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Thermoresponsive polymers in non-aqueous solutions†

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Thermoresponsive polymers are gaining increasing interest for numerous applications especially in the biomedical and nanotechnology fields. The thermoresponsive behaviour of polymers has been extensively studied in pure water or water/organic solvent systems, however, temperature-induced phase transitions in other organic solvents are less common. Polymers in organic solvents exhibit a broad range of temperature-driven solution behaviours, from LCST and UCST, to sol–gel transitions, to micellization processes, among others, with potential applications as smart materials in electronics, in the lubricant industry, and in the biomedical field. This review article will focus on the thermoresponsive behaviour of polymers in different classes of organic solvents and mixtures thereof to emphasize and demonstrate the versatility and potential of these polymers.

1. Introduction

Smart polymers are able to respond to various external triggers such as temperature, light, magnetic fields, mechanical forces, pH and other chemical stimuli, emerging as valuable materials for numerous applications ranging from drug delivery, biosensors to tissue-/surface engineering among many others.[1–3] To date, temperature remains the most utilized trigger for the design of stimuli responsive polymers predominantly in aqueous media, which is reflected by a plethora of available reports and review articles discussing and summarizing their synthesis and application.[4–13] Thermoresponsive polymers exhibit a miscibility gap in the phase diagram for polymer/solvent mixtures (Fig. 1). Below the lower critical solution temperature (LCST) and above the upper critical solution temperature (UCST), a polymer in a solvents is miscible at any ratio.[14]

It is important to note, that LCST and UCST are exact temperature values describing the minimum or maximum of the binodal curves, respectively. Therefore, constructing the binodal curve of a phase diagram for a given polymer/solvent system is essential for the determination of the exact values for LCST and UCST. Furthermore, the critical solution temperatures are dependent on polymer molecular weight and polydispersity as well as solution components and additives.[15–18] Consequently, LCST/UCST values are often inaccurately reported by determining cloud point temperatures (T_{CP}), which refer to the temperature at which phase separation occurs for a specific polymer concentration in solution. Hence, the T_{CP} may be any value on the binodal curve. Additionally, different experimental approaches for the measurement of T_{CP} result in further deviations, impeding the valid comparison of reported data.[19,20] As a result, many efforts have been undertaken to facilitate and improve the characterization of thermo-

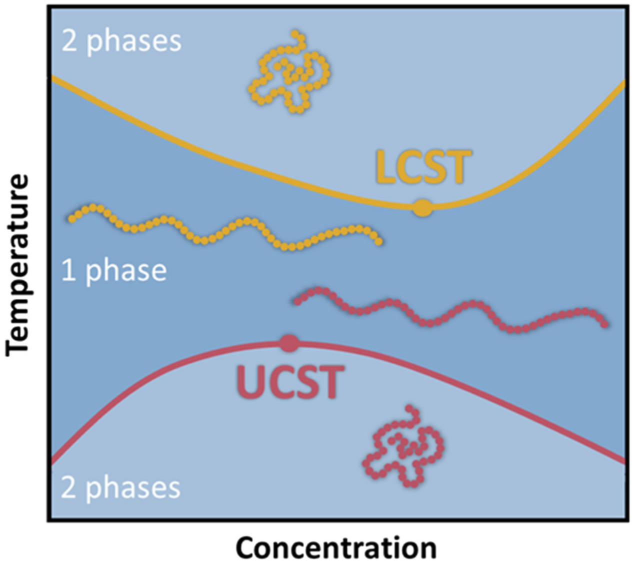

Fig. 1 Phase diagram showing the UCST and LCST for a binary mixture of a thermoresponsive polymer.

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responsive polymers. Predominantly, thermooptical techniques, such as turbidimetry, are utilized for the determination of T_{CP}.[21,22] However, the accuracy is strongly correlated to the heating rate and possible sediment formation of the sample.[19] Therefore, various analytical approaches have been developed to increase the accuracy of measured T_{CP}, while reducing the sample size and accelerating the analysis in a high-throughput fashion.[19,23–28] Furthermore, thermoresponsive polymers have been analyzed by NMR spectroscopy,[29] fluorescence microscopy,[30] infrared spectroscopy (IR),[31,32] dynamic light scattering (DLS),[33–35] and calorimetric techniques.[15,36–38]

In 1967, the thermal phase transition of poly(*N*-isopropylacrylamide) (PNIPAM) in aqueous solution was reported for the first time using hydrogen–deuterium exchange experiments.[39] Since then, PNIPAM advanced to become one of the most studied polymers in the field of thermoresponsive biomaterials.[20,40–43] Similarly, triblock copolymers from poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO), which are summarized under the trademark name Pluronics, are powerful thermoresponsive materials for various applications.[44] More recently, copolymers of poly(meth)acrylates with ethylene glycol-derived side chains gained growing attention due to a sharp phase transition and tunable T_{CP} by copolymerizing different monomers.[45–48] Similarly, polypeptides and poly(2-oxazolines) are discussed as potential PNIPAM substitutes, showing thermoresponsive behavior in the physiological temperature range (Fig. 2).[49–51]

The vast number of reports discussing water-soluble polymers with a LCST-type behavior exceeds the scope of this work and the reader is referred to exhaustive literature reviews addressing the topic and summarizing different polymer types.[4,6] Instead, we would like to emphasize the current state of thermoresponsive polymers in solvent mixtures and non-aqueous media, while also highlighting polymers with UCST-type phase transitions. Polymers with a UCST behavior are often overlooked in literature reviews or remain merely a side note due to the large quantity of articles discussing materials with LCST-type phase transition in aqueous media for biomedical applications.[55,56] For the same reasons, polymers with phase transitions in non-aqueous media are not sufficiently addressed and summarized in literature. In the following, the thermoresponsive behavior of polymers in solvent mixtures and non-aqueous media will be outlined and discussed.

2. Binary mixtures of water and other organic solvents

As explained above, water remains the most used media for the design and study of thermoresponsive polymers. Moreover, its binary mixtures with other organic solvents have also been thoroughly investigated. Among all, the thermoresponsive behaviour of PNIPAM and its copolymers has been widely studied in water/alcohol,[57–66] water/DMSO,[31,60,67] water/acetone,[68] water/THF,[58] and water/dioxane binary mixtures.[58,69–71] Furthermore, other acrylamide homo and copolymers, such as poly(*N*,*N*-dimethylacrylamide) and poly[*N*-acryloylpiperidine-*random*-*N*-acryloylpyrrolidine], have been shown to undergo a phase transition in water/alcohol, water/dioxane, and water/acetone mixtures upon changes in temperature.[72–75]

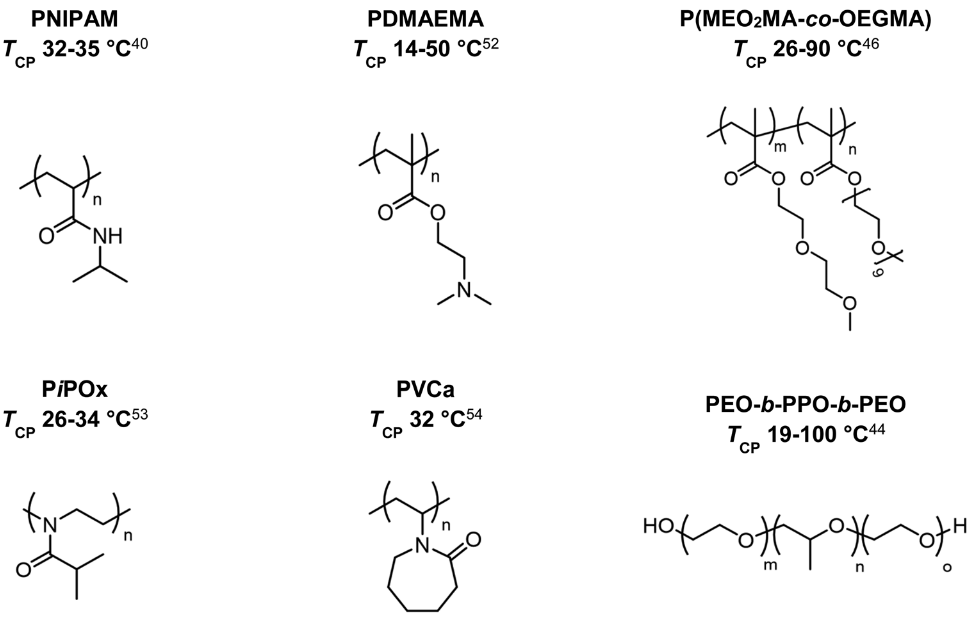


Fig. 2 Examples for thermoresponsive polymers in aqueous media with corresponding T_{CP} range tunable depending on chain length, monomer ratio and additives (*e.g.* salts). PNIPAM = poly(*N*-isopropylacrylamide), PDMAEMA = poly(*N*,*N*-dimethylaminoethyl methacrylate), P(MEO$_2$MA-*co*-OEGMA) = poly(2-(2-methoxyethoxy)ethyl methacrylate-*co*-oligo(ethylene glycol) methacrylate), PiPOx = poly(2-isopropyl-2-oxazoline), PVCa = poly(*N*-vinylcaprolactam), PEO-*b*-PPO-*b*-PEO = poly((ethylene oxide)-*b*-(propylene oxide)-*b*-(ethylene oxide)).

Another widely-studied class of polymers with thermoresponsiveness especially in water/alcohol mixtures is poly(methyl methacrylate) (PMMA) and its derivatives.[76–80] Poly(ethylene glycol) and its derivatives have also been well established as thermoresponsive polymer systems in water/alcohol mixtures, showing LCST,[81] UCST,[82–84] or both transitions depending on the polymer and mixed solvents composition.[85]

Additionally, the solution behaviour of poly(2-alkyl-2-oxazoline) homo and copolymers has been studied in detail especially in binary ethanol/water solutions, in which they show both LCST and UCST depending on the length of the alkyl side chains and on the ethanol content.[86–90] Polypeptides and glycopeptides have been investigated in water/alcohol mixtures, showing a tuneable UCST transition.[91–93]

Other classes of polymers showing thermoresponsiveness in water/organic solvent solutions are poly(boronic acid) and its derivatives in water/DMSO, water/DMF, and water/THF solutions,[67,94,95] and polysiloxanes in water/acetonitrile and water/ethylene carbonate mixtures.[96]

Literature offers insight to a plethora of thermoresponsive polymers in water/organic solvents binary mixtures and the reader is referred to an exhaustive review for further information and examples on the UCST behaviour of polymers in alcohol/water mixtures.[97] In the following sections, thermoresponsive polymers in pure organic solvents and mixtures thereof will be evaluated and discussed in more detail.

3. Pure alcohols

Apart from water and its binary mixtures, the thermoresponsive behaviour of polymers has been extensively investigated in alcoholic solvents. However, to the best of our knowledge, there are no literature reviews on this topic. For this reason, the thermoresponsive behaviour of polymers in alcohols will be discussed in detail in this section. The examples are grouped by solvents and, therefore, the same polymer classes will recur in the different subsections. In Tables S1–S5,† a complete overview of all examples discussed is provided for more clarity. Representative examples of thermoresponsive polymers in methanol (Table 1), ethanol (Table 2), 1-propanol (Table 3), 2-propanol (Table 4), and other alcoholic solvents (Table 5) are shown below.

3.1. Thermoresponsive behaviour in methanol (MeOH)

Methanol is one of the most studied alcoholic solvents for the evaluation of the thermoresponsive behaviour of polymers in solution. The temperature-induced phase transitions of synthetic polypeptides in alcohols and, in particular, in methanol has been widely studied especially for their potential application in the biomedical field as smart materials. For example, the polypeptide poly((γ-4-oligo(ethylene glycol) benzyl-L-glutamate)-*random*-(γ-benzyl-L-glutamate)) containing an oligo(ethylene glycol) (OEG) molar content of 0.75 mol% and a degree of

Table 1 Representative examples of polymers showing a thermoresponsive behaviour in methanol

Solvent	Type of polymer	Polymer conc.	Phase transition type (Temp. °C)	Ref.
MeOH	Poly(γ-4-(propoxycarbonyl)benzyl-L-glutamate)-oligo(ethylene glycol) derived from azido functionalized triethylene glycol monomethylether	1 mg mL^{-1}	UCST (~55)	93
MeOH	Poly(γ-4-(2-(2-methoxyethoxy) ethoxycarbonyl)benzyl-L-glutamate)	1 mg mL^{-1}	UCST(@36.4)	98
MeOH	Poly(γ-4-(2-(2-(2-methoxyethoxy) ethoxy)ethoxycarbonyl) benzyl-L-glutamate)	1 mg mL^{-1}	UCST (@16.0)	98
MeOH	Poly(γ-propyl-L-glutamate) with *p*-tolyl pendants and 3-methyl-1,2,3-triazolium iodide linkages	0.5 mg mL^{-1}	UCST (~26.8)	99
MeOH	Poly(γ-propyl-L-glutamate) tetra-*O*-acetyl-D-(+)-mannopyranoside conjugate	5 mg mL^{-1}	UCST (@27.4)	100
MeOH	Poly(2-(2-(2-acetoxyethoxy)ethoxy)ethyl methacrylate)	1 wt%	UCST (@26)	101
MeOH	Imidazolium ionic liquid-based nanogels	4.5 wt%	Sol–gel transition (~7)	102
MeOH	Poly(*N*-cyclopropyl-2-cyanohex-4-enamide)	10 mg mL^{-1}	UCST (~63)	103
MeOH	Poly(methyl 4-(2-(acryloyloxy)propanamido)butanoate)	1 wt%	UCST (@6–27)	104
MeOH	Poly(1-(cyclohexylamino)-1-oxopropan-2-yl acrylate)	1 wt%	UCST (@−37 to −20)	104

Table 2 Representative examples of polymers showing a thermoresponsive behaviour in ethanol

Solvent	Type of polymer	Polymer conc.	Phase transition type (Temp. °C)	Ref.
EtOH	Polypeptide bearing azobenzene and triethylene glycol spacers and 1-butylimidazolium side-chain end groups	8 mg mL^{-1}	UCST (~30)	105
EtOH	Poly(2-(2-(2-(2-((tetrahydrofuran-2-yl)oxy)ethoxy)-ethoxy)ethoxy) ethyl methacrylate)	1 wt%	UCST (~25)	106
EtOH	Poly(2-(dimethylamino) ethyl methacrylate-*co*-methacrylic acid-*co*-oligo(ethylene glycol) methyl ether methacrylate)	1 mg mL^{-1}	UCST (~10)	107
EtOH	Poly(2-(dimethylamino)ethyl methacrylate-*b*-3-phenylpropyl methacrylate)	21 wt%	Sol–gel transition (~70)	108
EtOH	Poly(*N*-isopropyl-2-cyanohex-4-enamide)	10 mg mL^{-1}	UCST(@40)	103
EtOH	Poly(2-nonyl-2-oxazoline)	5 mg mL^{-1}	UCST (~48)	86
EtOH	Poly(octadecyl vinyl ether-*random*-2-methoxyethyl vinyl ether)	1 wt%	UCST (~25)	109

Table 3 Representative examples of polymers showing a thermoresponsive behaviour in 1-propanol

Solvent	Type of polymer	Polymer conc.	Phase transition type (Temp. °C)	Ref.
PrOH	Poly((γ-4-oligo(ethylene glycol) benzyl-L-glutamate)-*random*-(γ-benzyl-L-glutamate))	0.2 mg mL^{-1}	UCST (@25.6–90)	110
PrOH	Poly(2-(2-(2-(2-((tetrahydrofuran-2-yl)oxy)ethoxy)-ethoxy)ethoxy) ethyl methacrylate)	1 wt%	UCST (~22)	106
PrOH	Poly(2-hydroxyethy methacrylate)	1 wt%	UCST (@35.8–45.9)	111
PrOH	Poly(*N*-(4-vinylbenzyl)-*N*,*N*-dibutylamine)	2 wt%	UCST (@48.0)	112

Table 4 Representative examples of polymers showing a thermoresponsive behaviour in 2-propanol

Solvent	Type of polymer	Polymer conc	Phase transition type (Temp °C)	Ref.
iPrOH	Poly(ethylene glycol) 6 kDa	0.050 wt%	UCST (@21)	113
iPrOH	Poly(poly(ethylene glycol) methacrylate)	0.0625 wt%	UCST (<5)	113
iPrOH	Poly(acrylic acid)/poly(poly(ethylene glycol) methacrylate) blend	0.0625/0.0625 wt%	UCST (@42)	113
iPrOH	PEG-armed star polymers, poly((ethylene glycol) methyl ether methacrylate-*b*-methyl methacrylate-*b*-ethylene glycol dimethyl acrylate)	3 wt%	UCST (~30)	114
iPrOH	PEG-armed Ru(II)-star polymers, poly((ethylene glycol) methyl ether methacrylate-*b*-methyl methacrylate-*b*-ethylene glycol dimethylacrylate-*b*-4-(diphenylphosphino) styrene-Ru(II))	3 wt%	UCST (~31)	114
iPrOH	Poly(oligo(ethylene glycol) methyl ether methacrylate-*b*-*N*-isopropylacrylamide)	5 mg mL^{-1}	UCST (<0)	115
iPrOH	Poly(oligo(ethylene glycol) methyl ether methacrylate-*b*-*N*,*N*-diethylacrylamide)	5 mg mL^{-1}	UCST (@0.5)	115
iPrOH	Poly(2-(dimethylamino) ethyl methacrylate-*co*-methacrylic acid)-*graft*-oligo(ethylene glycol) methyl ether methacrylate	1 mg mL^{-1}	UCST (@50)	107
iPrOH	Poly(vinylidene fluoride)-*graft*-poly(diethylene glycol methyl ether methacrylate)	0.09%w/v	UCST (@27.5)	85
iPrOH	Poly(*N*-(2-methacrylaoyxyethyl)pyrrolidone-*b*-methyl methacrylate)	5 wt%	Sol–gel transition (@27–50)	116

Table 5 Representative examples of polymers showing a thermoresponsive behaviour in other alcoholic solvents

Solvent	Type of polymer	Polymer conc.	Phase transition type (Temp. °C)	Ref.
BuOH	Poly(*N*-phenyl maleimide-*co*-*n*-octadecyl vinyl ether)	0.1 wt%	UCST (@67)	117
iBuOH	Poly(oligo(ethylene glycol) methyl ether methacrylate)	16 mg mL^{-1}	UCST (@30.4)	82
iBuOH	Poly(2-hydroxyethyl methacrylate)	1 wt%	UCST (@68.8–71.4)	111
*sec*BuOH	Poly(oligo(ethylene glycol) methyl ether methacrylate)	16 mg mL^{-1}	UCST (@26.4)	82
*sec*BuOH	Poly(2-hydroxyethyl methacrylate)	1 wt%	UCST (@13.5–14.0)	111
2-Methyl-1-butanol	Poly(oligo(ethylene glycol) methyl ether methacrylate)	16 mg mL^{-1}	UCST (@22.2)	82
Glycerol	Poly(2-hydroxyethyl methacrylate)	1 wt%	UCST (@71.8–83.6)	111
PeOH	Poly((γ-4-oligo(ethylene glycol) benzyl-L-glutamate)-*random*-(γ-benzyl-L-glutamate))	0.2 mg mL^{-1}	UCST (@43.3–86)	110
PeOH	Poly(oligo(ethylene glycol) methyl ether methacrylate)	16 mg mL^{-1}	UCST (@40.9)	82
iPeOH	Poly(oligo(ethylene glycol) methyl ether methacrylate)	16 mg mL^{-1}	UCST (@35.7)	82
4-Methyl-2-pentanol	Poly(oligo(ethylene glycol) methyl ether methacrylate)	16 mg mL^{-1}	UCST (@34.0)	82
HexOH	Poly(*N*-phenyl maleimide-*co*-*n*-octadecyl vinyl ether)	0.1 wt%	UCST (~47)	117
HepOH	Poly(oligo(ethylene glycol) methyl ether methacrylate)	16 mg mL^{-1}	UCST (@53.3)	82
2-Octanol	Poly(oligo(ethylene glycol) methyl ether methacrylate)	16 mg mL^{-1}	UCST (@47.7)	82
OctOH	Poly(*N*-phenyl maleimide-*co*-*n*-octadecyl vinyl ether)	0.1 wt%	UCST (~35)	117
OctOH	Poly(oligo(ethylene glycol) methyl ether methacrylate-*b*-(*N*-isopropylacrylamide-*co*-pentafluorophenyl acrylate))	1 mg mL^{-1}	Self-assembly (@0)	115
Dodecanol	Poly(oligo(ethylene glycol) methyl ether methacrylate)	16 mg mL^{-1}	UCST (@75.4)	82
CyclohexOH	Poly(styrene-*b*-methyl methacrylate)	~0.15–20 wt%	UCST (~65–75)	118
BnOH	Poly(γ-benzyl L-glutamate)	15–40 wt%	Sol–gel transition (@60–70)	119

polymerization (DP) of 3 prepared *via* triethylamine-initiated ring-opening polymerization (ROP) exhibited a UCST-type phase transition in methanol.[110] The T_{CP} increased from 4 to 34.2 °C with increased concentration from 0.2 to 1 mg mL^{-1}, as demonstrated by visual inspection and UV-vis analyses.

In another report, polypeptides containing OEG pendants synthesized *via* copper-mediated [3 + 2] alkyne–azide 1,3-dipolar cycloaddition (CuAAC) between poly(γ-4-(propargoxycarbonyl)benzyl-L-glutamate) (**P1**) or poly(γ-4-(4-propargoxyphenoxycarbonyl)benzyl-L-glutamate) (**P2**) and azido functiona-

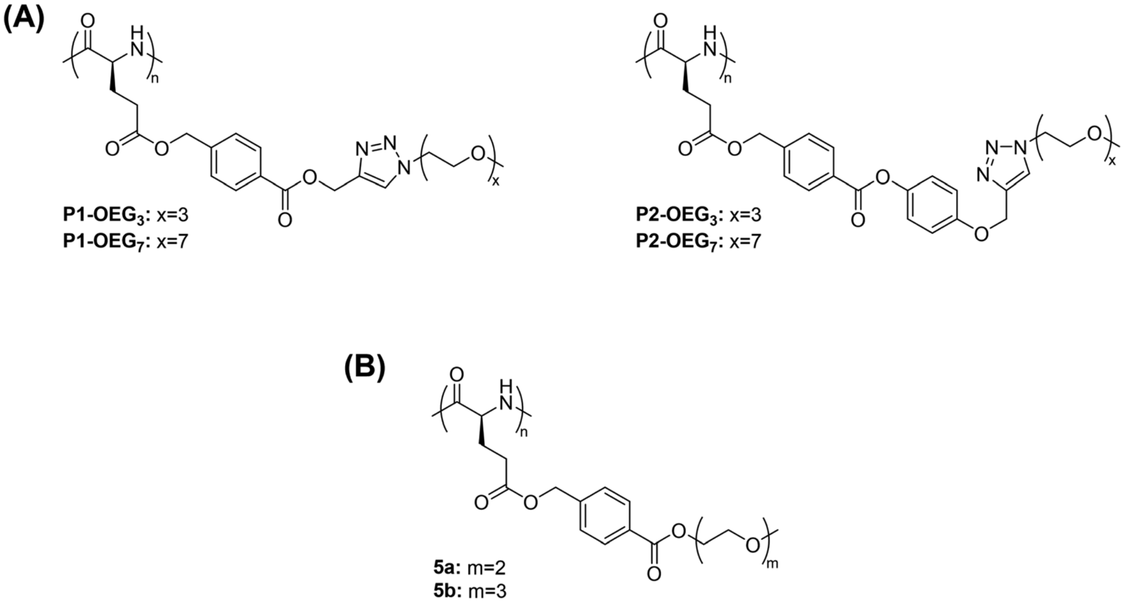


Fig. 3 Chemical structure of polypeptides with OEG pendants. (A) Polypeptides obtained by reacting poly(γ-4-(propargoxycarbonyl)benzyl-L-glutamate) (**P1**) or poly(γ-4-(4-propargoxyphenoxycarbonyl)benzyl-L-glutamate) (**P2**) with azido functionalized OEG,[93] and (B) poly(γ-4-(2-(2-methoxyethoxy) ethoxycarbonyl)benzyl-L-glutamate) (**5a**) and poly(γ-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxycarbonyl) benzyl-L-glutamate).[98]

lized OEG (N_3-OEG$_x$) were also found to have thermoresponsive behaviour in MeOH (Fig. 3A).[93]

The thermoresponsive behaviour was dependent on both the type of linkage (*i.e.* phenylene or benzoic acid phenyl ester linkages) and the length of the OEG pendants. On the one hand, **P1-OEG$_3$** with phenylene linkages and short OEG pendants exhibited a UCST phase transition in MeOH at around 55 °C at a polymer concentration of 1 mg mL^{-1}, as showed by variable-temperature UV-vis spectroscopy measurements. On the other hand, **P2-OEG$_7$** with benzoic acid phenyl ester linkages and long OEG pendants underwent a UCST phase transition at 49.5 °C at the same polymer concentration. At low temperatures, the polymers aggregated, but at elevated temperatures the hydrogen bonding interactions between the polar linkages, such as the ester bonds and 1,2,3-triazole groups, the OEG pendants of the polymers and the alcoholic molecules, became more favoured compared to the polymer–polymer ones resulting in the dissolution of the polymer.[93]

In another example, polypeptides with OEG pendants synthesised from OEGylated *N*-carboxyanhydride monomers by ROP using triethylamine as initiator, namely poly(γ-4-(2-(2-methoxyethoxy) ethoxycarbonyl)benzyl-L-glutamate) (**5a**) and poly(γ-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxycarbonyl) benzyl-L-glutamate) (**5b**), exhibited a UCST-type phase transition in MeOH (Fig. 3B).[98] In the transmittance curves, no hysteresis between the heating a cooling cycles was observed due to a lack of intra- and intermolecular hydrogen bonding interactions between the OEG pendants, which prevented the formation of large aggregates. The thermoresponsive behaviour was attributed to H bonding interactions between the ether groups on the OEG pendants and the OH groups of the alcoholic solvent, which became greater with the increase in temperature, as demonstrated by variable-temperature UV-vis spectroscopy, variable-temperature ^{1}H NMR, and DLS measurements. Furthermore, the UCST phase transition was found to be strongly dependent on the polymer concentration, the length of the OEG pendants, and the length of the main chain.

In a recent report, polypeptides bearing *p*-tolyl pendants and 3-methyl-1,2,3-triazolium linkages synthesized *via N*-alkylation of poly(γ-propyl-L-glutamate)-*graft*-(4-methylbenzene) and subsequent ion-exchange reactions, underwent a UCST-type phase transition in MeOH (Fig. 4).[99] It was shown by transmittance measurements that poly(γ-propyl-L-glutamate) with *p*-tolyl pendants and 3-methyl-1,2,3-triazolium iodide linkages (**P2**) with a DP of 54 or 92 had similar T_{CP} values around 26.8 °C at a polymer concentration of 0.5 mg mL^{-1}. However, P2$_{54}$ with a shorter main chain length exhibited a lower initial aggregation temperature and a sharper solution phase transition compared to P2$_{92}$ (Fig. 4). The thermoresponsive behaviour of **P2** and its solubilization upon increase in temperature were attributed to the van der Waals interactions between the hydrophobic groups and the alkyl groups of the alcoholic solvent, and to the H bonding interactions between the polar ester and ether bonds and the hydroxyl groups of the solvent molecules. A similar behaviour was also observed in the case of poly(γ-propyl-L-glutamate) with *p*-tolyl pendants and 3-methyl-1,2,3-triazolium tetrafluoroborate linkages (**P4**) at a high concentration (10 mg mL^{-1}), but a value for its T_{CP} was not reported.

In another example, polypeptides containing 1-butyl, 1-hexyl, or 1-dodecyl side-chains synthesized by CuAAC between poly(γ-4-(propargoxycarbonyl)benzyl-L-glutamate) and 1-azidoalkanes exhibited a UCST phase transition in MeOH, which was dependent on the length of both the alkyl side-

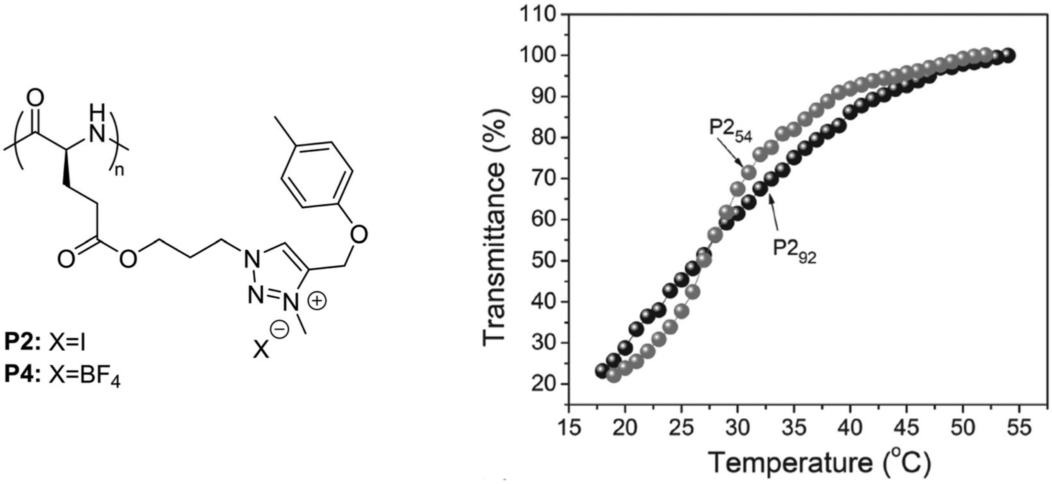


Fig. 4 Chemical structure of the polypeptides bearing *p*-tolyl pendants and 3-methyl-1,2,3-triazolium linkages, and plots of transmittance *versus* temperature of 0.5 mg mL^{-1} MeOH solutions of P2$_{54}$ and P2$_{92}$. Adapted from ref. 99 Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

chains and the main chain.[91] While polypeptides with a long main chain (DP ≥ 62) were insoluble in MeOH, polypeptides with a short main chain (*i.e.* DP = 41–44) showed UCST behaviour, with T_{CP} of 55, 50 and 54.7 °C when the length of the alkyl pendants was varied from 1-butyl, to 1-hexyl, to 1-dodecyl, respectively. Furthermore, lowering the polymer concentration resulted in a decrease in the T_{CP} values.

