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REVIEW

Diels–Alder "click" reactions: recent applications in polymer and material science

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The "click" chemistry concept is based on utilizing rapid reactions which are efficient, versatile, and selective. Indeed, Diels–Alder (DA) reactions fulfill most of the requirements for the "click" chemistry concept. In this review, we discuss the recent reports concerned with the use of DA "click" reactions in the synthesis of various macromolecular architectures, bioconjugates and hybrid materials.

1 Introduction

Diels–Alder (DA) reaction is one of the most common reactions used in organic chemistry and invented by Otto Diels and Kurt Alder who received the Nobel Prize in 1950 for their discovery.[1] DA reaction involves a straightforward [4 + 2] cycloaddition reaction between an electron-rich diene (furan and its derivatives, 1,3 cyclopentadiene and its derivatives, *etc.*) and an electron-poor dienophile (maleic acid and its derivatives, vinyl ketone, *etc.*) to form a stable cyclohexene adduct as illustrated in Fig. 1.[2,3] This reaction requires a very low energy to form a cyclohexene ring and it allows the formation and functionalization of numerous molecules. DA cycloaddition reaction forms not only carbon–carbon bonds but also heteroatom–heteroatom bonds (hetero-Diels–Alder, HDA) and it is widely used synthetically to prepare six-membered rings.[4] Some attractive features of DA reactions (retro-Diels–Alder, rDA) are thermal reversibility and the decomposition reaction of the cyclic system that can be controlled by temperature.[5]

Over the last decade, increasing attention has been devoted to the use of rapid reactions that meet the three main criteria of an ideal synthesis: efficiency, versatility, and selectivity. The extensively studied reactions that have been adapted to fulfill these criteria are known as "click" reactions. They are classified into four categories: (i) cycloaddition reactions (most commonly Huisgen 1,3-dipolar cycloaddition,[6–9] but also Diels–Alder reaction), (ii) nucleophilic ring-opening reactions of strained heterocyclic electrophiles (epoxides, aziridines and aziridinium ions),[10] (iii) non-aldol carbonyl chemistry (ureas, oximes and hydrazones)[11,12] and (iv) additions to carbon–carbon multiple bonds (especially thiol–ene chemistry but also Michael additions).[13–16] Among these, the most widely used reaction is copper catalyzed Huisgen 1,3-dipolar cycloaddition of terminal azides and alkynes to form triazole rings.[17] Apparently, some Diels–Alder reactions easily accomplish the several requirements of "click" chemistry.[18] Additionally, an advantage of these reactions is that they can proceed in the absence of a metal catalyst. The chemical structures of well-known dienes, dienophiles and adducts and reaction conditions are shown in Table 1. In order to assess whether a reaction may be classified as a "click" reaction, a modified definition in the context of polymer chemistry has been proposed by a group of polymer chemists.[19] In the adapted definition, a few more requirements have been added to the original definition of Sharpless' because of major differences in the macromolecular synthesis: (i) to use equimolar amounts of the building blocks, (ii) a simple large-scale purification process and (iii) a reasonable timescale and require no tedious fine-tuning

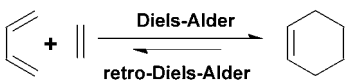

Fig. 1 General mechanism of Diels–Alder/retro Diels–Alder reactions of dienophile and diene.

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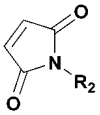
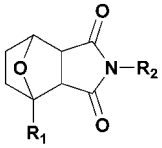
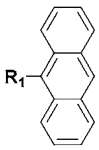
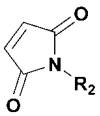
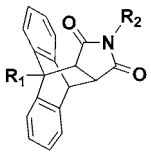
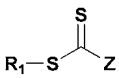
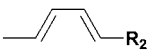
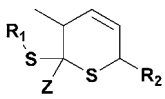
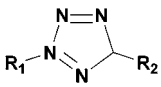
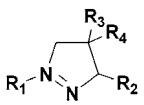
Table 1 Selected well-known Diels–Alder reactions in polymer and material science

Reagent A	Reagent B	Mechanism	Adduct	Conditions
furan 	maleimide 	[4 + 2] rDA cycloaddition reaction[5,20–23]		Between 25 and 120 °C without a catalyst reversible at temperatures higher than 120 °C
anthracene 	maleimide 	[4 + 2] DA cycloaddition reaction[24,25]		2 days under reflux in toluene without a catalyst
dithioester 	diene 	[4 + 2] HDA cycloaddition reaction[26]		10 min at r.t. catalyzed by trifluoroacetic acid
tetrazine 	cyclooctene 	[4 + 2] DA cycloaddition reactioninverse[27–30]		40 min at 25 °C (100% yield) N_2 is the only by-product

of reaction conditions. Therefore, it is more appropriate to call some Diels–Alder reactions as "click-type" or simply "efficient conjugation" methods.

A large number of specialized reviews have been published during the last decade on both copper-catalyzed azide–alkyne cycloaddition (CuAAC) and thiol–ene "click" reactions, however, only limited literature address the use of Diels–Alder (DA) cycloaddition reactions as "click" or "click-type" reactions in polymer and material science.[9,18,31–35] From this point, this review summarizes the potential use of DA "click" reactions in these fields and presents the recent examples to demonstrate the current state-of-the-art.

2 Macromolecular architectures *via* DA "click" chemistry

Synthesis of macromolecules with advanced architectures (*e.g.* homopolymers, telechelic, dendronized and star polymers, and block and graft copolymers) has been the essential aim of polymer chemists.[9,35,36] DA "click" reactions in combination with living/controlled polymerization methods (including reversible addition-fragmentation chain transfer polymerization (RAFT),[18,26,37,38] nitroxide mediated radical polymerization (NMRP),[25,39] atom transfer radical polymerization (ATRP),[24,40,41] ring-opening polymerization (ROP)[37,40,42,43]) are a facile route to access various architectures.

2.1 Homopolymers

A simple and efficient DA cycloaddition reaction can be employed in the preparation of linear thermoplastic[44] and thermosetting polymers[45] such as polyimides,[46–55] polyphenylenes,[56–59] ladder polymers, *etc.*[60,61] The polymerization by the DA cycloaddition reaction can be achieved by starting with monomers containing both diene and dienophile functional groups (A–B type monomer) in a single molecule or *via* the intermolecular reaction of bisdienes with bisdienophiles (A–A and B–B co-monomers) (Fig. 2).[62] Although, the DA polymerization proceeds *via* the reaction of unsaturated compounds and the resulting polymers do not have a structure typical for condensation products, the polymerization process is similar to polycondensation.[63–65] Diels–Alder linkages on the polymer backbone are desirable for adjusting the chain length,[44] control of processing viscosity[66] and for improved recyclability.[67]

2.2 Telechelic polymers

Telechelic polymers are defined as macromolecules containing reactive end groups that have the capacity to enter into further polymerization or other reactions.[68] The efficiencies of DA cycloaddition reactions have allowed that they can be used for the preparation of telechelic polymers. For example, Haddleton and co-workers reported an alternative synthetic route to prepare maleimido-functionalized telechelic polymers *via*

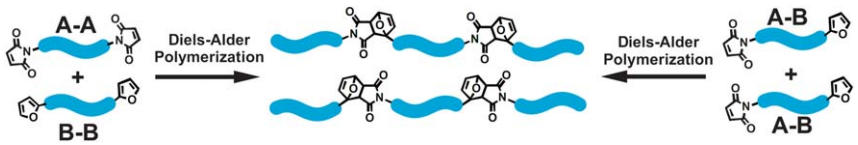


Fig. 2 Diels–Alder polymerization of A–B and A–A/B–B type monomers.

retro-Diels–Alder reaction. Well-defined telechelic polymethacrylates can be prepared by this strategy, which avoided the potential cross-linking side-reactions.[69]

Similarly, bismaleimide end-functionalized poly(ethylene oxide) (PEO) or poly(polypropylene oxide) (PPO) was reacted with an anthracene molecule having 2,2,6,6-tetramethylpiperidin-1-oxy (TEMPO) and *tert*-bromide groups *via* DA cycloaddition reaction. The obtained telechelic polymer with tertiary bromide and TEMPO functional groups was subsequently used for ATRP of *tert*-butyl acrylate (*t*BA) and for NMRP of styrene (St) to produce the heteroarm H-shaped terpolymers.[70] DA "click" reaction was also successfully combined with RAFT polymerization for the preparation of telechelic polymers. Sumerlin *et al.* presented a general strategy for end group functionalization of RAFT-generated polymers by DA "click" reaction.[71] Thiol terminated poly(*N*-isopropylacrylamide) (PNIPAM), prepared by RAFT/aminolysis, was reacted with excess of 1,8-bismaleimide derivatives to yield maleimido terminated PNIPAM. The maleimide dienophile allowed efficient coupling with 9-anthracene methanol by DA "click" reaction to yield a hydroxy monotelechelic polymer (Fig. 3).

