NJC

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *New J. Chem.*, 2022, **46**, 15321

RAFT solution copolymerization of styrene and 1,3-butadiene and its application as a tool for block copolymer preparation†

Abdullah Gunaydin,[ab] Patrick Grysan,[a] Daniel F. Schmidt,[a] Reiner Dieden,[a] Marc Weydert[c] and Alexander S. Shaplov *[a]

Received 10th May 2022,
Accepted 28th June 2022

DOI: 10.1039/d2nj02286a

rsc.li/njc

For the first time, random copolymers of styrene (St) and 1,3-butadiene (Bd) (poly(St_n-*r*-Bd_m), styrene butadiene rubber, SBR) were successfully prepared *via* solution reversible addition-fragmentation-transfer (RAFT) polymerization by employing dithio- and trithiocarbonate chain transfer agents (CTAs). The influence of various reaction parameters such as temperature and duration of polymerization, type of CTA, solvent and initiator, on molecular weight, molecular weight distribution (M_w/M_n) and the yield of the copolymers was investigated in detail. Determination of optimal reaction conditions allowed for the successful preparation of linear poly(St_n-*r*-Bd_m) having M_n of up to 26 000 g mol^{-1} and $M_w/M_n \leq$ 1.6, with an isolated yield of up to 39 wt%. According to NMR the obtained copolymers were random and did not contain any styrene blocks (more than 5 units in sequence). The composition of poly(St-r-Bd) was found to be nearly independent of reaction conditions and consisted of 19.6–24.0, 15.0–15.5 and 60.5–64.5 wt% of styrene, (1,2)-Bd and (1,4)-Bd units, respectively. The glass transition temperature (T_g) of the copolymers (measured *via* DSC) varied between −55 and −62 °C, while T_{onset} (measured *via* TGA) ranged between 385 and 390 °C. The optimized synthetic method for production of poly(St_n-*r*-Bd_m) copolymers was then extended to produce various poly[X_n-*b*-(St_m-*r*-Bd_k)] block copolymers, where X represents different methacrylic or styrenic monomeric units. The molecular weight of the poly[X_n-*b*-(St_m-*r*-Bd_k)] block copolymers was mainly dependent on the molar mass of the starting poly(X_n) macro-CTA and reached as high as 72 000 g mol^{-1}, with the SBR segment varying between 11 800 and 39 600 g mol^{-1}. These materials, believed to be the first of their kind reported in the literature, show clear evidence of nanostructure formation *via* AFM and promise unique and attractive combinations of stiffness, toughness, thermomechanical performance and chemical reactivity. This work opens up new avenues for the synthesis of novel copolymers with exceptional levels of structural control, thus providing additional tools to the polymer research community as far as the design and creation of materials with new and useful properties is concerned.

Introduction

Styrene butadiene rubber (SBR) is a synthetic rubber copolymer that finds widespread use in the tire industry. In addition to tires, many other industrial products (hoses, belts, flooring, shoe soles, mats, *etc.*) have benefited from SBR's introduction.[1] Generally, the application area of a given SBR depends on its composition, thermal and tensile properties.[2] SBR is industrially produced *via* the emulsion radical or solution anionic copolymerization of styrene (St) and 1,3-butadiene (Bd).[3] Each of these methods possesses certain advantages and limitations.

Despite the commercial realization of the methods mentioned above, many studies have explored other approaches for the preparation of SBR-based block copolymers.[4–8] Among these, reversible addition-fragmentation-transfer (RAFT) polymerization is promising given its ability to provide a high level of control over molecular weight and unprecedented tolerance of functional groups.[9,10] Moreover, in comparison with anionic polymerization, RAFT is less sensitive to moisture,[11] while

---

[a] *Luxembourg Institute of Science and Technology (LIST), 5 Avenue des Hauts-Fourneaux, L-4362 Esch-sur-Alzette, Luxembourg. E-mail: alexander.shaplov@list.lu*

[b] *University of Luxembourg, 2 Avenue de l'Université, L-4365 Esch-sur-Alzette, Luxembourg*

[c] *Goodyear Innovation Center Luxembourg, Avenue Gordon Smith, L-7750 Colmar-Berg, Luxembourg*

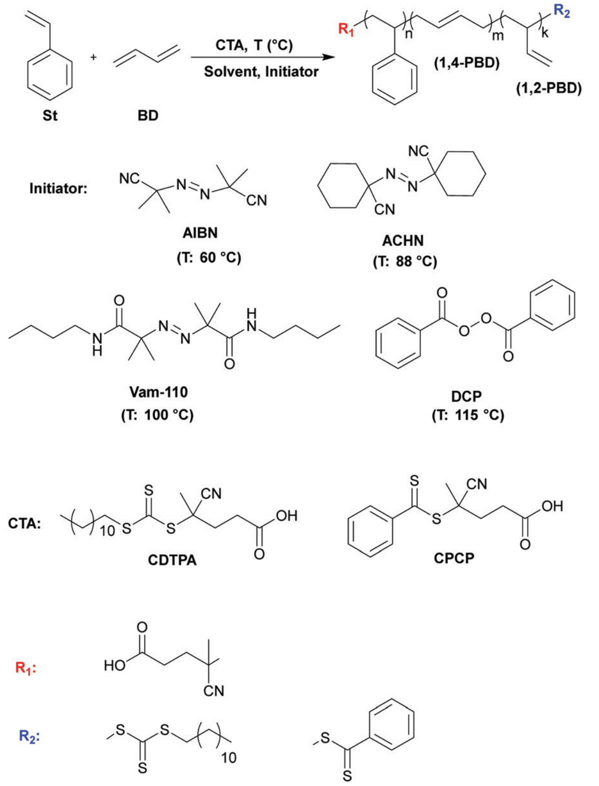
† Electronic supplementary information (ESI) available: Kinetics of styrene RAFT polymerization, assigned ^{1}H, ^{13}C NMR and IR spectra of poly(MMA)$_n$ macro-CTA, poly(St_n-*r*-Bd_m) and poly[MMA_n-*b*-(St_m-*r*-Bd_k)] copolymers, TGA plot of poly(St_n-*r*-Bd_m). See DOI: **https://doi.org/10.1039/d2nj02286a**

compared to emulsion radical polymerization, RAFT offers reduced branching and narrower molecular weight distributions.[12–14] Although attempts to produce Bd-based copolymers using several chain transfer agents (CTA) and macro-CTA agents have been carried out *via* emulsion RAFT polymerization[15–17] (for a recent review, see[18]), or *via* photo RAFT polymerization in the continuous-flow reactor,[19] the studies dedicated to Bd RAFT (co)polymerization in solution are few and far between. As of this writing, the authors are aware of only seven published reports describing the solution RAFT homopolymerization of Bd[20–22] and its copolymerization with acrylonitrile.[23–25]

Boutevin and coworkers[20] conducted RAFT polymerization of Bd in acetonitrile and isopropanol with various fluorinated dithioester CTAs. Reactions were carried out using *tert*-butyl peroxy-3,5,5-trimethylhexanoate (Trigonox 42 S) and di-*tert*-butyl peroxide initiators at 105 and 150 °C, respectively.[20] In spite of high reaction temperatures, the polymerization of Bd resulted in polymers with low molecular weights (M_n = 1300–1400 g mol^{-1}), albeit with narrow molecular weight distributions (M_w/M_n = 1.2–1.5). The conversion was limited as well (12–16 wt%).[20] Transitioning to a trithiocarbonate-based CTA (2-(dodecylthiocarbonothioylthio)propanoic acid, DoPAT) allowed for an increase in the molecular weight of resultant poly(Bd) to 3200 g mol^{-1} ($M_w/M_n \approx 1.5$), although in this case polymerization was performed at a lower temperature (70[22] *vs.* 105–150 °C[20]) with 2,2′-azobis(2-methylpropionitrile) (AIBN) as initiator and toluene as solvent.[22] The kinetics of the polymerization were found to be extremely slow, explained partly by the low k_p value and partly by the low initiator concentration in the system (the Bd : CTA : AIBN molar ratio was 1077 : 1 : 0.2).[22] By switching to another trithiocarbonate-based CTA, namely 2-(dodecyl thiocarbonothioylthio)-2-methylpropanoic acid (DDMAT), increasing the reaction temperature to 95 °C and using dicumyl peroxide (DCP) as the initiator, Abdollahi *et al.*[21] were able to increase the molecular weight of the resultant poly(Bd) up to ~11 000 g mol^{-1} ($M_w/M_n \approx$ 1.4–1.9). At all studied Bd:DDMAT:DCP ratios M_n was found to be linearly dependent on conversion, but after 35 h the conversion remained limited to 20%. In contrast to DoPAT,[20] however, DDMAT[21] did not retard or inhibit polymerization and provided good control over chain growth. Thus, the type of the CTA and the temperature of the reaction were found to be the most crucial parameters influencing Bd solution RAFT polymerization.[20–22]

Solution RAFT copolymerization of Bd and acrylonitrile (AN) was studied by the group of Barner-Kowollik *et al.*[23–25] The monomers were employed in their azeotropic ratio of AN : Bd = 38 : 62 and the overall monomer concentration was fixed at 9.4 M. In their first publication, copolymerization was carried out in *N*,*N*-dimethylacetamide (DMAc) at temperatures as high as 100 °C using 1,10-azobis(cyclohexanecarbonitrile) (ACHN, Vazo 88) as initiator.[24] Both trithiocarbonate-(DoPAT and dibenzyltrithiocarbonate (DiBenT)) and dithioacetate-based (cumyl phenyl dithioacetate (CPDA)) CTAs were tested. The influence of the initiator to RAFT-agent ratio as well as the influence of the CTA and ACHN concentrations on the evolution of conversion with time was explored, and near-linear trends were observed under the investigated reaction conditions.[24] Linear poly(An$_n$-*r*-Bd$_m$) copolymers were obtained with M_n up to 59 700 g mol^{-1} and M_w/M_n ratios of 1.2–2.0 depending on the extent of conversion.[24] CTA type did not significantly affect the overal conversion (42–51%), but did influence the molecular weight of the obtained poly(An$_n$-*r*-Bd$_m$) copolymer: DoPAT (M_n = 58 500 g mol^{-1}) > CPDA (42 000) > DiBenT (31 600).[24] For a 9 h reaction time, the presence of acrylonitrile increased conversion (55%) as compared to the case of Bd homopolymerization (42–51%).[20] Finally, the theoretically predicted values of molecular weight were found to be in agreement with those determined experimentally. In their next study, Barner-Kowollik *et al.*[24] investigated the influence of various solvents and initiators on the rate of Bd : AN copolymerization and the molecular weight of the obtained poly(An$_n$-*r*-Bd$_m$) copolymers. Copolymerization was studied in DMAc, chlorobenzene (PhCl), 1,4-dioxane, *tert*-butanol, isobutyronitrile, toluene, trimethylacetonitrile, dimethyl carbonate, acetonitrile, methyl acetate, acetone and methyl *tert*-butyl ether (MTBE) at 100 °C with 2,2′-azobis(*N*-butyl-2-methylpropionamide) (VAm-110). Conversions after 22 h ranged from 15 wt% for methyl acetate to 35 wt% for DMAc.[24] Such differences were explained by changes in the decomposition behaviour of the employed VAm-110 azo initiator as studied by ultraviolet-visible (UV-vis) spectroscopy. While copolymerization in DMAc with VAm-110 led to a conversion-dependent M_n values very close to theoretical expectations, the utilization of ACHN or 1-[(1-cyano-1-methylethyl)azo]formamide (V30) resulted in a strong deviation from linearity. The highest conversion (34%) and molecular weight (M_n = 100 000 g mol^{-1}) for poly(An$_n$-*r*-Bd$_m$) were achieved when polymerization was conducted in DMAc with DoPAT and VAm-110 as CTA and initiator, respectively.[24] Finally, attempts were made to increase NBR molecular weight through the combination of the RAFT technique with either copper-mediated alkyne–azide cycloaddition[25] or Diels–Alder reactions.[26] The optimal parameters for poly(An$_n$-*r*-Bd$_m$) synthesis as determined in[24] were used to produce NBR segments with M_n in the range of 1000–42 000 g mol^{-1} and having either propargyl or cyclopentene end groups. These NBR building blocks were further reacted with 1,4-bis(azidomethyl)benzene or polymer segments with pyridine end groups to produce NBRs with molecular weights of up to 97 000 g mol^{-1}.[25,26]