Sugar-containing polypeptides have also shown temperature-induced solution behaviours in methanol. This is the case of glycopolypeptides with different contents of tetra-*O*-acetyl-D-(+)-mannopyranoside and tetra-*O*-hydroxyl-D-(+)-mannopyranoside pendants synthesised *via* CuAAC, which showed a UCST-type phase transition in MeOH, that was dependent on both the content and DP of the two monosaccharides (Fig. 5).[100] On the one hand, glycopolypeptides containing only tetra-*O*-acetyl-D-(+)-mannopyranoside pendants (*i.e.* **5a**, DP = 36) exhibited a UCST phase transition at 7.4 °C at 1 mg mL^{-1}, which increased to 27.4 °C at 5 mg mL^{-1}, as shown by variable-temperature UV-vis spectroscopy, Fourier Transform Infrared (FTIR) spectroscopy, and dynamic light scattering (DLS). On the other hand, the thermoresponsive behaviour of glycopolypeptides containing both tetra-*O*-acetyl-D-(+)-mannopyranoside and tetra-*O*-hydroxyl-D-(+)-mannopyranoside pendants (*i.e.* **5c** and **5d**) was highly dependent on the ratio (x and y, respectively) of the two monosaccharide units. The T_{CP} of the glycopolypeptides in MeOH (5 mg mL^{-1}) increased from 33.4 to 35 °C, when decreasing the molar content of the acetylated sugar unit from 85 to 44 mol%. A mechanism for the UCST-type phase transition of the obtained glycopolypeptides based on the competition between side-chain/side-chain interactions and side-chain/solvent interactions was proposed. At high temperatures, the hydrogen bonding interactions between the acetyl groups and the alcoholic molecules resulted in the solvation of the polymer, while the hydrophobic interactions led to polymer aggregation at low temperatures. Moreover, the incorporation of proton donating groups, such as tetra-*O*-hydroxyl-D-(+)-mannopyranoside, led to the formation of hydrogen bonds between the side-chains, resulting in higher T_{CP} values due to the need of higher energy to break the polymer aggregates. The authors stated that these thermoresponsive glycopolypeptides could be potentially applied as smart stationary phases for chromatography.

Polypeptoides are another class of polymers showing thermoresponsiveness in alcoholic media. For instance, the ROP of *N*-allyl glycine (NAG) and *N*-octyl glycine (NOG) using benzylamine as initiator followed by the thiol–ene/yne coupling reaction with mercaptoacetic acid resulted in the synthesis of carboxylic acid-containing polypeptoides with a UCST-type solution behaviour.[120] A random copolymer with a 49 : 14 ratio between the average DP of NAG and NOG (PNAG$_{49}$-*r*-PNOG$_{14}$-COOH) underwent a UCST phase transition at 50.8 °C in MeOH at a polymer concentration of 2 mg mL^{-1}, as demonstrated by transmittance measurements. The T_{CP} values were dependent on the polymer concentration, and, at a fixed concentration, it increased upon increasing the DP of NOG due to a reduced solubility of the polymer in the alcoholic solvent caused by the longer alkyl chains.

Other classes of OEG-containing polymers resulted to be thermoresponsive in methanol. For example, a series of poly(oligo(ethylene glycol) (acyloxy)methacrylate)s (PAEEO$_n$MA) containing OEG units and different ester substituents synthesised *via* RAFT polymerization exhibited a UCST behaviour, which was dependent on the molecular structure, molecular weight, and concentration of the polymer, as shown by turbidity measurements (Fig. 6).[101] It was demonstrated that the T_{CP} decreased with increasing number of OEG units and carbon atoms in the alkyl substituents of the ester groups. For example, the increase of the OEG units from 2 to 4 resulted in a decrease of the T_{CP} from 26 to 4.5 °C, for 1 wt% polymer solutions in MeOH. Moreover, for polymers with similar DP

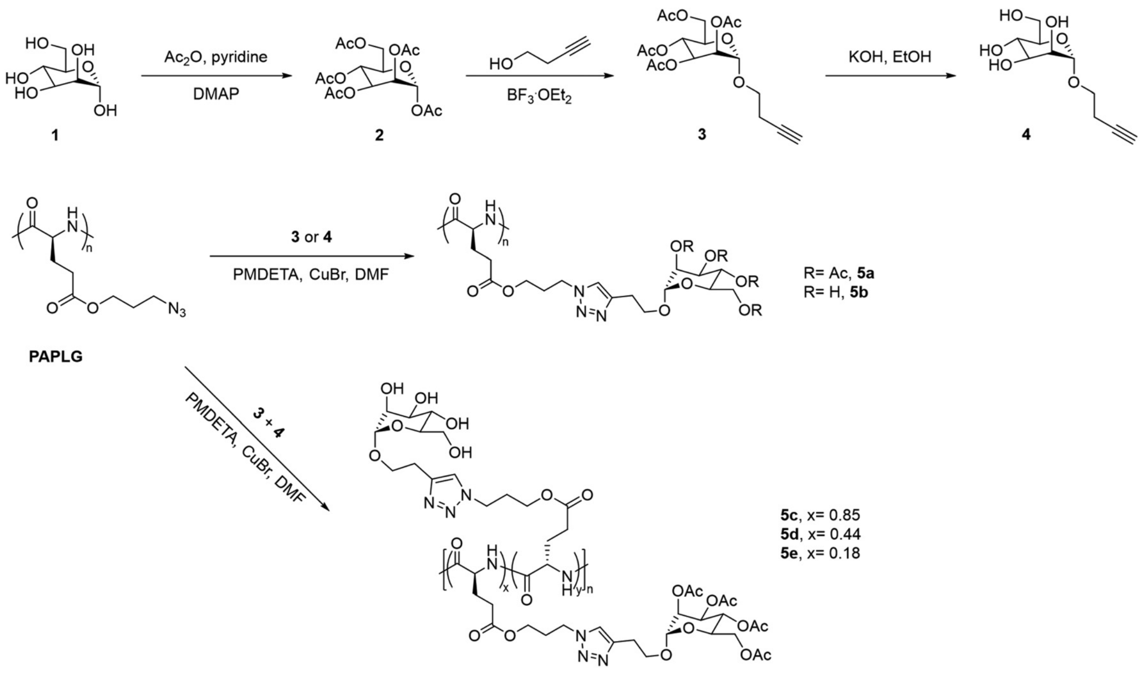
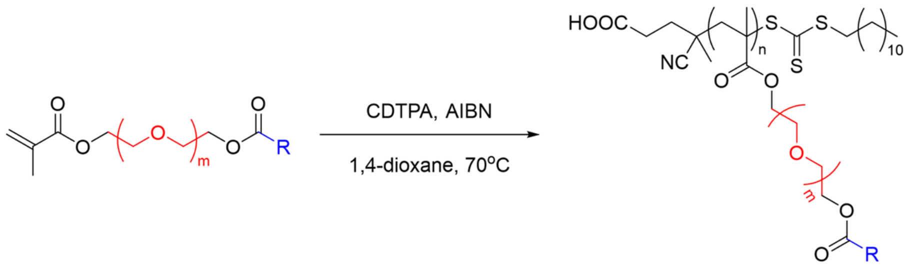


Fig. 5 Synthetic route of the glycopolypeptides with mannose pendants.[100]



R	m	Monomer	Polymer
CH_3	2	$AEEO_2MA$	$PAEEO_2MA$
CH_3	3	$AEEO_3MA$	$PAEEO_3MA$
CH_3	4	$AEEO_4MA$	$PAEEO_4MA$
CH_2CH_3	4	$PEEO_4MA$	$PPEEO_4MA$
$CH_2CH_2CH_3$	4	$BEEO_4MA$	$PBEEO_4MA$

Fig. 6 Schematic representation of the synthetic procedure used to synthesize a series of poly(oligo(ethylene glycol) (acyloxy)methacrylate)s.[101]

and the same number of OEG units, the increase in the number of carbon atoms in the alkyl groups of the ester resulted in the complete solubilization of the polymers bearing longer alkyl chains (*i.e.* R = CH_2CH_3 and $CH_2CH_2CH_3$).

It has also been reported that poly(*N*-propionyl-aspartic acid/ethylene glycol) (PPAE) synthesized by polycondensation of L-aspartic acid and ethylene glycol exhibited a UCST-type phase transition in MeOH.[121] However, no T_{CP} values or analyses on the polymer solution have been stated. The polymers were non-toxic and biocompatible, making them promising candidates for biomedical applications.

A ethylene glycol dimethacrylate (EGDMA) cross-linker was used for the synthesis of imidazolium ionic liquid-based cross-linked polymeric nanogels (ImIL-based CLPNs) obtained *via* FRP of 1,4-butanediyl-3,3′-bis-1-vinyl imidazolium halides ([BVIm]X = 1·X, X = Cl, Br), which showed both a UCST and a

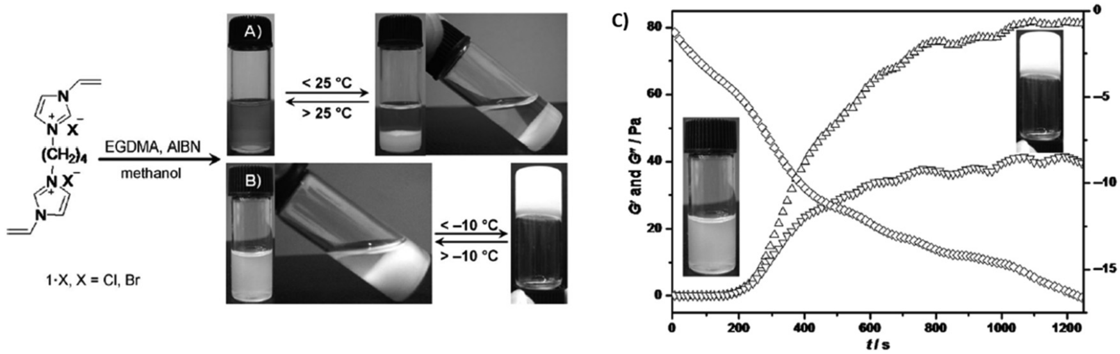


Fig. 7 One-step synthesis of ImIL-based CLPN, and images of the thermoresponsive behaviour of CLPN solution with a 1·Br/EGDMA feed ratio of (A) 5 : 1 mol/mol, and (B) 10 : 1 mol mol^{-1}. (C) Shear storage modulus (G', ▲) and shear loss modulus (G''; ▼) as a function of temperature (◆) for a 4.5 wt% CLPN MeOH solution with a 10 : 1 1·Br/EGDMA feed ratio and corresponding appearance of the sample. Adapted from ref. 102 Copyright 2012 WILEY-VCH Verlag GmbH & Co. KGaA.

sol–gel transition in MeOH depending on the feed ratio between 1·Br and EGDMA (Fig. 7).[102] On the one hand, at a 1·Br/EGDMA feed ratio of 5 : 1 mol/mol, the 4.5 wt% CLPN solution was translucent at temperatures above 28 °C and became cloudy when cooled below 25 °C, as shown by turbidity and DLS measurements. On the other hand, when the feed ratio was increased to 10 : 1 mol/mol, the polymer solution turned into a gel at temperatures below −7 °C, as supported by temperature-dependent oscillatory shear rheological measurements (Fig. 7C). The increase in the 1·Br content resulted in the enhancement of the interactions between CLPN and the methanol molecules. In addition, ^{1}H NMR spectroscopy, IR spectroscopy, and X-ray diffraction were used to elucidate the interactions between the ImIL-based CLPN and MeOH. All analyses showed that the formation of a solution of CLPN in MeOH was related to the partial replacement of C–H—Br$^-$ bonds with hydrogen bonding interactions between the imidazolium ring and the methanol molecules. Therefore, the formation of a thermoresponsive CLPN gel in MeOH at low temperatures required the enhancement in the hydrogen bonds between the imidazolium ring, Br$^-$, and MeOH, while at high temperatures the H-bond network was destroyed resulting in the formation of a CLPN MeOH solution.

Other classes of polymers undergo temperature-induced phase transitions in MeOH, as shown by the examples given below.

Poly(*N*-cyclopropyl-2-cyanohex-4-enamide) synthesized *via* ROP of 1-cyano-1-pentafluorophenoxycarbonyl-2-vinylcyclopropane and post-polymerization modification of the obtained homopolymer with cyclopropylamine exhibited a UCST-type behaviour in MeOH.[103] The polymer phase transition was dependent on the polymer concentration, with T_{CP} values decreasing from around 63 to around 54 °C at 10 and 2.5 mg mL^{-1}, respectively, as shown by turbidity measurements.

Turbidity measurements of a 1 mg mL^{-1} MeOH solution of poly(*N*-(6-acetamidopyridin-2-yl)acrylamide) obtained by free radical polymerization (FRP) demonstrated the UCST-type thermoresponsive behaviour of the polymer with a T_{CP} of 50 °C.[73]

In another report, poly(methyl 4-(2-(acryloyloxy)propanamido)butanoate) and poly(1-(cyclohexylamino)-1-oxopropan-2-yl acrylate) were synthesized by FRP using functionalized acrylate monomers obtained from the Passerini three-component reaction (Passerini-3CR) of acrylic acid and a series of isocyanides and aldehydes (Fig. 8).[104] Because of the hydrophilicity/hydrophobicity balance, the resulting polyacrylates showed a UCST behaviour in MeOH at 6–27 and −37 to −20 °C, respectively, as shown by UV-vis analyses of 1 wt% polymer solutions.

Magnetic fluids based on magnetite coated with a covalently bonded polymeric shell of poly(2-methoxyethyl methacrylate) (PMEMA) have been reported to show a UCST-type behaviour in MeOH, forming stable dispersions above UCST and precipitated below it.[122] From turbidity measurements, the T_{CP} was found to decrease from around 38 to 19 °C with the increase in the length of the PMEMA arms from to 11 to 35.1 kDa, which was not observed for the free polymers in solution. This behaviour was attributed to the surface attachment of the arms, which resulted in a less beneficial entropic contribution to the solvation process compared to free polymer chains. This effect was less pronounced for long chains since the free volume of chain segments increased with increasing distance from the solid core. These core–shell particles, which combine the properties of both thermoresponsive polymers and magnetic fluids, could be promising materials for easily recoverable polymer supported magnetic separation kits and catalytic systems.

In another example, a random copolymer of octadecyl vinyl ether (ODVE) and 2-methoxyethyl vinyl ether obtained *via* living cationic polymerization underwent a UCST-type phase transition in methanol at around 20 °C, which was attributed to the crystallization of the long alkyl chains of the octadecyl vinyl ether monomer.[109]

Finally, poly(*N*-(4-vinylbenzyl)-*N*,*N*-diethylamine) (PVEA) obtained by RAFT polymerization exhibited a LCST phase transition in MeOH, which was strongly dependent on the polymer DP and concentration.[112,123] The effect of the addition of a cosolvent on the LCST-type behaviour was also evaluated by analysing PVEA DP = 104 MeOH/EtOH solutions. The T_{CP}

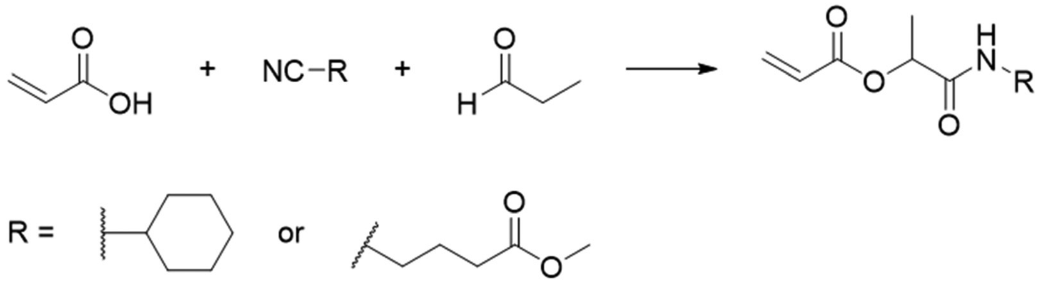


Fig. 8 Passerini-3CR of acrylic acid, different isocyanides, and propionaldehyde yielding the acrylates used in the synthesis of thermoresponsive polymers with a UCST-type phase transition in MeOH.[104]

increased from 39.5 to 65 °C with increased EtOH content from 0 to 50 wt%, and the polymer became soluble above 50 w% of EtOH.

3.2. Thermoresponsive behaviour in ethanol (EtOH)

The thermoresponsive behaviour of polymers in ethanol has also been widely investigated. Many of the previously mentioned polymers have similar thermoresponsive behaviours in both MeOH and EtOH, therefore, they will appear again in this subsection.

As expected, PEO-containing or OEGylated polymers have shown thermoresponsiveness also in ethanol. For example, PEO homopolymer exhibited a UCST phase transition due to the dissolution of the crystalline areas formed upon quenching of a polymer solution at temperatures above the melting temperature.[124] The T_{CP} varied from around −5 to 10 °C when the polymer concentration was increased from 0.01 to 0.165 vol%, as extrapolated from small-angle neutron scattering (SANS) measurements.

Various OEGylated polypeptides exhibited a UCST-type behaviour in EtOH.[93,110] Polypeptides obtained from CuAAC of poly(γ-4-(propargoxycarbonyl)benzyl-L-glutamate) with azido functionalized triethylene glycol monomethylether (**P1-OEG$_3$**) or azido functionalized poly(ethylene glycol) methyl ether 350 (**P1-OEG$_7$**), and poly(γ-4-(4-propargoxyphenoxycarbonyl)benzyl-L-glutamate) with azido functionalized poly(ethylene glycol) methyl ether 350 (**P2-OEG$_7$**) exhibited UCST phase transition in ethanol (Fig. 3A).[93] At a polymer concentration of 1 mg mL^{-1}, the T_{CP} of **P1-OEG$_3$** was higher than the one of **P1-OEG$_7$** (70.5 °C and 53.1 °C, respectively) due to a decrease in the hydrogen bonding interactions between the OEG side chains and the alcoholic molecules as the length of the OEG pendants decreased. Moreover, the T_{CP} of **P2-OEG$_7$** was higher than that of **P1-OEG$_7$** (*i.e.* 64 °C) due to the presence of more hydrophobic linkages.

Poly((γ-4-oligo(ethylene glycol) benzyl-L-glutamate)-*random*-(γ-benzyl-L-glutamate)) copolymers also exhibited a UCST-type behaviour in EtOH at a maximal concentration above 0.2 mg mL^{-1}.[110] For polymers with the same OEG DP, a decrease in the T_{CP} values was observed with increasing OEG molar content due to an enhancement of the H bonding interactions between the oxygen of the OEG pendants and the hydroxyl groups of the alcoholic solvent, which facilitated the solvation of the polymers.

In another example, poly(γ-4-(2-(2-methoxyethoxy) ethoxycarbonyl)benzyl-L-glutamate) and poly(γ-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxycarbonyl) benzyl-L-glutamate), OEGylated polypeptides obtained from the ROP of *N*-carboxyanhydrides, showed a UCST phase transition in ethanol, which was dependent on the polymer concentration, and on the DP of both the side and the main chains.[98]

Furthermore, a homopolypeptide bearing azobenzene and triethylene glycol spacers and 1-butylimidazolium pendants with iodide counter anions (P(Azo-OEG$_3$-ImI)) showed a UCST-type phase transition in EtOH at around 30 °C at a polymer concentration of 8 mg mL^{-1}, which was strongly affected by the polymer concentration in solution (Fig. 9).[105]

As in the case of methanol, polypeptides containing 1-butyl, 1-hexyl, or 1-dodecyl side-chains showed a UCST-type behaviour in EtOH.[91] For polymers having similar main chain length, a decrease in the T_{CP} from 71.1 to 56.9 °C was observed with the increase in the alkyl side-chain length from 4 to 12 carbon atoms. For the same polymer type, higher T_{CP} values were recorded with increasing main chain length or polymer concentration due to an enhancement of

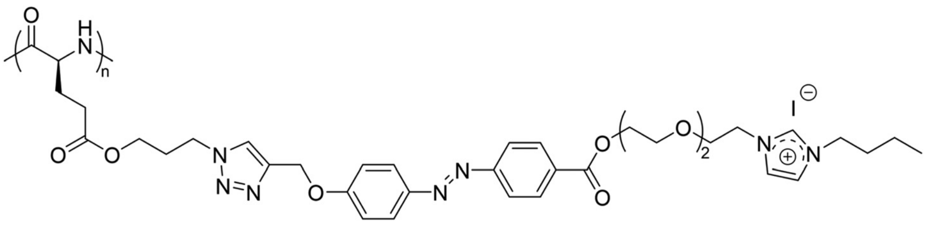


Fig. 9 Chemical structure of the homopolypeptide P(Azo-OEG$_3$-ImI).[105]

hydrophobic interactions and entanglement between polymer chains.

Glycopolymers also displayed thermoresponsive behaviour in EtOH. For example, glycopolypeptides containing different amounts of tetra-*O*-acetyl-D-(+)-mannopyranoside and tetra-*O*-hydroxyl-D-(+)-mannopyranoside pendants exhibited UCST-type phase transition with T_{CP} values dependent on the content and the DP of the monosaccharides.[100] Glycopolymers containing only tetra-*O*-acetyl-D-(+)-mannopyranoside pendants showed a T_{CP} of 51.9 °C, but when the tetra-*O*-acetyl-D-(+)-mannopyranoside molar content was decreased from 100 to 44, the T_{CP} increased from 51.9, to around 60 °C, respectively, due to an enhancement of the H bonding interactions between the proton donating groups in the side-chains.

Another class of OEGylated polymers which have been studied for their thermoresponsive behaviour in EtOH are poly(methacrylate)s. For example, poly(oligo(ethylene glycol) methyl ether methacrylate) (POEGMA) with a molecular weight of 23.2 kDa synthesised *via* RAFT polymerization exhibited a UCST-type behaviour in EtOH at 21.9 °C at a polymer concentration of 16 mg mL^{-1}, as showed by cloud point measurements.[82] Furthermore, it has been shown that poly(oligo(ethylene glycol) (acyloxy)methacrylate)s containing OEG units and various ester substituents obtained *via* RAFT polymerization exhibited a tunable UCST-type phase transition, depending on the polymer structure, molecular weight, and concentration (Fig. 6).[101] For example, a 1 wt% poly(2-(2-(2-acetoxyethoxy)ethoxy)ethyl methacrylate) solution exhibited a T_{CP} at 55 °C, which decreased to 36 °C when the number of OEG units was increased from 2 to 4. Moreover, the alkyl substituents in the ester groups also affected the T_{CP} values. In fact, the increase in the number of carbon atoms resulted in a decreased T_{CP} from 36 °C for poly(2-(2-(2-(2-(2-(acetoxy)ethoxy)ethoxy)ethoxy)ethoxy) ethyl methacrylate), to 8 °C for poly(2-(2-(2-(2-(2-(butyrylacyloxy)ethoxy)ethoxy)ethoxy)ethoxy) ethyl methacrylate).

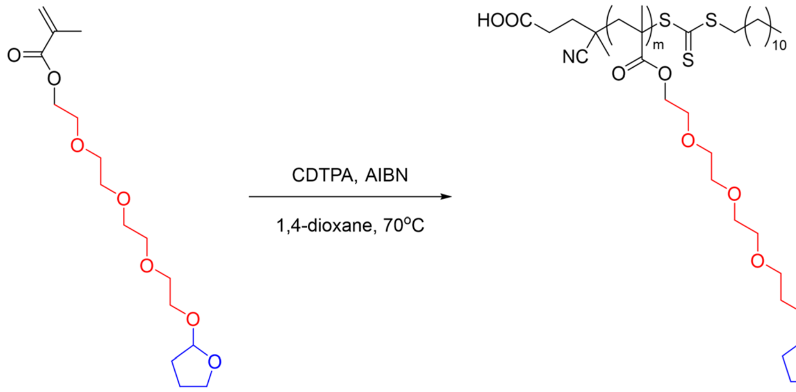
A UCST-type phase transition was also observed for poly(2-(2-methoxyethoxy)ethyl methacrylate), which was strongly dependent on the polymer molecular weight.[123] In fact, at a polymer concentration of 2 wt%, the T_{CP} increased from 13.4 to 20.6 °C when the polymer DP was increased from 29 to 89. At higher DP, the polymer–polymer interactions were more favourable, and higher temperatures were required to disrupt these interactions, resulting in higher T_{CP} values.

Another example is poly(2-(2-(2-(2-((tetrahydrofuran-2-yl)oxy)ethoxy)-ethoxy)ethoxy) ethyl methacrylate) ($PTFEO_4MA$) containing oligo ethylene glycol moieties and acetal groups synthesised *via* RAFT polymerization, which showed a UCST-type phase transition in EtOH with a T_{CP} at around 25 °C (Fig. 10).[106]

Furthermore, the RAFT copolymerization of a neutral oligo(ethylene glycol)methyl ether methacrylate (M_n = 480 Da) with two charged co-monomers, namely 2-(dimethylamino)ethyl methacrylate and methacrylic acid, yielded a thermoresponsive brush copolymer polyampholyte with a UCST phase transition in EtOH (Fig. 11).[107] At temperatures higher than 10 °C the polymer was completely soluble with particle size of 6 nm corresponding to unimers, as shown by DLS analysis. When the temperature was decreased to 5 °C, the particle size increased to about 45 nm, indicating the formation of nanostructures. This thermoresponsive behaviour was attributed to the collapse of the polymer due to strong electrostatic interactions between positive and negative charges, while the ethylene glycol side chains acted as solvophilic corona, stabilizing the nanostructures and preventing their aggregation.

Furthermore, block copolymers consisting of a poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) segment (DP = 20) and a 3-phenylpropyl methacrylate (PPPMA) block (DP = 47) ($PDMAEMA_{20}$-*b*-$PPPMA_{47}$) obtained by RAFT dispersion polymerization formed a pure worm phase at 21 wt% solids in ethanol at room temperature.[108] The block copolymer exhibited a gradual macroscopic thermoreversible degelation–gelation behaviour when heated up to 70 °C due to a worm-to-sphere morphological transition, as supported by ^1H NMR, DLS, and TEM analyses (Fig. 12).

Various poly(acrylate)s have also shown to undergo temperature-induced phase transition in EtOH, as in the case of



$TFEO_4MA$ **$PTFEO_4MA$**

Fig. 10 Schematic depiction of the RAFT polymerization of poly(2-(2-(2-(2-((tetrahydrofuran-2-yl)oxy)ethoxy)-ethoxy)ethoxy) ethyl methacrylate) ($PTFEO_4MA$).[106]

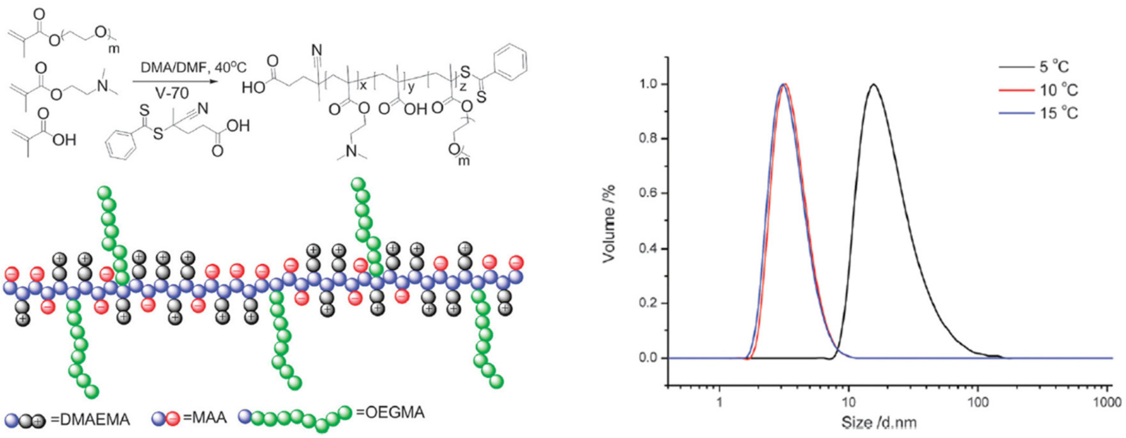


Fig. 11 Schematic representation of the synthesis and structure of the brush copolymer polyampholyte (left), and size distribution at various temperatures for a 1 mg mL^{-1} ethanol solution of the brush copolymer determined by DLS (right). Adapted from ref. 107 Copyright 2015 Royal Society of Chemistry.

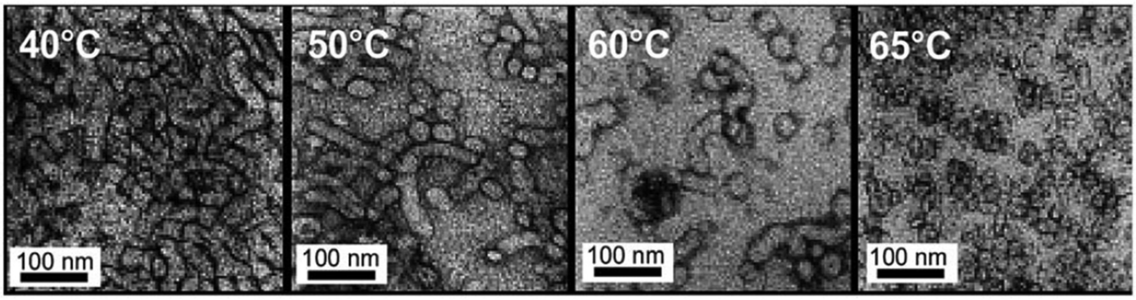


Fig. 12 TEM images of the $PDMAEMA_{20}$-*b*-$PPPMA_{47}$ block copolymer at 40, 50, 60 and 65 °C demonstrating the gradual temperature-induced worm-to-sphere morphology transition. Reproduced from ref. 108 Copyright 2014 Royal Society of Chemistry.

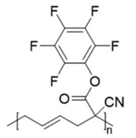
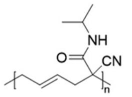
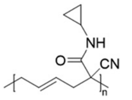
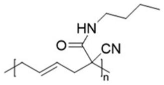
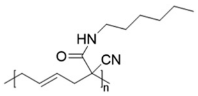
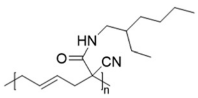
poly(methyl acrylate) and its copolymers. Poly(methyl acrylate) with a DP of 60 synthesised *via* solution atom transfer radical polymerization (ATRP) exhibited a UCST behaviour at 60 °C at a concentration of 5 mg mL^{-1}.[125] The T_{CP} could be tuned by copolymerization of poly(methyl acrylate) with other monomers, such a styrene and diethylene glycol ethyl ether acrylate, into diblock copolymers. In the latter case, the UCST was attributed to the transition from micelles to individually dissolved polymer chains, as demonstrated by turbidity and DLS measurements.[84]

In another example, poly(1-(benzylamino)-1-oxopropan-2-yl acrylate) and poly(methyl 4-(2-(acryloyloxy)propanamido) butanoate) obtained by FRP using acrylates synthesised *via* the Passerini-3CR showed UCST-type phase transition in ethanol in a temperature range of 55–74 °C and 6–19 °C, respectively, as demonstrated by visual inspection and UV-vis analyses of 1 wt% polymer solutions.[104]

Vinylcyclopropane-derivatives could also undergo UCST phase transition in EtOH. For example, poly(1-cyano-*N*-propylcarboxyamidovinylcyclopropane) obtained by post-polymerization modification of poly(1-cyano-1-pentafluorophenoxycarbonyl-2-vinylcyclopropane) with *n*-propylamine showed a UCST-type behaviour in EtOH at around 34 °C at a concentration of 1 mg mL^{-1}.[126] As expected, the T_{CP} was found to slightly decrease with the decrease in the polymer concentration. Furthermore, polymers obtained from the ROP of poly(1-cyano-1-pentafuorophenoxycarbonyl-2-vinylcyclopropane) (**PCPFPCVP**) and its further post-polymerization modification with five different primary amines showed UCST behaviour in ethanol (Table 6).[103] At a concentration of 10 mg mL^{-1}, poly(*N*-isopropyl-2-cyanohex-4-enamide) (**VCP2J1**) exhibited the highest T_{CP} at 40 °C, while the butylamide-derivative **VCP2J3** showed a T_{CP} of 23 °C. The increase in the chain hydrophobicity resulted in a further decrease of the T_{CP} to 15 °C for poly (*N*-hexyl-2-cyanohex-4-enamide) (**VCP2J4**). Interestingly, the polymer with 2-(ethyl)hexyl alkyl chains (**VCP2J5**) exhibited a higher T_{CP} at 25 °C. It was also found that the increase in size and, thus, in hydrophobicity of the amine moiety, led to an increase in the minimal concentration required to observe UCST behaviour due to an enhancement of the polymer solubility in the alcoholic solvent.