In another study, thioxanthone end-functionalized PEO was successfully synthesized by using the DA "click" chemistry strategy. The final polymer could be used as photoinitiator for water-borne photopolymerization of several hydrophilic vinyl monomers, such as acrylic acid, acrylamide, 2-hydroxyethyl acrylate, and 1-vinyl-2-pyrrolidone.[72]

2.3 Block copolymers

As a model case, the preparation of block copolymers would be a suitable platform to show that DA cycloaddition reactions allow a facile access to more complex macromolecular architectures. For example, DA "click" reaction, [4 + 2] system, based on the coupling of furan protected maleimide- and anthracene-end functionalized polymers has been successfully used to generate numerous block copolymers.[24,73] Well-defined functional precursors, PEO, polystyrene (PSt) and poly(methyl methacrylate) (PMMA), were prepared by anionic ROP, NRMP and ATRP techniques, respectively.[24,25,70] The overall strategy is represented in Fig. 4 by the preparation of PEO-*b*-PSt and PEO-*b*-PMMA.

Recently, Kimura and co-workers prepared an anthracene-terminated poly(L-lactide) and a maleimide-terminated poly(D-lactide) by tin-catalyzed ROP of the corresponding lactide with 2-hydroxy-methylanthracene or *N*-(2-hydroxyethyl)maleimide as the initiator. Simple heating of these polymers could generate the poly(L-lactide)-*b*-poly(D-lactide) copolymer through anthracene–maleimide type DA "click" reaction.[74]

The HDA reactions between heterodienophiles such as imines, aldehydes or thiocarbonyl compounds with suitable dienes are also powerful method in the synthesis of heterocycles.[4,75,76] Barner-Kowollik and co-workers have recently introduced an efficient HDA type "click" reaction between diene- and dithioester-functional polymers.[26,77,78] In the first example of the HDA "click" reaction, they reported the synthesis of polystyrene-*b*-poly(ε-caprolactone) (PSt-*b*-PCL) by heating a solution of dithioester-terminated polystyrene and a diene-terminated PCL in the presence of catalyst at 50 °C between 2 and 24 h depending upon the nature of the dithioester end-group (Fig. 5).[37] Precursor polymers could be obtained by RAFT and ROP methods using benzyl(diethoxyphosphoryl)dithioformate or benzylpyridin-2-yl dithioformate and *trans*,*trans*-2,4-hexadienol, respectively.[37] In this approach, an electron-withdrawing dithioester played a key role regarding the controlling agent in a RAFT polymerization and subsequently as the reactive heterodienophile in an HDA "click" reaction. The reaction was catalyzed by the addition of either Lewis acids such as zinc chloride in the case of the diethoxyphosphoryl dithioester end-group or trifluoroacetic acid in the case of the pyridinyl dithioester end-group. These catalysts coordinate to sulfur atoms of the dithioester end-group in order to increase the electrophilicity on the thiocarbonyl bond.

The efficiency of HDA "click" reaction is dramatically accelerated by changing the open-chain diene to a cyclic one such as cyclopentadiene, even at ambient temperature in just a few minutes without the addition of catalyst. This ultrafast HDA "click" reaction was extremely efficient and resulted in almost

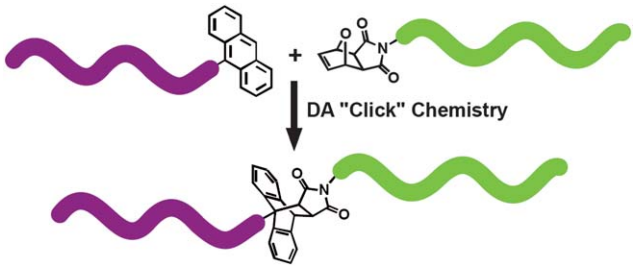


Fig. 4 Synthesis of block copolymers *via* anthracene–maleimide type DA "click" reaction.

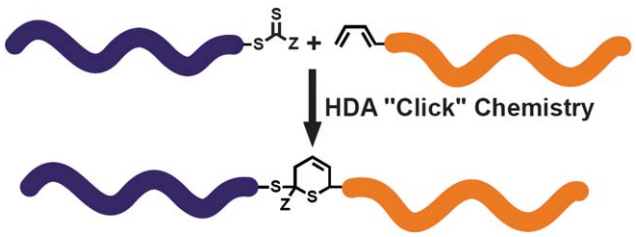


Fig. 5 Synthesis of block copolymer *via* HDA "click".

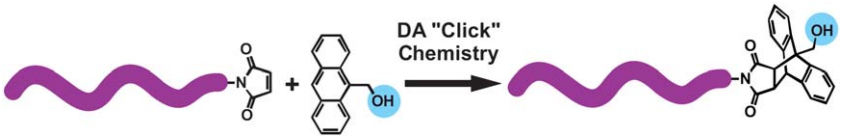


Fig. 3 Synthesis of hydroxyl-functionalized telechelic polymer *via* anthracene–maleimide type DA "click" reaction.

complete conversion of macromolecular coupling just by shaking the reaction flask at room temperature.[26,79,80] Furthermore, this "click" reaction can also provide an access to high molecular weight block copolymers ranging from 34 000 to over 100 000 and with low polydispersities (PDI < 1.2).[81]

Durmaz *et al.*[82] elegantly achieved a one-pot "click" construction of an ABC triblock copolymers such as PEO-*b*-PSt-*b*-PMMA and PCL-*b*-PSt-*b*-PMMA by utilizing tandem CuAAC and DA "click" reactions (Fig. 6). Well-defined polymeric precursors were obtained by either ROP of EO and CL or ATRP of St and MMA. The middle block was heterobifunctional PSt containing anthracene at the initiator end and azide at the termination end. Copper catalytic system was used to catalyze both CuAAC and DA "click" reactions at high temperature, and the triblock copolymer was obtained with high coupling efficiencies in a one-pot strategy.

2.4 Graft copolymers

Yagci, Tunca and Hizal *et al.* reported on the preparation of well-defined graft copolymers on the basis of the DA "click" chemistry between polymer backbone bearing anthryl pendant groups and maleimide end-functionalized polymers.[25] The "grafting onto" processes were carried out at the reflux temperature of toluene with a quantitative yield and without need for an additional purification step. Two series of well-defined PSt-*g*-PEO and PSt-*g*-PMMA copolymers were successfully prepared through the DA "click" reaction.

Later on, Barner-Kowollik and Stenzel demonstrated the synthesis of a graft copolymer *via* a combination of RAFT and HDA "click" methods.[83,84] The diene functionalized poly(*trans*-hexa-2,4-dienylacrylate-*r*-styrene) backbone and various dienophile functionalized polymers were prepared *via* RAFT polymerization of corresponding monomers, independently. Then, the HDA "click" reaction of these two polymers led to the formation of graft copolymer in 12 to 24 hours at 50 °C.