In the present study, we report for the first time the controlled random copolymerization of Bd with styrene (St) *via* the solution RAFT technique (Scheme 1). Optimization of the reaction parameters (type of CTA and initiator, CTA:initiator ratio, reaction temperature and time) enabled the preparation of linear poly(St$_n$-*r*-Bd$_m$) copolymers with molecular weights as high as $M_{n(SEC)}$ = 29 500 g mol^{-1} and M_w/M_n values in the range of 1.3–1.6. Furthermore, this approach was successfully applied to the preparation of various high molecular weight ($M_{n(SEC)}$ = 52 000–72 400 g mol^{-1}) poly[X$_n$-*b*-(St$_m$-*r*-Bd$_k$)] block copolymers, where X represents different methacrylic or styrenic monomeric units. The latter highlights the versatility of this method and demonstrates how it may be used to prepare novel random and block copolymers with complex, highly engineered sequence distributions that promise interesting performance profiles. While practical application of this approach would require



Scheme 1 Synthesis of poly(St_n-*r*-Bd_m) *via* solution RAFT polymerization.

significant improvements in reaction kinetics and yield, this work nonetheless demonstrates a simpler, more accessible route to elastomeric block copolymers than traditional anionic polymerization.

Experimental section

Materials

Chlorobenzene (PhCl, 99+%, Acros), anhydrous *N*,*N*-dimethylacetamide (DMAc, 99.8+%, Acros), anhydrous *N*,*N* dimethylformamide (DMF, 99.8%, Acros), scandium(III) trifluoromethanesulfonate ($Sc(OTf)_3$, 99%, Aldrich), 4-cyano-4-[(dodecylsulfanyl thiocarbonyl)sulfanyl]pentanoic acid (CDTPA, 97%, Aldrich), 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPCP), (97%, Aldrich), 1,1′-azobis(cyclohexanecarbonitrile) (ACHN, 98%, Aldrich), dicumyl peroxide (DCP, 98%, Aldrich), 2,2′-azobis(*N*-butyl-2-methylpropionamide) (VAm-110, >95%, Wako) and 4-methoxyphenol (99%, Aldrich) were used without further purification. Anhydrous tetrahydrofuran (THF) and toluene (>99%, Acros) were produced using an SPS solvent purification system (MBraun, Germany, aluminum oxide and 4 Å sieves columns). 1,1,2-Trichloroethane (TCA, 97%, Aldrich) and 1-methylnaphthalene (95%, Aldrich) were purified by distillation over CaH_2. Trihexyltetradecyl phosphonium chloride (≥95.0%, Aldrich) was dried at 55 °C/1 mbar for 24 hours. 2,2′-Azobis(2-methylpropionitrile) (AIBN, 98%, Aldrich) and 4,4′-azobis(4-cyanovaleric acid) (ACVA, ≥98.0%, Aldrich) were crystallized from methanol. 1,3-Butadiene (Bd, ≥99.3%, Linde Gas Benelux B. V.) was distilled through a column filled with 5 Å molecular sieves and activated aluminum oxide spherical balls (BASF F-200). Isobornyl methacrylate (IBOMA, VISIOMER® Terra IBOMA, 99%, EVONIK Operations GmbH), methyl methacrylate (MMA, ≥99%, Aldrich) and styrene (St, 99.9%, Aldrich) were distilled over CaH_2 prior to use.

Methods

NMR spectra were recorded on an AMX-600 spectrometer (Bruker, Germany) at 25 °C in the indicated deuterated solvents and listed in ppm. The signal corresponding to the residual protons of the deuterated solvent was used as an internal standard for ^1H and ^{13}C NMR. Signal assignment was performed using 2D NMR techniques: heteronuclear single quantum coherence (HSQC), heteronuclear multiple bond correlation (HMBC), H–H correlation spectroscopy (H–H COSY). IR spectra were acquired on a Bruker Tensor 27 Fourier IR-spectrometer (Bruker, USA) using ATR technology (128 scans, 2 cm^{-1} resolution).

A 1260 Infinity II gel permeation chromatograph (GPC, Agilent Technologies, USA) was used to determine M_n, M_w and M_w/M_n of the polymers. The chromatograph was equipped with an integrated IR detector, a PLgel 5 mm MIXED-C, PLgel 5 mm MIXED-D columns and a PLgel guard column (Agilent Technologies, USA). $CHCl_3$ or THF was used as an eluent with a flow rate of 1.0 mL min^{-1} at 40 °C. Polystyrene standards (Agilent Technologies, $M_p = 162–1500 \times 10^3$ g mol^{-1}) were used to perform calibration for poly(St_n-*r*-Bd_m) and poly[St_n-*b*-(St_m-*r*-Bd_k)]. Polymethylmethacrylate (Agilent Technologies, $M_p = 500–1500 \times 10^3$ g mol^{-1}) were used to perform calibration for the poly(IBOMA), poly(MMA), poly[$IBOMA_n$-*b*-(St_m-*r*-Bd_k)] and poly[MMA_n-*b*-(St_m-*r*-Bd_k)].

Thermogravimetric analysis (TGA) was carried out in air on a TGA2 STARe System (Mettler Toledo, Switzerland), applying a heating rate of 5 °C min^{-1}. The onset weight loss temperature (T_{onset}) was determined as the point in the TGA curve at which a significant deviation from the horizontal was observed. The resulting temperature was then rounded to the nearest 1 °C. DSC experiments were performed on a DSC3+ STARe System differential calorimeter (Mettler Toledo, Switzerland) with a heating rate of 10 °C min^{-1} in the range of −80 to 150 °C for SBR. Thermal mechanical analysis (TMA) of poly[X_n-*b*-(St_m-*r*-Bd_k)] block copolymer samples was performed under inert atmosphere (He) using a DIL 402 select Expedis dilatometer (NETZSCH, Germany) with a constant load of 0.3 N at a heating rate of 3 °C min^{-1} in the range of −80 to 60 °C for the low T_g block (SBR block) and a heating rate of 10 °C min^{-1} in the range of −80 to 200 °C for the high T_g block (PIBOMA, PMMA, and PS).

Atomic force microscopy (AFM) images were recorded with an MFP-3D Infinity microscope (Asylum Instruments/Oxford Instruments, United Kingdom) in tapping mode (−20 °C, in air). AC160TS-R3 (Olympus, Japan) cantilevers were applied with a stiffness of 26 N m^{-1} and resonance frequency of 300 KHz. The domain periodicity was evaluated from three different 1 × 1 μm^2 images. On each image, two profiles were taken, and for each, the distance over ten consecutive periods was recorded. The images were recorded in the so-called 'soft tapping mode', to avoid deformation and indentation of the polymer surface by the tip. All the images were collected with the maximum available number of pixels (512) in each direction. The general procedure for the preparation of the samples for AFM was as follows: 150 mg of block copolymer were dissolved in 1.5 ml of chloroform and cast onto a glass slide at 22 °C. An inverted glass funnel with the neck filled with cotton was then place over top of the glass slide in order to ensure gradual evaporation (over the course of hours), thus enabling reorganization of the films to achieve (near-) equilibrium morphologies. Finally, the films were dried at 55 °C/1 mbar for 12 h. This approach was chosen in preference to standard thermal of the films (as commonly practiced in the block copolymer literature) given the tendency of the SBR blocks to undergo thermally induced crosslinking.

Solution RAFT copolymerization of styrene and 1.3-butadiene

Poly(St_n-*r*-Bd_m) copolymers were prepared varying reaction conditions *via* the RAFT technique. Depending on the initiator type, the temperature was set to 60, 88, 100, and 115 °C for AIBN, ACHN, VAm-110, and DCP, respectively. A typical procedure for the synthesis of SBR with CDTPA RAFT agent and VAm-110 initiator is given below as an example of copoly10 (Table 1, entry 10):

Bd (20.00 g, 370 mmol) was distilled into a pressure stable glass reactor (Büchiglasuster, Switzerland) pre-cooled at −20 °C under vacuum. The autoclave was equipped with a manometer, a gas inlet valve, a sampling valve closed with septum, a security disk and a magnetic stirrer. After the distillation of Bd, the reactor was filled with an inert atmosphere (Ar) up to 0.1 bar overpressure.