Poly(2-alkyl-oxazoline)s are another class of polymers that shows temperature-driven phase transitions not only in water/alcohol mixtures, but also in pure alcohols, such as ethanol. To exemplify, poly(2-nonyl-2-oxazoline) and poly(2-benzyl-2-oxazoline) obtained by cationic ring-opening polymerization

Table 6 Label, chemical structure, M_n and M_w/M_n of PCPFPCVP and the amine-modified polymers[103]

Polymer	Structure	M_n [Da]	M_w/M_n
PCPFPVCP		64 900	2.80
VCP2J1		76 400	2.14
VCP2J2		32 200	2.36
VCP2J3		68 600	2.55
VCP2J4		82 800	2.58
VCP2J5		82 600	2.68

underwent a UCST-type phase transition in ethanol at a concentration of 5 mg mL^{-1} at around 48 and −12 °C, respectively.[86] In the case of poly(2-phenyl-2-oxazoline) solutions at the same polymer concentration, two T_{CP} values at around 40 and at 48.1 °C have been reported.[88,89] Nevertheless, the copolymerization of 2-phenyl-2-oxaozline with 2-nonyl-2-oxazoline in a 90 : 10 ratio resulted in a drastic decrease in the T_{CP} to around 10 °C due to an increased solubility of the statistical copolymer in EtOH.[89]

As shown above for solutions in methanol, poly(octadecyl vinyl ether-*random*-2-methoxyethyl vinyl ether) also exhibited a fully reversible UCST-type phase transition at around 25 °C in ethanol at a concentration of 1 wt% due to the crystallization of the side chains of the octadecyl vinyl ether units.[109]

3.3. Thermoresponsive behaviour in 1-propanol (PrOH)

Polymers also exhibit thermoresponsive behaviours in 1-propanol (PrOH) As shown above for MeOH and EtOH, various polypeptides show temperature-induced phase transitions in this alcohol. For example, poly((γ-4-oligo(ethylene glycol) benzyl-L-glutamate)-*random*-(γ-benzyl-L-glutamate)) with different OEG molar content and DP underwent a UCST-type phase transition with a maximal concentration (C_m) dependent on the OEG content and on the side-chain length.[110] OEGylated poly(γ-4-(propargoxycarbonyl)benzyl-L-glutamate) and poly(γ-4-(4-propargoxyphenoxycarbonyl)benzyl-L-glutamate) derived from azido functionalized triethylene glycol monomethylether (**P1-OEG$_3$**), or azido functionalized poly(ethylene glycol) methyl ether 350 (**P1-OEG$_7$** and **P2-OEG$_7$**), exhibited a UCST phase transition in PrOH at a polymer concentration of 1 mg mL^{-1} (Fig. 3A).[93] The T_{CP} decreased with increasing OEG chain length, due to decreased hydrogen-bonding interactions between the OEG pendants and the alcoholic solvent, and increased with the presence of more hydrophobic linkages.

The UCST phase transition of the polypeptides poly(γ-4-(2-(2-methoxyethoxy) ethoxycarbonyl)benzyl-L-glutamate) and poly(γ-4-(2-(2-(2-methoxyethoxy)ethoxy)ethoxycarbonyl) benzyl-L-glutamate) in PrOH was also strongly dependent on the polymer concentration and on the length of both the OEG pendants and of the main chain.[98]

The glycopolypeptide poly(γ-propyl-L-glutamate) tetra-*O*-acetyl-D-(+)-mannopyranoside containing poly(L-glutamate) main-chain and mannose pendants also underwent a UCST phase transition at 58.3 °C in PrOH at a concentration of 1 mg mL^{-1} (Fig. 6).[100]

Furthermore, it has been shown that the non-linear PEG analogue POEGMA exhibited a UCST-type phase transition in PrOH at 29.1 °C at a concentration of 16 mg mL^{-1}, as demonstrated by the measurement of the cloud point values by optical transmission analysis.[82] In another example, poly(2-(2-(2-(2-((tetrahydrofuran-2-yl)oxy)ethoxy)-ethoxy)ethoxy) ethyl methacrylate) (PTFEO$_4$MA) exhibited a UCST behaviour in PrOH with a T_{CP} around 22 °C at a polymer concentration of 1 wt%.[106]

Another poly(methacrylate) exhibiting a UCST behaviour in PrOH is poly(2-hydroxyethyl methacrylate), with T_{CP} shifting to higher values with increased molecular weight and concentration of the polymer in solution.[111]

Finally, poly[*N*-(4-vinylbenzyl)-*N*,*N*-dibutylamine] with a DP of 72 showed a UCST-type behaviour in 1-propanol with a T_{CP} of 48 °C.[112] It has also been demonstrated that the addition of a 10 wt% of cosolvent (*i.e. n*-butanol) to a 2 wt% polymer solution in PrOH resulted in the decrease of the T_{CP} from 48 to 29 °C, while the addition of 10 wt% of nonsolvents (*i.e.* methanol, ethanol, or 2-propanol) led to a rise in the T_{CP} value from 48 to 75 °C.

3.4. Thermoresponsive behaviour in 2-propanol (iPrOH)

The thermoresponsive behaviour of polymers has also been studied in the structural isomer of PrOH, 2-propanol (iPrOH). Examples of thermoresponsive (glycol)polypeptides in iPrOH are present in literature, although this solvent has been less studied than the previously mentioned alcoholic solvents. For instance, a glycopolymer consisting of a poly(γ-propyl-L-glutamate) main-chain and tetra-*O*-acetyl-D-(+)-mannopyranoside side chains underwent a UCST phase transition at 62.2 °C at a concentration of 1 mg mL^{-1}. This thermoresponsive behaviour was attributed to hydrophobic interactions and H-bonding interactions between polymer chains, and the formation of hydrogen bonds between the acetyl groups on the polymer and the OH groups of the solvent, as confirmed by FTIR spectroscopy.[100] As expected, OEGylated polypeptides with different hydrophobic linkage groups (*i.e.* phenyl and benzoic acid phenyl ester linkages) and OEG pendants with different lengths also showed a UCST behaviour in iPrOH at a concentration of 1 mg mL^{-1}, which was strongly influenced by the OEG chain length and the hydrophobicity of the linkage groups.[93]

Apart from OEGylated polypeptides, Pegylated and OEGylated polymers often show thermoresponsive behaviour and, in particular, UCST phase transition in alcoholic media. For instance, the thermoresponsive behaviour of PEG and its analogues has been extensively studied in iPrOH. It has been shown *via* turbidity measurements that a 5 mg mL^{-1} iPrOH solution of PEG homopolymer with a molecular weight of 6 kDa exhibited a UCST-type phase transition at 15.8 °C accompanied by a large hysteresis.[127] In another example, PEG 6 kDa homopolymer synthesised *via* ATRP exhibited a UCST behaviour in iPrOH (C = 0.05 wt%) at 21 and 39 °C during the cooling and heating cycles of transmittance measurements, respectively.[113]

Interestingly, the T_{CP} of PEG could be tuned by blending PEG with poly(acrylic acid) (PEG/PAA), and poly(poly(ethylene glycol) methacrylate) with PAA (PPEGMA/PAA), exhibiting a UCST phase transition in iPrOH, where the PAA alone is insoluble.[113] In both cases, the thermoresponsive behaviour was found to be dependent on the ratio between the polymers (Fig. 13), and on the molecular weight of both the proton acceptor (PEG and PPEGMA) and proton donor (PAA) polymers. In the case of the PEG/PAA blends, the thermoresponsive behaviour was attributed to significant interactions between the H-donor COOH groups of PAA and the H-acceptor oxygen atoms of PEG. The solubility of the polymers blend decreased with decreasing temperature until a critical value was reached at the T_{CP} below which a polymer-rich phase appeared due to the presence of interpolymer H bonding interactions. The temperature-induced behaviour of PPEGMA/PAA blends was attributed to the formation of interpolymer complexes by H bonding interactions between the PAA and the comb-like polymacromonomer brushes bearing short PEG side chains. The solution behaviour of the polymers pairs was also analysed in MeOH/iPrOH mixtures. Since MeOH was a good solvent for all polymers, a decrease in the T_{CP} values with increasing content of MeOH was expected. However, changes in the transition temperature were observed only above 20%v/v MeOH content in iPrOH.

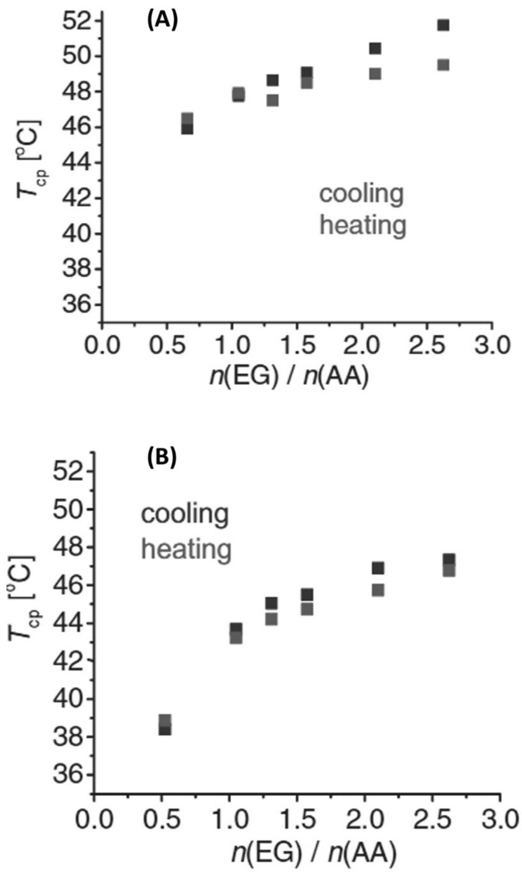


Fig. 13 Cloud point temperatures of (A) PEG/PAA and (B) PPEGMA/PAA solutions in iPrOH as a function of EG : AA monomeric unit molar ratios with 0.0625 wt% PAA concentration. Reproduced from ref. 113 Copyright 2017 WILEY-VCH Verlag GmbH & Co KGaA, Weinheim.

PEG has also been used for the synthesis of more sophisticated architectures showing thermoresponsiveness in iPrOH. As an example, PEG-armed star polymers with Ru(II)-enclosed microgel cores have been synthesised by cross-linking the living PEGMA arms with a dimethacrylate linking agent in the presence of a phosphine-ligand functionalized styrene and $RuCl_2(PPh_3)_3$ as catalyst (Fig. 14).[114] The solution behaviour of the PEGMA prepolymer, PEGMA-methyl methacrylate diblock copolymer (PEGMA-MMA block), and unreacted PEGMA-MMA diblock copolymer containing the ruthenium catalyst (PEG-Ru block), as well as star polymers consisting of only PEG (PEG star), and PEG-Ru star polymers was analysed in iPrOH. The PEG-Ru star polymers exhibited a UCST behaviour at around 31 °C, which was dependent on both the structure and the composition. The star polymers resulted in a higher T_{CP} compared to the linear counterparts due to the higher hydrophobic content (*i.e.* MMA, phosphine, linking agent). Moreover, the introduction of the Ru catalyst resulted in an increase of the UCST for both linear and star polymers.

Among all PEG analogues, the solution behaviour of POEGMA and its copolymers has been extensively investigated in 2-propanol. POEGMA homopolymers bearing a pentafluorophenyl ester end group and a dithioester end group showed UCST phase transitions in iPrOH, which was strongly dependent on the polymer molecular weight and concentration.[82,114,115] The phase transition behaviour was also influenced by the addition of cosolvents and nonsolvents, resulting in an increased polymer solubility and, thus, a decreased T_{CP} when chloroform, a good solvent, was added, and in a lowered solubility and increased T_{CP} when hexane, a non-solvent, was used.[82] In another report, the RAFT copolymerization of OEGMA with the commercially available oligo (ethylene glycol)phenyl ether acrylate (OEGPhA) in different ratios, resulted in the synthesis of a series of thermoresponsive copolymers exhibiting UCST-type behaviour in iPrOH at a concentration of 10 mg mL^{-1}.[83] A linear relationship between the phenyl ether content and the T_{CP} value was found, with T_{CP} increasing from 35.1 to 75.4 °C with increasing OEGPhA

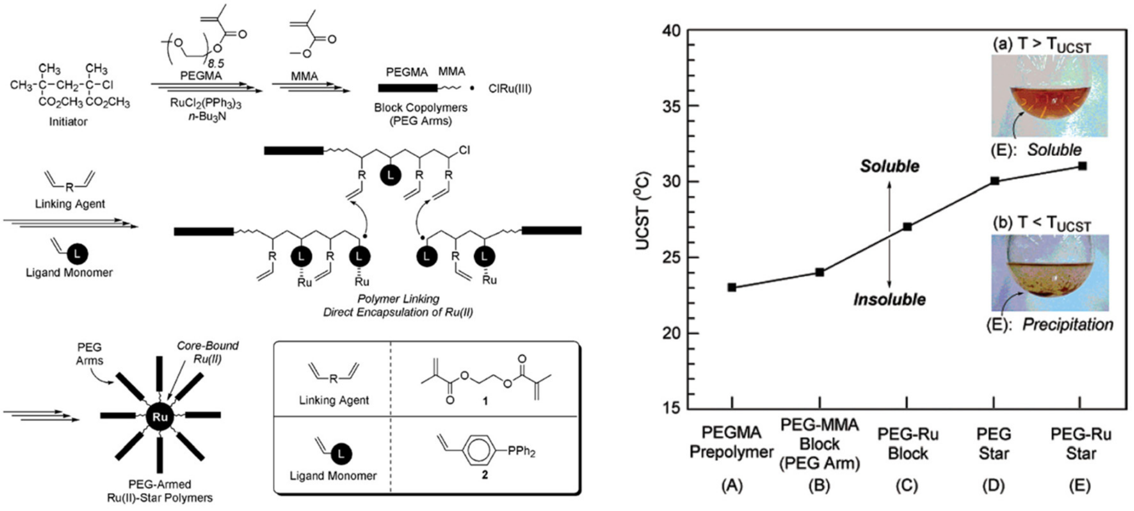


Fig. 14 (Right) Schematic depiction of the synthesis of PEG armed star polymers with Ru(II)-enclosed microgel core *via* Ru(II)-catalysed living radical polymerization. (Left) UCST of 3 wt% solutions of various PEGMA polymers in iPrOH. Inset pictures: (a) PEG-Ru star (E) in iPrOH above UCST, (b) PEG-Ru star (E) in iPrOH below UCST. Adapted from ref. 114 Copyright 2007 American Chemical Society.

content from 21 to 73 mol% due to a decreased solubility of the polymer in the solvent. Furthermore, block copolymers consisting of a POEGMA segment and a PNIPAM (POEGMA-*b*-PNIPAM) or *N*,*N*-diethylacrylamide (PDEAM) block (POEGMA-*b*-PDEAM) exhibited a UCST phase transition in iPrOH, forming micellar aggregates upon cooling, as shown by turbidity and DLS measurements.[115,128]

As previously mentioned for EtOH, a brush copolymer polyampholyte composed of OEGMA, 2-(dimethylamino)ethyl methacrylate and methacrylic acid underwent a UCST temperature induced self-assembly at 50 °C in iPrOH at a concentration of 1 mg mL^{-1}.[107] This behaviour was ascribed to the collapse of the copolymer caused by the strong electrostatic interactions between the opposite charges into nanostructures stabilized by the solvophilic ethylene glycol side chains. By decreasing the temperature to 50 °C, particles of around 35 nm were observed *via* DLS analyses (Fig. 15). However, an increase in the particles size was measured when the temperature was further decreased due to the formation of larger agglomerates caused by a less efficient electrostatic stabilization of the OEG side chains in iPrOH compared to the strong electrostatic attractive interactions between the charges. Additionally, a graft-copolymer consisting of a poly(vinylidene fluoride) backbone and poly(diethylene glycol methyl ether methacrylate) side chains exhibited a UCST-type thermoresponsive behaviour at 27.5 °C in iPrOH at a critical composition of 0.09% (w/v), as shown by DLS measurements.[85]

In another example, poly(2-(2-methoxyethoxy)ethyl methacrylate) ($PMEO_2MA$) and poly(*N*-(4-vinylbenyl)-*N*,*N*-diethylamine) (PVEA) homopolymers showed a UCST-type phase transition in iPrOH, greatly influenced by the polymer DP.[112,123] When $PMEO_2MA$ was polymerised in a diblock manner with PVEA, the resulting diblock copolymer exhibited a UCST phase transition at lower temperatures compared to the one of the $PMEO_2MA$ homopolymer with the same DP, and closer to the one of the PVEA homopolymer. This was attributed to the increased solubility of the $PMEO_2MA$ segment by the highly soluble PVEA block, resulting in a lower T_{CP} than that of the $PMEO_2MA$ homopolymer.[123]

Another ethylene glycol-based polymer exhibiting a UCST thermoresponsive behaviour in iPrOH is poly(2-(2-(2-(2-((tetrahydrofuran-2-yl)oxy)ethoxy)-ethoxy)ethoxy) ethyl methacrylate) with a T_{CP} around 35 °C at a polymer concentration of 1 wt%.[106]

Poly(oligo(ethylene glycol) methyl ether acrylate) (POEGMeA) and its copolymers with oligo(ethylene glycol) phenyl ether acrylate (OEGPhA) are another class of intensively studied PEG analogues. In iPrOH, the (co)polymers exhibited a UCST behaviour with T_{CP} linearly increasing with increased OEGPhA content.[83] In order to elucidate molecular events, a diblock copolymer consisting of a random poly(OEGMeA-*co*-OEGPhA) block comprising 45 mol% of OEGPhA units, and a soluble poly(dimethylacrylamide) segment (pDMA) was synthesised and analysed *via* variable temperature NMR spectroscopy in iPrOD-d8 at a concentration of 20 mg mL^{-1}, in which it exhibited a T_{CP} of 45.2 °C. From the analyses, it has been elucidated that the decrease in solubility in alcohols of polymers containing phenyl groups was caused by a promotion of favourable attractive polymer–polymer interactions and a decreased contribution to mixing entropy due to rigidity and lack of conformational isomers of rigid rings, resulting in the broadening of the insolubility regime of the phase diagrams of the phenyl ether-containing polymers.

Poly(oligo(ethylene glycol) (meth)acrylamide)s are other widely studied biocompatible PEG analogues showing a UCST behaviour in iPrOH, as in the case of poly(oligo(ethylene glycol) acrylamide)s (polyOEGAM) and poly(oligo(ethylene glycol) methacrylamide)s (polyOEGMAM).[127] The T_{CP} values

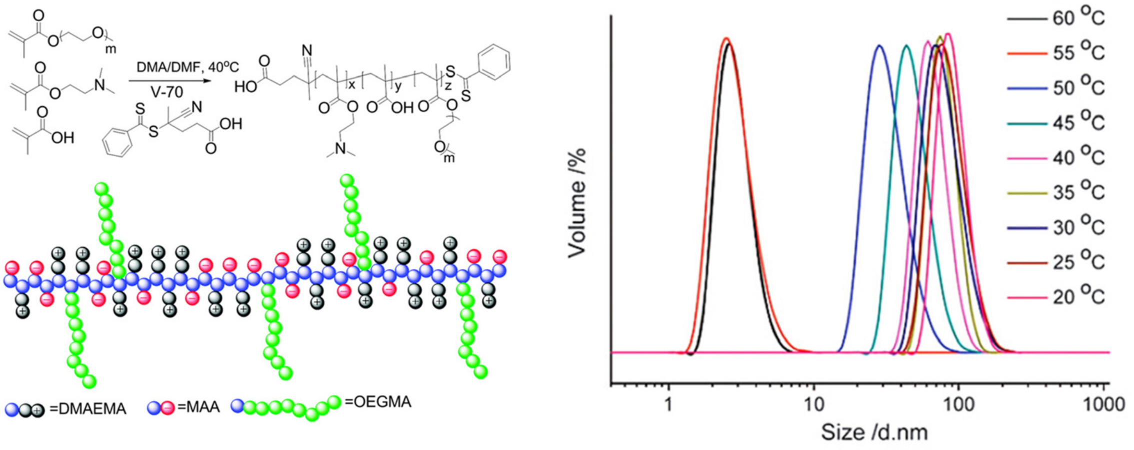


Fig. 15 Chemical structure and size distribution measured by DLS at various temperatures of a 1 mg mL^{-1} iPrOH solution of poly(2-(dimethylamino) ethyl methacrylate-*co*-methacrylic acid)-*graft*-oligo(ethylene glycol) methyl ether methacrylate. Adapted from ref. 107 Copyright 2015 Royal Society of Chemistry.

increased with increasing length of the OEG side chains due to a decreased solubility of the polymer in the alcohol. Moreover, at comparable lengths of the OEG side chains, polyOEGMAMs exhibited higher T_{CP} values compared to polyOEGAMs counterparts.

In a final interesting example, a series of amphiphilic pyrrolidone diblock copolymers consisting of a *N*-(2-methacrylaoyxyethyl)pyrrolidone block with a fixed DP of 37 and a methyl methacrylate segment with a DP between 117 and 230 was able to form thermoresponsive organogels composed of 3D micellar networks in iPrOH (Fig. 16).[116] The organogels underwent a thermoreversible sol–gel transition, which was dependent on the DP of the PMMA block and on the polymer concentration in solution. Because of their biocompatibility and interesting temperature-induced behaviour, these diblock copolymers might be potentially applied in the development of new nanomaterials, in biotechnology, and in transdermal drug delivery.

3.5. Thermoresponsive behaviour in other alcohols

Thermoresponsive polymers have also been investigated in alcohols with slightly longer alkyl chains, such as 1-butanol (BuOH) and its structural isomers, and pentanol (PeOH). As expected, OEGylated polymers have shown thermoresponsive behaviours in these solvents. As an example, POEGMA and its diblock copolymers with PNIPAM or PDEAM exhibited a sharp and reversible UCST phase transition in 1-butanol, which was dependent on both the polymer molecular weight and polymer concentration.[82,115] Experiments in different butanol isomers revealed that branching of the alkyl chains had an effect on the solution behaviour of POEGMA polymers. To exemplify, the T_{CP} value of solutions of a 23.2 kg mol^{-1} POEGMA polymer (C = 16 mg mL^{-1}) decreased from 36.6 °C in BuOH, to 30.4 °C in 2-methyl-1-propanol (iBuOH), to 26.4 °C in 2-butanol (*sec*BuOH), and further to 22.2 °C in 2-methyl-1-butanol. A similar trend was also observed in alcohols with longer chain lengths. Additionally, a linear increase in the T_{CP} with increasing chain length of the alcohol was found, with T_{CP} values ranging from 40.9 °C in 1-pentanol up to 75.4 °C in dodecanol.[82]

(Glyco)polypeptides also show thermoresponsiveness in alcoholic solvents with longer alkyl chains. For example, the T_{CP} values of the glycopolypeptide poly(γ-propyl-L-glutamate) tetra-*O*-acetyl-D-(+)-mannopyranoside conjugate were found to increase with the number of carbon in the alcoholic solvent due to increased hydrophobic interactions and decreased H bonding interactions between the polymer and the solvent molecules, reaching 69.9 °C and 77.9 °C in BuOH and PeOH, respectively.[100] Other polypeptides previously mentioned, such as those obtained by reacting azido functionalized OEG with poly(γ-4-(propargoxycarbonyl)benzyl-L-glutamate) or poly(γ-4-(4-propargoxyphenoxycarbonyl)benzyl-L-glutamate),[93] poly((γ-4-oligo(ethylene glycol) benzyl-L-glutamate)-*random*-(γ-benzyl-L-glutamate)),[110] poly(γ-4-(2-(2-methoxyethoxy) ethoxycarbonyl) benzyl-L-glutamate) and poly(γ-4-(2-(2-(2-methoxyethoxy) ethoxy)ethoxycarbonyl) benzyl-L-glutamate),[98] also showed a UCST phase transitions in both BuOH and PeOH, with T_{CP} values influenced by the OEG chain length and content.

Another thermoresponsive polymer undergoing a phase transition in a series of aliphatic alcohols at high temperatures is poly(2-hydroxyethyl)methacrylate.[111] The solubility of the polymer decreased with increasing molecular weight, which was found to be similar in BuOH and iBuOH (*i.e.* between 60.8 and 73 °C depending on the polymer molecular weight). On the contrary, the solubility of the polymer in glycerol was very low (T_{CP} between 71.8 and 83.6 °C), while it was highly soluble in *sec*BuOH, resulting in a low T_{CP} at around 14 °C.

Finally, comb-like copolymers obtained from the free radical solution polymerization of *n*-octadecyl vinyl ether and *N*-phenyl maleimide underwent a reversible UCST-type behaviour at 67 °C in BuOH at a concentration of 0.1 wt% (Fig. 17).[117] This behaviour was dependent on the polymer concentration and it was ascribed to the aggregation of the

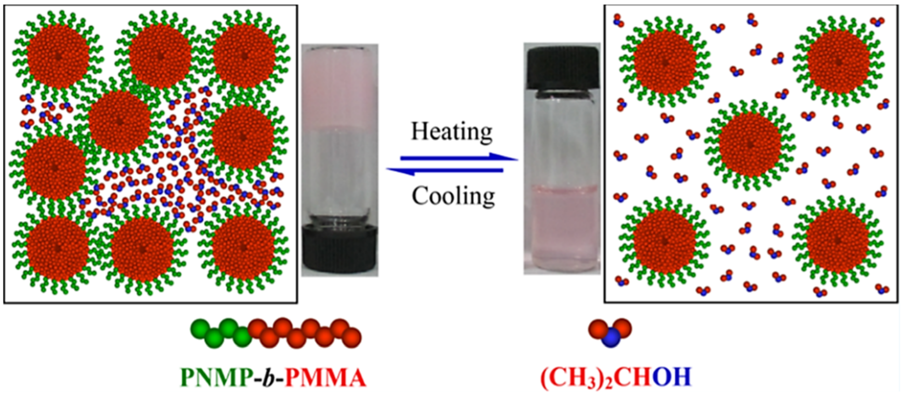


Fig. 16 Proposed mechanism of the thermally-induced sol–gel transition of poly(*N*-(2-methacrylaoyxyethyl)pyrrolidone-*block*-methyl methacrylate) organogels in iPrOH. Reproduced from ref. 116 Copyright 2017 American Chemical Society.

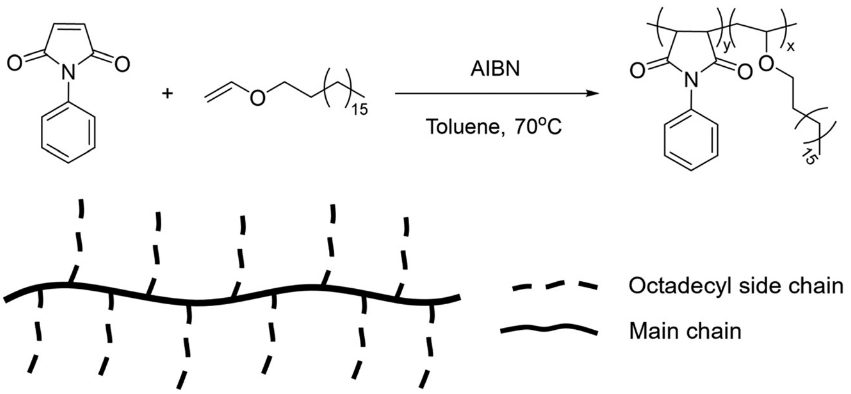


Fig. 17 Schematic representation of the synthetic route and chemical structure of the comb-like copolymers.[117]

long alkyl chains of the vinyl ether monomer at low temperatures. Furthermore, the T_{CP} value decreased with increasing chain length of the alcoholic solvent due to an enhanced solubility of the polymer in longer alkyl chain alcohols, such as 1-hexanol (HexOH) and 1-octanol (OctOH). The T_{CP} in BuOH could be tuned by adding proper co-solvents. In fact, the addition of toluene as good solvent resulted in a decrease in the T_{CP}, while the addition of ethylene glycol as nonsolvent increased the T_{CP}.

The most studied long-chained alcohol for the solution behaviour of polymers is 1-octanol. Based on the thermoresponsive behaviour of POEGMA, its block copolymers with PNIPAM (POEGMA-*b*-PNIPAM) and PDEAM (POEGMA-*b*-PDEAM), and two polymers of POEGMA-*b*-[PNIPAM-*co*-poly(pentafluorophenyl acrylate) poly(pentafluorophenyl acrylate) (POEGMA-*b*-(PNIPAM-*co*-PPFPA))] containing different amounts of PFP ester, formed well-defined spherical inverted micelles in OctOH upon cooling, with T_{CP} values around room temperature, as demonstrated by DLS and UV-vis analyses.[115,128] Interestingly, the PNIPAM and PDEAM blocks did not significantly influence the transition temperature of the final diblock copolymers.

Furthermore, PEG analogues obtained from the post-polymerization of poly(pentafluorophenyl(meth)acrylate) with α-amino, ω-methoxy functionalized di(ethylene glycol), tri(ethylene glycol), and PEG-350, PEG-750 and PEG-5k showed thermoresponsiveness in OctOH.[127] Polymers with long ethylene glycol side chains, longer than PEG-750 for polyacrylamides and longer than tri(ethylene glycol) for polymethacrylamides, underwent a UCST phase transition in OctOH, with T_{CP} values increasing with increased EG length. However, the increase in the EG side chain length also resulted in the broadening of the hysteresis between the heating and cooling transition temperatures of the polymers (Fig. 18). This behaviour was attributed to the PEG analogues behaving as pure PEG in terms of redissolution characteristics when the OEG side chain length was increased.