The orthogonality of DA and CuAAC "click" reactions was also demonstrated by preparing modular hetero-graft copolymers from maleimide-terminated P*t*BA, alkyne-terminated PEO, and anthracene- and azide-functionalized PSt backbone in a one-pot strategy (Fig. 7).[39] The graft copolymers were obtained with high grafting efficiency in the range from about 90% to nearly 100% showing low polydispersity indices (1.15–1.17). The use of consecutive DA and CuAAC "click" chemistries in a one-pot reaction was a versatile and straightforward strategy for the preparation of well-defined heterograft copolymer which cannot be obtained by using only one of the "click" reactions.

In another study, graft and graft-block copolymers were synthesized by either combination of ring-opening metathesis polymerization/Diels–Alder (ROMP/DA) or CuAAC/ROMP/DA strategies. First, anthracene end-functionalized polystyrene macromonomer was synthesized through CuAAC "click" reaction of an oxanorbornenyl alkyne with azido terminated polystyrene. Then the obtained macromonomer or anthracene-functionalized oxanorbornene was polymerized *via* ROMP using the first-generation Grubbs' catalyst. Finally, poly(oxanorbornenyl anthracene) or poly(oxanorbornene)-*g*-polystyrene-anthracene copolymer was coupled with maleimide end-functionalized polymers, such as PEO, PMMA and poly(*n*-butyl acrylate) *via* DA "click" reactions to yield corresponding graft and graft-block copolymers, respectively.[85] Recently, this strategy was applied to synthesise brush copolymers with AB block-brush architectures containing polyoxanorbornene backbone and PCL, PMMA or P*t*BA side chains.[86]

2.5 Complex macromolecular architectures

Diels–Alder cycloaddition reaction is a very useful and versatile toolbox to construct complex macromolecular architectures because of its quantitative yield, mild reaction conditions and tolerance of numerous functional groups. The Tunca and Hizal group demonstrated that a number of these examples were

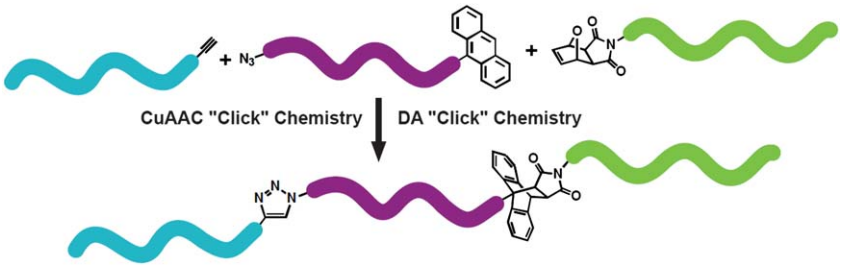


Fig. 6 Synthesis of ABC triblock copolymer *via* one-pot CuAAC and DA "click" reactions.

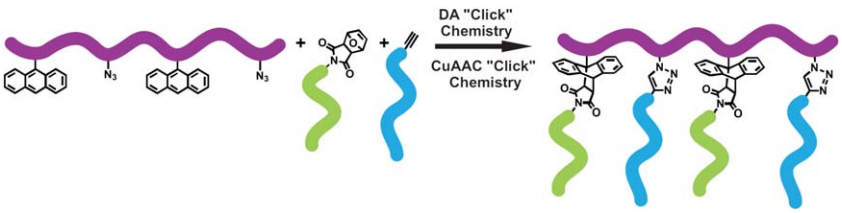


Fig. 7 Synthesis of hetero-graft copolymer *via* one-pot CuAAC and DA "click" reactions.

accessible by DA "click" reactions, sometimes in combination with CuAAC, thus representing the wide scope and modularity. For example, several A_3 type star polymers containing PEO, PMMA and P*t*BA arms were efficiently synthesized by DA "click" reactions using furan protected maleimide end-functional polymers and a trianthracene core.[87] ABC type miktoarm star polymers were prepared by combination of DA "click", ATRP and NMRP processes.[88] In this case, DA cycloaddition was performed with a maleimide-terminated PEO and an anthracene functionalized dual initiator which is capable to initiate both NMRP and ATRP of St and *t*-BA, respectively (Table 2).

The orthogonality of DA and CuAAC "click" reactions was demonstrated by preparing modular three-arm star block copolymers ((PSt-*b*-PMMA)$_3$ and (PSt-*b*-PEO)$_3$) from maleimide-terminated PMMA or PEO and α-anthracene-ω-azide-terminated polystyrene.[92] Linear PEO, PSt, and PMMA precursors were prepared *via* ATRP of related monomers, except a commercially available PEO. Similarly, a one-pot "double-click" approach was employed to prepare H-shaped ABCDE quinto-polymers.[90]

Barner-Kowollik and co-workers recently reported synthesis of star-shaped polymers by combination of RAFT/HDA "click", RAFT and ATRP/HDA "click" or ROP and RAFT/CuAAC and HDA "click" processes. In the first example, RAFT polymerization of styrene was followed by a HDA "click" reaction to yield star polymers with up to four arms.[38] In general, the coupling efficiencies were found to decrease with increasing number of arms. When a diethoxyphosphoryldithioformate terminated polymer was used the yields of 2-arm star, 3-arm star, and 4-arm star polymers were 81%, 77% and 65%, respectively, and when a pyridin-2-yl dithioformate terminated polymer was used, the yields of 2-arm star, 3-arm star and 4-arm star polymers were 91%, 86% and 82% respectively.

The synthesis of three-arm (PSt-*b*-PCL)$_3$ star-block copolymers by a sequential combination of the CuAAC and HDA "click" reactions was successfully performed through an arm-first and core-first strategy.[95] The strategy involves the preparation of an α-diene-ω-alkyne functionalized PCL by AROP, a PSt equipped with an electron-deficient dithioester end group by RAFT, and a triazide coupling agent as the corresponding building blocks. In addition, a twelve-armed star-block copolymer composed of P*i*BorA internal and PSt external blocks was synthesized by combination of ATRP, RAFT and HDA "click" reactions.[98] In this system, bromine functionality of an ATRP polymerized multi-functional (PiBorA-Br)$_{12}$ was converted into diene end groups and subsequently coupled with dithioester functionality of a RAFT-polymerized PSt *via* HDA "click" chemistry.

In a recent study, Tunca *et al.* synthesized cyclic homo and block copolymers by combination of double CuAAC and DA "click" reaction strategy.[99] First, well-defined linear precursors were obtained *via* combination of ATRP, anionic ROP and CuAAC methods. Afterwards, these linear homo or block copolymers were efficiently coupled *via* DA "click" reaction to give their corresponding cyclic homo and block copolymers. Combination of CuAAC and DA "click" reactions strategy enabled us to prepare cyclic block copolymers, which cannot be achieved by using a single "click" reaction (Fig. 8).