A solution of styrene (3.53 g, 34 mmol), CDTPA (0.0950 g, 0.235 mmol) and VAm-110 (0.0735 g, 0.235 mmol, CDTPA:Vam −110 = 1 : 1 by mol) in 31 ml of anhydrous DMAc was placed into a separate Schlenk flask and degassed *via* three freeze-pump-thaw cycles. This solution was further injected *via* syringe into the reactor containing Bd under overpressure of the inert atmosphere (Ar) at −20 °C. The reactor was heated to 100 °C under vigorous stirring (300–350 rpm), and the reaction was continued for 72 h (**Caution**: high pressure (5.5 bars) is reached very quickly). The course of the reaction was monitored by the pressure drop caused by 1,3-butadiene consumption. After the completion of the reaction, the glass autoclave was cooled down to 50 °C, the unreacted Bd was released from the reactor, and 0.06 g (0.48 mmol) of 4-methoxyphenol (inhibitor) in 4 ml of dichloromethane was added to quench polymerization. The resultant polymer was purified by double precipitation into the methanol excess, collected by decantation and dried at 55 °C/1 mbar for 12 hours. Yield: 4.96 g (21%); $M_{n(SEC)}$ = 22 300 g mol^{-1}; M_w/M_n = 1.8; ^{1}H NMR (600.2 MHz, $CDCl_3$): δ = 7.45–6.80 (br. m, 5H, H6), 5.48 (br. m, H, H13), 5.40–5.00 (br. m, 2H, H9), 5.00–4.77 (br. m, 2H, H14), 3.90 (d, 2H, *J* = 7.3Hz, H7′), 3.27 (t, 2H, *J* = 7.5Hz, Alk-5), 2.48 (br. m, 2H, H8), 2.19 (br. m, 2H, H7), 2.10–1.68 (br. m, 6H, H10, H12), 1.63 (br. m, 2H, Alk-4), 1.35 (br. m, 2H, Alk-3), 1.28–1.03 (br. m, 9H, H1′, H1′, H2, H15), 0.80 (t, 3H, *J* = 14.0 Hz, H1); ^{13}C NMR (150.9 MHz, CDCl3): δ = 145.4 (br. m, C6i), 142.7 (br. m, C13), 132.5–125.3 (br. m, C6, C9), 114.2 (br. m, C14), 45.7 (br. m, C8), 43.5 (br. m, C12), 42.9–42.0 (br. m, C15a), 40.1 (br. m, C7), 38.1 (br. s, C11), 36.9 (s, Alk-5), 35.6 (br. m, C16), 32.7 (br. m, C10b), 31.9 (s, Alk-1″), 29.6–28.8 (multiple s, Alk-2, Alk-3), 28.0 (s, Alk-4), 27.4 (br. m, C10a), 25.5–24.7 (br. m, C15), 22.7 (s, Alk-1′), 14.1 (s, Alk-1) (see ESI† file for full assignment); IR (ATR-mode): 3063 (w, aromatic CH), 3025 (w, aromatic CH), 3003 (w, *cis* CH), 2915 (s, CH), 2843 (m, CH), 1712 (w, C═O (CTA)), 1639 (w, *cis* –CH═CH–), 1602 (w, C═C aromatic), 1493 (m, C═C aromatic),

Table 1 RAFT copolymerization of 1,3-butadiene and styrene[a]

Entry	Poly(St_n-*r*-Bd_m)	CTA	Solvent	Initiator	Temperature (°C)	$M_{n(target)}$	$M_{n(SEC)}$[b] (g mol^{-1})	M_w/M_n[b]	Yield[c] (%)
1	Copoly 1	CPCP	Chlorobenzene	AIBN	60	100 000	6 800	1.3	3
2	Copoly 2	CPCP	Chlorobenzene	ACHN	88	100 000	14 160	2.3	6
3	Copoly 3	CPCP	Chlorobenzene	VAm-110	100	100 000	16 000	4.1	8
4	Copoly 4	CPCP	Chlorobenzene	DCP	115	100 000	23 000[d]	3.3	20
5	Copoly 5	CPCP	DMF	VAm-110	100	100 000	23 300	3.1	6
6	Copoly 6	CPCP	DMAc	VAm-110	100	100 000	19 800	2.5	12
7	Copoly 7	CPCP	TCA	VAm-110	100	100 000	18 000	2.0	5
8	Copoly 8	CDTPA	THF	VAm-110	100	100 000	11 000	2.1	9
9	Copoly 9	CDTPA	Chlorobenzene	VAm-110	100	100 000	12 300	1.3	9
10	Copoly 10	CDTPA	DMAc	VAm-110	100	100 000	22 300	1.8	16
11	Copoly 11	CDTPA	TCA	VAm-110	100	100 000	15 500	1.3	8
12	Copoly 12	CDTPA	DMAc	DCP	115	100 000	28 300[d]	2.5	39
13	Copoly 13	CDTPA	TCA	DCP	115	100 000	26 000[d]	1.6	27
14	Copoly 14	CDTPA[e]	DMAc	VAm-110	100	100 000	29 500	1.6	22
15	Copoly 15	CDTPA	DMAc	VAm-110	100	50 000	12 400	1.4	14
16	Copoly 16	CDTPA	DMAc	VAm-110	100	150 000	27 600	1.5	22
17	Copoly 17	CDTPA	DMAc	VAm-110	115	100 000	18 300	1.3	10
18	Copoly 18	CDTPA[f]	DMAc	VAm-110	100	100 000	19 500	1.5	13
19	Copoly 19	CDTPA[g]	DMAc	VAm-110	100	100 000	20 600	1.7	21
20	Copoly 20	CDTPA	DMAc/IL[h]	VAm-110	100	100 000	16 000	2.0	8
21	Copoly 21	CDTPA	DMAc/$Sc(CF_3SO_3)_3$[i]	VAm-110	100	100 000	17 000	1.7	19

[a] Reaction time 72 h, [Bd] : [St] = 85 : 15 by weight, [Bd + St] = 50 wt%, [CTA] : [initiator] = 5 : 1 by mol. [b] By GPC in $CHCl_3$ at 40 °C (calibration with PS standards). [c] Isolated yield. [d] M_n of soluble fraction. [e] Reaction time 192 h (8 days). [f] Addition of 3 portions of VAm-110. [g] [CTA] : [initiator] = 5 : 5 by mol. [h] Ionic liquid (IL): trihexyltetradecylphosphonium chloride, [DMAc] : [IL] = 50 : 50 by volume. [i] [$Sc(CF_3SO_3)_3$] : [styrene + butadiene] = 1 : 73 by mol.

1449 (s), 1436 (s), 1349 (w), 1308 (w), 1261 (w), 1074 (m), 1029 (w), 993 (m, vinyl CH_2), 965 (vs, *trans* –CH═CH–), 910 (vs, vinyl CH_2), 805 (m), 759 (m, CH aromatic), 699 (vs, CH aromatic) cm^{-1}; T_g = −58 °C (DSC); T_{onset} = 387 °C (TGA).

Synthesis of macro-chain transfer agents (macro-CTA)

A set of macro-CTAs, namely, poly(IBOMA)$_{12K}$, poly(IBOMA)$_{26K}$, poly(IBOMA)$_{36K}$, poly(IBOMA)$_{46K}$, poly(MMA)$_{40K}$ and poly(St)$_{43K}$ was prepared by solution RAFT polymerization. A typical procedure for the synthesis of a macro-CTA is described below by an example of poly(MMA)$_{40K}$ (Table 3, entry 6) preparation:

MMA (10.00 g, 100 mmol), CDTPA (0.0504 g, 0.125 mmol) and AIBN (0.0051 g, 0.031 mmol, CDTPA : AIBN = 4 : 1 by mol) were dissolved in 7 ml of anhydrous TCA in a Schlenk flask. The solution was deoxygenated by three freeze-pump-thaw cycles and sealed under an inert atmosphere (Ar). The reaction was conducted at 60 °C for 24 h. Polymerization was quenched by the injection of 0.06 g (0.48 mmol) of 4-methoxyphenol (inhibitor) solution in 4 ml of dichloromethane, and then the reaction mixture was diluted with dichloromethane. The resultant polymer was isolated by double precipitation into the excess of methanol and dried at 55 °C/1 mbar for 12 h. Yield: 9.5 g (95%); $M_{n(SEC)}$ = 40 300 g mol^{-1}; M_w/M_n = 1.1; ^1H NMR (600.2 MHz, $CDCl_3$): δ = 3.54 (s, 3H, H8), 2.04–1.93 (br. m, 2H, H10), 1.93–1.69 (br. m, 2H, H6), 1.20 (br. s, 2H, H11), 1.15 (br. t, 3H, J = 6 Hz, H7mm), 0.96 (s, 3H, H7mr), 0.79 (s, 3H, H7rr); ^{13}C NMR (150.9 MHz, CDCl3): δ = 178.3–176.1 (br. m, C13), 55.0–52.1 (br. m, C6), 51.8 (s, C8), 45.5 (s, C14mm), 44.8 (s, C14mr), 44.5 (s, C14rr), 31.7 (s, C11), 29.6–28.7, (m, Alk-2, Alk-3, Alk-4), 22.6 (s, Alk-1′), 21.0, (s, C7mm), 18.7 (s, C7mr), 16.4 (s, C7rr), 14.0 (s, Alk-1) (see ESI† file for full assignment); IR (ATR-mode): 2993 (w, CH), 2950 (m, CH), 2844 (w, CH), 1722 (vs, C═O), 1479 (m, αCH_2), 1435 (s), 1387 (w,–OCH_3), 1266 (m), 1239 (s, asC–O–C), 1189 (s), 1143 (vs, sC–O–C), 1063 (m), 986 (m), 965 (m), 917 (w), 842 (m), 749 (m, αCH_2) cm^{-1}; T_g = 130 °C (TMA); T_{onset} = 267 °C (TGA).

Synthesis of poly[X_n-*b*-(St_m-*r*-Bd_k)] block copolymers

A set of poly[X_n-*b*-(St_m-*r*-Bd_k)] block copolymers was synthesized from the respective macro-CTAs by conducting solution RAFT random copolymerization of styrene and 1,3-butadiene. A typical procedure is provided by the example of the poly[MMA$_{40K}$-*b*-(St-*r*-Bd)$_{23K}$] synthesis (Table 3, entry 6):

Bd (20.00 g, 370 mmol) was distilled into a pressure stable glass reactor (Büchiglasuster, Switzerland) pre-cooled at −20 °C under vacuum. Afterwards, the reactor was filled with an inert atmosphere (Ar) up to 0.1 bar overpressure. A solution of styrene (3.53 g, 34 mmol), poly(MMA)$_{40K}$ (9.41 g, 0.235 mmol), VAm-110 (0.0735 g, 0.235 mmol), poly(MMA)$_{40K}$: VAm-110 = 1 : 1 (molar ratio), in 136 ml of anhydrous TCA was placed into a separate Schlenk flask and degassed *via* three freeze-pump-thaw cycles. The degassed solution was transferred *via* syringe into the reactor containing Bd at −20 °C. The mixture was stirred until the formation of a clear solution and the reactor was heated to 100 °C (**Caution**: Pressure reached 5.5 bars in 20 minutes). Polymerization was continued under stirring at 100 °C for 72 h. Then the reactor was cooled down to 50 °C, the unreacted Bd was released and a solution of 0.06 g (0.48 mmol) of 4-methoxyphenol (inhibitor) in 4 ml of dichloromethane was added to quench polymerization. The resultant viscous solution was diluted with dichloromethane and the copolymer was purified by double precipitation into the methanol excess. Product, representing yellow powder, was dried at 55 °C/1 mbar for 12 hours. Yield: 11.2 g (34%); $M_{n(SEC)}$ = 63 800 g mol^{-1}; M_w/M_n = 1.4; ^1H NMR (600.2 MHz, $CDCl_3$): δ = 7.30–6.98 (br. m, 5H, H6), 5.54 (br. m, 1H, H13), 5.48–5.15 (br. m, 2H, H9), 5.03–4.84 (br. m, 2H, H14), 3.95 (d, 2H, J = 6Hz, H17), 3.58 (s, 3H, H19), 2.53 (s, 2H, H8), 2.24 (s, 2H, H7), 2.05–1.80 (br. m, H10, H12, H21), 1.24 (br. s, H22), 1.19 (br. t, 3H, J = 13 Hz, H16mm), 1.00 (br. t, 3H, H16mr), 0.83 (br. t, 3H, H16rr); ^{13}C NMR (150.9 MHz, CDCl3): δ = 178.4–176.2 (br. m, C18), 145.3 (s, C6i), 142.6 (br. m, C13), 131.6–125.8 (br. m, C6, C9), 114.8–113.8 (br. m, C14), 54.7–52.2 (m, C15), 51.7 (s, C19), 45.7 (br. m, C8), 45.5 (s, C17mm), 44.9 (s, C17mr), 44.52 (s, C17rr), 43.5 (br. m, C12), 40.0 (br. m, C7), 38.1 (br. m, C11), 35.7 (br. m, C21), 32.7 (br. m, C10b, C22), 32.0–31.8 (br. m, C1″), 30.5–29.9 (br. m, C2, C3, C4), 27.3 (s, C10a), 22.6 (s, C1′), 21.1 (br. m, C16mm), 18.7 (br. m, C16rm), 16.5 (s, C16rr) (see ESI† for full assignment); IR (ATR-mode): 2999 (w, CH), 2946 (m, CH), 2916 (m, CH), 2843 (m, CH), 1725 (vs, C═O), 1640 (w, *cis* –CH═CH–), 1483 (m, αCH_2), 1435 (s), 1387 (m, –OCH_3), 1364 (w), 1269 (m), 1241 (s, asC–O–C), 1190 (s), 1145 (vs, sC–O–C), 1064 (m), 993 (w, vinyl CH_2), 965 (s, *trans* –CH═CH–), 911 (m, vinyl CH_2), 842 (w), 810 (w), 781 (w), 749 (w, αCH_2), 730 (w), 700 (m, CH aromatic) cm^{-1}. T_{g1} = −8.5 °C and T_{g2} = 132.1 °C (TMA).