Cyclic alcohols are not intensively studied in relation to the thermoresponsive behaviour of polymers, indicated by the few reports present in literature. One example is the thermoresponsive behaviour of polystyrene and poly(methyl methacrylate) homopolymers, which exhibited a UCST phase transition in cyclohexanol, with T_{CP} increasing with increasing molecular weight of the polymer, as demonstrated by thermooptical analyses.[118] This behaviour was more accentuated for PS than for PMMA. A diblock copolymer consisting of a PS and a PMMA block exhibited T_{CP} in between those of the two homopolymers

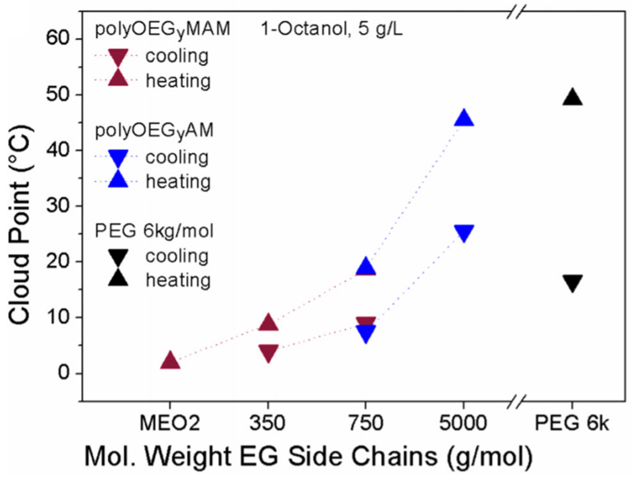


Fig. 18 Cloud points of poly(acrylamide)s (blue), poly(methacrylamide)s (purple) and reference PEG 6k (black) measured during cooling (▼) and heating (▲) OctOH at a polymer concentration of 5 mg mL^{-1}, showing an increased hysteresis with an increase of OEG chain length. Adapted from ref. 127 Copyright 2012 American Chemical Society.

with similar molecular weight. In another example, poly (γ-benzyl L-glutamate) have demonstrated to undergo a reversible sol–gel transition in benzyl alcohol (BnOH), forming crystalline fibrillar aggregates at room temperature and having melting temperatures in the range 60–70 °C depending on the sample preparation.[119]

In this section, we have thoroughly discussed the thermoresponsive behaviour of different classes of polymers in alcoholic solvents with increasing alkyl chain length. Thermoresponsive polymers predominantly exhibit a UCST-type phase transition in pure alcoholic systems, even though a few examples of polymers with a LCST or sol–gel transitions have also been highlighted. As discussed above, the thermoresponsive behaviour of polymers in alcohols is strongly dependent on various parameters, such as polymer composition (*e.g.* DP, functional groups, *etc.*), architecture and concentration, as well as on the choice of the solvent and the addition of cosolvents and nonsolvents in the binary system. By carefully selecting these parameters, a precise tuning of the T_{CP} can be achieved. Although many examples of thermoresponsive polymers in alcoholic solvents are present in literature, their potential applications are still limited. For instance, these polymers are often synthesised and their thermoresponsive behaviour in alcohols studied to gain a fundamental understanding about the structure–properties relationship of specific polymer/solvent systems, and their potential applications, especially in the biomedical field, are not generally discussed or investigated.

4. Hydrocarbons

In the previous sections of this review, the solution behaviour of polymers in aqueous media, alcohol water mixtures, and pure alcohols was discussed. It was further pointed out that macromolecules with thermoresponsive properties are omnipresent for water-based applications. However, pure organic systems are less common, with (aliphatic) hydrocarbons catching even less attention. However, polymers showing a thermoresponsive behaviour in hydrocarbons are gaining an increasing interest especially in the lubricant industry for their application as polymeric oil additives, such as viscosity modifiers, oil thickeners, and friction reducers. Therefore, in this section, we would like to discuss polymer solutions with temperature-induced phase transitions in aliphatic and aromatic hydrocarbons, and in oils in more detail (Table S6†). Representative examples are highlighted in Table 7.

4.1. Thermoresponsive behaviour in aliphatic solvents

Despite the few studies on thermoresponsive polymers in aliphatic solvents, unique solution behaviours and self-assembly of polymers upon changes in temperature have been reported in literature. It has to be noticed that in the case of some solvents, only a few examples have been found in literature. Nevertheless, also in this case, the polymers will be classified based on the solvent, following the order of increasing number of carbons in the aliphatic chain.

Hexane is the shortest aliphatic hydrocarbon that has been used in the study of the temperature-responsive behaviour of polymers.

In a recent example, a phenylacetylene homopolymer having two hydroxyl groups and a chiral pinanyl substituent (Fig. 19) underwent a reversible twist in the conformation from optical inactive *cis*-transoidal to one handed helical *cis*-cisoidal at a critical twisting temperature (CTT) of 3 °C upon heating a 1 mmol L^{-1} hexane solution in the presence of achiral benzyl amine (20 vol%), as shown by absorption and circular dichroism (CD) measurements.[129] Furthermore, copolymers consisting of a chiral unit and an achiral unit, both bearing OH groups, showed a thermotropic twisting behaviour in hexane/benzyl amine with a CTT of 16 °C, which was found to be independent of the polymer concentration. However, this thermoresponsive behaviour was strongly dependent on both the amine concentration and chemical structure, as well as on the composition of the copolymer. The thermoresponsive behaviour was attributed to the release of the amine from the polymer upon heating and the presence of chiral moieties in the polymer, which resulted in the twisting of the polymer in a specific direction, as shown by ^1H NMR analyses.

Linear poly(octadecyl vinyl ether) (poly(ODVE)) obtained *via* living cationic polymerization has also shown a UCST phase transition at around 9 °C in hexane due to the crystallization of the long alkyl side chains, as shown by UV-vis spectrometry measurements of the transmittance of 1 wt% polymer solutions.[109,147]

The solution behaviour of polystyrene homopolymers with different molecular weight distributions has been studied in various aliphatic solvents, such as cyclohexane and methylcyclohexane, using thermooptical analyses (TOA) and cloud point measurements.[21,130] The homopolymers showed both

Table 7 Examples of thermoresponsive polymers in aliphatic hydrocarbons, aromatic hydrocarbons, and oils

Solvent	Type of polymer	Polymer conc.	Phase transition type (Temp. °C)	Ref.
Hexane/achiral benzyl amine	Substituted chiral poly(phenylacetylene)	1 mmol L^{-1}	Conformational transition (@3)	129
Hexane/achiral benzyl amine	Substituted chiral/achiral copoly (phenylacetylene)	1 mmol L^{-1}	Conformational transition (@16)	129
Hexane	Poly(octadecyl vinyl ether)	1 wt%	UCST (~9)	109
Methylcyclohexane	Polystyrene	1–25 wt%	LCST (~215–250), UCST (~35–70)	130
Cyclohexane	Polystyrene	1–25 wt%	LCST (~215–240), UCST (~10–30)	130
Heptane	Polystyrene-*b*-polyisoprene	0.001–10 mg mL^{-1}	Cylinders-to-spheres (~35) and vesicles-to-cylinders transition (~40)	131
n-Octane	Poly(stearyl methacrylate-*b*-3-phenylpropyl methacrylate)	20–30 wt%	Worm-to-sphere transition (~70)	132
Decane	Poly(octadecyl vinyl ether)-*b*-poly(isobutyl vinyl ether)ODVE and IBVE	20 wt%	Sol–gel transition (~17)	109
n-Dodecane	Poly(benzyl methacrylate-*b*-lauryl methacrylate)	5–20 wt%	Worm-to-sphere transition (~50)	133
n-Dodecane	Graft-copolymers with polyolefin backbones and poly(butyl methacrylate-*stat*-lauryl methacrylate) side chains	2 mg mL^{-1}	UCST (~80)	134
n-Dodecane	Poly(lauryl acrylate-*b*-benzyl acrylate)	15 wt%	Worm-to-sphere transition (~15)	135
n-Tetradecane	Poly(stearyl methacrylate-*b*-3-phenylpropyl methacrylate)	20 wt%	Worm-to-sphere transition (~85)	136
n-Hexadecane	Poly(*tert*-octyl acrylamide-*b*-*N*,*N*-dimethylacrylamide)	1.0 wt%	UCST (@55)	137
Isohexadecane	Poly(lauryl acrylate-*b*-benzyl acrylate)	15 wt%	Worm-to-sphere transition (~67)	135
Toluene	Poly(octadecyl vinyl ether)	1 wt%	UCST (~4)	109
Toluene	Poly(3-((4*R*,5*R*)-4,5-bis (hydroxydiphenylmethyl)-2-methyl-1,3-dioxolane-2-yl)propyl acrylate) + chiral effectors	10 mg mL^{-1}	UCST or sol–gel transition (ND)	138
Toluene	Poly(3-((4*R*,5*R*)-4,5-bis (hydroxydiphenylmethyl)-2-methyl-1,3-dioxolane-2-yl)propyl acrylate) + (*S*) or (*R*)-2-methylpiperidine	25 mg mL^{-1}	UCST (~10–30)-LCST (~20–60)-UCST (~45–75)	138
Toluene	Poly(vinyl phenol-*alt*-*N*-octadecyl maleimide)	5 wt%	Sol–gel transition (~RT)	139
1,2,4-Triethylbenzene	Poly(11-(4-((*E*)-4-butylstyryl)phenoxy) undecyl methacrylate)	2 wt%	UCST (@49.7)	140
Dioctyl phthalate, dibutyl phthalate, diethyl phthalate	Poly(styrene-*b*-dimethylsiloxane)	1 wt%	Thermotropic transition (@70)	141
Hydrocarbon oil	Poly(lauryl methacrylate-*b*-styrene-*b*-lauryl methacrylate)	0.1–16 wt%	Swelling of micelles (~80)	142
Mineral oil	Poly(stearyl methacrylate-*b*-benzyl methacrylate)	10 wt%	Vesicle-to-worm transition (@135)	143
Polyalphaolefin	Poly(alkyl methacrylate)s with different alkyl side chain lengths	1 wt%	UCST (0.5–138)	144
Polyalphaolefin	Poly(*n*-butyl methacrylate-*co*-*n*-hexyl methacrylate)-*b*-poly(2-ethylhexyl methacrylate-*co*-lauryl methacrylate)-*b*-poly (*n*-butyl methacrylate-*co*-*n*-hexyl methacrylate)	14.3–15 wt%	Sol–gel transition (~0–63.5)	144
Decamethylcyclopentasiloxane silicone oil	Poly(dimethylsiloxane-*b*-2-(dimethylamino) ethyl methacrylate)	0.25–25 wt%	Worm-to-sphere transition (@32)	145
Yubase-4 oil	Poly(2-stearyl-2-oxazoline-*co*-2-ethyl-2-oxazoline)	5 mg mL^{-1}	UCST (~80–49)	146
Yubase-4 oil	Poly(methacrylic acid-*co*-2-ethylhexyl methacrylate)-*graft*-poly(2-stearyl-2-oxazoline-*co*-2-ethyl-2-oxazoline)	5 mg mL^{-1}	UCST (~40–51)	146

LCST and UCST phase transitions with T_{CP} values strongly influenced by the polymer molecular weight and concentration. The incorporation of polystyrene into more complex architectures, such as star polystyrene polymers, resulted in a temperature-induced phase transition in the same solvent at a concentration of 5 mg mL^{-1}, which was more pronounced for the star polymers compared to the linear analogues, as shown by field-flow fractionation (ThFFF) and DLS analyses.[148]

The copolymerization of styrene into diblock copolymers composed of a polystyrene block of 21.6 kDa and a polyisoprene block of 4.3 or 6 kDa *via* sequential anionic polymerization resulted in copolymers showing a temperature dependant self-assembly behaviour in heptane, a good solvent for

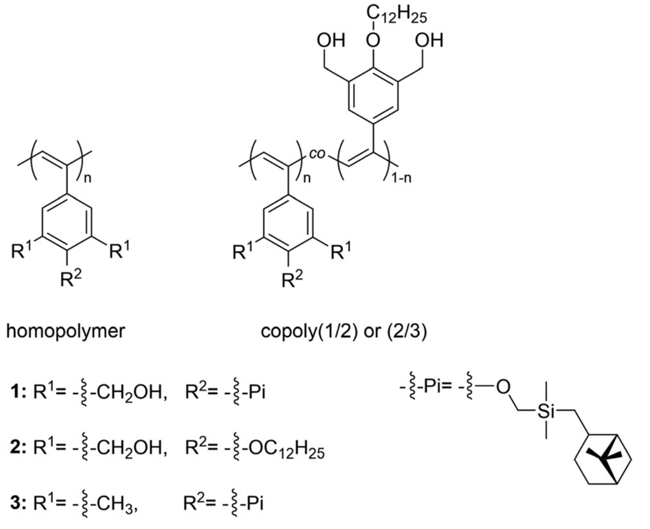


Fig. 19 Schematic depiction of the chemical structure of phenylacetylene homo and copolymers.[129]

the isoprene block.[131] Their thermoresponsive behaviour was studied and visualized by light scattering measurements and atomic force microscopy (AFM) at a concentration range of 0.001–10 mg mL^{-1}. Depending on the length of the isoprene segment, the block copolymers were able to self-assemble into micelles or vesicles at room temperature. Upon heating the mixture to 40 °C, a reversible transition into spherical micelles for the polymer with the shorter polyisoprene segment, and into cylindrical micelles for the longer polyisoprene segment, was observed due to a change in the quality of the solvent, as demonstrated by the calculation of the temperature variation of the second virial coefficient (A_2) for linear polyisoprene in heptane. The initial morphologies were once again obtained upon cooling back to 25 °C. However, it has been noticed that the growth rates of both the cylindrical micelles and the vesicles were slower compared to the rate of dissolution at high temperatures, which was attributed to slow kinetics near the glass transition temperature (T_g).

Macro-chain transfer agents (macro-CTAs) consisting of poly(stearyl methacrylate) homopolymers (PSMA) have been used for the non-polar RAFT dispersion polymerization of 3-phenylpropyl methacrylate (PPPMA) in *n*-octane.[132] At 20 wt%, a series of diblock copolymers showing the full range of morphologies (*i.e.* spheres, cylinders and vesicles) was obtained *via* polymerization induced self-assembly (PISA) by using low DP macro-CTAs (*i.e.* 18 and 19 units of SMA) and by varying the DP of the PPPMA block. The complexity of the nanoparticles increased from spheres to worms to vesicles by increasing the DP of the PPPMA block from 31 to 130, as confirmed by transmission electron microscopy (TEM) studies. By heating the polymer solutions from 25 to 70 °C, block copolymers forming only pure worm phases (*i.e.* $PSMA_{18}$-*b*-$PPPMA_{71}$) could undergo a fast reversible thermally-induced shift from gels to free-flowing solutions due to a worm-to-sphere transition (Fig. 20). This fast morphological transition was facilitated by the change in the relative solvation of the PPPMA core-forming block and by its low T_g.

Block copolymers consisting of a thermoresponsive poly (ODVE) segment with a DP of 200 and a decane-soluble poly (isobutyl vinyl ether) block (DP = 200) were shown to exhibit a thermoreversible sol–gel transition in decane.[109] The polymer solution was a transparent sol at room temperature, and it turned into a stiff opaque gel upon cooling, as demonstrated by dynamic viscoelasticity measurements. Moreover, thermally induced reversible physical gelation was achieved in various organic solvents for different block copolymers by varying the thermosensitive segment corresponding to a solvent.

In another report, sterically-stabilized nanoparticles consisting of a poly(*tert*-octyl acrylamide) segment (DP = 82), and a poly(dimethylacrylamide) block (DP = 150) ($POAAPDMAC_{150}$) directly synthesised in decane *via* PISA underwent a UCST phase transition at 2 °C at a concentration of 1 wt%, as demonstrated by turbidity measurements and DLS analyses.[137]

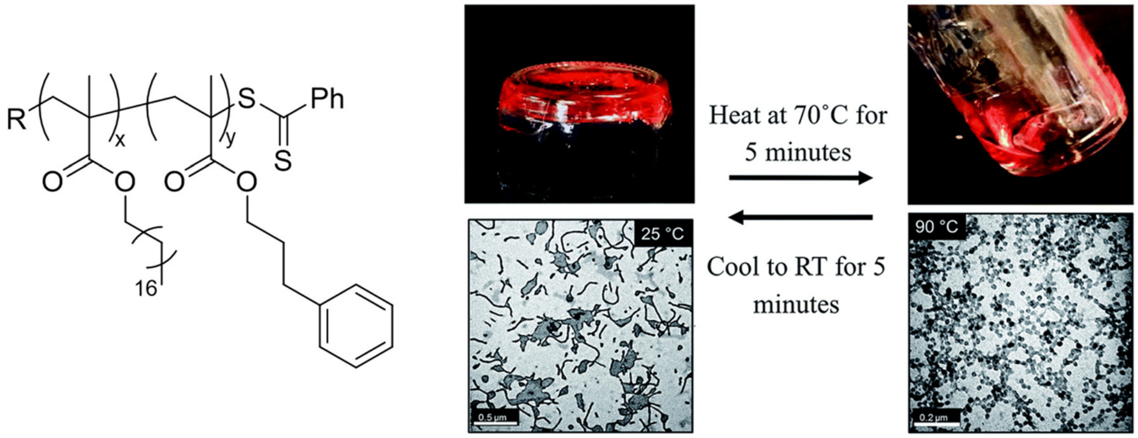


Fig. 20 Chemical structure and digital images showing the reversible, temperature-induced degelation–gelation for the $PSMA_{18}$-*b*-$PPPMA_{71}$ copolymer at 30 wt% in *n*-octane (top), and TEM images of the $PSMA_{18}$-*b*-$PPPMA_{71}$ block copolymer nanoparticles prepared at 30 wt% in *n*-octane (bottom). Reproduced from ref. 132 Copyright 2015 Royal Society of Chemistry.

Interestingly, alternating copolymers of 2-chloroethyl vinyl ether and maleic anhydride showed a LCST behaviour in propyl acetate/*n*-alkanes mixed solvents at a fixed polymer concentration, with T_{CP} values shifting to higher temperatures by increasing the length and the dielectric constant of the *n*-alkane (*i.e.* hexane < octane < decane < dodecane).[149,150] Additionally, a linear relationship between the content of *n*-octane in the mixed solvents and the change in the T_{CP} was observed. The LCST of the alternated copolymer could be tuned from 76.3 to 30.9 °C by increasing the *n*-octane content in the mixed solvents from 6 to 16 wt%, with the T_{CP} decreasing with increasing polymer concentration in the dilute region, and becoming almost constant in the high concentration region.[150]

Among all aliphatic hydrocarbons, *n*-dodecane is probably one of the most studied ones, usually used as model alkane for the evaluation of the properties of potential polymeric oil additives. Diblock copolymers of lauryl methacrylate and benzyl methacrylate (PLMA-*b*-PBzMA) obtained by RAFT polymerization were demonstrated to form spheres, worms or vesicles *via* PISA at 20 wt% solid content in *n*-dodecane at 70 °C when the DP of the PLMA stabilizer block was relatively low.[133] The worm state (*i.e.* $PLMA_{16}$-$PBzMA_{37}$) formed a free-standing gel at 20 °C, which underwent degelation upon heating above 50 °C due to a worm-to-sphere transition. This morphological transition was irreversible for dilute solutions (0.10%w/w), but it became reversible when the polymer concentration was increased up to 20%w/w, as confirmed by TEM images (Fig. 21). The reversible worm-to-sphere transition was attributed to a change in the relative volume fractions occupied by the PBzMA core-forming and stabilizer blocks caused by surface plasticization of the PBzMA block, as confirmed by variable temperature ^1H NMR analyses and small-angle X-ray scattering (SAXS) studies. Two possible mechanisms have been proposed for the observed morphological transition upon heating: (A) the sequential budding of spheres, and (B) a series of random worm cleavages (Fig. 22). However, the appearance of a second minor population of isolated spheres in the TEM image (Fig. 21B, red arrows) suggested that the former mechanism was more likely to occur.[133]

Similarly, poly(alkyl methacrylate)s have been employed to obtain thermoresponsive copolymers with more complex architectures. For example, well-defined graft-copolymers consisting of polyolefin backbones and poly(alkyl methacrylate) side chains have been synthesised *via* a combination of ring-opening metathesis polymerization of cyclic monomers (*i.e.* cyclooctene COE, 3-ethyl cyclooctene EtCOE, and α-bromoisobutyrate functionalized *cis*-cyclooctene BrICOE), ATRP of the alkyl methacrylates (*i.e.* butyl methacrylate BuMA, and lauryl methacrylate LMA), and subsequent hydrogenation

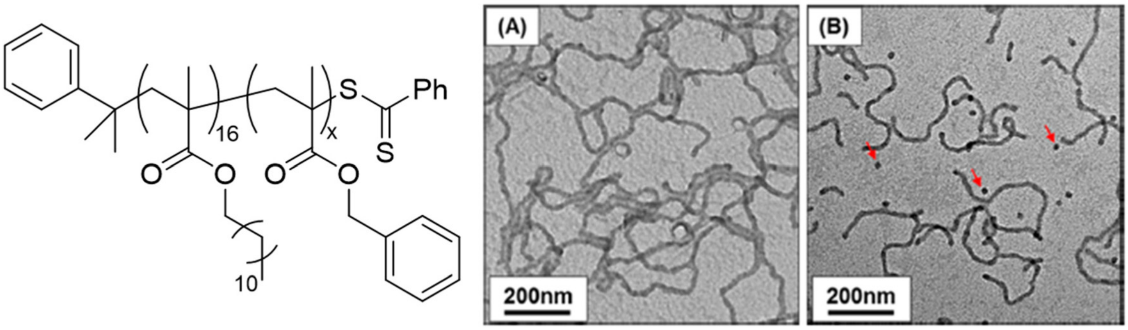


Fig. 21 Chemical structure and TEM images showing the thermoreversible morphological transition of a 20%w/w $PLMA_{16}$-$PBzMA_{37}$ worm gel diluted to 0.01% w/w solid prior to prepare the TEM grids, at (A) 20 °C, and (B) after heating to 90 °C and cooling back to 20 °C. Reproduced from ref. 133 Copyright 2014 American Chemical Society.

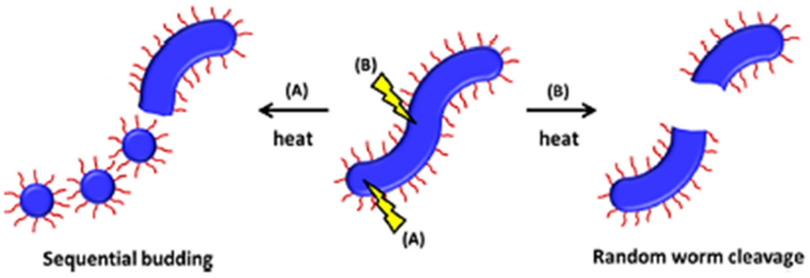


Fig. 22 Schematic representation of the two possible mechanisms for the worm-to-sphere transition of a $PLMA_{16}$–$PBzMA_{37}$ diblock copolymer dispersion in *n*-dodecane upon heating: (A) sequential budding of spheres, and (B) random worm cleavage. Reproduced from ref. 133 Copyright 2014 American Chemical Society.

of the unsaturated backbone.[134] The graft-copolymers having a COE backbone containing 8 mol% of BrICOE and side chains with a [LMA] : [BuMA] molar ratio of 39 : 61 ($L_{40}B_{60}$-C50) showed a UCST-type phase transition in *n*-dodecane. As suggested by SANS measurements, clusters containing methacrylate-rich domains were observed at low temperatures due to the low solubility of the side chains in the solvent, while the high temperature favoured the "deaggregation" into individual polymer chains due to an increase in the solubility of the methacrylate side chains.

By changing the methacrylate backbone into the acrylate counterpart, a series of all-acrylic poly(lauryl acrylate)-*block*-poly(benzyl acrylate) (PLA-*b*-PBzA) diblock copolymers was synthesised *via* RAFT polymerization in aliphatic hydrocarbon solvents.[135] The whole range of morphologies (*i.e.* spheres, worms, and vesicles), confirmed by conventional TEM, DLS and cryo-TEM, was obtained by PISA depending on the polymer concentration, DP of the core and stabilizer blocks, as well as on the choice of the solvent (Fig. 23). For 15%w/w PLA_{14}-$PBzA_{60}$ dispersions in both *n*-dodecane and isohexadecane, the formation of a free-standing gel at 20 °C was observed. The gel underwent a worm-to-sphere transition when the temperature was increased up to 80 °C. Additionally, as demonstrated by rheology measurements, the copolymer presented a second critical gelation temperature upon cooling below 15 °C, which was attributed to the stiffening of the worms on approaching the T_g of the benzyl acrylate block.

In another report, sterically-stabilized nanoparticles consisting of a poly(*tert*-octyl acrylamide) segment (DP = 85), and a poly(dimethylacrylamide) block (DP = 150) directly synthetized in dodecane *via* PISA exhibited a UCST-type phase transition with a T_{CP} of 27 °C. This behaviour was attributed to the poor solvation of the poly(*tert*-octyl acrylamide) stabilizer block in the hydrocarbon at lower temperatures.[137]

Poly(ε-allyl-ε-caprolactone) (PCL) synthesised *via* ROP using $Mg(BHT)_2(THF)_2$ and post-polymerized *via* photoinitiated thiol–ene addition using a series of commercially available alkyl thiols (*i.e.* 1-hexanethiol, 1-octanethiol, 1-ethyl hexanethiol, 1-decanethiol, 1-dodecanethiol, and 1-hexadecanethiol) was also found to be thermoresponsive in *n*-dodecane.[151] The alkyl-functionalized polymers exhibited a UCST phase transition, which was dependent on the length of the alkyl thiol and the polymer concentration. The increase in the alkyl chain length on the PCL backbone from C6 to C12 resulted in an enhancement of its solubility in the hydrocarbon, and the polymers became semi-crystalline when the alkyl chain length reached 10 carbons, as demonstrated by DLS and UV-vis analyses.

Interestingly, the possibility of using temperature as stimulus to control the foamability of an emulsion system in *n*-dodecane/water has also been investigated.[152] In this example, a system composed of four components, *n*-dodecane and aqueous 0.3 M $NaNO_3$ solution (1 : 1), tetraethylene glycol monododecyl ether (surfactant), and azobenzene randomly modified poly(acrylic acid sodium salt) (1 mol% modification) as the amphiphilic photoresponsive polymer (PRP), was studied as a "proof-of-principle" for the design of stimuli-responsive foams. The surfactant could stabilize both direct and inverse emulsions below and above the phase inversion temperature (PIT). Above the PIT, a decreased foamability was observed, which was attributed to an increased ability of emulsion drops to enter the air–water interface due to the different interfacial organization. The foamability was recovered by decreasing the temperature below the PIT.

The temperature-responsive solution behaviour of polymers in longer aliphatic hydrocarbon has also been investigated, even though only a few studies are present in literature. For example, the thermoresponsive behaviour of diblock copolymers of 3-phenylpropyl methacrylate (PPMA) and stearyl methacrylate (SMA) obtained *via* RAFT dispersion polymerization in *n*-tetradecane using SMA homopolymers as macro-CTAs has been evaluated.[136] At 20 wt% solids, nanoparticles with spherical, worm and vesicular morphologies were obtained *in situ* by employing a PSMA macro-CTA with a fixed DP of 19 ($PSMA_{19}$), which was chain extended with PPMA ($PPPMA_x$). To exemplify, the diblock copolymer consisting of a $PSMA_{19}$ segment and a $PPPMA_{85}$ block was able to form a soft physical gel at 20 wt% solids at ambient temperature due to worm nanoparticle entanglements. Also in this case, the gel underwent degelation upon heating up to 95 °C. This process was completely reversible, and it was attributed to a worm-to-sphere transition

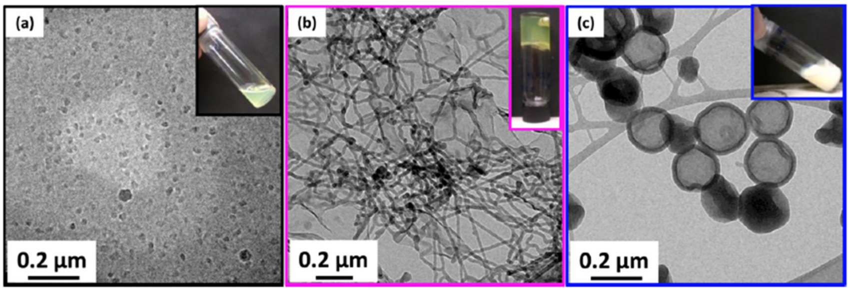


Fig. 23 Cryo-TEM images of poly(lauryl acrylate)-*block*-poly(benzyl acrylate) copolymers in *n*-heptane, forming (a) spheres, (b) worms, and (c) vesicles depending on the polymer concentration and DP of the blocks. Digital photographs of the concentrated dispersions are also shown. Reproduced from ref. 135 Copyright 2015 American Chemical Society.

caused by an increase in the solvation of the core-forming PPPMA block, as confirmed by DLS and TEM analyses.

Finally, nanoparticles consisting of block copolymers of *tert*-octyl acrylamide (DP = 85) and dimethylacrylamide (DP = 150) obtained *via* PISA showed a UCST-type phase transition in *n*-tetradecane and *n*-hexadecane, which was attributed to the poor solubility of the *tert*-octyl acrylamide block in the hydrocarbons at lower temperatures.[137]

4.2. Thermoresponsive behaviour in aromatic solvents

Aromatic hydrocarbons have also been employed for the evaluation of the thermoresponsive behaviour of polymers. Among all, toluene is the most studied one. Linear poly(octadecyl vinyl ether) and linear poly(2-(4-biphenyloxy)ethyl vinyl ether) (poly(BPOVE)) underwent a UCST phase transition in toluene around 4 °C and 12 °C, respectively.[109] As explained above, the UCST phase transition of poly(ODVE) was due to the crystallization of the long alkyl chains (Fig. 24), while the solution behaviour of poly(BPOVE) was caused by the strong interactions between the liquid crystalline mesogenic structures.

Furthermore, it has been shown that a partially fluorinated poly(vinyl ether), namely poly[2-(4,4,5,5,6,6,7,7,7-nonafluoroheptyloxy)ethyl vinyl ether] (poly(9FVE)), synthesised by living cationic polymerization exhibited a UCST-type phase transition in toluene, with the polymer solution being completely transparent at 70 °C, and becoming heterogeneous at 69 °C, as demonstrated by a sharp drop in transmittance in the transmittance *vs.* temperature plot.[153] The polymer thermoresponsiveness was completely reversible with little hysteresis, and it was strongly dependent on the balance between polymer-solvent and polymer–polymer interactions based on their affinity towards each other.

In another report, poly(3-((4*R*,5*R*)-4,5-bis(hydroxydiphenylmethyl)-2-methyl-1,3-dioxolane-2-yl)propyl acrylate) (poly(T5)) synthesised *via* ATRP containing *α*,*α*,*α*′,*α*′-tetraaryl-2,2-disubstituted 1,3-dioxolane-4,5-dimethanol (TADDOL) moiety in the side chains exhibited single or triple thermoresponsive behaviour in toluene in the presence of chiral guests as effectors (Fig. 25).[138] The addition of hydrogen bond acceptors or donors, such as camphor, methanol and borneol, resulted in single thermoresponsiveness, while the addition of quinine, containing four hydrogen bonding sites, led to a sol–gel transition due to the bonding of multiple polymer chains, inducing gelation of the polymer.

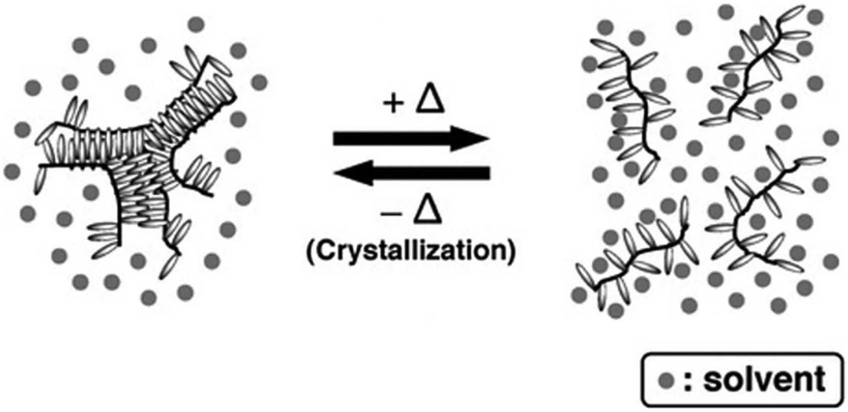


Fig. 24 Schematic depiction of the UCST phase transition of poly(ODVE) caused by the crystallization of the long alkyl chains. Adapted from ref. 109 Copyright 2008 Wiley Periodicals, Inc.