2.6 Dendrimer and dendronized polymers

Diels–Alder cycloaddition reaction between anthracene and maleimide derivatives has proven to produce excellent results in the formation of dendrimers and dendronized polymers in a modular approach. First, McElhanon and co-workers reported the use of thermally reversible furan–maleimide DA

Table 2 Various macromolecular complex architectures obtained by DA "click" reactions

Type of reactions	Polymerization methods	Topology	Polymer[a]
DA	ATRP/AROP	Linear AB block copolymer[24,73]	PMMA-*b*-PSt, PEO-*b*-PSt, P*t*BA-*b*-PSt, PMMA-*b*-PEO, PCL-*b*-P*t*BA
CuAAC and DA	ATRP/ATRP/AROP	Linear ABC block copolymer[82]	PEO-PSt-PMMA PCL-PSt-PMMA
CuAAC and DA	AROP/ATRP/NMRP	Hetero-graft copolymer[39]	PSt-*g*-(PMMA-PEO)
CuAAC and DA	ATRP/AROP	Multiblock-graft copolymer[89]	PSt-*g*-PMMA, PSt-*g*-PEO, PSt-*g*-P*t*BA
DA	AROP/ATRP/NMRP	H-shaped A_2B_2C block copolymer[70]	PSt-*b*-P*t*BA-*b*-PEO-*b*-P*t*BA-*b*-PSt PSt-*b*-P*t*BA-*b*-PPO-*b*-P*t*BA-*b*-PSt
DA	AROP/ATRP/NMRP/ROP	H-shaped ABCDE quintopolymer[90]	PEO-*b*-PMMA-*b*-P*t*BA-*b*-PCL-*b*-PSt
DA	AROP/ATRP	Star polymer A_3[87]	PEO-PMMA-P*t*BA
CuAAC and DA	ROP	Star polymer A_4 and A_8[91]	PCL_4, PCL_8
HDA	RAFT	Star polymers A_2, A_3, A_4[38]	PSt_2, PSt_3, PSt_4
CuAAC and DA	ATRP/AROP	Mikto-arm star A_3B_3[92]	(PSt-*b*-PMMA)$_3$ (PSt-*b*-PEO)$_3$
DA	ATRP	Multi-arm star-block polymer[93]	PMMA-PSt P*t*BA-PSt
CuAAC and DA	ATRP/AROP	Multi-arm star triblock terpolymers[94]	$(PtBA)_k$-$(PMMA)_n$-$(PSt)_m$-PDVB
CuAAC and HDA	ROP/RAFT	Multi-arm star block copolymers[95]	(PSt-*b*-PCL)$_3$
CuAAC and DA	ATRP	Multi-arm star polymers with peripheral dendritic PMMA[96]	$(PMMA)_{2n}$-$(PSt)_m$-PDVB and $(PMMA)_{4n}$-$(PSt)_m$-PDVB
CuAAC and DA	ATRP	Multi-miktoarm star block copolymers[97]	$(PtBA)_n$-$(PSt)_m$-PDVB-$(PSt)_m$-$(PMMA)_k$
HDA	ATRP/RAFT	Multi-arm star block copolymers[98]	(P*i*BorA-*b*-PSt)$_{12}$

[a] PSt, polystyrene; PMMA, poly(methyl methacrylate); PEO, poly(ethylene oxide); PPO, poly(propylene oxide); P*t*BA, poly(*t*-butyl acrylate); PCL, poly(ε-caprolactone); P*i*BorA, poly(isobornyl acrylate); PDVB, poly(divinyl benzene).

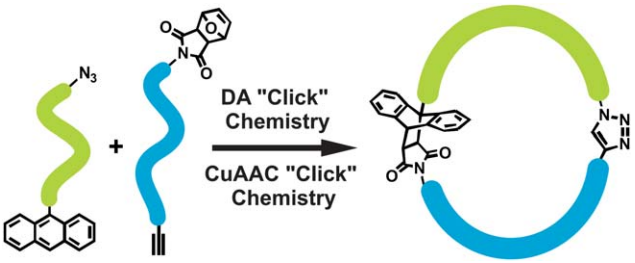


Fig. 8 Synthesis of cyclic block copolymers *via* tandem CuAAC and DA "click" reactions.

cycloaddition reactions for a convergent approach towards benzyl aryl ether dendrimers up to the third generation (Fig. 9).[22] The system required a disubstituted furan that could serve as an AB_2 monomer and an *N*-substituted maleimide with a reactive hydroxyl focal point, which was finally coupled with the 1,3,5-benzenetricarbonyl trichloride central linker in the presence of triethylamine in tetrahydrofuran. This work was the first example of a new class of thermally reversible dendrimer taking advantage of the DA/rDA approach. Later on, the same group[20] reported a similar system with a bismaleimide core and fourth generation benzyl aryl ether based dendrons that contained furan moieties at their focal point to access first through fourth generation Diels–Alder dendrimers. The DA cycloaddition reactions have also been used in peripheral modification of carbosilane dendrimers and represent a facile example of covalent structural modification.[100–103]

Sanyal's group[104] recently reported the synthesis of unsymmetrical (AB type) dendrimers by DA "click" reaction of furan functionalized polyaryl ether dendrons and maleimide functionalized polyester dendrons. Precursor dendrons were prepared by coupling of acid-functionalized Frechet dendrons with furfuryl alcohol and divergently starting with a furan-protected *N*-hydroxypropylmaleimide. The DA cycloaddition reaction of dendrons in benzene at 85 °C for 24 h led to the three different generations of unsymmetrical dendrimers (G1, G2 and G3) with 98%, 76%, and 79%, respectively.

Similarly, dendronized polymers (linear polymer chains with bulky side dendrons) have been prepared by DA "click" reaction using an anthracene-bearing PSt backbone and third-generation polyester dendrons containing reactive maleimide at the focal point.[105] Kakkar *et al.* have designed appropriate building blocks to construct thermoresponsive dendrimers by combination of CuAAC and furan–maleimide type DA "click" reactions, in a sequential manner.[106] These thermally labile dendrimers, which can undergo facile retro-DA disassembly, led to a suite of new nanoscopic materials for a variety of applications. McElhanon and co-workers also reported the synthesis of a linear dendronized step polymer utilizing sequential "double-click" reactions.[107] First, third generation of dendritic bisfuran monomers could be prepared by CuAAC "click" reaction, followed by thermally reversible polymerization by DA "click" reaction between the bisfurans and bismaleimides.

2.7 Cross-linked and mendable polymers

Utilization of the DA "click" reactions in the preparation of polymer networks has resulted in a new class of thermally reversible cross-linked polymers[108] and hydrogels[109] which are widely tested in encapsulants, self-healing materials and coatings applications.[109–111] Three synthetic strategies can be employed for the synthesis of polymer networks, namely (i) direct DA cycloaddition reactions involving multifunctional monomers, *e.g.* a di- or tri-furan derivative and a bismaleimide,[48,112–116] (ii) DA cycloaddition of linear polymers bearing pendant furan and/or maleimide[111,117–132] and (iii) a cross-linker or an initiator containing a Diels–Alder linkage in the polymerization (Fig. 10).[133,134]

For the first strategy, Wudl and co-workers reported that the synthesis of a highly cross-linked polymer network can be formed *via* the DA cycloaddition reaction of a multi-diene (four furan-functionalized monomer) and multi-dienophile (three maleimide-functionalized monomer) and thermal reversibility of this network can be accomplished by the retro-DA reaction.[135] For the second strategy, thermoresponsive hydrogels based on the aqueous Diels–Alder reaction of various polymer backbone bearing pendant furfuryl groups and PEO bismaleimide were reported by Wei and co-workers.[136–138] For the last strategy, a cross-linker or an initiator containing a Diels–Alder linkage can be synthesized by a series of reactions involving DA, retro-DA cycloaddition and esterification. The thermally labile cross-linker or initiator was successfully converted to polymer networks *via* different polymerization methods.[133,134] Recently, Barner-Kowollik *et al.* reported an alternative approach for the synthesis of a reversible cross-linked polymer *via* the HDA "click" reaction of biscyclopentadiene end-functionalized

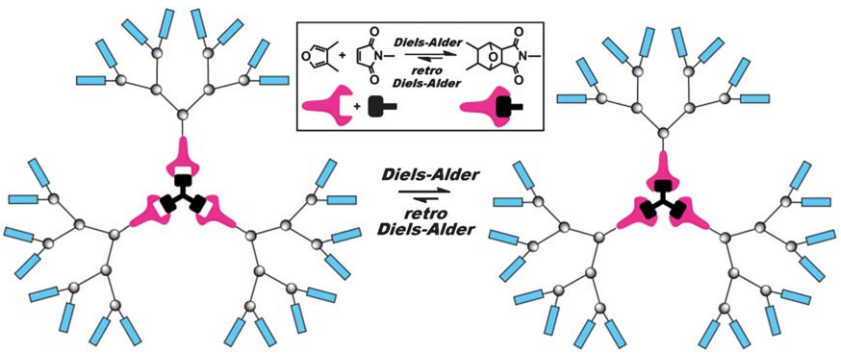


Fig. 9 Reversible furan–maleimide Diels–Alder reaction for the formation and controlled cleavage of dendrimers around a plurifunctional core.