Results and discussion part

Choosing a proper RAFT or chain transfer (CTA) agent is essential to achieve an effective control over molecular weight, realize a narrow molecular weight distribution, and construct macromolecules with well-defined architectures, including random, block or gradient copolymers.[27] The goal of the study was to use RAFT polymerization as a versatile technique for the preparation of SBR-based block copolymers. Thus, the selection of the RAFT agent was limited by the condition that it should be able to polymerize monomers having different vinyl groups, namely, styrene, 1,3-butadiene and various methacrylates. As discussed in the introduction, for (co)polymerization of Bd the various RAFT agents based on dithioesters, trithiocarbonates and dithiobenzoates have been successfully applied.[20–25] Similar CTAs were found to be quite effective in the controlled polymerization of styrene.[28,29] However, not all of the above mentioned RAFT agents are capable of effectively polymerizing (meth)acrylates. Only those trithiocarbonate and dithiobenzoate CTAs (R–S–C═S–Z), that possess an R leaving group with tertiary carbon having three different substituents including one cyano (CN) group, were reported to polymerize (meth)arcylates in a controlled manner.[30–32] Such leaving groups with a tertiary radical show higher transfer constants and produce more stable radical species in comparison to groups containing primary or secondary carbons. Moreover, the electron-withdrawing effect of CN substituents increases the capability of the R group to reinitiate monomers as an expelled radical, leading to better control over the polymerization.[33,34] Thus, to fulfill the requirement for effective and controlled polymerization of the various monomers mentioned above, the 4-cyano-4-[(dodecylsulfanylthiocarbonyl)-sulfanyl] pentanoic acid (CDTPA, trithiocarbonate-type) and 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPCP, dithiobenzoate-type) having a tertiary carbon with a cyano group were selected (Scheme 1). Afterwards, the study continued with the investigation of the influence of various reaction parameters (the type of RAFT agent, solvent and initiator, the temperature and the duration of polymerization, *etc.*) on solution RAFT copolymerization of styrene and butadiene, enabling the determination of the optimum conditions for the synthesis of poly(St_n-*r*-Bd_m) with highest molecular weight and in highest yield (Table 1). Because of this goal, the results of the various polymerizations will be compared in terms of molecular weight, M_w/M_n ratios and yield. Finally, in order to ensure that the poly(St_n-*r*-Bd_m) would possess the desired elastomeric character and low T_g, it was decided to fix the Bd : St ratio at 85 : 15 (w/w).

Effect of the RAFT agent

The influence of the RAFT agent on the synthesis of poly(St_n-*r*-Bd_m) was examined in two different solvents, namely in *N*,*N*-dimethylacetamide (DMAc) and chlorobenzene (PhCl), at 100 °C with the VAm-110 (Table 1, entries 3, 6, 9 and 10) initiator. In terms of SBR molecular weight, the results obtained were ambiguous. The utilization of CDTPA in DMAc led to the synthesis of poly(St_n-*r*-Bd_m) with higher molecular weight ($M_{n(SEC)}$ = 22 300 g mol^{-1}) in comparison with SBR prepared in the same solvent with CPCP (19 800 g mol^{-1}) (Table 1, entries 6 and 10). In contrast, in chlorobenzene poly(St_n-*r*-Bd_m) synthesized with CPCP showed higher molecular weight than with CDTPA: 16 000 and 12 300 g mol^{-1}, respectively (Table 1, entries 3 and 9). It was observed that both RAFT agents influenced the M_w/M_n ratios of the resultant poly(St_n-*r*-Bd_m). While the M_w/M_n ratios obtained with CDTPA were quite satisfactory (~1.3–1.8), the dispersity of SBR synthesized with CPCP indicated a loss of control (M_w/M_n = 2.5 and 4.1 in DMAc and PhCl, respectively). In both solvents, the application of CDTPA resulted in slightly higher isolated yields of poly(St_n-*r*-Bd_m) (16 and 9%) in comparison with utilization of CPCP (12 and 8%, correspondingly) (Table 1, entries 3,6 and 9,10). The discussed trends can be summarized as follows:

$$\text{CPCP } (M_{n(SEC)} = 19\,800 \text{ g mol}^{-1}) < \text{CDTPA } (22\,300) \text{ in DMAc}$$

$$\text{CDTPA } (M_{n(SEC)} = 12\,300 \text{ g mol}^{-1}) < \text{CPCP } (16\,000) \text{ in PhCl}$$

$$\text{CDTPA } (M_w/M_n = 1.8) < \text{CPCP } (2.5) \text{ in DMAc}$$

$$\text{CDTPA } (M_w/M_n = 1.3) < \text{CPCP } (4.1) \text{ in PhCl}$$

It can be concluded that for the RAFT synthesis of poly(St_n-*r*-Bd_m), the CDTPA agent was more preferable due to the achievement of a copolymer with lower molecular weight distribution and in higher yield. These results were found to be in agreement with those reported previously for the styrene RAFT homopolymerization.[35]

Effect of [CTA]/[initiator] ratio

The [CTA]/[initiator] ratio is a critical parameter that can affect the control over polymerization.[36] The increase in the CTA : initiator ratio from 5 : 1 to 5 : 5 resulted in the improvement of the SBR's yield from 16 to 21%, but at the same time led to the decrease in M_n from 22 300 to 20 600 g mol^{-1} (Table 1, entries 10 and 19). Thus, for all future experiments the CTA : initiator ratio was fixed as 5 : 1 (Table 1). A reduction in initiator concentration might be expected to increase the livingness of the polymerization and the molecular weight of the product. However, this would also tend to reduce the yield still further, and was therefore not considered in the scope of the current effort.

Effect of initiator

The influence of initiator type on the copolymerization of styrene and Bd was studied through use of a set of azo-compounds, namely AIBN, ACHN and VAm-110, as well as DCP, as a representative of peroxide type initiators. The reaction temperatures were selected based on the initiator's 10 h half-life temperatures and ranged from 60 °C to 110 °C (Scheme 1). Utilization of azo-initiators in PhCl in combination with CPCP RAFT agent resulted in the synthesis of poly(St_n-*r*-Bd_m) with the yields ranging from 3 to 8% (Table 1, entries 1–3). The overall evolution of molecular weight, molecular weight distribution and yields of SBRs in accordance with the nature of initiator used can be summarized as follows:

$$\text{AIBN (SBR } M_{n(SEC)} = 6800 \text{ g mol}^{-1}) < \text{ACHN } (14\,160) < \text{Vam } -110 \ (16\,000)$$

$$\text{VAm-110 } (M_w/M_n = 4.1) > \text{ACHN } (2.3) > \text{AIBN } (1.3)$$

$$\text{AIBN (SBR yield: 3\%)} < \text{ACHN } (6) < \text{VAm-110 } (8)$$

It was found that among azo-initiators, the VAm-110 provided the SBR with highest molecular weight (16 000 g mol^{-1}) and in highest yield (8%), although simultaneously with the broadest molecular weight distribution (M_w/M_n= 4.1) (Table 1, entries 1–3).

With the aim to study the influence of other initiators, the peroxide type DCP, having a working temperature closed to that of VAm-110, was selected. The utilization of DCP allowed for a significant increase in the molecular weight (up to 23 000 g mol^{-1}) and yield (up to 20%) of poly(St_n-*r*-Bd_m) (Table 1, entries 1–4). One explanation for this is that DCP was promoting partial cross-linking as was supported by the presence of insoluble polymer parts. To confirm this conclusion, the copolymerization was conducted in the presence of DCP in two other solvents (Table 1, entries 12 and 13). In both TCA and DMAc, the utilization of DCP significantly increased the copolymer's yield and molecular weight, but again resulted in partial cross-linking. Analyzing all obtained results (Table 1), it is possible to conclude that higher polymerization temperatures (associated with different initiators) resulted in higher molecular weights and yields of SBR copolymers.

Keeping in mind that the duration of the reaction (72 h) was far longer than the half-life (10 h) of the VAm-110 at the chosen temperature (100 °C), the low copolymers yields were at first explained by the insufficient amount of initiating radicals/species. To test this assumption, additional amounts of VAm-110 solution in DMAc were injected at equal intervals, *i.e.* after 24 and 48 h of reaction (Table 1, entry 18). This led only to little change in copolymers yield (16 to 13%) and M_n (22 300 to 19 500 g mol^{-1}) (Table 1, entry entries 10 and 18). The first possible explanation for low M_n and yield can be the low reactivity of 1.3-butadiene in radical polymerizations.[22] For example, the kinetic study of 1,3-butadiene RAFT homopolymerization conducted by P. Xu and coworkers in toluene with AIBN initiator and DoPAT RAFT agent at 70 °C revealed that even for a target M_n of 3000 the conversion reached only 6% within 45 h of reaction, indicating the rate of homopolymerization was notably slow.[22] In another study, the RAFT solution homopolymerization of 1.3-butadiene in acetonitrile with *tert*-butyl peroxy-3.5.5-trimethylhexonoate and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl-2-phenyl-2-((phenylcarbonothioyl)thio)ace-tate at higher temperature (110 °C) over 50 h resulted in an M_n of only 1400 g mol^{-1} and 16% conversion.[20] The second possible reason for low molecular weight of SBR as detected by GPC may be branching of the obtained copolymer thanks to the presence of double bonds in the Bd repeats, though proving this would require an in-depth study beyond the scope of the current investigations.