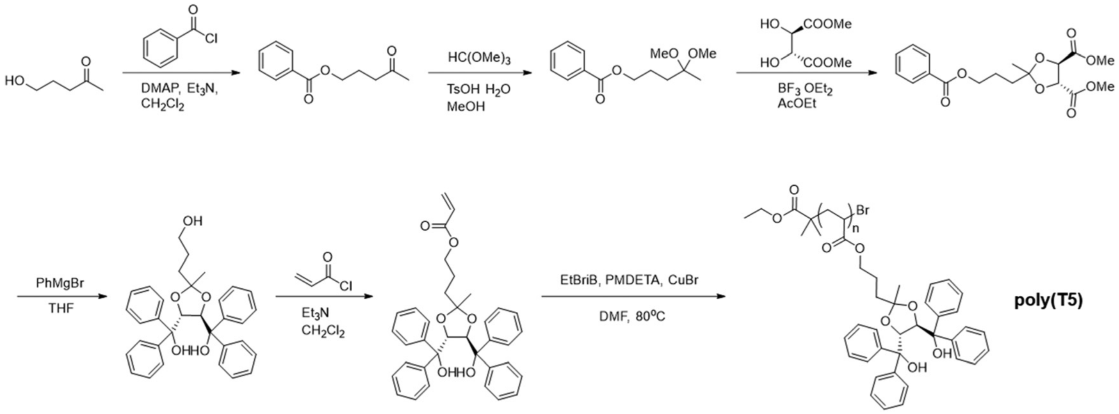


Fig. 25 Schematic depiction of the synthesis of poly(3-((4*R*,5*R*)-4,5-bis(hydroxydiphenylmethyl)-2-methyl-1,3-dioxolane-2-yl)propyl acrylate) (poly(T5)).[138]

Interestingly, a triple thermoresponsive behaviour was observed in the presence of (*S*) or (*R*)-2-methylpiperidine.[138] Upon heating, the polymer solution underwent a UCST phase transition, followed by a LCST transition and again by a UCST transition. This unique triple thermoresponsiveness was attributed to the formation of multiple supramolecular complexes between the host polymer and the guest molecules, and it was dependent on the stoichiometry change between the host and the guest, and the concentration of both the polymer and the effector, as demonstrated by transmittance, DLS, and NMR studies (Fig. 26). This supramolecular strategy is believed to be of importance for the design of highly ordered responsiveness of functional polymer materials.

Alternating copolymers of vinyl phenol and alkyl-substituted maleimide with an appropriate alkyl chain length also exhibited interesting thermoresponsive behaviours in toluene (Fig. 27).[139] A 1 wt% poly(vinyl phenol-*alt*-*N*-dodecyl maleimide) (50 : 50) solution showed a UCST-type phase transition at around 60 °C in toluene, and a sol–gel transition around room temperature when the polymer concentration was increased to 5 wt%. Comparatively, a 50 : 50 poly(vinyl phenol-*alt*-*N*-octadecyl maleimide) exhibited a reversible sol–gel transition in toluene around room temperature at both analysed polymer concentrations. The two copolymers underwent a sol–gel transition also in other aromatic solvents, such as anisole, *p*-cymene, cumene, 1,2,4-trichlorobenzene, and nitrobenzene at a concentration of 5 wt%. This thermoresponsive behaviour was attributed to hydrogen bonding interactions between phenol units, which became weaker on heating, resulting in the temperature-induced phase transition, as shown by variable temperature ^{1}H NMR measurements. Moreover, it was demonstrated that the transition temperature was dependent on the molecular weight of the alternating copolymer as well as on the amount of phenol groups in the polymer chains.

In another report, the solution behaviour of the liquid crystalline polymer poly(11-(4-((*E*)-4-butylstyryl)phenoxy)undecyl methacrylate) (PMAS) synthesised by RAFT polymerization was evaluated in both toluene and 1,2,4-triethylbenzene.[140] The polymer exhibited a UCST phase transition at 26.3 and 49.7 °C in 2 wt% polymer solutions in toluene and 1,2,4-triethylbenzene, respectively, characterized by a large hysteresis. The thermoresponsive behaviour was dependent on both the polymer concentration and molecular weight. Scanning electron microscopy (SEM) and TEM imaging of the PMAS at temperatures above and below the UCST, and the investigation of the polymer after dimerization with stilbene using UV light

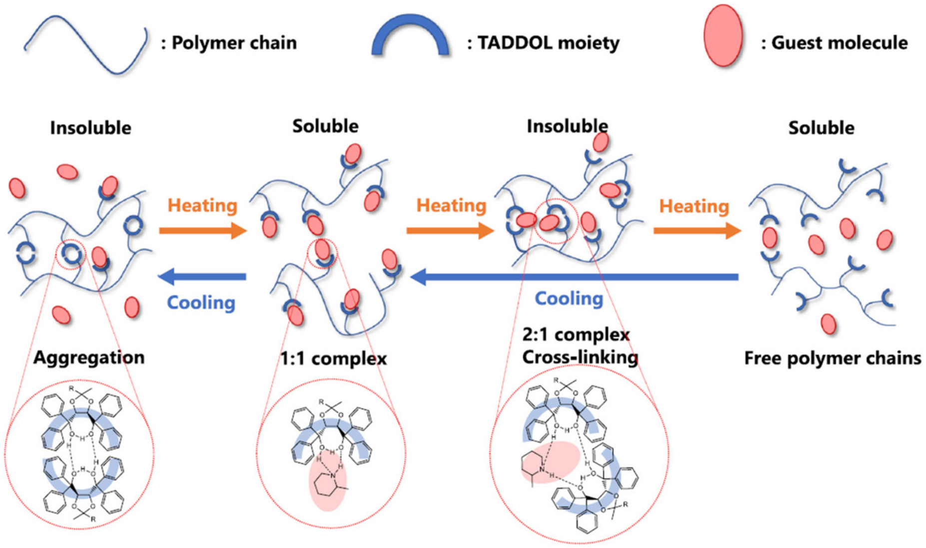


Fig. 26 Schematic depiction of the process of the schizophrenic thermoresponsive behaviour of poly(T5) in presence of (*S*) or (*R*)-2-methylpiperidine in toluene. Reproduced from ref. 138 Copyright 2020 American Chemical Society.

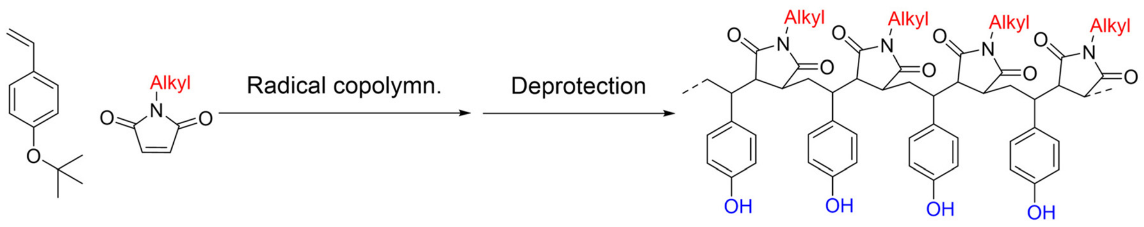


Fig. 27 Schematic depiction of the synthesis of alternating copolymers of vinyl phenol and alkyl substituted maleimide.[139]

irradiation confirmed that the thermoresponsive behaviour was driven by the crystallization of PMAS in the evaluated solvents.

Poly(γ-benzyl-L-glutamate) homopolymers synthesised *via* nickel-mediated ROP formed thermoreversible gels in toluene with gel–sol transition temperature between 48 and 53 °C depending on the polymer molecular weight and concentration.[154] From TEM and AFM imaging, it has been demonstrated that gels formed at a very low concentration (0.05 wt%) consisted of spherical aggregates sticking together, with thin nanofibers radiating from them. The increase in the polymer concentration resulted in the formation of a self-supportive gel with a nanofiber 3D network.

The effect of the addition of a second solvent on the thermoresponsive behaviour of polymer solutions in toluene has also been studied. For example, poly[2-(vinyloxy)-ethyl-1-butylimidazolium chloride] (poly([BuIm][Cl])) bearing imidazolium pendants underwent a LCST-type phase transition at around 60 °C in a mixture of toluene/1-butanol (90/10% w/w), which was induced by the addition of the good solvent, 1-butanol, in the nonpolar solvent, toluene.[155] It was demonstrated by ^{1}H NMR and differential scanning calorimetry (DSC) measurements that, at low temperatures, the interactions between the polymer pendants and the alcohol resulted in the polymer solubilization, while the increase in temperature led to the weakening of the aforementioned interactions resulting in favoured counter anion-induced pendant–pendant interactions and, eventually, in the phase separation.

Furthermore, a reversible twist in the conformation from optical inactive *cis*-transoidal to *cis*-cisoidal has been reported for a phenylacetylene homopolymer having two hydroxyl groups and a chiral pinanyl substituent in toluene/2-amino-1-butanol and toluene/DMSO mixtures (4/1 v/v) upon a change in temperature.[129]

The thermoresponsive behaviour of polymers in aromatic solvents has been further investigated with polystyrene block copolymers. A poly(styrene-*b*-dimethylsiloxane) diblock copolymer with block molecular weights of 4 and 12 kDa, respectively, was synthesised *via* anionic polymerization in a series of styrene-selective dialkyl phthalates: dioctyl phthalate (DOP), dibutyl phthalate (DBP), and diethyl phthalate (DEP).[141] The increase in the selectivity of the mixed solvent at room temperature resulted in a change in the morphology of the equilibrium micelles from spheres (DOP) to cylinders (DBP) to vesicles (DEP). By increasing the temperature above 70 °C, the selectivity of the solvent decreased, leading to a reverse transition from cylinders to spheres in DBP, and from vesicles to cylinders to spheres in DEP. These thermotropic transitions were dependent only on the thermodynamic interactions between the solvent and the blocks in the copolymer, which could be varied by changing the nature of the solvent or the temperature.

4.3. Thermoresponsive behaviour in oils

The thermoresponsive behaviour of polymers has been investigated also in more complex alkane mixtures. For example, poly(lauryl methacrylate-*block*-styrene-*block*-lauryl methacrylate) (PLMA-*b*-PS-*b*-PLMA) gradient copolymers synthesised *via* nitroxide-mediated radical polymerization (NMP) were able to form spherical colloidal micelles in a commercially available hydrocarbon oil, as shown by SAXS measurements.[142] These micelles, consisting of a pure PS core, an interfacial layer of mixed PS and PLMA, and a pure PLMA corona, swelled upon heating due to the gradual solubilization of the domains in which the two monomers were mixed. On the one hand, the high incompatibility of the PS core with the oil resulted in no swelling and hindered plasticization. On the other hand, the increase in temperature led to the extension of the PLMA corona and in the solubilization of the mixed layer, resulting in the micelles swelling.

Another example is the thermally induced morphological transition of diblock copolymer vesicles consisting of stearyl and benzyl methacrylates formed *via* PISA in mineral oil.[143] At appropriate block length, the diblock copolymers underwent a vesicle-to-worm phase transition upon heating from 20 to 150 °C, as assessed by TEM, SAXS, rheology and variable temperature ^{1}H NMR studies. The latter technique showed that at elevated temperatures, the BMA core-forming block was better solvated, resulting in a change in the preferred morphology of the diblock copolymer *via* surface plasticization. SAXS studies also indicated that on average, three worms were formed per vesicle.

Similarly, a UCST-type behaviour in polyalphaolefin (PAO) was observed for homopolymers and random copolymers of alkyl methacrylates with an appropriate alkyl pendant length (Fig. 28).[144] It has been shown that the T_{CP} was strongly dependent on the number of carbon atoms in the alkyl pendant groups for polymers with a similar DP: the longer the alkyl side chain, the lower the UCST in PAO. For instance, the T_{CP} could be tuned from 0.5 °C to 138 °C by decreasing the number of carbons in the alkyl side chains from 8 to 4. Additionally, a series of ABA triblock copolymers containing a PAO-philic middle block (*i.e.* 2-ethylhexyl methacrylate and lauryl methacrylate copolymers) and temperature-responsive outer blocks (*i.e.* *n*-butyl methacrylate and *n*-hexyl methacrylate copolymers) synthesised by RAFT polymerization using a difunctional chain transfer agent, showed a reversible thermally-induced sol–gel transition in PAO (Fig. 28). This transition could be efficiently tuned from around 0 to 63.5 °C by varying the composition and length of the blocks, as well as the polymer concentration in solution.[144]

Furthermore, linear polydimethylsiloxane-poly(2-(dimethylamino)ethyl methacrylate diblock copolymers formed a well-defined worm phase at 25% w/w in decamethylcyclopentasiloxane (D5) silicone oil.[145] The worms underwent a worm-to-sphere transition upon heating up to 100 °C. This change in morphology was driven by a reversible solvent plasticization of the poly(2-(dimethylamino)ethyl methacrylate cores, as shown by TEM, variable temperature ^{1}H NMR, DLS, and SAXS experiments. It has been observed by both oscillatory rheology studies and shear-induced polarized light imaging measurements that the degelation occurred at around

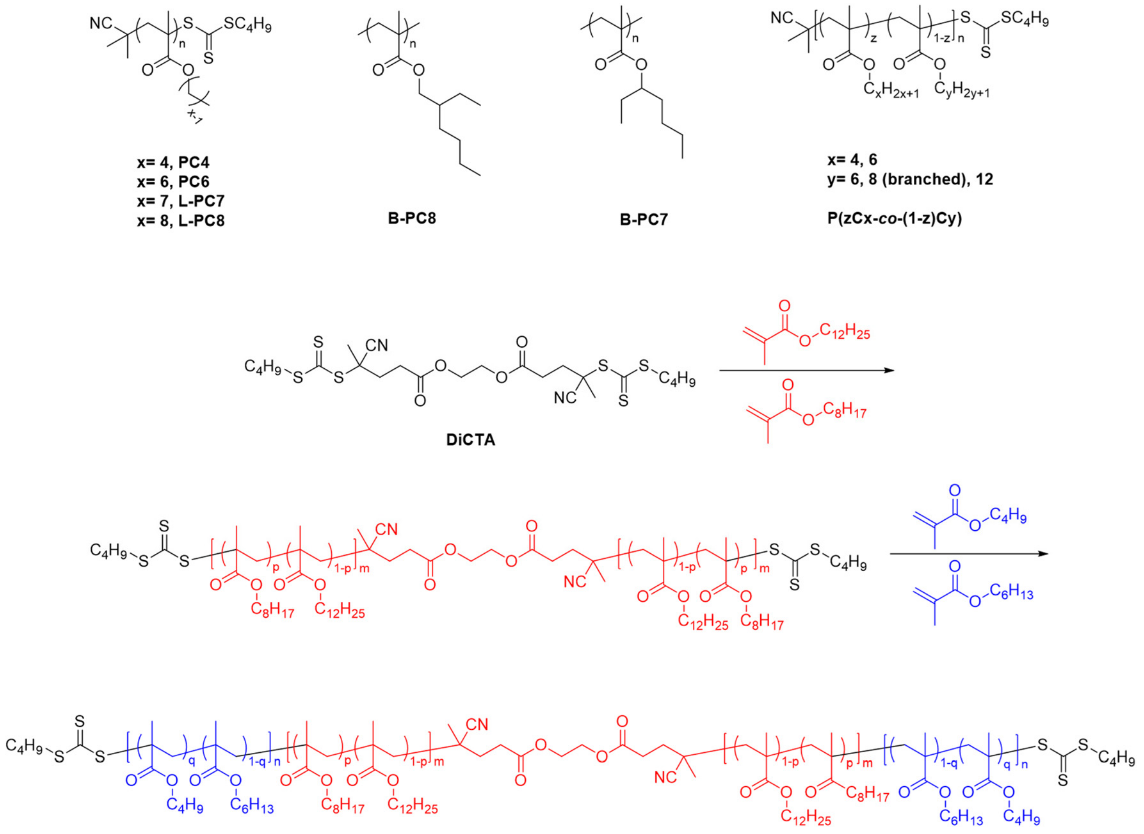


Fig. 28 Schematic depiction of the chemical structure of homopolymers and random copolymers of alkyl methacrylates with linear and branched alkyl side chains (top), and synthetic route of ABA triblock copolymers composed of a PAO-philic middle block and two thermoresponsive outer blocks (bottom).[144]

32 °C, while the full worm-to-sphere conversion required higher temperatures (~110 °C). The thermoresponsive behaviour of the worms upon the addition of a cross-linker was also evaluated. TEM analyses showed that the covalently-stabilized worms failed to undergo the worm-to-sphere transition when heated to 100 °C.

In another report, linear random copolymers of 2-ethyl-2-oxazoline (EtOx) and 2-stearyl-2-oxazoline (SteOx) obtained *via* cationic ring opening polymerization (CROP) characterized by different ratios between the two monomers exhibited a UCST-type phase transition in Yubase-4 oil.[146] The solution behaviour was attributed to the packing of the long alkyl chains of the SteOx units, and the T_{CP} values of the copolymers could be tuned by varying the ratios between the two monomers. Moreover, DSC analyses demonstrated the presence of exothermic crystallization peaks for all copolymers, and the resulting crystallization temperatures (T_c) could be correlated with the T_{CP} values obtained by transmittance measurements. It has been shown that by increasing the overall order of the copolymer structure (*i.e.* copolymer composition), an increase in the T_c and T_{CP} values in oil was observed due to a better alignment of the polymer chains, which could pack and form crystalline areas. Furthermore, graft copolymers consisting of a methacrylic acid-*co*-2-ethylhexyl methacrylate backbone and SteOx-*co*-EtOx side chains, obtained *via* the grafting-onto method (Fig. 29), also exhibited a UCST solution behaviour, which was found to be dependent on various parameters, such as the conversion, DP, and composition of the side chains, as well as on the grafting density. Also in this case, it was possible to correlate the T_c values obtained *via* DSC measurements with the T_{CP} values determined by transmittance measurements.

In this section, the temperature-induced phase transitions of polymers in aliphatic and aromatic hydrocarbons as well as complex alkane mixtures have been meticulously described. In these solvents, polymers mainly exhibit UCST-type solution behaviours and sol–gel transitions caused by their self-assembly in solution, but a few examples of LCST and triple thermoresponsiveness are also present in literature. Furthermore, other interesting phenomena include conformational transitions and controlled foamability upon changes in temperature. The thermoresponsive behaviour could be tuned not only by the structural and chemical characteristics of the polymers, but also by the addition of solvents, effectors, and other small molecules, which could trigger and vary the temperature-induced behaviour. This class of polymers have gained an increase interest especially for their possible application in the lubricant industry for the production of oil additives.

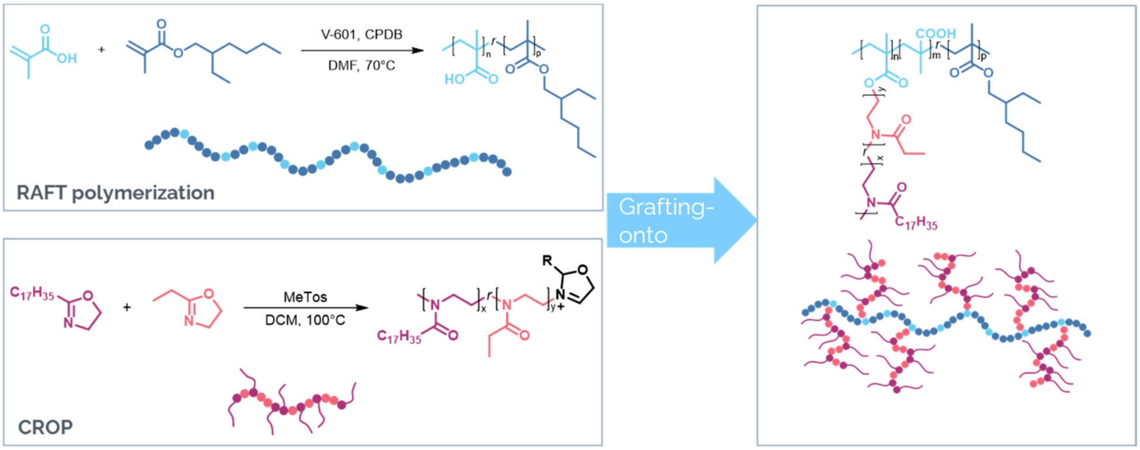


Fig. 29 Schematic representation of the synthetic route used to synthesize graft copolymers consisting of a methacrylic acid-*co*-2-ethyhexyl methacrylate backbone and SteOx-*co*-EtOx side chains.[146]

5. Halogenated solvents

In this section, the thermoresponsive behaviour of polymers in halogenated solvents will be described in detail. Although halogenated solvents have not been intensively investigated in relation to thermoresponsive polymers, in the few examples presented in the literature, it has been demonstrated that polymers have interesting temperature-responsive solution behaviours in these solvents (Table 8 and Table S7†).

Among all halogenated solvents, chlorinated solvents and, especially, chloroform ($CHCl_3$), are the most studied in relation to the temperature-induced solution behaviour of polymers. As discussed above, poly(ODVE) showed a UCST-type phase transition in hexane due to the crystallization of the long alkyl side chains. In a similar fashion, the miscibility

Table 8 Representative examples of thermoresponsive polymers in halogenated solvents

Solvent	Type of polymer	Polymer conc.	Phase transition type (Temp. °C)	Ref.
$CHCl_3$	Poly[2-(vinyloxy)-ethyl-1-butylimidazolium chloride]	2 wt%	LCST (@30)	155
$CHCl_3$	Poly[2-(4,4,5,5,6,6,7,7,7-nonafluoroheptyloxy)ethyl vinyl ether]	1 wt%	UCST (~20)	153
$CHCl_3$	Poly(isobutyl vinyl ether)-*b*-(2-(4,4,5,5,6,6,7,7,7-nonafluoroheptyloxy) ethyl vinyl ether)	0.5 wt%	Self-assembly (~25)	153
$CHCl_3$	Poly(isobutyl vinyl ether)-*b*-(2-(4,4,5,5,6,6,7,7,7-nonafluoroheptyloxy) ethyl vinyl ether)	20 wt%	Sol–gel transition (~25)	153
$CHCl_3$ (+2%EtOH)	Chiral-polymeric ionic liquids (CPILs) with benzyl *N*-substituent and an imidazole derived from (L)-valine	0.5 mg mL^{-1}	LCST (@48.5)	156
$CHCl_3$	CPIL-stabilized AuNPs	1 mg mL^{-1}	LCST (@31)	156
$CHCl_3$	Poly(7-methacryloyloxycoumarin)	0.1 wt%	LCST (@28)	157
$CHCl_3$	Poly((−)-3-methoxycarbonyl-5-(*N*-methyl-*N*-(*S*)-(1-phenylethyl) carbamoyl)phenylacetylene)	0.0001 mol L^{-1}	*cis–trans* isomerization (~15–20)	158
DCM	Poly(7-methacryloyloxycoumarin)	0.3wt%	LCST (~39)	157
DCM	Poly(3-((4*R*,5*R*)-4,5-bis(hydroxydiphenylmethyl)-2-methyl-1,3-dioxolane-2-yl)propyl acrylate)	10 mg mL^{-1}	UCST (~43)	138
DCE	Poly(2-(3-butylureido)propyl acrylate) + effectors	25 mg mL^{-1}	LCST (@43–57) and UCST (@32–71)	159
DCE	Poly(3-(3-butylureido)propyl acrylate) (PUA) + effector	25 mg mL^{-1}	LCST (~33) and UCST (~38)	160
DCE	Poly(3-(3-butylureido)propyl methacrylate (PUMA) + effector	25 mg mL^{-1}	LCST (~30) and UCST (~24)	160
DCE	Poly(3-(3-butylureido)propyl vinyl ether) (PUVE) + effector	25 mg mL^{-1}	LCST (~47) and UCST (~20)	160
DCE	Poly((1-pyrene)methyl acrylate) + effectors	10 mg mL^{-1}	LCST (@43)	161
1,1,2-Trichloroethane	Poly(7-methacryloyloxycoumarin)	0.3 wt%	LCST (ND)	157
o-Dichlorobenzene	Poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-*alt*-(3,3‴-di(2-octyldodecyl)-2,2′,5′,2″,5″,2‴-quaterthiophen-5,5‴-diyl)]	5 mg mL^{-1}	Disaggregation (~75)	162
Perfluoro (methylcyclohexane)	Poly[2-(4,4,5,5,6,6,7,7,7-nonafluoroheptyloxy)ethyl vinyl ether]	1 wt%	UCST (~10)	153
Perfluorodecalin	Poly[2-(4,4,5,5,6,6,7,7,7-nonafluoroheptyloxy)ethyl vinyl ether]	1 wt%	UCST (~20)	153

gap of a 1 wt% solution of poly(ODVE) in chloroform was demonstrated, exhibiting a UCST behaviour with a T_{CP} of −2 °C.[109,147] Interestingly, vinyl ether polymers functionalized with imidazolium or pyridinium salt pendants underwent a LCST-type phase separation in $CHCl_3$.[155] In fact, a solution of poly[2-(vinyloxy)-ethyl-1-butylimidazolium chloride] in $CHCl_3$ displayed a LCST-type behaviour at 30 °C with no hysteresis, which was found to be dependent on the polymer DP, polymer concentration, the type of pendant counter anions, and the length of the alkyl side chains. Moreover, poly[2-(vinyloxy) ethyl-4-methylpyridinium chloride] (poly([MePy][Cl])) exhibited a fully reversible LCST phase transition at around 35 °C in $CHCl_3$/MeOH mixtures (97/3%w/w), which was strongly affected by the content of MeOH in the mixed solvents. The authors believe that these thermoresponsive polymers might have a potential application in sensor systems and other interactive materials.

Furthermore, poly[2-(4,4,5,5,6,6,7,7,7-nonafluoroheptyloxy) ethyl vinyl ether] (poly9FVE), a partially fluorinated vinyl ether polymer, underwent a UCST phase transition at around 20 °C in $CHCl_3$, which was dependent on the DP of the polymer (Fig. 30).[153] Additionally, when 9FVE was copolymerized with isobutyl vinyl ether (IBVE), the resulting block copolymer self-assembled in $CHCl_3$. It was demonstrated by DLS measurements that the diblock copolymer adopted either individual polymer chains or small aggregates at 30 °C at a concentration of 0.5 wt%, whereas the aggregates size sharply increased upon cooling. Moreover, when the diblock copolymer concentration was increased to 20 wt%, the polymer solution underwent a thermally induced sol–gel transition, forming a transparent gel upon cooling from 50 °C to ambient temperature. It was also shown that poly9FVE underwent a UCST-type transition in fluorinated solvents, namely perfluoro(methylcyclohexane) and perfluorodecalin, at around 10 °C and 20 °C, respectively.

Similarly, when dissolving chiral-polymeric ionic liquids (CPILs) in $CHCl_3$, thermoresponsive properties were observed.[156] CPILs were synthesised from the corresponding linear poly(vinylbenzyl chloride) polymers *via* substitution of the chloride groups with chiral imidazoles obtained from several amino acids (Fig. 31). CPILs bearing a benzyl *N*-substituent and an imidazole derived from (L)-valine (CPIL-4a) exhibited a LCST-type thermoresponsive behaviour at 48.5 °C in $CHCl_3$ (stabilized by 2% EtOH), as shown by transmittance measurements. This thermoresponsive behaviour was attributed to the self-assembly of the IL-like moieties, which resulted in a high-order supramolecular structure with a hierarchical architecture that provided the thermoresponsiveness. The LCST could be tuned over a wide range of temperatures, from 58.8 to 12.5 °C, by varying the substitution at the chiral stereocentres and the amide substitution, the nature of the counter ion and the CPILs concentration. Poly(vinylbenzyl chloride) homopolymer was then used to stabilize gold nanoparticles (AuNPs) by direct synthesis from $AuCl_4^-$ in the pres-

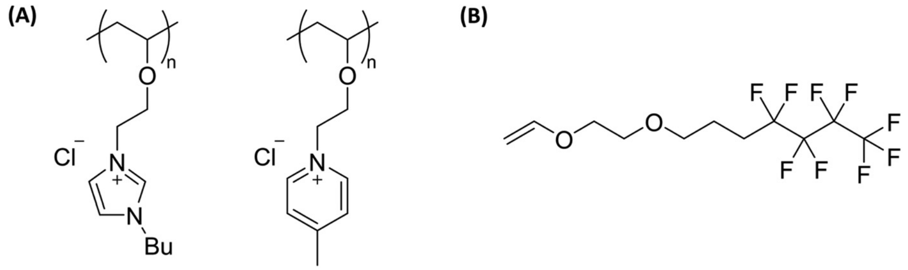


Fig. 30 Chemical structure of (A) poly[2-(vinyloxy)-ethyl-1-butylimidazolium chloride] and poly[2-(vinyloxy)ethyl-4-methylpyridinium chloride],[155] and (B) the 2-(4,4,5,5,6,6,7,7,7-nonafluoroheptyloxy)ethyl vinyl ether (9FVE) partially fluorinated monomer.[153]

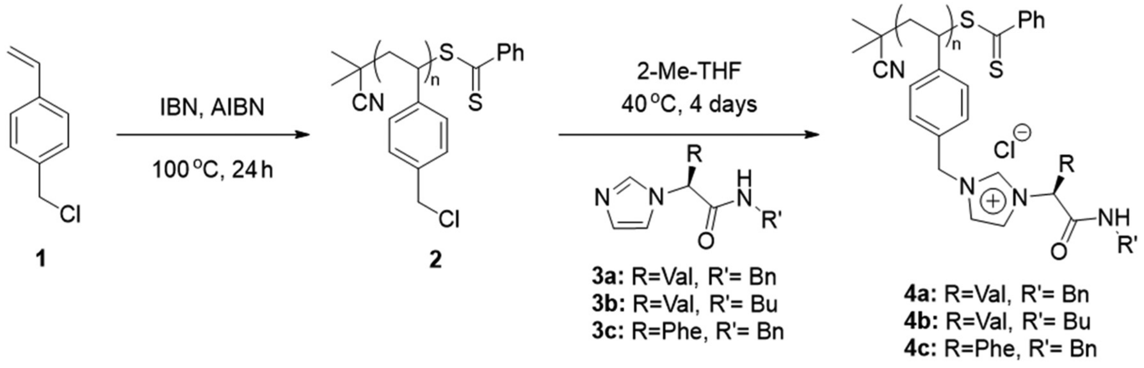
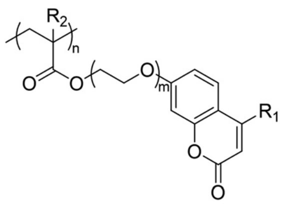


Fig. 31 Schematic depiction of the synthesis of chiral polymeric ionic liquids (CPILs).[156]

ence of the polymer prepared *via* RAFT polymerization, followed by the modification of the chloromethyl groups into chiral imidazolium units. Interestingly, this nanocomposite system also showed a LCST phase transition at 31.0 °C in $CHCl_3$ at a concentration of 1 mg mL^{-1}. These systems may open a new avenue for the preparation of chiral polymeric IL-stabilized AuNPs for various applications.