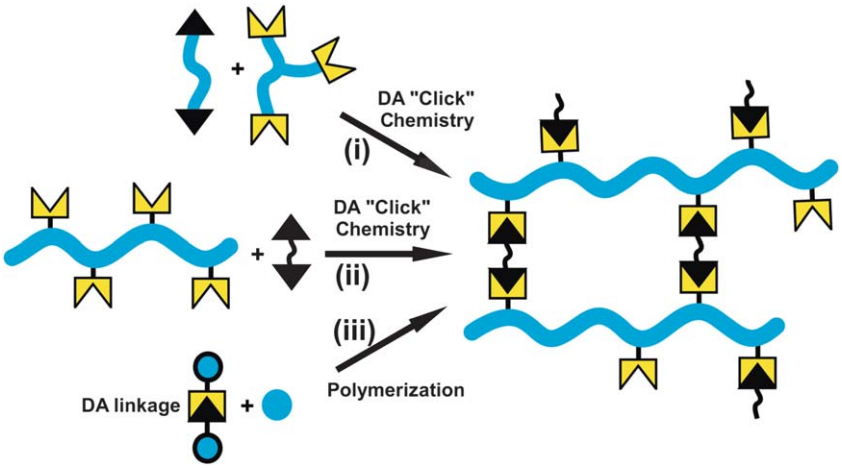


Fig. 10 General strategies for the synthesis of polymer network *via* DA cycloaddition reactions.

PMMA and trifunctional pyridinyldithioformate cross-linker.[139] The reversibility of rapid HDA reactions allows regeneration of the highly reversibly stimuli-responsive cross-linked polymer network.

It is clear that DA "click" chemistry is the most frequently studied reaction for the synthesis of thermoreversible cross-linked networks including polymer gels and thermoset networks. This 'thermoreversibility' enables the fabrication of re-mendable polymers carrying diene and dienophile functionalities, either as the polymer chain-end or in the repeating units.[140] In these polymers, when the fractured polymers are reheated, first DA linkages should disconnect but then the diene and dienophile moieties should reconnect upon cooling and the cracks, or fractures, should repair. This fracture/repair cycle can be repeated multiple times, and it does not require additional chemicals such as a catalyst, monomer, or special surface treatment of the fractured interface. There are a number of Diels–Alder systems based on furan–maleimide,[23,124,132,135,141–147] cyclopentadiene[148–155] and anthracene–maleimide[134,156] couples for re-mendable polymers (Fig. 11). Recent reviews on re-mendable polymers are available in the literature.[140,157–160]

2.8 Side-chain functionalization

Side-chain functionalization is the process by which desired groups are introduced into the side chain unit of the polymer backbone. Typically side chain functional polymers can be simply prepared by DA "click" chemistry. In this context, Jen and co-workers have used the DA "click" reaction between polymer backbone bearing side-chain anthracene molecules and maleimide-containing nonlinear optical (NLO) chromophores to yield high-performance NLO polymers.[161] DA "click" reaction was also applied using the opposite end functional (side-chain maleimide) polymer backbone and anthryl-containing chromophores.[162] The resulting polymers exhibited high dielectric strength and thermal stability, excellent optical and poling efficiencies, and good processability. The facile access of these polymers highlighted the importance of the reagent-free DA "click" reactions. Moreover, DA click reactions have a significant advantage over the CuAAC "click" reaction because of the high reactivity of azides, towards cyano-containing acceptors that are the most used NLO chromophores.

Another example of side chain functionalization was the incorporation of photoactive groups onto polystyrene backbone by using a "double-click" chemistry strategy (Fig. 12).[163] For this purpose, thioxanthone–anthracene, *N*-propargyl-7-oxy-norbornene acted as a "click-linker", and polystyrene with side-chain azide moieties were reacted in *N*,*N*-dimethylformamide for 36 h at 120 °C. The obtained polymeric photoinitiators were shown to efficiently initiate the free radical polymerization of

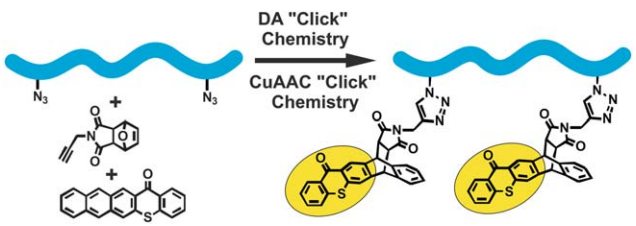


Fig. 12 Side-chain functionalization of polymers *via* one-pot CuAAC and DA "click" reactions.

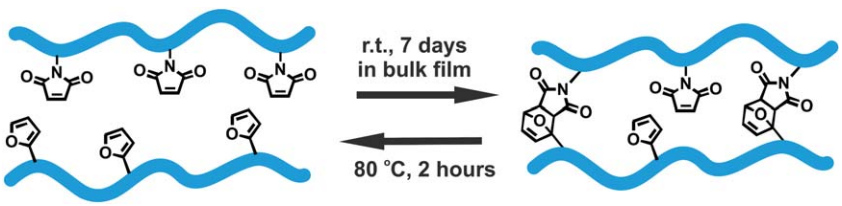


Fig. 11 Example of a re-mendable network with furan and maleimide pendant end groups *via* DA cycloaddition reactions.

mono- and multi-functional monomers *via type II* photo-initiation mechanism.

3 Bioconjugates and modification of biomolecules *via* DA "click" chemistry

3.1 Modification of nucleic acids and oligonucleotides

The modification of biomolecules with synthetic polymers offers many advantages over unmodified counterparts, including increased stability and solubility, the ability to modulate protein activity, and increased bioavailability for therapeutic applications.[164–166] The DA cycloaddition reactions are a promising tool for the bioconjugation of biomolecules since it occurs within a short period (hours), with very high yields and under mild conditions (at room temperature in aqueous solution). The high compatibility of DA cycloaddition reactions with biomolecules has been operated elegantly in the bioconjugation or immobilization of oligonucleotides, protein, peptides, carbohydrates and antibodies. For example, a number of studies described the use of DA "click" chemistry with oligonucleotides[167] bearing a diene or dienophile moiety with small molecules (carboxylic acid, activated ester, benzophenone, pyrene, fluorescent dye, TEMPO, biotin, *etc.*),[168–180] polymers,[170,171,181] gold nanoparticles,[171,182] and glass surfaces.[183–187] The reactions were carried out without interference of the many functional groups presented in RNA and DNA. The yields were greater than 80% and often as much as 90–95% within several hours at room or slightly higher temperature (*e.g.*, 30 °C).