Effect of solvent

The effect of solvent was investigated by first conducting the RAFT copolymerization in PhCl, DMF, DMAc and TCA with VAm-110 initiator and CPCP RAFT agent (Table 1, entries 3, 5, 6, and 7). The copolymerization at 100 °C for 72 h resulted in the preparation of SBRs with molecular weights ranging from 16 000 to 23 300 g mol^{-1}. An acceptably narrow molecular weight distribution (M_w/M_n = 2.0) was obtained only in TCA, while the use of PhCl, DMF, and DMAC provided broader molecular weight distributions (M_w/M_n = 4.1, 3.1, and 2.5, respectively). Although by conducting the reaction in DMAc it was possible to increase the yield of the copolymer up 12%, the range of the obtained yields (5–12%) was generally low (Table 1, entries 3, 5, 6, and 7). The impact of solvent type on molecular weight, molecular weight distribution and yield of obtained poly(St$_n$-*r*-Bd$_m$) copolymers can be summarized as follows:

$$\text{PhCl } (M_n = 16\,000 \text{ g mol}^{-1}) < \text{TCA } (18\,000) < \text{DMAc } (19\,800) < \text{DMF } (23\,300)$$

$$\text{PhCl } (M_w/M_n = 4.1) > \text{DMF } (3.1) > \text{DMAc } (2.5) > \text{TCA } (2.0)$$

$$\text{TCA (Yield of SBR: 5\%)} < \text{DMF } (6) < \text{PhCl } (8) < \text{DMAc } (12)$$

As previously noted, CDTPA was found to be the most effective RAFT agent for the copolymerization of Bd with styrene. Thus, the investigation of solvent effects was continued in the same set of solvents, but in the presence of the CDTPA RAFT agent (Table 1, entries 8–11). As a common observation, the transfer to CDTPA led to the slight increase in the molecular weight and yields of the obtained copolymers. At the same time, much lower M_w/M_n values in the range of 1.3–2.1 were observed.

Consistent with this observation, the GPC traces of poly(St$_n$-*r*-Bd$_m$) copolymers produced in this fashion became remarkably narrow (Fig. 1). The obtained results can be arranged in the following order:

$$\text{THF } (M_n = 11\,000 \text{ g mol}^{-1}) < \text{PhCl } (12\,300) < \text{TCA } (15\,500) < \text{DMAc } (22\,300)$$

$$\text{THF } (M_w/M_n = 2.1) > \text{DMAc } (1.8) > \text{PhCl } (1.3) \sim \text{TCA } (1.3)$$

$$\text{TCA (Yield of SBR: 8\%)} < \text{THF } (9) \sim \text{PhCl } (9) < \text{DMAc } (16).$$

Providing a combination of high molecular weight and high yield at the cost of a small increase in M_w/M_n ratio, DMAc was identified as the optimal solvent for RAFT copolymerization of styrene and 1,3-butadiene at a given conditions (Table 1, entry 10).

Effect of temperature

The influence of temperature on the synthesis of poly(St$_n$-*r*-Bd$_m$) copolymers was briefly mentioned in the section on the initiator effects. It was established that the increase in reaction temperature from 60 to 100 °C increased copolymer molecular weight and yield (Table 1, entries 1–3). While the recommended working temperature (the temperature of the 10 h half-life) for VAm-110 initiator is 110 °C, one additional experiment was performed in DMAc with CDTPA and VAm-110 at 115 °C (Table 1, entry 17). The increase of reaction temperature from 100 °C to 115 °C led to a reduction in the molecular weight (18 300 g mol^{-1}), molecular weight distribution (M_w/M_n: 1.3), and the yield (10%) in comparison to the polymerization performed at 100 °C (Table 1, entries 10 and 17). Thus, 100 °C was found to be optimal for copolymerization.

Effect of reaction duration

Although, 72 h of polymerization can be considered as excessive, especially taking into account the half-life of VAm-110 initiator equal to approximately 25 h at 100 °C, another experiment was carried out for 192 h (Table 1, entry 14). The prolongation of the reaction duration up to 8 days gave an increase in the molecular weight from 22 300 to 29 500 g mol^{-1}, and the yield from 16 to 22% (Table 1, entries 10 and 14). This is consistent with the fact that, even after more than 8 days (approximately 8 half-lives), we would still expect to have $\left(\frac{1}{2}\right)^8$ = 0.4% of unreacted VAm-110 remaining – meaning that VAm-110 decomposition and initiation is continuously occurring during the entire period. Taking into account the low reactivity of Bd *vs.* radical polymerization reactions, this provides additional time for molecular weight increase. Furthermore, it should also be noted that the presence of the RAFT agent ensures the formation of more stable, longer-lived radicals than would otherwise be generated through VAm-110 decomposition alone.

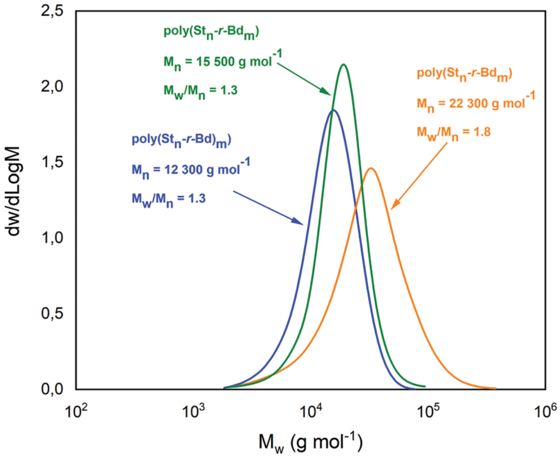


Fig. 1 GPC traces of poly(St$_n$-*r*-Bd$_m$) copolymers (CHCl$_3$, PS standards) obtained by solution RAFT process (Table 1, entries 9–11).

Effect of additives

Several attempts to increase the molecular weight and the yield of poly(St$_n$-*r*-Bd$_m$) copolymer by application of various catalytic additives were also made.

It was established previously that the conducting of polymerization in ionic liquids (ILs) as reaction medium[37–41] or adding small amounts of ILs during bulk polymerization[42] led to pronounced effects: (1) significant increase in the molecular weight of the resultant polymer; (2) improved yields of polymers (close to quantitative); (3) accelerated reaction rate. Thus, the first catalytic additive to test was the trihexyltetradecylphosphonium chloride IL. As styrene was not soluble in the neat IL, a [DMAc] : [IL] = 50 : 50 v/v ratio mixture was used for RAFT copolymerization (Table 1, entry 20). Unfortunately, however, the obtained poly(St$_n$-*r*-Bd$_m$) copolymer precipitated during the reaction, decreasing both the M_n and yield of the SBR in comparison with work performed in neat DMAc (Table 1, entries 10 and 20).

Moad *et al.*[43] investigated the modulation of the activity of an acid/base switchable dithiocarbamate RAFT agent, cyanomethyl (4-fluorophenyl)(pyridin-4-yl)carbamodithioate, with the Lewis acid scandium trifluoromethanesulfonate. It was revealed that Sc(OTf)$_3$ was able to deliver improved control over RAFT copolymerization of methyl acrylate and vinyl acetate, M_n close to the target one and decreased M_w/M_n ratios of copolymers.[43] Therefore, the effect of Sc(OTf)$_3$ on styrene/BD RAFT copolymerization was studied as well (Table 1, entry 21). The introduction of Sc(OTf)$_3$ to the RAFT system reduced the molecular weight from 22 300 to 17 000 g mol^{-1} and produced a bimodal molecular weight distribution as observed in the GPC curve (Table 1, entries 21 and 10), but slightly increased copolymer yield (from 16 to 19%).

Optimal conditions

Based on a detailed analysis of all the experiments in Table 1, it can be concluded that the optimal reaction conditions for the synthesis of poly(St$_n$-*r*-Bd$_m$) copolymer with highest possible molecular weight and in highest yield are as follows: DMAc (solvent), CDTPA (RAFT agent), VAm-110 (initiator), [BD + St] = 50 wt%, [CTA] : [initiator] = 5 : 1 by mol, 100 °C and 192 h (Table 1, entry 14).

At this point it is important to briefly address the question of absolute yields in more detail, given that the maximum yield reported in Table 1 is 39%. While this may appear low in comparison to other investigations, the origins of the limited yields observed here stem from the initial choice of the Bd : St ratio as 85 : 15 (w/w). This is because, in addition to already slow reaction kinetics of St RAFT polymerization (Fig. S1, ESI†), it is well-known that Bd polymerizes even more slowly *via* radical processes. For these reasons, the overall propagation kinetics are very slow, the yields are low, and St units are overrepresented in the final copolymer composition as compared to the composition of the monomer feed (Table 2). To address the issue of low yields, three strategies are envisioned. First, we note that prior work involving the RAFT solution copolymerization of acrylonitrile and Bd at a 64 : 36 w/w ratio[23–25] resulted in conversions of up to 62–64%. This shows that the presence of larger amounts of a more reactive monomer (such as St or acrylonitrile) favors greater conversion and a higher yield of the resulting copolymer. Second, while the additives studied here did not produce the desired increases in yield (Table 1, entries 20 and 21), this approach nonetheless deserves further attention, given the potential for novel additives to provide better performance. Third, in the case where some level of crosslinking may be tolerate in the final block copolymer, the use of peroxide initiators during the growth of the second block can provide significant increases in yield as well (Table 1, entry 4).

Living character of (co)polymerization

Ideally, the living character of a RAFT (co)polymerization is revealed through a detailed study of the reaction kinetics. In this case, however, the low reactivity of Bd requires its use in high concentrations. This, in turn, means all (co)polymerizations must take place at high pressures (5.5–6 bar), which makes the collection of samples for the purpose of a traditional kinetic analysis impossible. Nonetheless, given the critical importance of establishing whether the (co)polymerization is living or not, we have studied the effect of the monomer/initiator ratio on molecular weight ($M_{n(SEC)}$) obtained from GPC. On the one hand, the expected linear relationship between the monomer/initiator ratio and the measured

Table 2 Composition and properties of poly(St$_n$-*r*-Bd$_m$) obtained by RAFT solution copolymerization

Poly(St$_n$-*r*-Bd$_m$)	$M_{n(SEC)}$[a] (g mol^{-1})	St[b] (wt%)	(1,2)-Bd[b] (wt%)	(1,4)-Bd[bc] (wt%)	T_g[d] (°C)	T_{onset}[e] (°C)
Copoly 9	12 300	20.0	15.5	64.5	−60	315
Copoly 10	22 300	19.6	15.4	65.0	−62	310
Copoly 11	15 500	24.0	15.5	60.5	−55	310
Copoly 19	20 600	21.0	15.0	64.0	−58	315

[a] By GPC in CHCl$_3$ at 40 °C (calibration with PS standards). [b] Microstructure determined by ^{1}NMR using procedure published in.[44] [c] *cis* and *trans* content were not separated. [d] T_g determined by DSC. [e] T_{onset} determined by TGA under inert atmosphere.

molecular weight is indeed observed, confirming the living character of the polymerization. However, the absolute values of the measured molecular weights are approximately four times lower than would be expected based on theoretical concerns. This relationship may be seen graphically in Fig. S9 (see ESI†).