Similar to ionic charges, interactions with π-electron systems have also shown to induce thermoresponsive behaviour. For example, poly(7-methacryloyloxycoumarin) (**P1a**) and its derivatives as homopolymers containing photoreactive coumarin units synthesised *via* FRP exhibited a temperature-induced phase transition depending on the type of substituents (Fig. 32).[157] For example, **P1a** showed a LCST thermoresponsive behaviour in $CHCl_3$ around room temperature (*i.e.* 28 °C), attributed to the collapse of the CH/π interactions between the solvent molecules and the coumarin ring, and the formation of π/π interactions between the coumarin units. Additionally, for this polymer, a lower T_{CP} (21 °C) was measured for a 0.1 wt% polymer solution in deuterated $CDCl_3$ compared to $CHCl_3$, which was attributed to the deuterium isotope effect. It was further demonstrated that in distilled $CHCl_3$, the T_{CP} could be varied by photo-irradiation due to the reversible [2 + 2] cycloaddition of the coumarin units (dual-stimuli responsive units). The T_{CP} could be tuned from 28 to 57 °C by changing the polymer structure (*i.e.* by introducing ethyleneoxy spacer units and substituting the α-methyl group with hydrogen), and by introducing different substituents on the coumarin units. A similar LCST-type behaviour was also observed for **P1a** in 1,1,2-trichloroethane. As indicated by the authors, these polymers might have a potential application in the synthesis of dual-stimuli responsive functional materials.



P1a R_1= H, R_2= Me, m= 0
P1b R_1= H, R_2= Me, m= 1
P1c R_1= H, R_2= H, m= 0
P1d R_1= H, R_2= H, m= 1
P2a R_1= Me, R_2= Me, m= 0
P2b R_1= Me, R_2= Me, m= 1
P2c R_1= Me, R_2= H, m= 0
P2d R_1= Me, R_2= H, m= 1
P3a R_1= Ph, R_2= H, m= 0
P4a R_1= CO_2Et, R_2= Me, m= 0

Fig. 32 Chemical structure of the coumarin-containing polymers.[157]

In a similar fashion, a series of well-defined poly(arylene ether sulfone)s (PESs) with different molecular weight distributions obtained by chain-growth condensation polymerization showed a LCST-type phase transition in chloroform characterized by high T_{CP} values due to the high solubility of the polymer in the selected solvent.[163] As shown by UV-vis spectrophotometry, the T_{CP} was dependent on the length of the polymer chains, increasing with decreasing molecular weight.

Furthermore, it has been shown that poly(3-((4*R*,5*R*)-4,5-bis(hydroxydiphenylmethyl)-2-methyl-1,3-dioxolane-2-yl)propyl acrylate) exhibited a UCST-type thermoresponsive behaviour in $CHCl_3$ around 50 °C at a concentration of 10 mg mL^{-1} due to the cleavage of the self-associative interactions between TADDOL groups, which could be easily broken by heating, and the solvation of the polymer chains by the solvent molecules.[138] A similar thermoresponsive behaviour was also observed in dichloromethane and 1,2-dichlorethane. These polymers might find application for the design of stimuli-responsive polymers with highly ordered responsiveness.

Recently, it has been shown that temperature could also induce an helical inversion of poly((−)-3-methoxycarbonyl-5-(*N*-methyl-*N*-(*S*)-(1-phenylethyl)carbamoyl)phenylacetylene) in $CHCl_3$, which was related to the thermo-driven amide *cis–trans* isomerization, as shown by UV–vis spectroscopy, electronic circular dichroism (ECD), and vibrational circular dichroism (VCD).[158] For instance, at low temperatures the *trans* conformation was dominant, while the amide bond shifted toward the *cis* isomer when the temperature increased, causing a higher steric hindrance and, thus, the inversion of the helical sense (Fig. 33). As stated by the authors, this unique thermoresponsive behaviour brings a deeper understanding of the dynamic origin of biological one-handed helix, and it might also have potential as molecular thermoswitch in the field of smart materials.

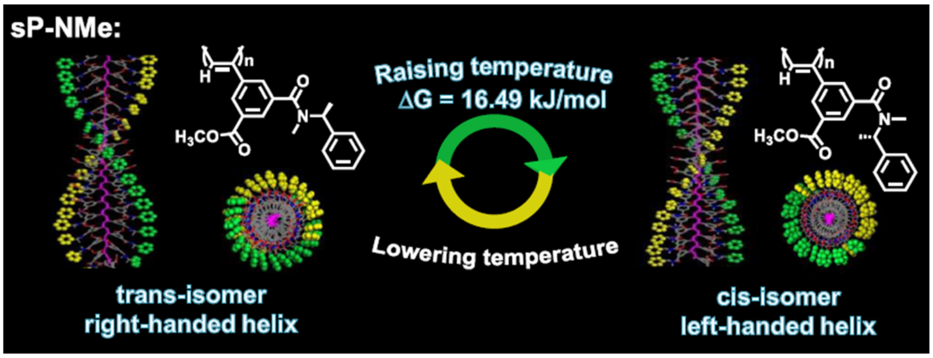


Fig. 33 Schematic depiction of the possible 3D helical models and the conformations of pendants for poly((−)-3-methoxycarbonyl-5-(*N*-methyl-*N*-(*S*)-(1-phenylethyl)carbamoyl)phenylacetylene) in $CHCl_3$. Adapted from ref. 158 Copyright 2021 American Chemical Society.

Similar to $CHCl_3$, vinyl ether polymers show thermoresponsiveness also in dichloromethane (DCM). For example, poly(ODVE) exhibited a UCST phase transition at 14 °C in DCM, due to the crystallization of the long alkyl chains, as confirmed by the appearance of an exothermic peak in the DSC curve at the phase separation of a poly(ODVE) DCM solution.[109,147] The UCST properties remained unchanged when reducing the side chain length to poly(hexadecyl vinyl ether) (poly(HDVE).[109]

In another report, poly(7-methacryloyloxycoumarin) also showed a temperature-induced solution behaviour in DCM, revealing a LCST-type phase separation near the boiling point of the solvent (~39 °C) at a concentration of 0.3 wt%, while being completely soluble at a polymer concentration of 0.1 wt%.[157]

1,2-Dichloroethane (DCE) has also been used for the investigation of polymers thermoresponsiveness in solution. As an example, the solubility and thermoresponsive behaviour of a series of well-defined urea-modified homopolymers obtained from the RAFT polymerization of 2-(3-butylureido)propyl acrylate in DCE was found to be dependent on the presence in solution of effectors, such as alcohols, amides, ureas, and carboxylic acids.[159] Upon the addition of the small molecules, solubility was achieved and a thermoresponsive behaviour was observed, as shown by transmittance measurements. It has been demonstrated that the thermosensitivity was strongly dependent on the strength of the hydrogen bonding between the urea groups and the effectors (Fig. 34). Effectors that strongly interacted with the urea groups, such as aliphatic carboxylic acids and dialkylureas, tended to induce UCST-type phase separation, while weakly interacting effectors, such as alcohols, induced an LCST-type behaviour. On the one hand, weak polymer–effector interactions were readily interrupted upon heating, leading to the insolubility of the polymer by aggregation (LCST-type). On the other hand, strong polymer–effector interactions resulted in the cleavage of the polymer–polymer interactions upon heating, leading to a UCST-type behaviour. Both the UCST and LCST phase transitions could be easily tuned by varying the type and the concentration of the effector in solution. Moreover, a quaternary system using two effectors, which were able to induce different thermoresponsive behaviours, namely 1-dodecanol (LCST) and *N*,*N*′-butyloctylurea (UCST), was also investigated. At appropriate amounts of the two effectors, both LCST and UCST were achieved, and the LCST + UCST regime could be easily adjusted by slight changes of the amount of the two effectors in the system. These polymer/effector systems might be used in the design of smart thermosensitive systems.

3-(3-Butylureido)propyl acrylate has also been copolymerized with *N*-[3-(acryloyloxy)propyl]-*N*,*N*,*N*-trihexylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (TFPB) *via* RAFT polymerization, resulting in copolymers with self-attractive urea units *via* hydrogen bonding, and self-repulsive lipophilic ion units *via* electrostatic interaction.[164] The copolymers exhibited a UCST-type thermoresponsive behaviour in DCE, which was dependent on the content of lipophilic units in the polymer. The TFPB units were able to induce the dissolution of the polymer due to ionic dissociation, decreasing the T_{CP} from 65 to 48 °C by increasing the TFPB content in the final copolymer from 4 to 5 mol%. Moreover, the self-association of the urea units was found to be strongly dependent on the temperature, while the ionic dissociation of the ion pairs was only slightly affected. Thus, a considerable decrease of the attractive interactions and a slight reduction of the repulsive forces occurred upon heating, resulting in the UCST-type phase transition (*i.e.* thermoresponsiveness achieved when the repulsive forces among TFPB units overcame the attractive

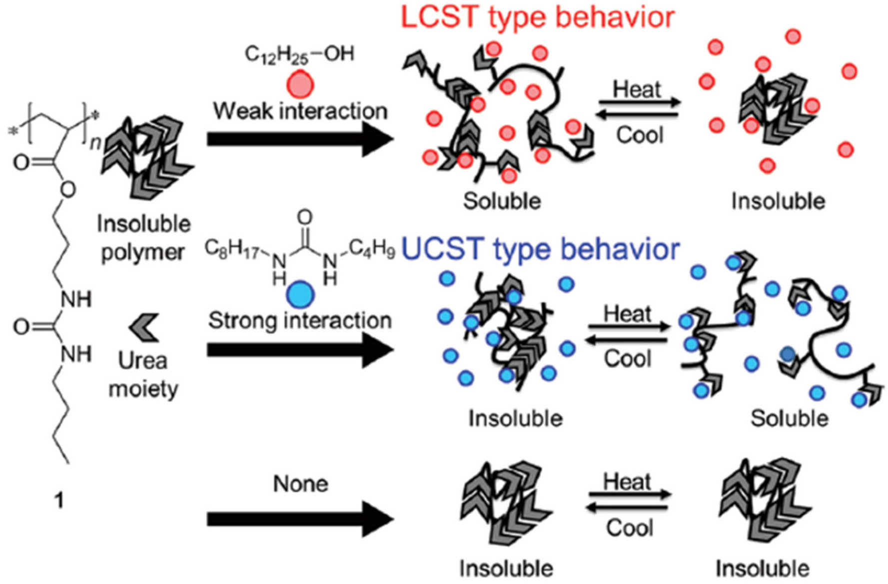


Fig. 34 Thermoresponsive behaviour of poly(2-(3-butylureido)propyl acrylate) induced by the addition of strongly interacting and weakly interacting effectors. Adapted from ref. 159 Copyright 2012 American Chemical Society.

interactions among urea units upon heating). Furthermore, the addition of salt decreased the concentration of dissociated species in the polymer, weakening the repulsive forces and, consequently, leading to increased T_{CP} values.

The attractive interactions between urea units have also been used to induce thermoresponsiveness to a series of polymers containing *N*-butylurea groups in the side chains and characterized by different backbones, namely poly(3-(3-butylureido)propyl acrylate) (PUA), poly(3-(3-butylureido)propyl methacrylate (PUMA), and poly(3-(3-butylureido)propyl vinyl ether) (PUVE), synthesised by RAFT polymerization (Fig. 35).[160] Their thermoresponsive behaviour was investigated in DCE in the presence of 1-hexanol. All polymers exhibited a LCST-type phase transition, which was attributed to the thermal cleavage of hydrogen bonds between urea groups in the polymer and hydroxyl groups in the effector, resulting in the self-association of the urea units and the precipitation of the polymer chains. By changing 1-hexanol with lauric acid, a UCST behaviour was observed for all polymers, with decreasing T_{CP} values when increasing the effector concentration. Additionally, thermoresponsive behaviour, either LCST or UCST, for these polymers was observed in other organic solvents (*e.g.* ethyl acetate, chloroform, toluene, cyclohexane, *etc.*) when 1-hexanol was added as an effector. This behaviour was not observed in more polar solvents, such as acetone. The temperature-induced phase transition could be controlled by varying the solvent polarity and the effector concentration.

The dependence of the thermoresponsive behaviour on the presence of effectors has also been investigated for a poly((1-pyrene)methyl acrylate) homopolymer (PPMA) synthesised *via* RAFT polymerization.[161] The solubilization of the polymer in DCE was hindered by the presence of the pyrene units, which were able to aggregate through π–π interactions. For this reason, the addition of electron-accepting molecules as effectors was required to form charge-transfer (CT) complexes with the polymer. Additionally, the low binding constant between the pyrene units and the effectors gave rise to the dissociation of the charge transfer complexes with increasing temperature. Upon heating, the dissociation of the charge transfer complexes between the PPMA and the electron-donating molecules resulted in a decrease in the solubility of the polymer leading to its aggregation and precipitation (Fig. 36). The T_{CP} increased with increasing effector concentration, and decreased at higher PPMA concentrations, indicating that the solubility of the polymer was strongly dependent on the degree of association between the PPMA and the effectors. It was also demonstrated by adding a competitive donor in solution that the solubility of the polymer could be tuned by controlling the degree of association between the pyrene units in the polymer chains and the effectors. Also in this case, these unique interactions and thermoresponsive behaviour might be use for the design of smart thermoresponsive systems.

In another report, poly[(5,6-difluoro-2,1,3-benzothiadiazol-4,7-diyl)-*alt*-(3,3‴-dialkyl-2,2′;5′,2″;5″,2‴-quaterthiophen-5,5‴-diyl)] (PffBT4T) polymers with varying side-chain lengths, namely 2-octyldodecyl (C8C12) and 2-nonyltridecyl (C9C13), exhibited an aggregation-to-dissolved chain transition in *o*-dichlorobenzene (*o*-DCB).[162] At room temperature, the polymers (5 mg mL^{-1}) aggregated into fabric structures, as shown by AFM, TEM and DLS analyses. Above 75 °C, the polymers were fully dissolved in *o*-DCB and adopted a semi-flexible coil conformation, as demonstrated by temperature-dependent SANS measurements. Interestingly, PffBT4T-C8C12 formed bigger aggregates compared to PffBT4T-C9C13 at the same temperature, indicating that the longer side chain hindered the further growth of aggregates.

In this section, the thermoresponsive behaviour of polymers in halogenated solvents, especially chlorinated, has been reviewed. In these solvents, polymers exhibit mostly LCST and UCST-type phase transitions, which are mainly caused by the interactions (repulsive or attractive) between specific functional groups present on the polymeric chains, the presence and the nature of effectors in solution, the nature of the counter ions, as well as by the DP and the concentration of the polymer. These polymers have shown interesting temperature-induced solution behaviours which might have a crucial impact on the design and production of polymers for the smart materials field.

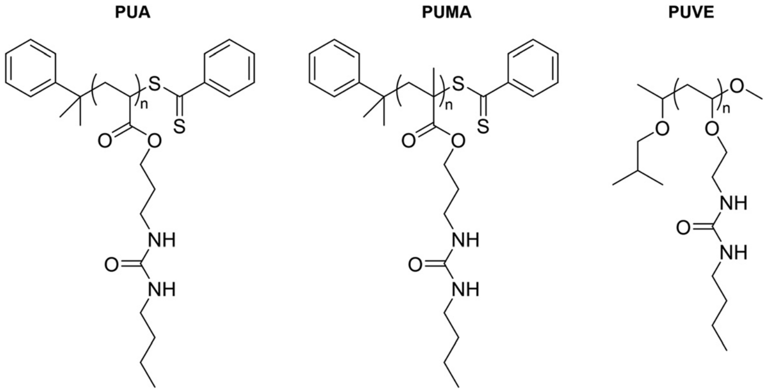


Fig. 35 Chemical structure of poly(3-(3-butylureido)propyl acrylate) (PUA), poly(3-(3-butylureido)propyl methacrylate (PUMA), and poly(3-(3-butylureido)propyl vinyl ether) (PUVE) having urea units in the side chains.[160]

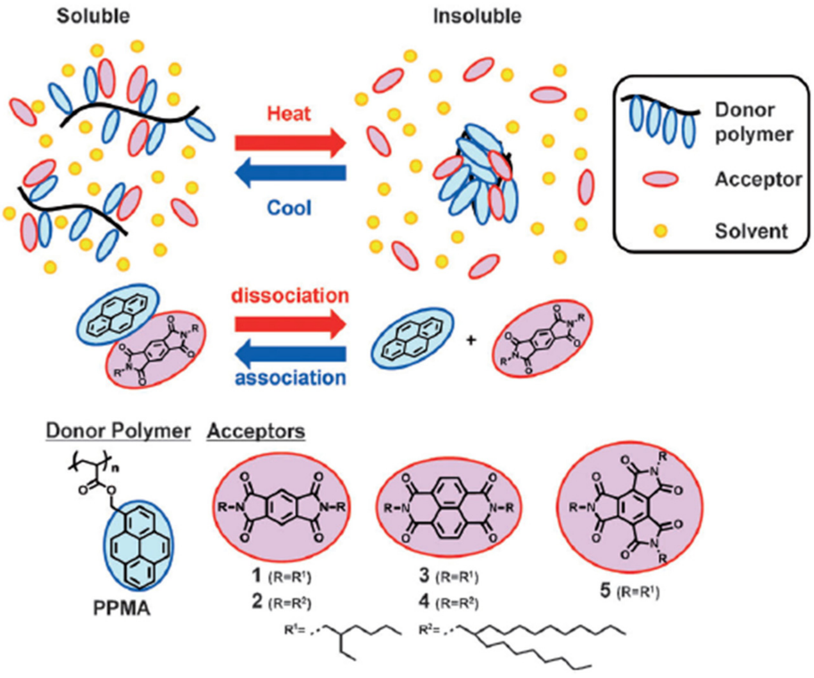


Fig. 36 Thermoresponsive behaviour of supramolecular complexes caused by CT interactions, and chemical structures of the PPMA polymer and used acceptors. Reproduced from ref. 161 Copyright 2013 WILEY-VCH Verlag GmbH&Co. KGaA, Weinheim.

6. Ionic liquids

In this section, the thermoresponsive behaviour of polymers in ionic liquids (ILs) will be thoroughly discussed (Table S8†). In Table 9, representative examples are divided depending on the type of IL used, as in the previous sections. However, for a better understanding of the polymer structure/IL structure relationship and its effect on the final temperature-induced behaviour, the examples will be discussed depending on the polymer type.

Poly(benzyl methacrylate) and its derivatives are the most studied polymers in relation with their thermoresponsive phase transitions in ionic liquids. For example, a 3 wt% PBzMA solution showed a LCST-type phase transition in 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfone) imide ([C_2mim][NTf_2]) with a T_{CP} of 105 °C.[165,166] The thermoresponsive behaviour was attributed to structure-forming solvation between the aromatic ring of PBzMA and the imidazolium cation of the IL, which led to a negative entropic mixing term and, thus, to the LCST-type behaviour.[181,182]

The effect of the structure of the IL on the thermoresponsive behaviour of PBzMA and its copolymers has been extensively studied by changing the alkyl chain length of the imidazolium substituent and the anion. In general, it has been observed that for ILs with [$C_n$mim] cations and [NTf_2] anion, the T_{CP} values of PBzMA solutions increased with the length of the alkyl chain of the imidazolium cation.[165,166] A similar trend was also observed for ILs having PF_6 as anion (Fig. 37).

Furthermore, the T_{CP} value of BzMA could be easily tuned by copolymerization with other solvophilic and solvophobic monomers (Fig. 38). For example, the copolymerization of benzyl methacrylate with the solvophobic styrene monomer resulted in a decrease of the T_{CP} in [C_2mim][NTf_2] with increasing styrene content.[166] When BzMA was copolymerized with the solvophilic methyl methacrylate (MMA), higher T_{CP} values were recorded for polymers with higher MMA contents. Furthermore, diblock copolymers consisting of a MMA block and a BzMA segment showed a LCST-type behaviour in [C_2mim][NTf_2] (2 wt%), resulting in the formation of micelles at a lower critical micellization temperature (LCMT) of around 120 °C, as demonstrated by DLS measurements.[167] Interestingly, copolymers of St and MMA also exhibited thermoresponsive phase transitions in [C_2mim][NTf_2], which were strongly dependent on the St content.[168] To exemplify, depending on the St content, the copolymers were insoluble or showed LCST or UCST phase transitions in the selected IL. Interestingly, those containing 42.2–45.6 mol% of St exhibited both LCST (~165–170 °C) and UCST (~−5 °C) behaviours.

In another report, BzMA was copolymerized with 4-phenylazophenyl methacrylate (AzoMA) and the resulting polymers exhibited a LCST-type phase transition in [C_2mim][NTf_2], which was found to be strongly dependent on the content and on the *cis*/*trans* isomerization of the AzoMA units.[169] Turbidity measurements were performed either in the dark, to obtain copolymers with *trans*-AzoMa units, or under UV irradiation for *cis*-AzoMA-containing copolymers. The T_{CP} values of 3 wt% [C_2mim][NTf_2] solutions containing copolymers with 1.9 mol% of *cis*-AzoMA or *trans*-AzoMA were around 103 and 83 °C, respectively. When the AzoMA content

Table 9 Examples of thermoresponsive polymers in ionic liquids

Solvent	Type of polymer	Polymer conc.	Phase transition type (Temp. °C)	Ref.
[C_2mim][NTf_2]	Poly(benzyl methacrylate)	3 wt%	LCST (@105)	165
[C_2mim][NTf_2]	Poly(benzyl methacrylate-*co*-styrene)	3 wt%	LCST (~70–100)	166
[C_2mim][NTf_2]	Poly(benzyl methacrylate-*co*-methyl metacryalte)	3 wt%	LCST (~120–140)	166
[C_2mim][NTf_2]	Poly(methyl methacrylate)-*b*-poly(benzyl methacrylate)	2 wt%	LCST and LCMT (~120)	167
[C_2mim][NTf_2]	Poly(styrene-*co*-methyl methacrylate)	3 wt%	LCST (~85–170), UCST (~−5–10), LCST + UCST	168
[C_2mim][NTf_2]	Poly(*cis*-4-phenylazophenyl methacrylate-*co*-benzyl methacrylate)	3 wt%	LCST (~102–103)	169
[C_2mim][NTf_2]	Poly(*trans*-4-phenylazophenyl methacrylate-*co*-benzyl methacrylate)	3 wt%	LCST (~80–83)	169
[C_2mim][NTf_2]	Poly(*N*-isopropylacrylamide)	1 wt%	UCST (@34)	170
[C_2mim][NTf_2]	Poly(benzyl methacrylate)-*b*-poly(*N*-isopropylacrylamide)	1 wt%	LCMT (~140)	171
[C_2mim][NTf_2]	Poly(*N*-isopropylacrylamide)-*b*-poly(ethylene oxide)-*b*-poly(*N*-isopropylacrylamide)	10 wt%	Sol–gel (~20)	172
[C_2mim][NTf_2]	Poly(ethyl glycidyl ether)	10 wt%	LCST (@84.4)	173
[C_2mim][NTf_2]/[C_4mim]PF_6	Poly(benzyl methacrylate)-*b*-poly(*N*-isopropylacrylamide)	1 wt%	UCMT (~30) LCMT (~130)	171
[C_4mim][NTf_2]	Poly(*n*-butyl methacrylate) 48 kDa	0.25 wt%	LCST (@119)	174
[C_8mim][NTf_2]	Poly(3-methylbenzyl methacrylate)	3 wt%	LCST (@162)	175
[C_4dmim][NTf_2]	Poly(2-phenylethyl methacrylate)	3 wt%	LCST (@136)	175
[C_1mim][NTf_2]	Poly(2-phenylethyl methacrylate)-*b*-poly(methyl methacrylate)-*b*-poly(2-phenylethyl methacrylate)	30 wt%	Sol–gel (@23)	176
[Azo][NTf_2]/[C_1mim][NTf_2]	Poly(2-phenylethyl methacrylate)-*b*-poly(methyl methacrylate)-*b*-poly(2-phenylethyl methacrylate)	30 wt%	Sol–gel (@50.7–61.3)	176
[C_4mim][BF_4]	Poly(ethylene oxide)-*b*-poly(*N*-isopropylacrylamide)	1 wt%	UCMT (~60) LCMT (~207)	177
[C_2dmim][BF_4]	Poly(ethylene oxide) 2 kDa	60 wt%	LCST (~110)	178
[C_4mim][PF_6]	Poly(*trans*-4-phenylazophenyl methacrylate-*r*-*N*-isopropylacrylamide)-*b*-poly(ethylene oxide)-*b*-poly(*trans*-4-phenylazophenyl methacrylate-*r*-*N*-isopropylacrylamide)	1 wt%	UCMT (@60)	179
[C_4mim][PF_6]	Poly(*trans*-4-phenylazophenyl methacrylate-*r*-*N*-isopropylacrylamide)-*b*-poly(ethylene oxide)-*b*-poly(*trans*-4-phenylazophenyl methacrylate-*r*-*N*-isopropylacrylamide)	10 wt%	Sol–gel (@56)	179
[C_4mim][PF_6]	Poly(ethyl glycidyl ether)-*b*-poly(ethylene oxide)	1 wt%	LCMT (@15)	180
[C_8mim][PF_6]	Poly(ethyl glycidyl ether)	10 wt%	LCST (@67.0)	173

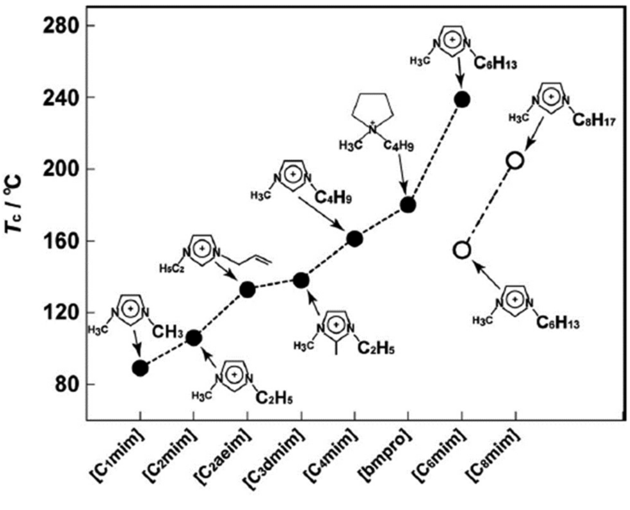


Fig. 37 T_{CP} values of PBnMA and chemical structure of IL cations with [NTf2] (●) and PF6 anions (○). Reproduced from ref. 165 Copyright 2009 IUPAC.

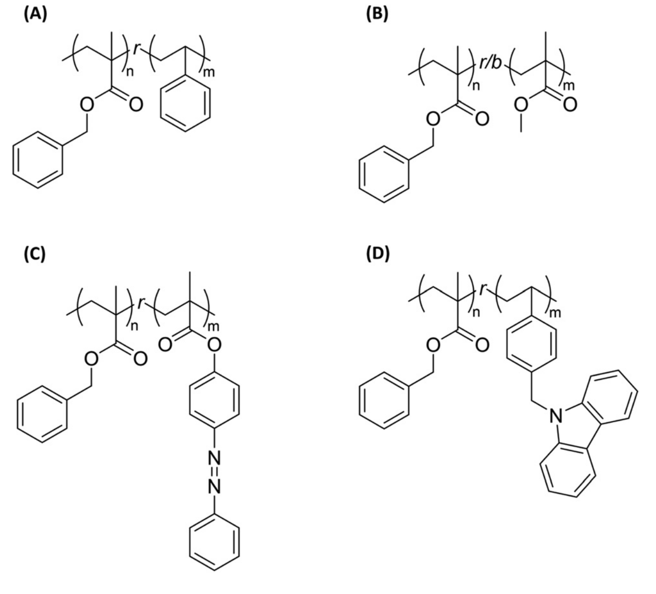


Fig. 38 Example of chemical structures of random and block copolymers of BzMA and (A) styrene, (B) methyl methacrylate, (C) 4-phenylazophenyl methacrylate, and (D) 9-(4-vinylbenzyl)-9*H*-carbazole.

was increased to 4.1 mol%, the T_{CP} decreased to 102 and 80 °C, for the *cis*- and *trans*-AzoMA copolymers, respectively. The difference in T_{CP} values between the two copolymers was attributed to the different strength of the cation–π interaction between the azo moieties of the copolymers in the *cis*- or *trans*-form and the IL, with the *trans*-form AzoMA units forming stronger interactions due to a higher planarity of the structure.

Furthermore, the NMP of BzMA with a small fraction of fluorescent controlling comonomer 9-(4-vinylbenzyl)-9*H*-carbazole (VBK, 2–11 mol% in the feed) yielded polymers exhibiting LCST-type behaviour in [C_2mim][NTf_2].[183] Since PVBK was insoluble in the selected IL, a decrease in the copolymers solubility with increasing VBK content was expected. For instance, the T_{CP} values of 3 wt% copolymer solutions decreased steeply from 86 to 68 °C when the amount of VBK was increased from 4 to 9 mol%. However, the thermoresponsive behaviour of these two copolymers was not reversible. The authors argued that the incorporation of VBK units resulted in a higher stiffness and lower solubility of the final copolymers which, combined with the π–π interactions between the aromatic structure of VBK and the benzyl groups of BzMA, hindered the diffusion of the IL into the polymer aggregates, resulting in an irreversible phase separation. However, it was also shown that chain extending macroinitiators of selected statistical copolymers with a solvophilic MMA-rich block containing 10 mol% of styrene resulted in diblock copolymers with a fully reversible LCST behaviour in the same IL at higher T_{CP} values.

In order to investigate the effect of the structures of polymers and ILs on the temperature-induced phase transition, a series of poly(benzyl methacrylate)-derivatives with different functional groups on their side chains was synthesised and their solution behaviour was studied in six different ILs (Fig. 39).[175] It has been observed from transmittance measurements that polymers with solvophobic substituents on the *m*-position of the phenyl group on the side chains (**1b–d**) were insoluble in [C_2mim][NTf_2]. Polymers containing methoxy (**1e**) and fluoro groups (**1f**) exhibited a LCST-type phase transition at 54 and 87 °C, respectively. The polymers with a 2-carbon spacer between the phenyl and the ester groups (**1g**) had a T_{CP} at 42 °C, while when the length of the alkyl spacer was increased to 4 carbon atoms (**1h**), the resulting polymer was insoluble. In contrast, poly(2-pyridylmethyl methacrylate) (**1i**), a polar polymethacrylate, was completely soluble over the whole examined temperature range. Also for these polymers, the T_{CP} values increased with increasing length of the alkyl chain on the imidazolium cation of the ILs with a fixed [NTf_2] cation. Furthermore, the polymers **1d** and **1h**, which were insoluble in [C_2mim][NTf_2], exhibited a LCST phase transition in 1-octyl-3-methylimidazolium bis(trifluoromethane sulfone)imide [C_8mim][NTf_2] at 162 and 242 °C, respectively. The solution behaviour of PBzMA and the **1g** derivative were also evaluated in 1-butyl-2,3-dimethylimidazolium bis(trifluoromethane sulfonyl)imide ([C_4dmim][NTf_2]), exhibiting T_{CP} values of 176 and 136 °C, respectively. Finally, the temperature-induced phase transition of **1g** was studied in binary mixtures of different ILs. The T_{CP} of **1g** in [C_2mim][NTf_2]/[C_4mim][NTf_2] mixture increased linearly from 42 to 118 °C as the weight fraction of [C_2mim][NTf_2] increased from 0 to 1. This linear relationship between the T_{CP} and the ratio of the two ILs was also observed for other ILs mixtures and different BzMA-derivatives, making it a useful tool for the prediction and estimation of T_{CP} values that are too low or too high to be directly measured.