The conjugation of diene-modified oligonucleotides with maleimide derivatives of peptides could also be done using DA cycloaddition reaction under mild conditions without additional catalysts (Fig. 13). The reaction was strongly affected by the size of the reagents and nature of dienes and dienophiles, but it was completed in 8–10 h with high yield.[176,188,189] The DA cycloaddition reactions allowed the straightforward synthesis of large peptide–oligonucleotide conjugates, however, maleimide was prone to Michael addition reactions with other nucleophilic centers on peptides or oligonucleotides and may lead to side reactions.[190]

3.2 Modification of amino acids, peptides, and proteins

The DA cycloaddition reactions can also offer many possibilities for the modification of peptides and proteins,[191–194] due to the compatibility with all amino acid side groups except for the thiol group on cysteine.[195] To prove the applicability of DA "click" chemistry, protein–cyclopentadiene conjugates were prepared and subsequently grafted onto maleimide modified glass,[196,197] self-assembled monolayer,[198–206] dendrimer[207] or hydrophilic resin[208] to give the cycloaddition product in high yield. The DA cycloaddition reactions have also been recognized as a promising chemoselective methodology to introduce fluorescent labels on proteins,[28,29,197,209–212] to prepare neo-glycoproteins,[213] or to chemically activated proteins.[27,214–216]

Recently, the Nolte group reported on an elegant spontaneous copper-free tandem 1,3-dipolar cycloaddition-retro-Diels–Alder (tandem crDA) reaction in which a trifluoromethyl-substituted oxanorbornadiene derivative reacts with an azide to form a stable 1,2,3-triazole linkage. The crDA reaction was successfully applied to the coupling of small molecules with proteins and polymers with peptides in various media at ambient temperature (Fig. 14). The key to the successful bioconjugation of this approach lay in the increased reactivity of the trifluoro-methyl substituted oxanorbornadiene derivatives as compared to the electron deficient alkynes. These molecules tended to react with azide under mild reaction conditions, even in the absence of transition metal catalysts like copper. It was proved that this crDA "click" reaction was faster than classical CuAAC "click" reaction at room temperature. Therefore, this method was successfully used in the modification of peptides and proteins. Later on, the crDA "click" reaction was tested in the biological media, indicating that the reaction was bioorthogonal and underwent independently of pH and also proceeded in serum and blood.[212,217,218]

An alternative bioorthogonal inverse-electron demand Diels–Alder reaction between strained *trans*-cyclooctene (dienophile) and *s*-tetrazine (diene) has been reported by several groups (Fig. 15).[27–29,219–223] In this method, first the reaction sites of the diene and the dienophile were reacted in a [4 + 2] cycloaddition and then formation of nitrogen gaseous made this reaction irreversible and produces the stable dihydro-pyridazines. Because of its high reactivity in organic solvents, in water, and in cell media, it may be used as a tool for the covalent and

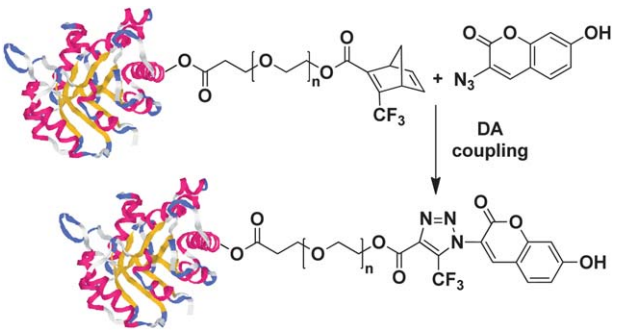


Fig. 14 Functionalization of oligopeptides with 3-azido-7-hydroxy-coumarin *via* tandem-crDA reaction.

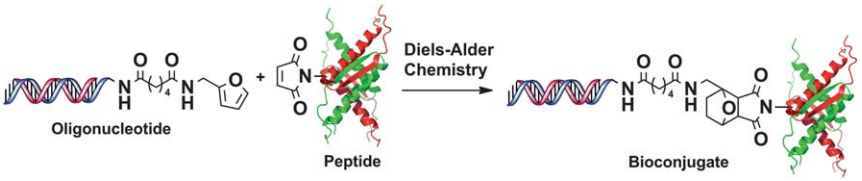


Fig. 13 Preparation of peptide-oligonucleotide bioconjugates by DA "click" reaction.

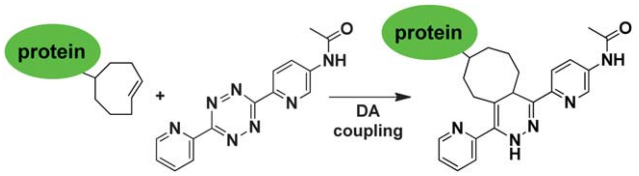


Fig. 15 Functionalization of protein with tetrazole-based diene *via* inverse-electron demand Diels–Alder reaction.

irreversible derivatization of various molecules such as peptides,[27] oligonucleotides[222] and small-molecule drugs.[29,220,223]

3.3 Modification of sugars, polysaccharides, and glycoconjugates

Other biomaterials including carbohydrates and derivatives have been immobilized onto various substrates (such as SAM,[224,225] protein,[213,226] human serum albumin[227] and glass[228]) by DA cycloaddition reactions.[229,230] Chaikof and co-workers reported on a protocol using sequential double "click" reactions (DA followed by CuAAC) for the immobilization of carbohydrates and proteins onto a solid surface. First, a PEO linker carrying alkyne and cyclodiene end groups was synthesized and attached onto an *N*-(ε-maleimidocaproyl)-functionalized (EMC) glass plate *via* an aqueous DA reaction. Subsequently, an alkyne-functionalized surface was provided for the conjugation of azide-containing biomolecules (proteins, biotin, and sugars) *via* CuAAC "click" chemistry, which proceeded to completion at low temperature and in aqueous solvent. The reactants, azide, alkyne, cyclodiene, and EMC groups were independently stable under bioconjugation conditions and do not react with common organic reagents or with themselves. Thus the potential of this strategy to immobilize a wide range of functionally complex substances onto solid surfaces has been significant.[231] Later on, the same group has extended to use of aqueous DA "click" chemistry for the immobilization of diverse biomolecules such as biotin, lactose and protein A onto EMC glass plate.[183]

3.4 Modification of antibodies

DA "click" chemistry has been recently employed for bioconjugation of maleimide-functional antibodies onto furan-functional polymeric nanoparticle surfaces.[232–235] The self-assembled polymeric nanoparticles were designed from poly (2-methyl, 2-carboxy trimethylene carbonate-*co*-D,L-lactide)-*graft*-poly(ethylene glycol) with furan groups located on the surface of the PEO corona. Coupling of maleimide-functional antibodies on the nanoparticle surface *via* DA chemistry led to the immuno-nanoparticles, which are promising tools for antibody-mediated targeted drug delivery. The DA "click" coupling reaction was performed in aqueous media (pH 5.5) at 37 °C achieving high coupling efficiency of antibody of up to 100% within several hours.

4 Hybrid materials *via* DA "click" chemistry

Owing to the efficiency and facile work-up, DA cycloaddition reactions have been extensively used for the functionalization of organic/inorganic nanostructures and surfaces.[45,236] The surface modification of divinylbenzene based microspheres and aromatic polyester by grafting 2,4-hexadienoyl-terminated poly(ε-caprolactone) and maleimide-terminated PEO chains afforded functional microspheres[42] and hydrophilic polymers.[237] In another approach, divinylbenzene based microspheres were firstly functionalized with a highly reactive diene (cyclopentadiene), and subsequently reacted with thiocarbonyl terminated polystyrene through HDA "click" reaction.[238]

The external graphene planes of carbon black,[239,240] nanotubes[241–250] and fibers[251–254] make these materials particularly suited for functionalization by DA cycloaddition reactions to their π-electrons. Abetz *et al.* have also shown that these carbon-rich materials behave both as diene and dienophile, depending on the reaction partner.[255] Preliminary results indicated that single walled carbon nanotubes were more reactive than corresponding multiwall tubes while the carbon nanofibers were the least reactive, presumably due to the less available surface area. For example, consecutive DA cycloadditions of 1,3-butadienes onto the carbon nanofiber led to a polymeric layer on the surface (Fig. 16).[252–254] This process offers a new and powerful methodology to obtain functional carbon nano-materials with better solubility for the technological applications.

Similarly, DA and HDA click reactions have been also used for selective modification of fullerenes.[240,256–260] For example, Barner-Kowollik and Nebhani reported a direct and rapid functionalization of fullerene with cyclopentadienyl functionalized PEO *via* DA reaction ambient temperature in the absence of

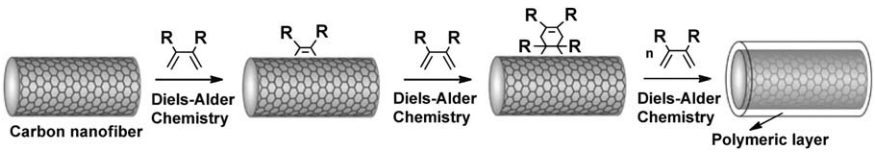


Fig. 16 Surface modification of carbon nanotubes with organic molecules *via* Diels–Alder reactions.