This data is correlated with the experiments presented in Table 1 (entries 10, 15 and 16). The discrepancy in molecular weights can be explained by several reasons: (1) the slope of the theoretical line is given at 100% of conversion, while the real conversions varied between 14 and 25%; (2) the obtained poly(St_n-*r*-Bd_m) copolymer may be branched due to the presence of residual double bonds (though proving this is challenging and beyond the scope of the current work); (3) slow polymerization kinetics of both Bd and St in the given conditions. Indeed, the study of styrene RAFT polymerization kinetics performed in the optimal conditions (Fig. S1, ESI†) revealed that after 72 h of reaction the conversion reached only 62% and the actual molecular weight was still lower than the calculated one (63 000 and 100 000 g mol^{-1}, respectively).

Properties of poly(St_n-*r*-Bd_m) copolymers

Several poly(St_n-*r*-Bd_m) copolymers, namely, copoly9-copoly11 and copoly19, have been selected from Table 1 for the investigation of their physical chemical properties (Table 2). These polymers were chosen as samples prepared in different solvents and with different [CTA]:[Initiator] ratios. At first, their structure and purity were proved by ^1H and ^{13}C NMR (Fig. 2 and Fig. S2, S3, ESI†). ^1H NMR showed the presence of St (7.60–7.20, 7.09–6.89, 2.48, 2.19 ppm) and Bd units (5.55–5.12, 4.95–4.79, 2.06–1.80 ppm) as well as the peaks attributed to the remains of CDTPA agent (Fig. S2, ESI†). Further on, the composition or the microstructure of the copolymers was identified by ^1H NMR in accordance with the previously published procedure.[44] The only deviation from above mentioned technique[44] was the choice of the deuterated solvent: instead of CS_2 : 1,1,2,2-tetrachloroethane-d_2 (2 : 1 v : v ratio) mixture the ^1H NMR analysis in this work was performed in deuterated chloroform (Fig. S2, ESI†). All selected poly(St_n-*r*-Bd_m) copolymers were found to be random. This statement is done based on the absence of any peak related to styrene blockiness (more than 5 units of styrene in a row) at 6.75–6.30 ppm (Fig. 2 and Fig. S2, ESI†). The styrene content slightly varied in the range of 19.6–24.0 wt%, while the vinyl content ((1,2)-Bd units) was practically fixed in between 15.0 and 15.5 wt% (Table 2). Accordingly, the (1,4)-Bd units fraction narrowly ranged from 60.5 to 65.0 wt%. Therefore, it can be concluded that the microstructure of poly(St_n-*r*-Bd_m) copolymers within the same loading of monomers was nearly independent on the reaction conditions. The structure of the obtained random copolymers was additionally confirmed by IR spectroscopy (Fig. S4, ESI†). The following characteristic absorption bands were observed: 699 and 759 cm^{-1} (C–H deformation vibrations from aromatic ring), 910 and 993 cm^{-1} (vinyl CH_2 vibrations), 964 cm^{-1} (*trans* –CH═CH– vibrations), 1493 and 1602 cm^{-1} (C═C vibrations from aromatic ring), 1639 cm^{-1} (*cis* –CH═CH– vibrations), 1712 cm^{-1} (C═O vibrations from RAFT agent), 2915 and 2843 cm^{-1} (aliphatic CH vibrations), 3003 (*cis* CH vibrations), 3025 and 3063 cm^{-1} (aromatic CH vibrations).

All tested copolymers were found to have similar solubility in organic solvents: they were soluble in chlorinated solvents ($CHCl_3$, TCA, CH_2Cl_2), hydrocarbons (cyclohexane, toluene, hexane (at 50 °C)), some polar solvents (THF, diethyl ether, DMAc (at 60 °C)). They were found to be insoluble in acetonitrile, acetone, some aprotic polar solvents (DMF, DMSO, NMP) and alcohols (MeOH, EtOH). The observed solubility of poly(St_n-*r*-Bd_m) copolymers was found to be almost identical to that of high molecular weight linear poly(St_n-*r*-Bd_m) prepared *via* traditional solution anionic polymerization.

Thermal properties of copolymers were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) (Table 2 and Fig. S10, S11, ESI†). According to DSC, poly(St_n-*r*-Bd_m) copolymers showed one single glass transition temperature (T_g) ranging from −55 to −62 °C (Fig. S10, ESI†). As the vinyl content in the copolymers was nearly unaltered (15.0–15.5 wt%), the obtained T_g values were well correlated with the styrene content.[45] Thus, the lower was the styrene fraction, the lower was the observed T_g (Table 2).

The thermal degradation behaviour of copolymers was assessed by TGA under inert atmosphere (Table 2). The weight loss profile of all copolymers revealed one-step degradation mechanism (Fig. S11, ESI†). It was found that the weight loss onset temperature T_{onset} varied in the range of 310–315 °C and the thermal stability of poly(St_n-*r*-Bd_m) copolymers was nearly independent on the molecular weight.

Synthesis of poly[X_n-*b*-(St_m-*r*-Bd_k)] block copolymers

To demonstrate the applicability of the suggested approach a set of different poly[X_n-*b*-(St_m-*r*-Bd_k)] block copolymers was prepared *via* solution RAFT method (Table 3 and Fig. S4, S7, S8, ESI†). To narrow the dispersity and to obtain the block copolymers with as little branching as possible it was decided to start the process with the synthesis of well-defined macro-CTAs and then

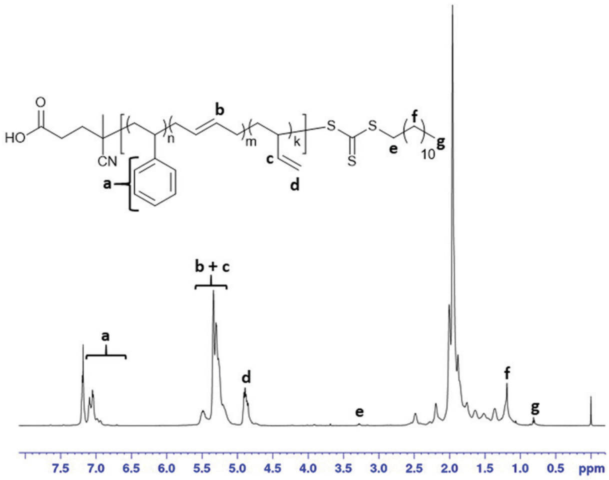


Fig. 2 ^1H NMR of poly(St_n-*r*-Bd_m) copolymer (Table 1, entry 11) produced by solution RAFT copolymerization (more detailed assignment is presented in Fig. S3a and S3b, see ESI†).

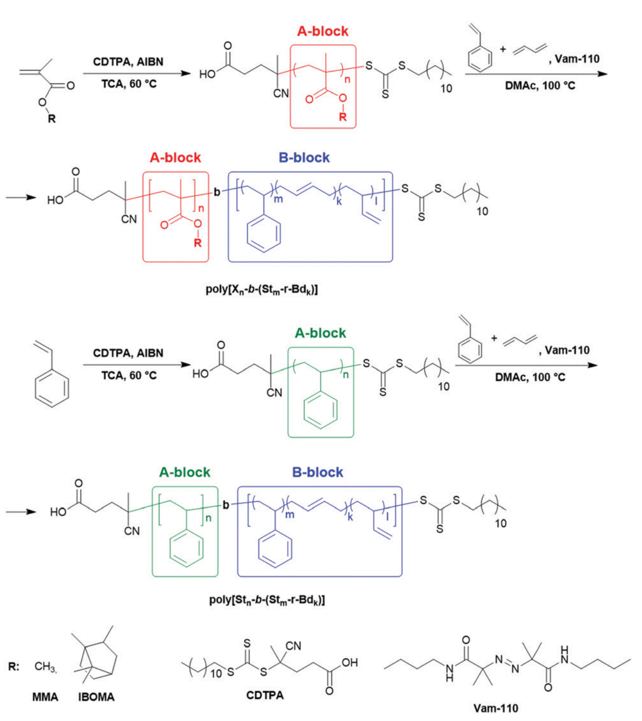
Table 3 Synthesis and selected properties of poly[X_n-*b*-(St_m-*r*-Bd_k)] block copolymers[a]

	A-block			B-block	poly[X_n-*b*-(St_m-*r*-Bd_k)] (A-*b*-B copolymer)								
Entry	Macro-CTA	$M_{n(SEC)}$[b] (g mol^{-1})	M_w/M_n[b]	M_n[b] (g mol^{-1})	Block copolymers	$M_{n(SEC)}$[b] (g mol^{-1})	M_w/M_n[b]	Yield[c] (%)	T_{g1}[d] (°C)	T_{g2}[d] (°C)	Type of morphology[e]	Characteristic size A (nm)	Characteristic size B (nm)
1	Poly(MMA)$_{40K}$	40 300	1.1	23 500	poly[MMA$_{40K}$-*b*-(St-*r*-Bd)$_{23K}$]	63 800	1.4	34	−9	132	L	72 ± 11	—
2	Poly(IBOMA)$_{12K}$	12 400	1.1	39 600	poly[IBOMA$_{12K}$-*b*-(St-*r*-Bd)$_{39K}$]	52 000	1.6	28	−68	152	D	—	—
3	Poly(IBOMA)$_{26K}$	26 000	1.2	28 700	poly[IBOMA$_{26K}$-*b*-(St-*r*-Bd)$_{28K}$]	54 700	1.6	28	−6	184	ML	185 ± 96	89 ± 21
4	Poly(IBOMA)$_{36K}$	36 700	1.2	26 300	poly[IBOMA$_{36K}$-*b*-(St-*r*-Bd)$_{26K}$]	63 000	1.5	33	−6	187	ML	290 ± 72	74 ± 11
5	Poly(IBOMA)$_{46K}$	46 500	1.2	25 900	poly[IBOMA$_{46K}$-*b*-(St-*r*-Bd)$_{25K}$]	72 400	1.5	40	−5	185	ML	201 ± 95	51 ± 14
6	Poly(St)$_{43K}$	43 500	1.4	15 000	poly[St$_{43K}$-*b*-(St-*r*-Bd)$_{15K}$]	58 500	1.6	36	4	102	ML	176 ± 44	64 ± 13

[a] Reaction conditions: VAm-110, 1,1,2-trichloroethane (TCA), [Bd] : [St] = 85 : 15 wt%, [Bd + St] = 13 wt%, [CTA] : [VAm-110] = 5 : 1 by mol, 100 °C, 72 h, $M_{n(target)}$ for SBR block = 100 000 g mol^{-1}. [b] By GPC in THF at 40 °C (calibration with PS standards). [c] Isolated yield. [d] Determined by TMA. [e] Determined by AFM: L-lamellar, D-disordered, ML-modulated lamellar (for detailed size characterisation see ESI).

to perform chain extension with random copolymerization of St and Bd (Scheme 2). Both methacrylic (poly(IBOMA), poly(MMA)) and styrenic (poly(St)) types of macro-CTAs were used to show the versatility of method. MMA and St were selected as "classical" representatives, while IBOMA was chosen because the isobornyl bicyclic structure gives rise to methacrylate polymers with enhanced thermal stability and outstanding heat-resistance with $T_g > 191$ °C.[46,47]

The various macro-CTAs were synthesized with CDTPA agent employing the optimal conditions determined previously.[47] For comparison three macro-CTAs were prepared with the same M_n of around 40 000 g mol^{-1} (Table 3, entries 1, 5, 6, ESI†), while for poly(IBOMA) the molecular weight was varied from 12 400 to 46 500 g mol^{-1} (Table 3, entries 1, 2–5). For methacrylic type macro-CTAs the M_w/M_n ratio did not exceed 1.2, implying excellent control over the polymerization. For poly(St)$_{43K}$ it was found to be slightly higher at M_w/M_n = 1.4 (Table 3, entry 6). The isolated macro-CTAs were further chain extended *via* the random copolymerization of Bd and St at an 85 : 15 monomer ratio (Scheme 2 and Table 3). The optimal conditions determined above were applied for this synthesis with the exception that DMAc was replaced with TCA due to the insolubility of some of macro-CTAs in DMAc. For all block copolymers SEC analysis showed monomodal peaks that were continuously shifted towards shorter elution times indicating the successful growth of the poly(St-*r*-Bd) chain (Fig. 3).