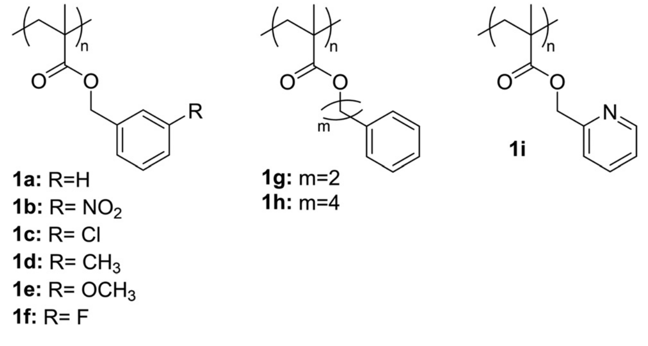


Fig. 39 Chemical structures of the PBzMA-derivatives.[175]

In another report, the solution behaviour (poly(benzyl methacrylate) and poly(2-phenylethyl methacrylate) (PPhEtMA)), a PBzMA derivative, was evaluated in mixed ILs (1,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide [C_1mim][NTf_2] and (1-butyl-3-(4-phenylazobenzyl)imidazolium bis(trifluoromethanesulfonyl)amide [Azo][NTf_2], as a small molecular photo trigger.[184] The [Azo][NTf_2] IL was mainly in its *trans* form in the absence of light (100%) or under visible light irradiation (85%), while the *cis* form was the predominant one under UV light irradiation (65%). Interestingly, PPhEtMA was completely soluble in [Azo][NTf_2], but insoluble in [C_1mim][NTf_2]. However, the addition of a small amount of [Azo][NTf_2] to [C_1mim][NTf_2] resulted in the dissolution of the polymer. It has been shown that PPhEtMA underwent a LCST-type phase transition in the solvent mixture, with T_{CP} increasing with increasing [Azo][NTf_2] content for both measurements performed in absence of light or under UV irradiation. Furthermore, at all contents, the T_{CP} values measured in the absence of light were higher than those obtained under UV irradiation. Interestingly, the mixture containing 30 wt% [Azo][NTf_2] exhibited a reversible phase separation and dissolution at 112 °C under alternating UV and visible light irradiation, due to the *cis–trans* isomerization of the [Azo][NTf_2] IL. A similar behaviour was also observed for PBzMA, with T_{CP} values increasing with increasing [Azo][NTf_2] content in the absence of light. However, the T_{CP} values of mixtures containing *cis*-[Azo][NTf_2] were higher than those containing *trans*-[Azo][NTf_2], an opposite behaviour compared to PPhEtMA, which was suggested to be caused by specific interactions of the two polymers with [Azo][NTf_2], as demonstrated by ^{1}H NMR measurements.

Furthermore, two thermoresponsive ABA triblock copolymers, PBnMA-*b*-PMMA-*b*-PBnMA (BMB) and PPhEtMA-*b*-PMMA-*b*-PPhEt, (PMP), exhibited a thermo- and photo-responsive micellization/demicellization in [Azo][NTf_2]/[C_1mim][NTf_2] mixtures.[185] As shown by DLS measurements performed in the dark, the size of a 0.1 wt% PMP solution in [Azo][NTf_2]/[C_1mim][NTf_2] (5/95) sharply increased at around 65 °C, a higher temperature compared to the T_{CP} of PPhEtMA homopolymer (49 °C) due to the presence of the solvophilic PMMA block. The increase in the scattering intensity was caused by the formation of micelles consisting of a PPhEtMA core and PMMA corona. As in the case of the PPhEtMA homopolymer,

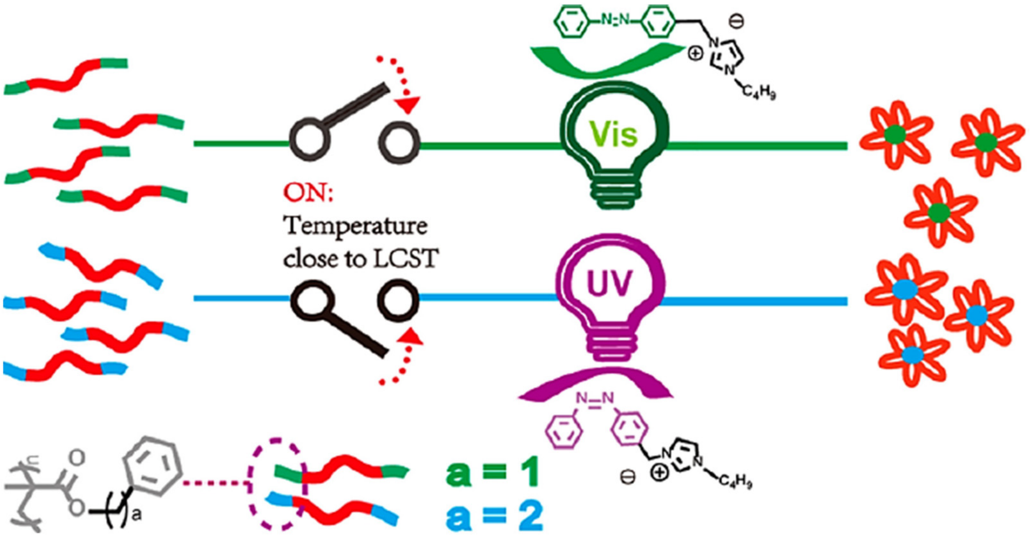


Fig. 40 Schematic representation of the micellization/demicellization process of PMP and BMB under UV and visible light irradiation. Reproduced from ref. 185 Copyright 2017 American Chemical Society.

the PMP triblock copolymer exhibited a lower T_{CP} (~55 °C) when the solution was heated under UV irradiation (*i.e.* prevalence of *cis*-IL). The BPB solution in the same ILs mixture in the absence of light showed a lower critical micellization temperature at around 110 °C. As in the case of the PBzMA homopolymer, the LCMT measured under UV irradiation was higher (~120 °C) compared to the one in *trans*-IL. Furthermore, at a temperature between the two LCMTs, UV irradiation induced a "unimer-to-micelle" transition for PMP, while a "micelle-to-unimer" transition was observed for BMB (Fig. 40). NMR analyses showed a shift in opposite directions of the chemical shifts for the two polymer/IL solutions, suggesting a strong influence of the photoisomerization of [Azo][NTf_2] and the structure of the polymers on the interaction between polymers and [C_1mim][NTf_2].

The thermoresponsive behaviour of crosslinked gels of PBzMA and its derivatives in ILs has also been extensively studied. For example, a gel obtained by crosslinking BzMA with ethylene glycol dimethacrylate exhibited a low-temperature swollen and a high-temperature shrunken phase in [C_2mim][NTf_2] with a phase transition temperature at around 100 °C. The authors believe that these gels could enable the development of environmentally stable smart gel materials for various applications.[166]

Furthermore, ABA triblock copolymers consisting of two outer PBzMA blocks and a middle PMMA segment (PBzMA-*b*-PMMA-*b*-PBzMA) were shown to undergo a low-temperature sol-high-temperature gel transition in [C_2mim][NTf_2] due to the formation of physical PBnMA cross-linking points.[186] At a polymer concentration of 20 wt%, viscoelastic measurements showed that the ABA triblock copolymer formed a viscous solution below 100 °C, and a gel at higher temperatures, due to the high concentration resulting in the aggregation of micelles. The evaluation of the sol–gel reversibility was demonstrated by temperature scanning (0–140 °C) over several days. These polymers may help the development of materials chemistry of soft materials using ILs.

In another example, the ABC triblock copolymer consisting of a PBzMA block, a middle PMMA segment, and a PPhEtMA block (PBzMA-*b*-PMMA-*b*-PPhEtMA) underwent a sol–gel transition in [C_2mim][NTf_2].[187] Also in this case, DLS analyses of a 0.1 wt% polymer solution showed the increase in the particle size above 70 °C, indicating the formation of micelles. However, above 120 °C a decrease in size was recorded. The authors suggested that this temperature responsive behaviour was caused by a unimer-to hairy micelle-to flower-like micelle transition due to the double thermosensitivity of the PPhEtMA and PBnMA blocks. Measurements of the frequency dependence of the dynamic moduli at selected temperatures of a 20 wt% PBzMA-*b*-PMMA-*b*-PPhEtMA solution showed that the ABC triblock copolymer formed a gel at temperatures above the T_{CP} of PBzMA (105 °C). However, between 40 and 100 °C, an intermediate state was observed, which was attributed to a sol-to-jamming micelles transition due to the LCST phase transition of the PPhEtMA block (~42 °C), as also confirmed by SAXS analyses. At high temperatures the PPhEtMA and PBnMA blocks connected by physical cross-linking, resulting in the gelation behaviour (Fig. 41).

Triblock copolymers of BzMA-derivatives have also shown sol–gel transitions in ILs. For example, an ABA triblock copolymer consisting of two outer PhEtMA blocks and a middle MMA segment (PMP) synthetized by ATRP of PhEtMA from a bifunctional PMMA macroinitiator exhibited a thermoresponsive behaviour in [C_2mim][NTf_2]/[C_4mim][NTf_2] mixtures.[188] DLS measurements of 0.1 wt% PMP dissolved in three [C_2mim][NTf_2]/[C_4mim][NTf_2] mixtures (100/0, 75/25, 50/50) showed the formation of micelles at higher temperatures. The LCMT of the triblock copolymer increased from 60 to

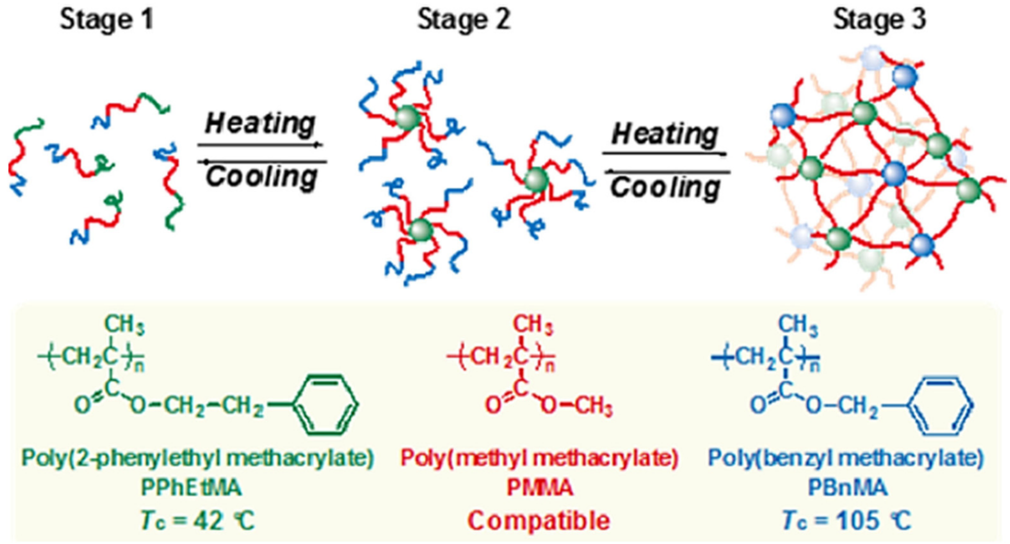


Fig. 41 Schematic representation of the sol-jamming micelles-gel transition of the PBzMA-*b*-PMMA-*b*-PPhEtMA ABC triblock copolymer. Reproduced from ref. 187 Copyright 2016 American Chemical Society.

100 °C with increasing $[C_4mim][NTf_2]$ fraction from 0 to 50 mol%. Furthermore, rheological measurements of the three 20 wt% PMP ILs solutions showed a low-temperature sol-high-temperature gel transition, with sol–gel transition temperatures increasing from 25 to 65 °C as the $[C_4mim][NTf_2]$ fraction increased from 0 to 50 mol%. The sol–gel transition temperatures were found to be concentration and solvent dependent.

The thermoresponsive behaviour of PMP has also been evaluated in $[C_1mim][NTf_2]$ and in a $[Azo][NTf_2]/[C_1mim][NTf_2]$ (10/90 w/w) mixture.[176] A 30 wt% PMP solution in $[C_1mim][NTf_2]$ exhibited a sol–gel transition at 23 °C due to the LCST-type behaviour of the PPhEtMA blocks, which resulted in percolated micellar networks consisting of aggregated PPhEtMA end blocks bridged by solvophilic PMMA middle blocks. To induce photo/thermoresponsive sol–gel transitions, $[C_1mim][NTf_2]$ was mixed with the photoresponsive $[Azo][NTf_2]$ IL. Temperature sweep measurements of viscoelastic moduli and dynamic frequency sweep measurements of a 30 wt% PMP solution in a 10/90 w/w $[Azo][NTf_2]/[C_1mim][NTf_2]$ mixture performed in the dark (*i.e.* $[Azo][NTf_2]$ in *trans*-state) showed that the PMP behaved as a viscous polymer solution below 40 °C. Above 40 °C, the solution still behaved as a viscoelastic fluid, but at higher temperatures it formed a gel. Under UV irradiation (*i.e.* photoisomerization of $[Azo][NTf_2]$ from *trans*- to *cis*-state), the measured gelation temperature was lower than the one measured in the dark, indicating a lower affinity of the PPhEtMA blocks towards the *cis*-$[Azo][NTf_2]$ compared to the *trans*-$[Azo][NTf_2]$.

Another widely studied thermoresponsive polymer in ILs is PNIPAM. Interestingly and contrarily to its thermoresponsive behaviour in aqueous solutions, PNIPAM with a molecular weight of 53 kDa showed a UCST-type phase transition in $[C_2mim][NTf_2]$ at around 34 °C at a polymer concentration on 1 wt%.[170] The T_{CP} values were strongly dependent on the polymer molecular weight and concentration, with T_{CP} increasing with increasing molecular weight and concentration, indicating a strong entropic contribution to the phase transition. Furthermore, PNIPAM gels obtained by using *N*,*N*′-methylenebisacrylamide as crosslinker exhibited a reversible swelling/deswelling behaviour in the IL, with a maximum swollen state at around 200 °C. The difference in the transition temperatures between the gels and the polymer in solution was attributed to the reduced conformational entropic effect for the gel due to the high molecular weight of the polymer. PNIPAM (40 kDa) also exhibited a UCST-type phase transition in other ILs, such as 1-ethyl-3-methylimidazolium tetrafluoroborate ($[C_2mim][BF_4]$) and 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim][BF_4]$).[177]

In order to tune its thermoresponsive behaviour in ILs, PNIPAM has been copolymerized with various comonomers (Fig. 42). For example, two block copolymers consisting of a BzMA block (11 kDa) and a PNIPAM segment (PBzMA(11)-*b*-PNIPAM), or a BzMA segment (22 kDa) and a block of NIPAM/acrylamide random copolymer (PBzMA(22)-*b*-P(NIPAM-*r*-AAM)) synthetized *via* RAFT polymerization showed a thermoresponsive behaviour in $[C_2mim][NTf_2]$, 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim]PF_6$), and in a 1 : 1 mixture of the two ILs.[171] In a 1 : 1 ILs mixture (wt%), the PBzMA(11)-*b*-PNIPAM diblock copolymer (C = 1 wt%) formed micelles below 30 °C (upper critical micellization temperature, UCMT), near the UCST of PNIPAM, and also above 130 °C, close to the LCST of PBzMA, with a regime of unimers at intermediate temperatures, as shown by DLS measurements. In pure $[C_2mim][NTf_2]$, the formation of micelles was observed only above 140 °C, however, no micellization at lower temperatures was detected. It has been reported that a 3 wt% PAAM homopolymer solution in $[C_2mim][NTf_2]$ exhibited a UCST-type phase transition above 150 °C, therefore, the copolymeri-

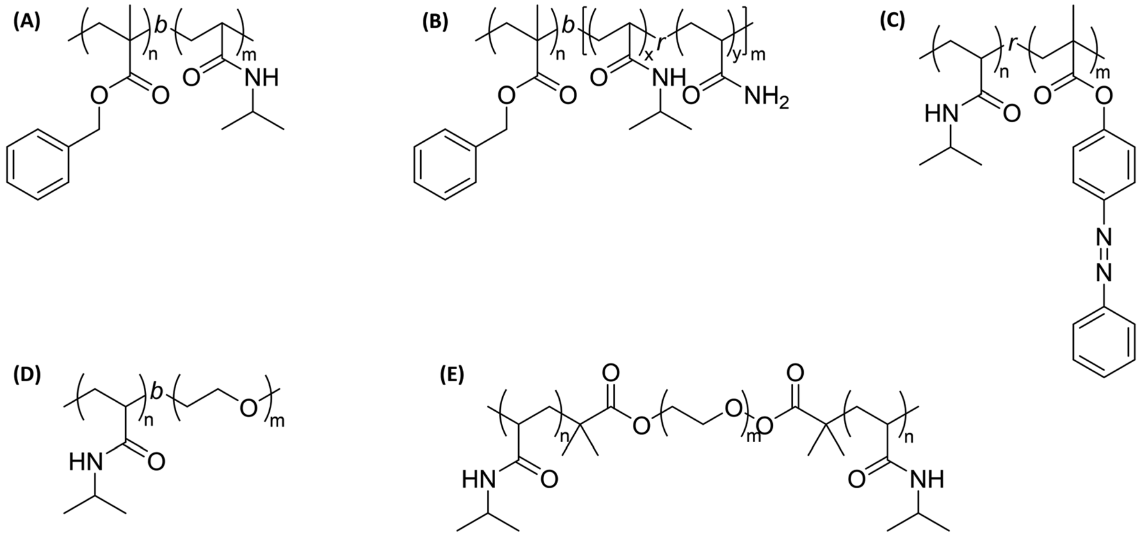


Fig. 42 Example of chemical structures of random and block copolymers of PNIPAM and (A) BzMA, (B) P(NIPAM-*r*-AAM), (C) AzoMA, (D) PEO, (E) PEO in ABA triblock copolymer.

zation of NIPAM with AAM, should induce a micellization of the diblock copolymer at lower temperatures. In fact, the diblock copolymer PBzMA(22)-*b*-P(NIPAM-*r*-AAM) underwent micellization at both low and high temperatures, with unimers at intermediate temperatures. This indicated that the self-assembly temperature of the diblock copolymers could be easily tuned, opening the route for the development of various smart materials.

In another example, the thermoresponsive behaviour of well-defined random copolymers of NIPAM and 4-phenylazophenyl methacrylate (AzoMA) synthesised *via* RAFT polymerization was evaluated in [C$_2$mim][NTf$_2$] in absence or under UV light irradiation.[189] The copolymers exhibited a UCST-type phase transition, which was strongly dependent on the AzoMA content and the photochromic state (Fig. 43). For example, the T_{CP} of *trans*-AzoMA-containing copolymers increased strongly with the increase in the AzoMA content, whereas that of *cis*-AzoMA-containing copolymers changed only slightly. This was attributed to the nature of the AzoMA monomer, which behaved as solvophobic monomer in its *trans*-form, and as solvophilic monomer in its *cis*-state, due to a change in polarity depending on its photoisomerization.

ABC triblock copolymers consisting of an IL-phobic poly(styrene) block, an IL-philic middle poly(*N*,*N*-dimethylacrylamide) segment and a photo/thermoresponsive final poly(4-phenylazophenyl methacrylate-*r*-*N*-isopropylacrylamide) block (PS-*b*-PDMAm-*b*-P(AzoBnAm-*r*-NIPAm) synthetized *via* RAFT polymerization exhibited temperature-induced phase transitions in [C$_2$mim][NTf$_2$].[190] As shown by DLS measurements performed in the dark, at a low polymer concentration (1 wt%), the triblock copolymer formed micelles consisting of a PS core and PDMAm-*b*-P(AzoBnAm-*r*-NIPAm) corona at 80 °C. By decreasing the temperature to 40 °C and further to 10 °C, the appearance of a bimodal distribution was observed, which was attributed to the formation of micellar aggregates due to the UCST behaviour of P(AzoBnAm-*r*-NIPAm). Rheological analysis of a 15 wt% triblock copolymer solution showed that the polymer could form percolated micellar networks at low temperatures due to the aggregation of the PS and P(AzoBnAm-*r*-NIPAm) blocks as physical crosslinks, bridged by the IL-philic PDMAm blocks. With the increase in temperature, a transition from micellar network to jammed micelles was observed, attributed to the disassembly of the thermoresponsive P(AzoBnAm-*r*-NIPAm) block, resulting in the softening of the gel. Also in this case, the temperature-induced phase transitions were strongly dependent on the photochromic state of the AzoBnAm units. The authors believe that this study might provide a promising strategy for controlling the rheological properties of nonvolatile soft materials *via* contactless light irradiation that could be used in various applications, such as photoresponsive and photo-healable actuators and soft materials.

The polymerization of PNIPAM with poly(ethylene oxide) into block copolymers showing temperature-induced phase transitions in ILs has also been thoroughly investigated. In contrast to the UCST behaviour of PNIPAM, PEO exhibited a LCST-type transition in ILs. For instance, PEO with a molecular weight of 20 kDa (PEO-20) underwent a reversible LCST behaviour in 1-ethyl-3-methylimidazolium tetrafluoroborate ([C$_2$mim] [BF$_4$]) with T_{CP} values decreasing with increasing polymer concentration.[191] Phase diagrams of two PEO homopolymers of 20 kDa and 5 kDa showed convex downward curves, with critical temperatures at 130 and 136 °C, respectively, showing that the T_{CP} values were only weakly dependent on the molecular weight of the polymer. The effect of the alkyl chain on the imidazolium cation of the IL was also evaluated by measuring the transmittance of a 2 wt% PEO-20 solution in [C$_4$mim] [BF$_4$]. The solution showed a LCST-type phase transition at 209 °C, approximately 45 °C higher than in [C$_2$mim] [BF$_4$]. Additionally, in a mixture of the two ILs, a 2 wt% PEO-20

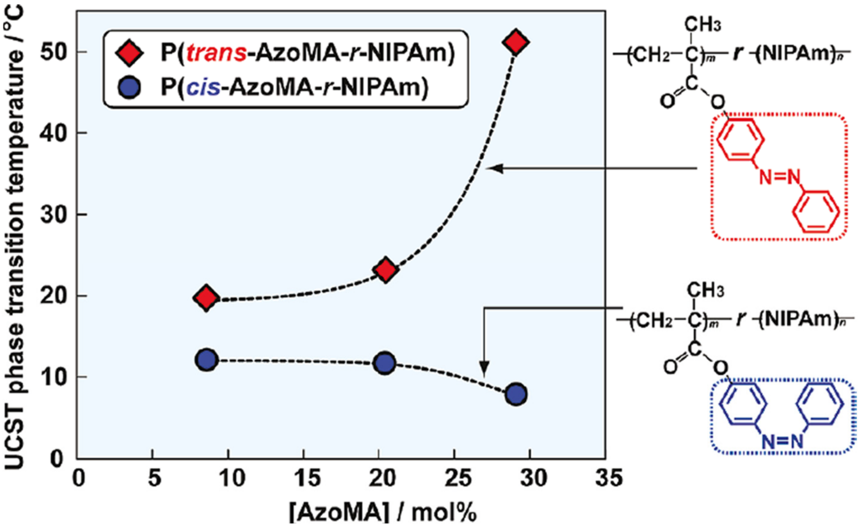


Fig. 43 Effect of AzoMA content and photochromic state on the T_{CP} values of random copolymers of NIPAM and AzoMA. Reproduced from ref. 189 Copyright 2011 American Chemical Society.

solution exhibited T_{CP} values which increased almost linearly with increasing weight fraction of [C_4mim] [BF_4].

Interestingly, a noticeable difference in the phase diagrams of 2 kDa PEO solutions in [C_2mim] [BF_4]and 1-ethyl-2,3-dimethylimidazolium tetrafluoroborate [C_2dmim] [BF_4], where the H atom in the C2 position of the imidazolium cation was replaced by a methyl group, was observed.[178] To exemplify, no changes were recorded at low PEO concentrations, however, a sharp decrease in the T_{CP} values was observed when the concentration was above 30 wt%. The substitution of the most acidic proton of the IL cation with a methyl group lowered the H bonding interactions with the PEO chains, decreasing the PEO miscibility in the IL and, consequently, shifting the T_{CP} to lower values.

By combining PNIPAM and PEO in a diblock copolymer, micelles and inverted micelles could be obtained in [C_4mim] [BF_4] with a UCMT around 60 °C and a LCMT around 207 °C, close to the T_{CP} of PNIPAM and PEO, respectively.[177] The authors concluded that the diblock formed PNIPAM-core micelles at low temperatures, and PEO-core micelles at high temperatures. Similarly to the behaviour of the corresponding homopolymers, in [C_4mim] [BF_4]/[C_2mim] [BF_4] mixtures, the UCMT and LCMT values of the diblock copolymer increased and decreased, respectively, with increasing [C_2mim] [BF_4] weight fraction.

In another report, triblock copolymers consisting of two PNIPAM outer blocks and a PEO middle segment obtained by RAFT polymerization of a PEO homopolymer end-capped with a chain transfer agent, showed a reversible sol–gel transition in [C_2mim][NTf_2] at a 10 wt% polymer concentration.[172] As demonstrated by dynamic shear measurements, the solution behaved as a liquid at high temperatures (~50 °C), and as a gel at −5 °C, with an intermediate behaviour at intermediate temperatures, and a gelation point around 20 °C. The gelation process was attributed to the noncovalent association of PNIPAM outer blocks undergoing the UCST, bridged by the IL-compatible PEO-middle block.

By incorporating a solvophobic poly(styrene) segment into a pentablock copolymer obtained by chain extension of a poly(styrene)-*b*-poly(ethylene oxide)-*b*-poly(styrene) triblock copolymers with NIPAM (PNIPAM-*b*-PS-*b*-PEO-*b*-PS-*b*-PNIPAM), the sol–gel transition temperatures of the resulting gels in [C_2mim][NTf_2] could be tuned over a wide temperature range (17–48 °C), as demonstrated by oscillatory shear and temperature-dependent dynamic shear moduli measurements, and DLS analyses.[192]

ABA triblock copolymers consisting of a middle IL-soluble PEO block and two outer segments of random copolymers of AzoMA and NIPAM exhibited temperature-induced reversible upper critical micellization and gelation in [C_4mim]PF_6 depending on the polymer concentration.[179,193,194] As already explained above, the AzoMA was in its *cis*-state under UV light irradiation, while it was in its *trans*-form under visible light irradiation or in the absence of light. As expected, the UCMT of the ABA copolymers (1 wt%) was found to be strongly dependent on the photochromic state of the AzoMA, with values of 60 °C and 44 °C for *trans*-ABA and *cis*-ABA copolymers, respectively.[179] In addition, a temperature-induced sol–gel transition was observed for 20 wt% ABA triblock copolymer solutions in both *cis*- and *trans*-states in [C_4mim]PF_6 under both UV or visible light. Also in this case, the gelation temperatures were strongly dependent on the *cis*- or *trans*-state of the azobenzene units.

PEO has also been copolymerized with poly(*n*-butyl methacrylate) (P*n*BMA) to form diblock copolymers undergoing temperature-induced micellization with tunable LCMT in ILs mixtures. P*n*BMA exhibited a LCST-type phase transition in [C_4mim][NTf_2], which was strongly influenced by the polymer concentration and molecular weight.[174] As also shown for other polymers, the T_{CP} value of P*n*BMA increased almost linearly with increasing length of the alkyl chain on the imidazolium cation. Additionally, in $[C_2mim][NTf_2]$/$[C_4mim][NTf_2]$ mixtures, the T_{CP} of 2 wt% P*n*BMA (48 kDa) decreased from 108 °C to room temperature when the $[C_4mim][NTf_2]$ weight fraction decreased. A similar trend was also observed in $[C_2mim][NTf_2]$/$[C_6mim][NTf_2]$ mixtures with T_{CP} values increasing from 108 to 247 °C when the $[C_6mim][NTf_2]$ weight fraction was increased from 0 to 75 wt%. In the case of PEO-*b*-PnBMA diblock copolymers containing a solvophilic PEO segment, a micellization process forming P*n*BMA-core and PEO-corona micelles in $[C_2mim][NTf_2]$/$[C_4mim][NTf_2]$ mixtures was observed *via* DLS analyses, with LCMT values increasing with increasing weight fraction of $[C_4mim][NTf_2]$.

The thermoresponsive behaviour of PEO-derivatives has also been investigated in various ionic liquids (Fig. 44). For example, poly(ethyl glycidyl ether) (PEGE) showed a LCST-type behaviour in various ILs, which was strongly dependent not only on the polymer molecular weight and concentration, but also on the nature and alkyl chain length of the IL cation and on the type on the IL anion.[173,195] For ILs with $[NTf_2]$ anion, PEGE (10 wt%) underwent a phase transition in imidazolium ILs, while it was soluble in pyridinium ILs and insoluble in ammonium and phosphonium ILs. Therefore, the hydrogen bonding interactions between the oxygen atoms of PEGE and the acidic hydrogens in the aromatic ILs were essential to increase its miscibility. The T_{CP} also increased with increasing alkyl chain length on the imidazolium cations. Furthermore, when the proton in the C2 position of the imidazolium cation was substituted with a methyl group, the T_{CP} significantly decreased (*e.g.* PEGE/$[C_4dmim][NTf2]$ has a T_{CP} 120 °C lower than PEGE/$[C_4mim][NTf_2]$). In contrast to PBzMA, the hydrogen bonding interactions between the ether oxygen atoms of PEGE and the hydrogen atoms of the IL cations played a crucial role in the temperature-induced phase transition. Also in this case, the T_{CP} values increased with increasing length of the alkyl chain on the IL cation. For ILs with imidazolium cations, PEGE exhibited an LCST phase transition in ILs containing imide anions, while it was immiscible in ILs with [OTf] and $[PF_6]$ anions. However, for imidazolium cations with longer alkyl chain length and $[PF_6]$ anion, a LCST behaviour was observed. Therefore, the thermoresponsive behaviour was also slightly influenced by the nature of the anion of the IL. In this study, the temperature-induced solution behaviour of other PEO-derivatives was also investigated. For example, poly(glycidyl methyl ether) (PGME) and poly(ethoxyethyl glycidyl ether) (PEEGE) were found to be completely miscible in ILs with [NTf2] anion, however, a LCST phase transition was observed in $[C_4mim][PF_6]$ at 53.5 and 56 °C, respectively, at a polymer concentration of 10 wt%. Additionally, poly(propylene oxide) (PPO) exhibited a LCST phase transition at 48 °C only in $[C_4mim][NTf_2]$, while it was completely immiscible in all the other tested ILs. Therefore, the ether oxygen atom of the PEO-derivatives played a crucial role in increasing their miscibility in the ILs through hydrogen bonding interactions.

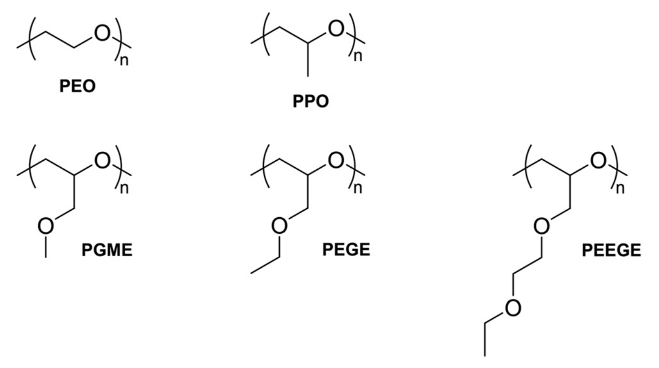


Fig. 44 Chemical structures of poly(ethylene oxide) (PEO) and its derivatives: poly(propylene oxide) (PPO), poly(glycidyl methyl ether) (PGME), poly(ethyl glycidyl ether) (PEGE), and poly(ethoxyethyl glycidyl ether) (PEEGE).