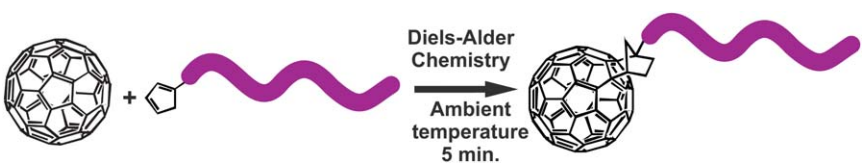


Fig. 17 Functionalization of fullerene with cyclopentadienyl functionalized polymer *via* Diels–Alder reaction.

any catalyst (Fig. 17).[259] In another case, DA "click" reaction was applied to synthesis of polymer hybrid materials from organic molecules onto silicon wafers,[261,262] gold nanoparticles[263–265] or tetraethoxysilanes.[147,266]

5 Conclusions and perspectives

In conclusion, DA "click" reactions show great potential for the construction of tailor-made functional materials such as telechelic polymers, block, graft, star, star-block, H-shaped polymers, dendrimers, bioconjugates and hybrid materials. DA "click" chemistry features several outstanding advantages including water-solubility, high reaction yields, no detectable side-reactions and no requirement for additional catalysts. Moreover, the reactive moieties of this method are inert for most functionalities such as –COOH, –OH and $–NH_2$ groups and biomolecules. It can be applied under particularly mild conditions (aqueous solution without solvents, neutral pH and moderate temperature). Another considerable advantage of these reactions is commercial availability of the suitable dienophiles in the form of maleimide-derivatives.

Overall, the DA "click" chemistry is a simple synthetic route to access organic and hybrid materials. While maleimides are used as dienophiles in most of the DA reactions developing new dienes and dienophiles should upgrade its ability in novel applications. On the other hand, sometimes longer reaction times are required for the complete conversion, which may be overcome by addition of suitable catalysts.

Notes and references

1 O. Diels and K. Alder, *Justus Liebigs Ann. Chem.*, 1928, **460**, 98–122.
2 J. Sauer and R. Sustmann, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 779–807.
3 K. C. Nicolaou, S. A. Snyder, T. Montagnon and G. Vassilikogiannakis, *Angew. Chem., Int. Ed.*, 2002, **41**, 1668–1698.
4 L. F. Tietze and G. Kettschau, *Top. Curr. Chem.*, 1997, **189**, 1–120.
5 J. L. Ripoll, A. Rouessac and F. Rouessac, *Tetrahedron*, 1978, **34**, 19–40.
6 H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004–2021.
7 V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew. Chem., Int. Ed.*, 2002, **41**, 2596–2599.
8 C. W. Tornoe, C. Christensen and M. Meldal, *J. Org. Chem.*, 2002, **67**, 3057–3064.
9 B. S. Sumerlin and A. P. Vogt, *Macromolecules*, 2010, **43**, 1–13.
10 G. Kumaraswamy, K. Ankamma and A. Pitchaiah, *J. Org. Chem.*, 2007, **72**, 9822–9825.
11 K. L. Heredia, Z. P. Tolstyka and H. D. Maynard, *Macromolecules*, 2007, **40**, 4772–4779.
12 A. Dirksen and P. E. Dawson, *Bioconjugate Chem.*, 2008, **19**, 2543–2548.
13 L. M. Campos, K. L. Killops, R. Sakai, J. M. J. Paulusse, D. Damiron, E. Drockenmuller, B. W. Messmore and C. J. Hawker, *Macromolecules*, 2008, **41**, 7063–7070.
14 K. L. Killops, L. M. Campos and C. J. Hawker, *J. Am. Chem. Soc.*, 2008, **130**, 5062–5064.
15 S. P. S. Koo, M. M. Stamenovic, R. A. Prasath, A. J. Inglis, F. E. Du Prez, C. Barner-Kowollik, W. Van Camp and T. Junkers, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 1699–1713.
16 R. A. Prasath, M. T. Gokmen, P. Espeel and F. E. Du Prez, *Polym. Chem.*, 2010, **1**, 685–692.
17 J. F. Lutz, *Angew. Chem., Int. Ed.*, 2007, **46**, 1018–1025.
18 A. J. Inglis and C. Barner-Kowollik, *Macromol. Rapid Commun.*, 2010, **31**, 1247–1266.
19 C. Barner-Kowollik, F. E. Du Prez, P. Espeel, C. J. Hawker, T. Junkers, H. Schlaad and W. Van Camp, *Angew. Chem., Int. Ed.*, 2011, **50**, 60–62.
20 M. L. Szalai, D. V. McGrath, D. R. Wheeler, T. Zifer and J. R. McElhanon, *Macromolecules*, 2007, **40**, 818–823.
21 A. Robertson, D. Philp and N. Spencer, *Tetrahedron*, 1999, **55**, 11365–11384.
22 J. R. McElhanon and D. R. Wheeler, *Org. Lett.*, 2001, **3**, 2681–2683.
23 Y. Chujo, K. Sada and T. Saegusa, *Macromolecules*, 1990, **23**, 2636–2641.
24 H. Durmaz, B. Colakoclu, U. Tunca and G. Hizal, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 1667–1675.
25 B. Gacal, H. Durmaz, M. A. Tasdelen, G. Hizal, U. Tunca, Y. Yagci and A. L. Demirel, *Macromolecules*, 2006, **39**, 5330–5336.
26 A. J. Inglis, S. Sinnwell, M. H. Stenzel and C. Barner-Kowollik, *Angew. Chem., Int. Ed.*, 2009, **48**, 2411–2414.
27 M. L. Blackman, M. Royzen and J. M. Fox, *J. Am. Chem. Soc.*, 2008, **130**, 13518–13519.
28 N. K. Devaraj, R. Weissleder and S. A. Hilderbrand, *Bioconjugate Chem.*, 2008, **19**, 2297–2299.
29 N. K. Devaraj, R. Upadhyay, J. B. Hatin, S. A. Hilderbrand and R. Weissleder, *Angew. Chem., Int. Ed.*, 2009, **48**, 7013–7016.
30 Z. Li, H. Cai, M. Hassink, M. L. Blackman, R. C. D. Brown, P. S. Conti and J. M. Fox, *Chem. Commun.*, 2010, **46**, 8043–8045.
31 G. Franc and A. K. Kakkar, *Chem.–Eur. J.*, 2009, **15**, 5630–5639.
32 A. Sanyal, *Macromol. Chem. Phys.*, 2010, **211**, 1417–1425.
33 C. R. Becer, R. Hoogenboom and U. S. Schubert, *Angew. Chem., Int. Ed.*, 2009, **48**, 4900–4908.
34 J. F. Lutz, *Angew. Chem., Int. Ed.*, 2008, **47**, 2182–2184.
35 R. K. Iha, K. L. Wooley, A. M. Nystrom, D. J. Burke, M. J. Kade and C. J. Hawker, *Chem. Rev.*, 2009, **109**, 5620–5686.
36 U. Mansfeld, C. Pietsch, R. Hoogenboom, C. R. Becer and U. S. Schubert, *Polym. Chem.*, 2010, **1**, 1560–1598.
37 S. Sinnwell, A. J. Inglis, T. P. Davis, M. H. Stenzel and C. Barner-Kowollik, *Chem. Commun.*, 2008, 2052–2054.
38 A. J. Inglis, S. Sinnwell, T. P. Davis, C. Barner-Kowollik and M. H. Stenzel, *Macromolecules*, 2008, **41**, 4120–4126.
39 A. Dag, H. Durmaz, E. Demir, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6969–6977.
40 O. Altintas, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 1218–1228.
41 O. Altintas, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 5699–5707.
42 L. Nebhani, S. Sinnwell, A. J. Inglis, M. H. Stenzel, C. Barner-Kowollik and L. Barner, *Macromol. Rapid Commun.*, 2008, **29**, 1431–1437.
43 H. Durmaz, A. Dag, O. Altintas, T. Erdogan, G. Hizal and U. Tunca, *Macromolecules*, 2007, **40**, 191–198.
44 J. P. Kennedy and G. M. Carlson, *J. Polym. Sci., Part A: Polym. Chem.*, 1983, **21**, 3551–3561.
45 G. W. Goodall and W. Hayes, *Chem. Soc. Rev.*, 2006, **35**, 280–312.
46 C. D. Diakoumakos and J. A. Mikroyannidis, *J. Polym. Sci., Part A: Polym. Chem.*, 1992, **30**, 2559–2567.
47 J. A. Mikroyannidis, *J. Polym. Sci., Part A: Polym. Chem.*, 1992, **30**, 125–132.
48 C. Gousse and A. Gandini, *Polym. Int.*, 1999, **48**, 723–731.
49 K. Kamahori, S. Tada, K. Ito and S. Itsuno, *Macromolecules*, 1999, **32**, 541–547.
50 S. E. Mallakpour, A. R. Hajipour, A. R. Mahdavian and S. Khoee, *J. Appl. Polym. Sci.*, 2000, **76**, 240–248.
51 J. A. Mikroyannidis, *J. Polym. Sci., Part A: Polym. Chem.*, 1992, **30**, 2017–2024.
52 G. Alhakimi, H. Gorls and E. Klemm, *Macromol. Chem. Phys.*, 1994, **195**, 1569–1576.
53 U. Kumar and T. X. Neenan, *ACS Symp. Ser.*, 1995, **614**, 518–526.
54 H. Ben Romdhane, M. Baklouti, M. R. Chaabouni, M. F. Grenier-Loustalot, F. Delolme and B. Sillion, *Polymer*, 2002, **43**, 255–268.
55 G. Alhakimi, E. Klemm and H. Görls, *J. Polym. Sci., Part A: Polym. Chem.*, 1995, **33**, 1133–1142.
56 J. K. Stille and G. K. Noren, *Macromolecules*, 1972, **5**, 49–55.
57 C. L. Schilling, J. A. Reed and J. K. Stille, *Macromolecules*, 1969, **2**, 85–88.
58 J. K. Stille, R. O. Rakutis, H. Mukamal and F. W. Harris, *Macromolecules*, 1968, **1**, 431–436.