Scheme 2 Synthetic approach for the preparation of poly[X_n-*b*-(St_m-*r*-Bd_k)] block copolymers.

The M_w/M_n ratio, ranging between 1.4 and 1.6, was considered satisfactory for RAFT polymerization. The molecular weight of the obtained block copolymers was in the range of 52 000–72 400 g mol^{-1} (Table 3). It was monotonously increasing from 25 900 to 39 600 g mol^{-1} with decreases in poly(IBOMA) macro-CTA M_n from 46 500 to 12 400 g mol^{-1}, respectively (Table 3, entries 2–5). The molar mass of the block copolymer was found to be dependent of the type of methacrylic macro-CTA: in both experiments with poly(IBOMA)$_{46K}$ and poly(MMA)$_{40K}$ the grown M_n of SBR block reached 23 500–39 600 g mol^{-1} (Table 3, entries 1 and 5). Compared to RAFT copolymerization of poly(St_n-*r*-Bd_m) alone, these molecular weights are higher, as expected, due to the higher initial viscosity of the reaction medium, which helps to suppress termination. At the same time, use of the styrenic macro-CTA allowed growth of only a 15 000 g mol^{-1} poly(St-*r*-Bd) block (Table 3, entry 6).

The T_gs of poly[X_n-*b*-(St_m-*r*-Bd_k)] block copolymers were evaluated using thermomechanical analysis (TMA). TMA method (Fig. S12, ESI†) was applied due to the uncertainty in high T_g determination *via* DSC as was reported previously for poly(IBOMA-*b*-Bd-*b*-IBOMA) triblock copolymers.[48] The resultant copolymers displayed two distinct T_g temperatures on the thermomechanical curve, consistent with the formation of

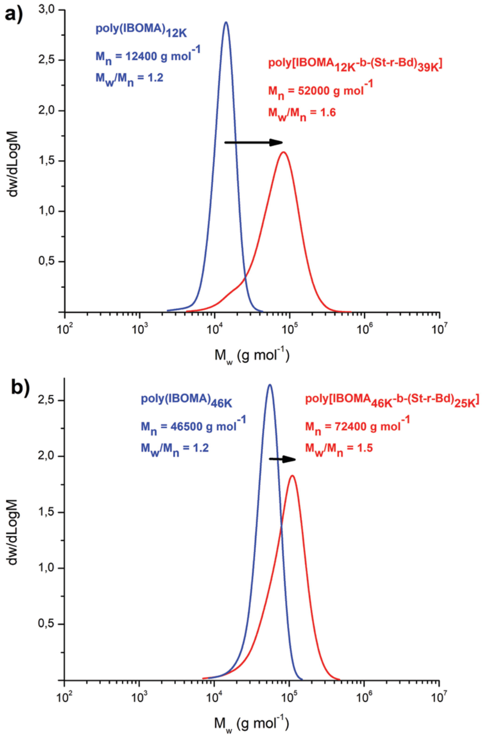


Fig. 3 GPC traces of macro-CTAs and respective block copolymers obtained *via* solution RAFT polymerization.

block copolymers (Table 3 and Fig. S12, ESI†). The transition at low temperatures (from −68 to 4 °C) was ascribed to the poly(St-*r*-Bd) block, whereas the T_g of poly(IBOMA), poly(MMA) and poly(St) blocks were observed in the high-temperature region at 184–187, 132 and 102 °C, respectively. The pronounced difference in the T_g of the poly(St-*r*-Bd) block can be explained by the variation in its size (M_n).

While the observation of a single GPC peak in combination with two separate T_g values, as detected here *via* TMA, is indeed consistent with the formation of a block copolymer, it is also true that a physical blend of homopolymers with similar molecular weights could also produce such a result. In order to fully exclude this possibility, one approach is to examine the phase behaviour of such systems. In the case of a blend of homopolymers, macroscopic phase-separation is expected on length-scales of tens to hundreds of microns or larger. In the case of block copolymers, on the other hand, phase-separation is inherently limited by molecular architecture resulting in the formation of nanoscale domains instead. Traditionally, such nanostructures are most often characterized either by microscopy (SEM, TEM, AFM, *etc.*) or scattering methods (SAXS, SANS, *etc.*), which are sensitive to the presence of such domains. Thus, to provide further evidence of successful poly[X_n-*b*-(St_m-*r*-Bd_k)] block copolymer formation, thin films were solvent cast onto glass substrates with slow solvent evaporation to encourage the formation of (near-)equilibrium morphologies, then studied by atomic force microscopy (AFM). AFM images of phase shift (Fig. 4 and Fig. S14, ESI†) revealed that

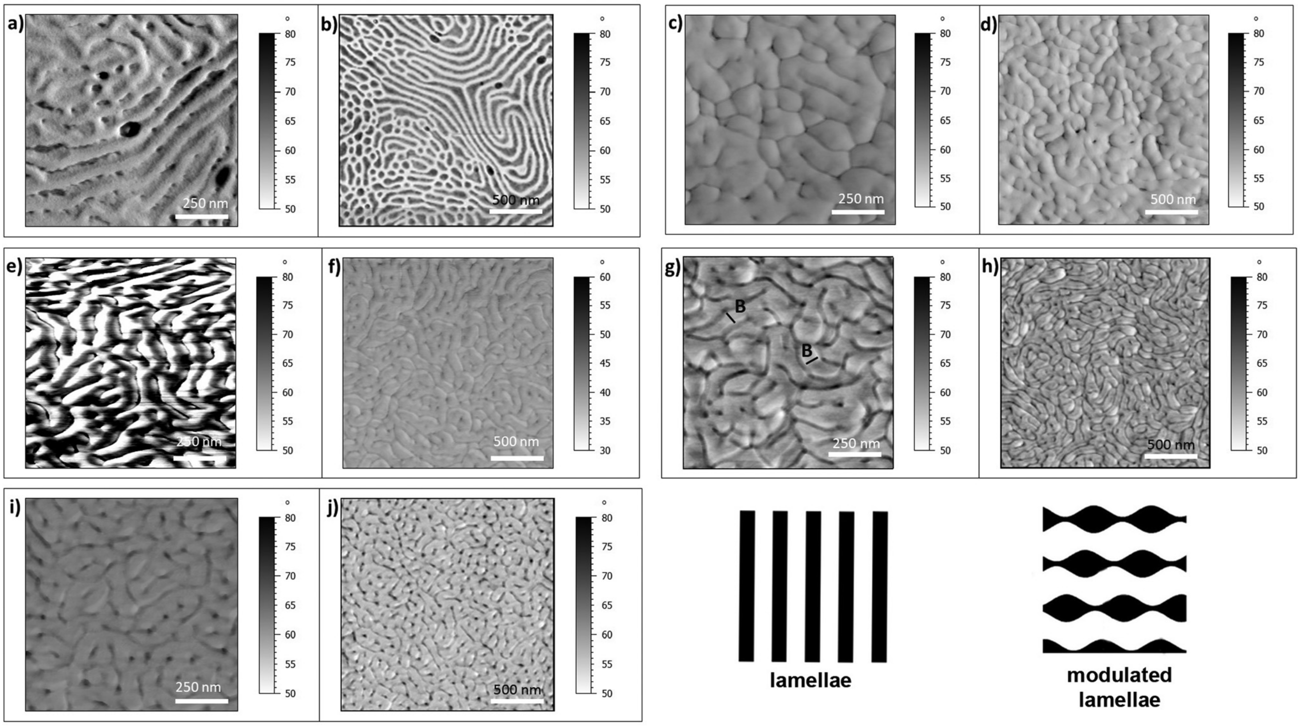


Fig. 4 AFM phase images of block copolymers: poly[MMA$_{40K}$-*b*-(St-*r*-Bd)$_{23K}$] (a) and (b), poly[IBOMA$_{26K}$-*b*-(St-*r*-Bd)$_{28K}$] (c) and (d), poly[IBOMA$_{36K}$-*b*-(St-*r*-Bd)$_{26K}$] (e) and (f), poly[IBOMA$_{46K}$-*b*-(St-*r*-Bd)$_{25K}$] (g), (h) and poly[St$_{43K}$-*b*-(St-*r*-Bd)$_{15K}$] (i) and (j). The dark areas show the soft part of the sample, while the bright domains represent the hard part.

phase separation mostly occurred at the nano-scale and the self-assembly can be attributed to three categories.[49] A clear lamellar morphology was observed for the poly[MMA$_{40K}$-*b*-(St-*r*-Bd)$_{23K}$] copolymer with a domain size of ~72 nm (Fig. 4(a) and (b)). For poly[IBOMA-*b*-(St-*r*-Bd)] copolymers the type of morphology was dependent on the ratio between the lengths of both blocks (Fig. 4(c)–(h)). When the poly(IBOMA) content was small in poly[IBOMA$_{12K}$-*b*-(St-*r*-Bd)$_{39K}$] the phase separation was found to be disordered. However, the increase in poly(IBOMA) content led to segregation in a modulated lamellar (ML) morphology (Fig. 4(c)–(h)). Here, the diameter of the ribbon-like structures decreased from 89 to 51 nm on transition from poly[IBOMA$_{26K}$-*b*-(St-*r*-Bd)$_{28K}$] to poly[IBOMA$_{46K}$-*b*-(St-*r*-Bd)$_{25K}$]. A similar ML morphology was demonstrated by the poly[St$_{43K}$-*b*-(St-*r*-Bd)$_{15K}$] block copolymer.