Finally, a diblock copolymer consisting of a PEGE block (DP = 104) and a PEO segment (DP = 178) synthesised *via* sequential anionic ring-opening polymerization exhibited a unimers-to-micelles transition in $[C_4mim][PF_6]$ with a LCMT of 15 °C at a polymer concentration of 1 wt%.[180]

In this section, the thermoresponsive solution behaviour of polymers in ionic liquids has been thoroughly discussed. In ILs, polymers exhibit a broad range of temperature-induced behaviours, from LCST, to UCST, to micellization and sol–gel transitions. The type of phase transition and the temperature at which it occurs are strongly dependent not only on the polymer composition, structure, molecular weight, and concentration, but also on the type of ionic liquid used, the length of the alkyl chain and the substitutions on the imidazolium cation, the nature of the anion, as well as the ratio between ILs mixtures. These polymers, especially crosslinked gels, might have a crucial impact on the development of environmentally stable smart gel materials for various applications. The reader is also referred to exhaustive reviews for further information on thermoresponsive polymers in ILs and their potential applications.[182,196–198]

7. Other organic solvents

In this last section, examples of polymers exhibiting temperature-induced phase transitions in organic solvents not previously mentioned are discussed (Table 10, and Table S9†). The solvents are displayed in order of polarity.

The thermoresponsive behaviour of various polymers was also investigated in a wide range of non-chlorinated organic solvents of different polarities. The polymers will be classified based on increasing solvent polarity. While some of the polymers, such as poly(ODVE), have been mentioned in previous paragraphs due to their solution behaviour in other solvents, novel polymer types will also be introduced in this section.

As mentioned before, poly(vinyl ether)s have interesting solution properties depending on the nature of the pendant side chains. Both poly(ODVE) and poly(HDVE) exhibited an UCST phase transition in diethyl ether.[109] Moreover, a UCST-type phase transition around 7 °C was observed for poly

Table 10 Examples of polymers exhibiting a thermoresponsive behaviour in other organic solvents in order of polarity

Solvent	Type of polymer	Polymer conc.	Phase transition type (Temp. °C)	Ref.
Diethyl ether	Poly(octadecyl vinyl ether)	1 wt%	UCST (~12)	109
THF	Hyperbranched 3-ethyl-3-(hydroxymethyl)oxetane core/glycidyl-*graft*-PEG shell copolymers	5 mg mL^{-1}	UCST (@13.4–17.4)	199
THF	Poly(*N*,*N*-diethylacrylamide)-*b*-poly(4-acryloylmorpholine)	6 wt%	UCST (~20–40)	200
THF	Poly-(*p*-biphenylylmethyl-L-glutamate	0.62–1.12 mg mL^{-1}	Chiral optical transition (~−2.5)	201
THF	Poly-γ-*p*-biphenylethoxy-L-glutamate and poly-γ-*p*-biphenylhexoxy-L-glutamate	~20 wt%	α-Helix reorientation (~7–37) gelation (~9–39)	202
1,4-Dioxane	Poly(11-(4-((*E*)-4-butylstyryl)phenoxy)undecyl methacrylate)	2 wt%	UCST (@52.3)	140
Methyl acetate	Polystyrene	0.003–0.078 wt%	LCST (@124.55–129.35) and UCST (@26.10–32.70)	21
Ethyl acetate	Poly(octadecyl vinyl ether-*random*-isobutyl vinyl ether)	1 wt%	UCST (~15)	109
n-Butyl acetate	Poly(2-chloroethyl vinyl ether-*alt*-maleic anhydride)	0.05 wt%	LCST (~85)	203
tert-Butyl acetate	Polystyrene	0.005–0.3 wt%	LCST (@117.9–165.5) and UCST (@−32.5–5.5)	21
Propyl acetate/DCE	Poly(2-chloroethyl vinyl ether-*alt*-maleic anhydride)	0.1 wt%	LCST (~42–70)	149
DME	Poly-(methacrylic acid-*alt*-hydroxyethyl acrylate)	8 mg mL^{-1}	LCST (~18)	204
DME	Poly(arylene ether sulfone)	2.5 mg mL^{-1}	LCST (@37)	163
DME	poly(arylene ether sulfonate)-*b*-polylactide	15 mg mL^{-1}	LCST (@27.4)	163
Acetone	Poly(octadecyl vinyl ether-*random*-isobutyl vinyl ether)	1 wt%	UCST (~38)	109
DMF	Comb-like copolymer of *N*-phenyl maleimide and *n*-octadecyl vinyl ether	1 wt%	UCST (@51)	117
DMF	Poly(thioether)-*b*-polysiloxane-*b*-furfuryl poly(thioether)-bismaleimide elastomer	n/a	De-crosslinking (@150)	205
DMAc	4,4′-Sulfonyldiphenol (SDP) based oligourethane derivative based on 1,6-hexamethylene diisocyanate	8 wt%	Sol–gel transition (ND)	206
DMSO	4,4′-Sulfonyldiphenol (SDP) based oligourethane derivative based on 1,6-hexamethylene diisocyanate	8 wt%	Sol–gel transition (ND)	206
ACN	Poly(3-(3-butylureido)propyl acrylate-*stat*-*N*-[3-(acryloyloxy)propyl]-*N*,*N*,*N*-trihexylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl) borate	100 mg mL^{-1}	UCST (@57)	164

(ODVE) in tetrahydrofuran (THF).[109,147] Similarly, the partially fluorinated poly(vinyl ether) poly(9FVE) also showed the same solution behaviour at around 8 °C, which was strongly affected by the polymer polydispersity and degree of polymerization.[153] In another example, poly(vinyl ether)s having imidazolium salt pendants, namely poly[2-(vinyloxy)-ethyl-1-butylimidazolium chloride], showed a LCST at around 40 °C in THF/1-butanol mixtures (86/14% w/w), characterized by a large hysteresis between the heating and the cooling cycles in the transmittance plots.[155]

Additionally, alternating copolymers of 2-chloroethyl vinyl ether and maleic anhydride synthesized by free radical solution polymerization exhibited a LCST behaviour in THF/hexane mixtures, as shown by static light scattering (SLS) analyses.[149,207] The T_{CP} could be tuned by varying the solvents mixture composition, the polymer molecular weight, and the copolymer concentration.[207] Since THF was a good solvent for the copolymer and hexane a non-solvent, an increasing amount of THF in the solvent mixture resulted in the shift of the cloud point to higher temperatures and in the widening of the homogeneous one-phase region below the T_{CP} curve. Increasing the THF fraction above 85 wt% resulted in the absence of a phase transition due to the complete solubility of the copolymer in the solvents mixture.[149]

In another study, core–shell copolymers consisting of a hyperbranched 3-ethyl-3-(hydroxymethyl)oxetane core and a glycidyl-*graft*-PEG shell (PEG-*g*-POG) with different DPs of the glycidyl segment exhibited a UCST phase transition in THF, which was attributed to the crystallization of the PEG side chains (Fig. 45).[199] The thermoresponsive behaviour was dependent on both the polymer concentration in solution and the DP of the glycidyl segment. To exemplify, the copolymers having PEG side chains with a M_n of 1900 g mol^{-1} and a glycidyl segment with DP = 5, 8, and 12 showed T_{CP} values of 13.4, 14.5 and 17.4 °C, respectively. The authors believe that these hyperbranched copolymers will help in the design and production of new intelligent materials for specialized applications in the biomedical field.

In a recent report, it has been shown that poly(4-acryloylmorpholine) (PAM) homopolymer with a molecular weight of 117 300 g mol^{-1} exhibited a UCST behaviour in THF around 10 °C at a polymer concentration of 3 wt%, which increased to 15 °C at 6 wt%.[200] Similarly, it was observed that block copolymers consisting of a poly(*N*,*N*-diethylacrylamide) block and a poly(4-acryloylmorpholine) segment (PDEA-*b*-PAM) showed a UCST phase transition in the same solvent, as demonstrated by turbidity and DLS measurements However, the thermoresponsive behaviour was strongly dependent on the molecular

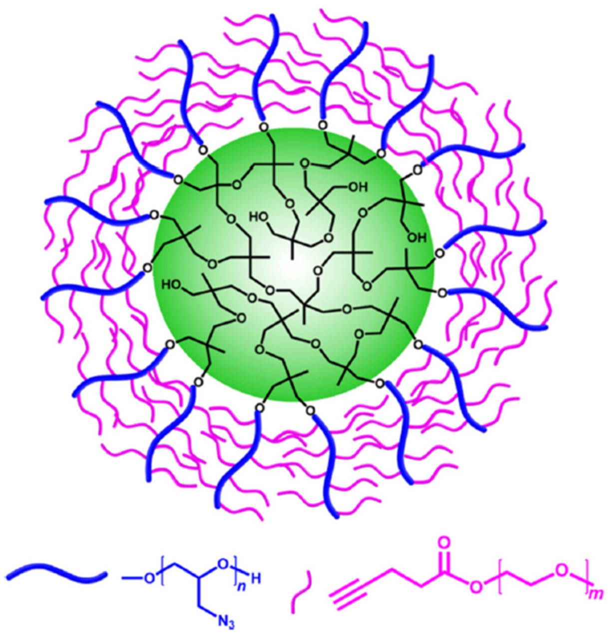


Fig. 45 Schematic representation of the core–shell copolymers with a hyperbranched 3-ethyl-3-(hydroxymethyl)oxetane core and a glycidyl-*graft*-PEG shell. Reproduced from ref. 199 Copyright 2021 American Chemical Society.

weight and on the concentration of the block polymer (Fig. 46). For instance, PDEA-*b*-PAM with a final molecular weight of 403 500 g mol^{-1} showed a UCST phase transition with a T_{CP} of around 10–12 °C at 3 wt%, which increased up to 40 °C at 6 wt%, with a broadening of the transition temperature range from 20 to 40 °C. The broader phase transition range was explained by the presence of the stabilizing THF-soluble PDEA blocks. For other shorter block copolymers and at lower concentrations, a thermoresponsive behaviour in THF was not observed.

Poly(*p*-biphenylylmethyl-L-glutamate), PBPMG, exhibited a temperature-induced phase transition in the helicogenic solvent THF at dilute concentrations.[201] It has been demonstrated by static and dynamic LS analyses and circular dichroism measurements, that at low temperatures the increasingly poor solvent conditions led to the ordered aggregation of the polymer chains whose association increased in parallel with a decrease in the optical rotation in solution. The increase in temperature resulted in the dissolution of the polymer chains. Poly-γ-*p*-biphenylethoxy-L-glutamate and poly-γ-*p*-biphenylhexoxy-L-glutamate, two PBPMG derivatives, showed two thermoresponsive behaviours in THF: a 90° reorientation of the polymer α-helix with respect to the external magnetic field and a thermoreversible gelation, as demonstrated by polarized optical microscopy, NMR and rheometric measurements.[202]

In another example, it has been shown that linear and star poly(styrene) polymers analysed using thermal field-flow fractionation and DLS, exhibited a temperature-induced phase transition in THF at a concentration of 5 mg mL^{-1}.[148] Both techniques demonstrated that the star polymers were more temperature-sensitive than the linear counterparts, which increased with increasing number of arms rather than with the length of the arms. This was explained by a difference in the rearrangement in solution of the linear and star polymers with increasing temperature. To exemplify, linear polymers would expand in a 3D manner when the temperature is raised, leading to an overall smaller size change compared to star polymers, which arms would preferably swell in 1D from the core in solution, resulting in an overall greater change in size. A similar trend but with smaller changes in size was also observed in dimethylacetamide.

Interestingly, the liquid crystalline polymer poly(11-(4-((*E*)-4-butylstyryl)phenoxy)undecyl methacrylate) is the only example of thermoresponsive polymers in pure 1,4-dioxane that we could find in literature.[140] The polymer exhibited a UCST-type phase transition at 52.3 °C at a polymer concentration of 2 wt%, which was demonstrated to be driven by the crystallization of the polymer in the solvent.

The thermoresponsive behaviour of polystyrene homopolymers has been investigated in methyl and ethyl acetate, in which both LCST and UCST-type transitions were observed.[21] As an example, a 770 kDa polymer solution in methyl acetate with a concentration of 0.05 wt% exhibited T_{CP} at around 125 and 30 °C for LCST and UCST-type behaviour, respectively, as measured by thermooptical analysis. It is important to notice that the apparatus used for the measurements required samples sealed by a vacuum in order to determine the cloud points of the polymer solutions at the saturated vapor pressure of the solvent, making possible the determination of temperature-induced phase transitions also in low boiling point

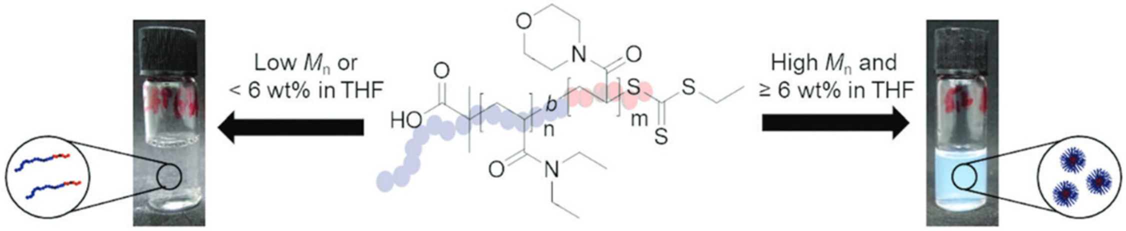


Fig. 46 Schematic representation of the aggregation behaviour of poly(*N*,*N*-diethylacrylamide)-*b*-poly(4-acryloylmorpholine) (PDEA-*b*-PAM) in THF, depending on the polymer molecular weight and concentration. Reproduced from ref. 200 Copyright 2021 The Authors. Macromolecular Rapid Communications published by Wiley-VCH GmbH.

solvents. Interestingly, 0.05 wt% ethyl acetate solutions of the polystyrene homopolymers only showed LCST-type phase transitions, with T_{CP} decreasing from 165.5 to 147.7 °C with increasing molecular weight from 100 to 600 kDa. A similar thermoresponsive behaviour was also observed in *tert*-butyl acetate.

As expected, poly(vinyl ether)s present temperature-induced phase transitions also in alkyl acetate solvents. For example, poly(dodecyl vinyl ether) (poly(DDVE)) and poly(cholesteryl 2-(vinyloxy)ethyl carbonate) (poly(ChVE)(Et)) exhibited a UCST transition in ethyl acetate around 45 °C and at 67 °C, respectively (Fig. 47).[109] Similarly, a UCST phase transition was observed for random copolymers of IBVE and ODVE at around 15 °C in the same solvent. In another example, the thermoresponsive behaviour of poly[2-(vinyloxy)-ethyl-1-butylimidazolium chloride] was achieved by combining ethyl acetate with a good solvent, 1-butanol (85/15% w/w).[155] The polymer exhibited a highly sensitive LCST-type phase transition at around 65 °C in the solvents mixture.

An LCST-type phase transition in *n*-butyl acetate was observed for poly(2-chloroethyl vinyl ether-*alt*-maleic anhydride) alternated copolymers obtained *via* free radical solution polymerization, which was attributed to specific polar interactions between the polymer and the solvent.[203] The T_{CP} was dependent on the polymer molecular weight and it could be tuned by adding co-solvents to the binary mixture. The addition of non-solvents (*i.e.* benzene, toluene, cyclohexane, 1,2-dichloroethane, *n*-octane) resulted in a decrease in the T_{CP}, while it increased when a good solvent (*i.e.* 2-hexanone, propyl acetate) was added. Interestingly, even when a low amount of DMSO was added (2 wt%), no thermoresponsive behaviour was observed up to 100 °C. These alternated copolymers also exhibited an LCST-type behaviour in propyl acetate/DCE mixtures.[149] Since DCE was a non-solvent for the polymer, the increase in the amount of DCE resulted in a decrease in the T_{CP} of the polymer and in the broadening of the hysteresis between heating and cooling cycles in the turbidity plot.

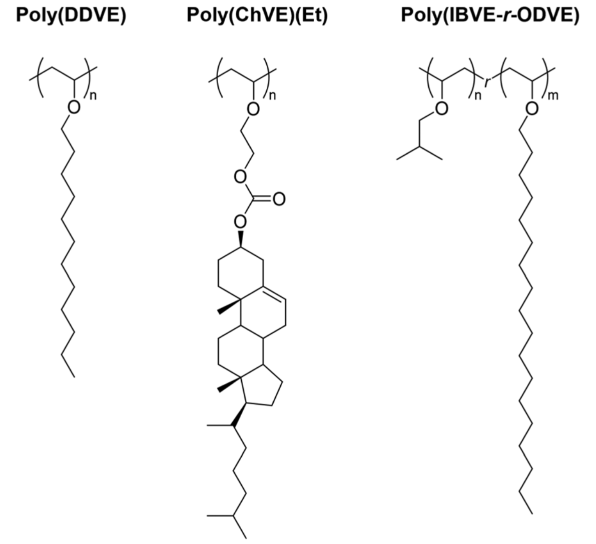


Fig. 47 Chemical structures of poly(dodecyl vinyl ether) (poly(DDVE)), poly(cholesteryl 2-(vinyloxy)ethyl carbonate) (poly(ChVE)(Et)), and poly(isobutyl vinyl ether-*random*-octadecyl vinyl ether) (poly(IBVE-*r*-ODVE)).[109]

In another example, an alternating copolymer of methacrylic acid (MAA) and hydroxyethyl acrylate (HEA) synthesised *via* cyclopolymerization of AB-type divinyl monomer with hemiacetal ester spacer followed by hydrolysis, revealed an interesting thermoresponsive behaviour in dimethoxyethane (DME) (Fig. 48).[204] It is important to notice that, in the paper, dimethyl ether is mentioned as the solvent used for the analyses. However, due to the low boiling point of dimethyl ether (*i.e.* − 24 °C) and the absence of information about the sample preparation, we suggest that the authors probably meant dimethoxyethane. The copolymer exhibited a LCST-type phase transition in DME at around 18 °C at a concentration of 8 mg mL^{-1}, suggested to be caused by the balance of two hydrogen bonding interactions: (i) the intra-chain interactions between neighbouring pendants (–COOH and –OH), and (ii) the inter-chain interactions between –COOH pendants. The adjacent hydroxyl group could affect the inter-chain interaction between carboxylic functional groups *via* H bonding with the –COOH group and/or its solvation, and the interaction preference might be altered with temperature changes, resulting in the thermoresponsive behaviour.

In order to better understand the thermoresponsiveness of the alternating copolymer, the solution behaviour of pMAA and pHEA homopolymers was investigated.[208] While pHEA was completely soluble in DME and failed to show thermoresponsiveness, pMAA exhibited a LCST around 25 °C. At temperatures lower than the LCST, the polymer chains were solvated through the formation of hydrogen bonds between the carboxylic acid groups and the solvent molecules that led to a reduction of the rotational and conformational degrees of freedom of the solvent. When the temperature was increased above the LCST, an entropy-driven desolvation occurred and the polymer chains aggregated through inter and intramolecular hydrogen bonding, resulting in the polymer precipitation.

Poly(arylene ether sulfone) and its diblock copolymers with DL-lactide also underwent LCST-type phase transitions in dimethoxyethane.[163] The T_{CP} of the homopolymers increased from 37 to more than 60 °C with increasing molecular weight and decreasing polymer concentration. Moreover, the T_{CP} of the diblock copolymers increased from 27.4 to 45 °C with the decrease in the DP of the PES block from 15 to 10. Reducing the polymer concentration from 15 to 5 mg mL^{-1} resulted in a further rise of the T_{CP} above 60 °C.

Vinyl ether polymers are intensively studied in various organic solvents and show thermoresponsiveness also in more polar solvents. For example, when a small amount of ODVE was polymerized with IBVE, the resulting random copolymer exhibited a UCST around 38 °C in acetone.[109] Similarly, the partially fluorinated poly(9FVE) underwent a UCST around 14 °C in the same polar solvent.[153] The comb-like copolymer resulting from the copolymerization of ODVE with *N*-phenyl

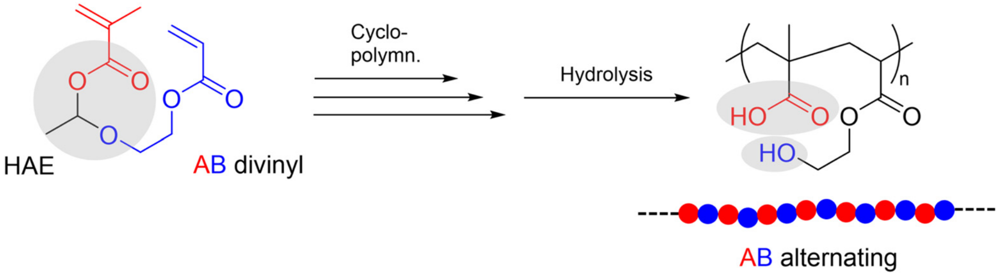


Fig. 48 Schematic depiction of the cyclopolymerization of AB-type divinyl monomer with hemiacetal ester spacer.[204]

maleimide showed a UCST behaviour at 51 °C in DMF due to the aggregation of the long alkyl chains of the vinyl ether monomer at low temperatures, as demonstrated by high resolution ^{1}H NMR analyses in DMF-d$_7$.[117] The UCST could be easily tuned by varying the polymer concentration and by adding co-solvents in the binary mixture.

The thermoresponsive behaviour of a series of blue-emitting 4,4′-sulfonyldiphenol (SDP)-based oligourethane derivatives (OUs) based on 1,6-hexamethylene diisocyanate (OUHDI), 4,4′-methylenebis(cyclohexyl isocyanate) (OUHMDI), and 2,4-diisocyanatotoluene (OUTDI) synthesised *via* a single-pot reaction has been investigated in several organic solvents.[206] For example, in solvents with hydrogen-bonding receptor units, such as DMF, dimethyl acetamide-DMAc, and DMSO, the polymers showed a spontaneous thermoreversible gelation, which facilitated the self-assembly of the polymer chains into nanotubes. As a result of the aggregation, these oligomers showed a blue fluorescence, while an enhanced bright deep-blue emission was achieved upon gelation due to inter-chain hydrogen bonding and oxygen cluster interactions. Among all the investigated polymers, OUHDI showed the most efficient thermoreversible gelation at 63 °C in DMF due to the greater ability of the higher symmetric linear structure to crystallize. Furthermore, the temperature-induced gelation was found to be both concentration and time-dependent. It was demonstrated that the gelation occurred more rapidly at high polymer concentrations due to increased inter-chain interactions, and the polymer solution changed from a viscous solution to a gel upon cooling over a period of 48 h. The synthetic approach used to introduce heteroatoms into the SDP-based thermoresponsive polymers might offer a new direction for the design and fabrication of blue luminescent gelators, which could be used in the development of high-quality displays and organic light-emitting diodes.

A thermoresponsive dielectric elastomer, poly(thioether)-*b*-polysiloxane-*b*-furfuryl poly(thioether) triblock copolymer, was obtained from the silicon alkoxide catalysed ROP of furfuryl glycidyl ether and carbonyl sulfide followed by the Diels–Alder reaction with bismaleimide (PSiFGE-BMI).[205] The triblock copolymer underwent a reversible de-crosslinking reaction when heated up from room temperature to 160 °C in DMF. DSC analyses revealed the appearance of an endothermic peak in the range 120–180 °C, with a maximum heat flow at around 150 °C, indicating the rupture of the crosslinking network. During the cooling process, the appearance of an exothermic peak at around 70 °C confirmed the reversible re-association of the crosslinking network. This study provides a new strategy for the synthesis of homogenous dielectric elastomers, which could have promising applications as actuated devices.

Poly(3-(3-butylureido)propyl acrylate-*stat*-*N*-[3-(acryloyloxy)propyl]-*N*,*N*,*N*-trihexylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate copolymers containing self-attractive urea units and self-repulsive lipophilic moieties exhibited a UCST behaviour in acetonitrile (ACN).[164] Also in this solvent, the T_{CP} decreased from 57 to 52 °C by increasing the content of the TFPB ion pair from 4 to 5 mol%, due to a more efficient dissolution of the polymer by ionic dissociation.

Finally, thermoresponsive polysiloxanes (TRPSis) synthesised *via* the catalyst-free aza-Michael addition of poly(aminopropylmethylsiloxane) to NIPAM have shown to undergo a UCST phase transition in ACN, with T_{CP} increasing by lowering the *N*-isopropyl content due to enhanced hydrogen bonding interactions of the polysiloxanes caused by the presence of more amino groups.[96] Moreover, TRPSis also exhibited a UCST in ACN/ethylene carbonate and in ACN/ethyl acetate mixtures. In the former solvent mixture, TRPSis showed higher UCST compared to pure solvents (Fig. 49A), while in the latter case the measured UCST was lower (Fig. 49C). This result was attributed to the co-effect of two *Hansen* solubility parameters during the mixing process: the energy from the dipolar intermolecular force between molecules (δ_{p}), and the energy from hydrogen bonds between molecules (δ_{h}). As can be observed in Fig. 49B, the increase in $n_{\text{ethylene carbonate}}$ resulted in decreased δ_{p} and increased δ_{h} values. On the contrary, upon increasing $n_{\text{ethylacetate}}$, δ_{p} increased, while δ_{h} decreased (Fig. 49D). These polymers could be promising candidates for the application as intelligent catalysts for extraction in non-aqueous conditions.

In this last section, the temperature-induced solution behaviour of polymers in various non-halogenated organic solvents with different polarities has been discussed. Also in this case, the thermoresponsive behaviour depends on various parameters, including, but not limited to, the polymer concentration and molecular weight, as well as the presence of specific functional groups or atoms, and the resulting intra- and inter-molecular interactions between polymer chains and/or solvent molecules. Using temperature to trigger different solution behaviours in a wide range of solvents with different polarities opens the possibility to design and develop new

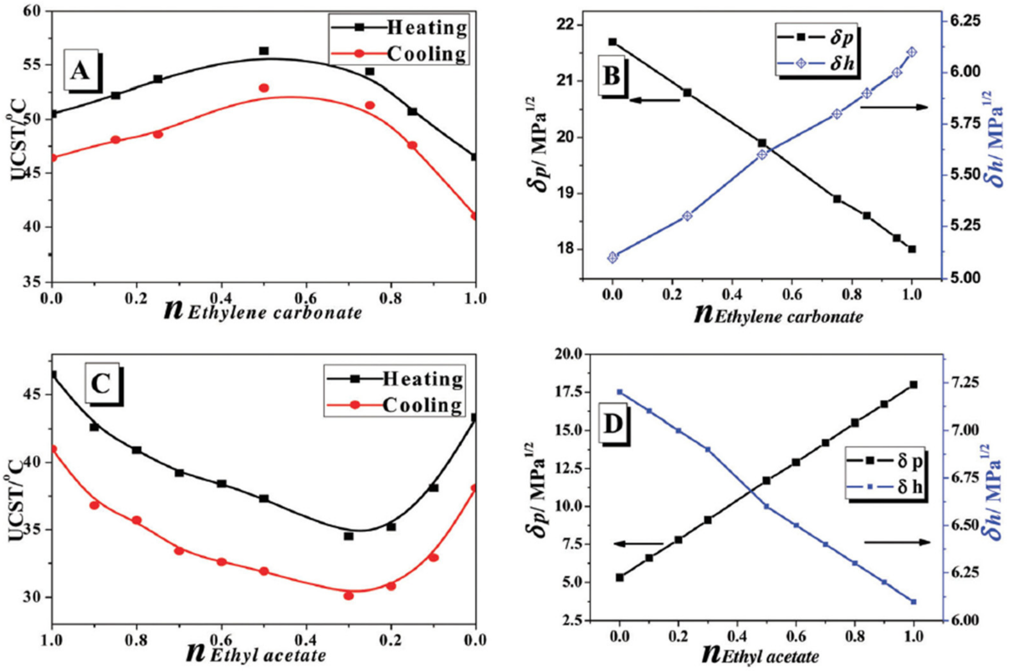


Fig. 49 (A) UCST and (B) and δ_p and δ_h of TRPSis in acetonitrile/ethylene carbonate mixed solvents as a function of the ethylene carbonate content; (C) UCST and (D) δ_p and δ_h of TRPSis in acetonitrile/ethyl acetate mixed solvents as a function of the ethyl acetate content. Reproduced from ref. 96 Copyright 2017 Royal Society of Chemistry and the Centre National de la Recherche Scientifique.

intelligent materials for a variety of potential applications in, for example, the electronic and biomedical fields.

8. Conclusions

The aim of this review article was to highlight the importance and variety of thermoresponsive polymers in non-aqueous systems present in literature. While the temperature-induced solution behaviour of polymers has been extensively investigated and reported in pure water or water/organic solvent mixtures, polymers showing thermoresponsiveness in other organic solvents are still not very common.

As explained above, the terms LCST and UCST refer to exact values corresponding to the minimum or the maximum of the binodal curve in the phase diagram of a polymer/solvent mixture and they should not be confused with cloud point temperatures. T_{CP}s correspond to any value on the binodal curve and refer to the temperature at which phase separation occurs at a specific polymer concentration in solution. For both water and organic solvents, these values are influenced by many parameters, such as the polymer molecular weight and polydispersity, its chemical composition, the presence of specific functional groups on the polymer chains, the addition and ratio of co-solvents, additives, and effectors, the type of solvent, as well as inter- and intra-molecular interactions between macromolecules and solvent molecules. Furthermore, the determination of the T_{CP} values strongly depends on the experimental method used, which makes the comparison of reported data more difficult. Many characterization approaches are used to evaluate the thermoresponsive behaviour of polymers in solution. Among all, the evaluation of the turbidity of a polymer solution upon the increase (or decrease) of temperature is the most common technique used for the determination of the T_{CP} value. Other widely employed methods for the characterization of thermoresponsive polymers are DLS, (variable temperature) NMR spectroscopy, FTIR spectroscopy, SANS, SAXS, and DSC. Additional less common techniques include circular dichroism, rheology and dynamic viscoelasticity measurements. Furthermore, microscopy methods, such as SEM, TEM, cryo-TEM and AFM, are also frequently used for the visualization of morphological changes in the self-assembly of polymers driven by temperature variations.

This detailed summary proves the versatility and potential of thermoresponsive polymers in non-aqueous systems, which show unique solution behaviour in a large variety of solvents with different polarities. However, while several types of potential applications have been proposed and reported for polymers in water and water/organic solvent mixtures, especially in the biomedical and personal care areas, only a few examples for non-aqueous systems are present in literature, mainly in the design of smart functional polymer materials for industrial applications as friction modifiers, and oil thickeners. Nevertheless, the easy synthesis, high stability and the tuneable thermoresponsive properties of these polymers make them promising candidates for their potential application not only in the lubricant industry, but also as smart materials for electronics and for the development of new sensors. Therefore, the understanding of the polymer/solvent relationship, the interactions involved, and the parameters affecting the behaviour in solution is crucial for the design of thermoresponsive polymers in non-aqueous systems. However, apart from the fundamental understanding, the focus should also be aimed to study the potential applications of these systems. Therefore, despite the lack in the literature of potential applications of these systems, we believe that this collection will help the chemistry community to better understand the chemistry required for the design of thermoresponsive polymers in non-aqueous systems and their emerging potential, with the hope that new ideas can arise from scientists reading this article.

Author contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

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