Conclusions

For the first time, the suitability in principle of a solution RAFT process (in contrast to the emulsion RAFT method) for the random copolymerization of styrene (St) and 1,3-butadiene (Bd) (poly(St$_n$-*r*-Bd$_m$)) was shown. It was demonstrated that the use of trithiocarbonate (4-Cyano-4 [(dodecylsulfanylthiocarbonyl)-sulfanyl]pentanoic acid (CDTPA)) chain transfer agent (CTA) leads to the desired copolymers in higher yield and with higher molecular weight in comparison with dithiocarbonate CTA. The optimization of reaction parameters such as polymerization temperature and time, type of CTA, solvent and initiator allowed for the successful preparation of soluble poly(St$_n$-*r*-Bd$_m$) copolymers in 39% isolated yield and with M_n values of up to 29 500 g mol^{-1} and $M_w/M_n \leq 1.6$. All obtained copolymers were random and did not contain any styrene blocks. Their composition was nearly independent of reaction conditions and consisted of 19.6–24.0, 15.0–15.5 and 60.5–64.5 wt% of styrene, (1,2)-Bd and (1,4)-Bd units, respectively.

To demonstrate the applicability and versatility of this approach, a range of poly[X$_n$-*b*-(St$_m$-*r*-Bd$_k$)] block copolymers was prepared *via* the solution RAFT method starting from well-defined macro-CTAs synthesized from various methacrylic (poly(IBOMA), poly(MMA)) and styrenic (poly(St)) monomers. Successful block copolymer synthesis was confirmed by different methods including SEC, TMA and AFM analyses. The molecular weight of poly[X$_n$-*b*-(St$_m$-*r*-Bd$_k$)] block copolymers was mainly dependent on the molar mass of the starting poly(X$_n$) macro-CTA and reached as high as 72 000 g mol^{-1}, with the attached SBR segment extension varying between 11 800 and 39 600 g mol^{-1}.

In sum, this approach provides a novel, readily accessible means of preparing copolymers with complex architectures based on a range of monomers, including those with functional groups, in order to generate high performance materials with tailored properties. The advantages of this method include (1) the relative simplicity of the reaction (no need for extreme purification of the monomers, less sensitivity towards moisture), (2) the control over the copolymer molecular weight and molecular weight distribution, and (3) the tolerance towards functional groups in monomers. This unique combination of useful characteristics highlights the promise of this approach (in spite of the long reaction times) as a new tool for the synthesis of next-generation copolymers with specifically designed and highly attractive performance profiles, where one of the blocks will possess rubbery properties and can be additionally cross-linked.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the Luxembourg National Research Fund (FNR) through the IPBG project TireMat-Tech (Grant No. 16/11514551). Authors would like to thank Prof. Barner-Kowollik (Queensland University of Technology (QUT), Brisbane, Australia) for providing valuable advices and discussions. EVONIK Operations GmbH (Germany, Essen, http://www.visiomer.com) is greatly acknowledged for the supplying of isobornyl methacrylate (VISIOMER® Terra IBOMA, IBOMA). Authors would like to warmly thank Benoit Marcolini (LIST) and Régis Vaudemont (LIST) for their help and advices related to materials characterization.

Notes and references

1 J. A. Brydson, in *Developments in Rubber Technology-2: Synthetic Rubbers*, ed. A. Whelan and K. S. Lee, Springer, Netherlands, Dordrecht, 1981, pp.21–49, DOI: , DOI: 10.1007/978-94-009-8108-9_2.
2 B. Rodgers and A. Halasa, in *Encyclopedia of Polymer Blends*, ed. A. I. Isayev, 2011, ch. 4, pp.163–206, DOI:, DOI: 10.1002/9783527805242.ch4.
3 M.-C. Iovu, S. Mapolie and A. G. Britchi, *Macromol. Symp.*, 2001, **165**, 55–62.
4 C. A. da Silva, H. Budde, M. Menzel, U. Wendler, M. Bartke, M. Weydert and M. Beiner, *RSC Adv.*, 2016, **6**, 50460–50470.
5 E. Kim, E. Lee, I. Park and T. Chang, *Polym. J.*, 2002, **34**, 674–681.
6 J. E. Kennedy, D. M. Devine, J. G. Lyons, L. M. Geever and C. L. Higginbotham, *J. Mater. Sci.*, 2009, **44**, 889–896.
7 L. Lei, L. Han, H. Ma, R. Zhang, X. Li, S. Zhang, C. Li, H. Bai and Y. Li, *Macromolecules*, 2021, **54**, 2691–2702.
8 E. Passaglia and F. Donati, *Polymer*, 2007, **48**, 35–42.
9 J. Chiefari, Y. K. Chong, F. Ercole, J. Krstina, J. Jeffery, T. P. T. Le, R. T. A. Mayadunne, G. F. Meijs, C. L. Moad, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 1998, **31**, 5559–5562.
10 A. B. Lowe and C. L. McCormick, in *Handbook of RAFT Polymerization*, ed. C. Barner-Kowollik, 2008, pp.235–284.
11 D. J. Keddie, *Chem. Soc. Rev.*, 2014, **43**, 496–505.
12 G. Moad, E. Rizzardo and S. H. Thang, *Aust. J. Chem.*, 2005, **58**, 379–410.
13 S. Pragliola, T. Acierno and P. Longo, *Polym. J.*, 2013, **45**, 904–908.
14 S. Perrier, *Macromolecules*, 2017, **50**, 7433–7447.

15 K. Nieswandt, P. Georgopanos, M. Held, E. Sperling and V. Abetz, *Polymers*, 2021, **14**, 62.

16 R. Wei, Y. Luo, W. Zeng, F. Wang and S. Xu, *Ind. Eng. Chem. Res.*, 2012, **51**, 15530–15535.

17 G. Bar-Nes, R. Hall, V. Sharma, M. Gaborieau, D. Lucas, P. Castignolles and R. G. Gilbert, *Eur. Polym. J.*, 2009, **45**, 3149–3163.

18 G. Moad, *Polym. Int.*, 2017, **66**, 26–41.

19 F. Lauterbach, M. Rubens, V. Abetz and T. Junkers, *Angew. Chem., Int. Ed.*, 2018, **57**, 14260–14264.

20 P. Lebreton, B. Ameduri, B. Boutevin and J.-M. Corpart, *Macromol. Chem. Phys.*, 2002, **203**, 522–537.

21 P. Ganjeh-Anzabi, V. Haddadi-Asl, M. Salami-Kalajahi and M. Abdollahi, *J. Polym. Res.*, 2013, **20**, 248.

22 R. Wei, Y. Luo and P. Xu, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 2980–2989.

23 A. Kaiser, S. Brandau, M. Klimpel and C. Barner-Kowollik, *Macromol. Rapid Commun.*, 2010, **31**, 1616–1621.

24 C. J. Dürr, S. G. J. Emmerling, A. Kaiser, S. Brandau, A. K. T. Habicht, M. Klimpel and C. Barner-Kowollik, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 174–180.

25 C. J. Dürr, S. G. J. Emmerling, P. Lederhose, A. Kaiser, S. Brandau, M. Klimpel and C. Barner-Kowollik, *Polym. Chem.*, 2012, **3**, 1048–1060.

26 C. J. Dürr, L. Hlalele, A. Kaiser, S. Brandau and C. Barner-Kowollik, *Macromolecules*, 2013, **46**, 49–62.

27 E. Rizzardo, G. Moad and S. H. Thang, *Handbook of RAFT Polymerization*, 2008, pp.189–234, DOI: , DOI: **10.1002/9783527622757.ch6**.

28 A. Goto, K. Sato, Y. Tsujii, T. Fukuda, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 2001, **34**, 402–408.

29 G. Moad, E. Rizzardo and S. H. Thang, *Polymer*, 2008, **49**, 1079–1131.

30 M. W. M. Fijten, R. M. Paulus and U. S. Schubert, *J. Polym. Sci., Part A: Polym. Chem.*, 2005, **43**, 3831–3839.

31 G. Moad, Y. K. Chong, A. Postma, E. Rizzardo and S. H. Thang, *Polymer*, 2005, **46**, 8458–8468.

32 Y. K. Chong, J. Krstina, T. P. T. Le, G. Moad, A. Postma, E. Rizzardo and S. H. Thang, *Macromolecules*, 2003, **36**, 2256–2272.

33 X. Zhang, O. Giani, S. Monge and J.-J. Robin, *Polymer*, 2010, **51**, 2947–2953.

34 C. Boyer, V. Bulmus, T. P. Davis, V. Ladmiral, J. Liu and S. Perrier, *Chem. Rev.*, 2009, **109**, 5402–5436.

35 Y. K. Chong, G. Moad, E. Rizzardo and S. H. Thang, *Macromolecules*, 2007, **40**, 4446–4455.

36 A. Favier and M.-T. Charreyre, *Macromol. Rapid Commun.*, 2006, **27**, 653–692.

37 S. Harrisson, S. R. Mackenzie and D. M. Haddleton, *Macromolecules*, 2003, **36**, 5072–5075.

38 Y. S. Vygodskii, O. A. Mel'nik, E. I. Lozinskaya, A. S. Shaplov, I. A. Malyshkina, N. D. Gavrilova, K. A. Lyssenko, M. Y. Antipin, D. G. Golovanov, A. A. Korlyukov, N. Ignat'ev and U. Welz-Biermann, *Polym. Adv. Technol.*, 2007, **18**, 50–63.

39 I. Woecht, G. Schmidt-Naake, S. Beuermann, M. Buback and N. García, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 1460–1469.

40 P. Kubisa, *Prog. Polym. Sci.*, 2009, **34**, 1333–1347.

41 E. Andrzejewska, M. Podgorska-Golubska, I. Stepniak and M. Andrzejewski, *Polymer*, 2009, **50**, 2040–2047.

42 S. A. Chesnokov, M. Y. Zakharina, A. S. Shaplov, E. I. Lozinskaya, I. A. Malyshkina, G. A. Abakumov, F. Vidal and Y. S. Vygodskii, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 2388–2409.

43 A. Tselepy, T. L. Schiller, S. Harrisson, C. Guerrero-Sanchez, G. Moad and D. J. Keddie, *Macromolecules*, 2018, **51**, 410–418.

44 A. F. Halasa, C. Jasiunas, B. Hsu, S. Henning and K. S. Seo, *J. Appl. Polym. Sci.*, 2013, **127**, 2116–2120.

45 A. F. Halasa, J. Prentis, B. Hsu and C. Jasiunas, *Polymer*, 2005, **46**, 4166–4174.

46 A. Matsumoto, K. Mizuta and T. Otsu, *J. Polym. Sci., Part A: Polym. Chem.*, 1993, **31**, 2531–2539.

47 A. Gunaydin, C. Mugemana, P. Grysan, C. Eloy Federico, R. Dieden, D. F. Schmidt, S. Westermann, M. Weydert and A. S. Shaplov, *Polymers*, 2021, **13**, 1626.

48 J. M. Yu, P. Dubois and R. Jérôme, *Macromolecules*, 1996, **29**, 7316–7322.

49 F. Bates, M. Schulz, A. Khandpur, S. Förster and J. Rosedale, *Faraday Discuss.*, 1994, **98**, 7.