59 H. Mukamal, F. W. Harris and J. K. Stille, *J. Polym. Sci., Part A-1*, 1967, **5**, 2721–2729.
60 A. D. Schluter, *Adv. Mater.*, 1991, **3**, 282–291.
61 U. Scherf and K. Mullen, *Adv. Polym. Sci.*, 1995, **123**, 1–40.
62 N. Teramoto, Y. Arai and M. Shibata, *Carbohydr. Polym.*, 2006, **64**, 78–84.
63 J. K. Stille and L. Plummer, *J. Org. Chem.*, 1961, **26**, 4026–4029.
64 E. S. Krongauz, *Usp. Khim.*, 1973, **42**, 1854–1891.
65 M. Grigoras, M. Sava, G. Colotin and C. I. Simionescu, *J. Appl. Polym. Sci.*, 2008, **107**, 846–853.
66 T. Brand and M. Klapper, *Des. Monomers Polym.*, 1999, **2**, 287–309.
67 K. B. Wagener and L. P. Engle, *J. Polym. Sci., Part A: Polym. Chem.*, 1993, **31**, 865–875.
68 M. A. Tasdelen, M. U. Kahveci and Y. Yagci, *Prog. Polym. Sci.*, 2011, **36**, 455–567.
69 G. Mantovani, F. Lecolley, L. Tao, D. M. Haddleton, J. Clerx, J. Cornelissen and K. Velonia, *J. Am. Chem. Soc.*, 2005, **127**, 2966–2973.
70 H. Durmaz, F. Karatas, U. Tunca and G. Hizal, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 3947–3957.
71 M. Li, P. De, S. R. Gondi and B. S. Sumerlin, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 5093–5100.
72 H. Akat, B. Gacal, D. K. Balta, N. Arsu and Y. Yagci, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 2109–2114.
73 O. Altintas, G. Hizal and U. Tunca, *Des. Monomers Polym.*, 2009, **12**, 83–98.
74 K. Masutani, S. Kawabata, T. Aoki and Y. Kimura, *Polym. Int.*, 2010, **59**, 1526–1530.
75 K. A. Jorgensen, *Angew. Chem., Int. Ed.*, 2000, **39**, 3558–3588.
76 H. Waldmann, *Synthesis*, 1994, 535–551.
77 L. Nebhani, S. Sinnwell, C. Y. Lin, M. L. Coote, M. H. Stenzel and C. Barner-Kowollik, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 6053–6071.
78 S. Sinnwell, C. V. Synatschke, T. Junkers, M. H. Stenzel and C. Barner-Kowollik, *Macromolecules*, 2008, **41**, 7904–7912.
79 A. J. Inglis and C. Barner-Kowollik, *Polym. Chem.*, 2011, **2**, 126–136.
80 M. Glassner, J. P. Blinco and C. Barner-Kowollik, *Polym. Chem.*, 2011, **2**, 83–87.
81 A. J. Inglis, M. H. Stenzel and C. Barner-Kowollik, *Macromol. Rapid Commun.*, 2009, **30**, 1792–1798.
82 H. Durmaz, A. Dag, O. Altintas, T. Erdogan, G. Hizal and U. Tunca, *Macromolecules*, 2007, **40**, 191–198.
83 A. Bousquet, C. Barner-Kowollik and M. H. Stenzel, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 1773–1781.
84 A. Bousquet, C. Boyer, T. P. Davis and M. H. Stenzel, *Polym. Chem.*, 2010, **1**, 1186–1195.
85 H. Durmaz, A. Dag, N. Cerit, O. Sirkecioglu, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 5982–5991.
86 A. Dag, H. Sahin, H. Durmaz, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 886–892.
87 A. Dag, H. Durmaz, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 302–313.
88 H. Durmaz, F. Karatas, U. Tunca and G. Hizal, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 499–509.
89 H. Durmaz, A. Dag, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 1195–1200.
90 E. Gungor, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 3409–3418.
91 X. Q. Xiong and Y. H. Xu, *Polym. Bull.*, 2010, **65**, 455–463.
92 H. Durmaz, A. Dag, A. Hizal, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 7091–7100.
93 A. Dag, H. Durmaz, U. Tunca and G. Hizal, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 178–187.
94 H. Durmaz, A. Dag, D. Gursoy, A. L. Demirel, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 1557–1564.
95 S. Sinnwell, A. J. Inglis, M. H. Stenzel and C. Barner-Kowollik, *Macromol. Rapid Commun.*, 2008, **29**, 1090–1096.
96 H. Durmaz, A. Dag, C. Onen, O. Gok, A. Sanyal, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 4842–4846.
97 A. Dag, H. Durmaz, V. Kirmizi, G. Hizal and U. Tunca, *Polym. Chem.*, 2010, **1**, 621–623.
98 S. Sinnwell, M. Lammens, M. H. Stenzel, F. E. Du Prez and C. Barner-Kowollik, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 2207–2213.
99 H. Durmaz, A. Dag, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 5083–5091.
100 C. Kim, H. Kim and K. Park, *J. Organomet. Chem.*, 2005, **690**, 4794–4800.
101 C. Kim, K. I. Lim and C. G. Song, *J. Organomet. Chem.*, 2005, **690**, 3278–3285.
102 H. J. Son, W. S. Han, H. Kim, C. Kim, J. Ko, C. Lee and S. O. Kang, *Organometallics*, 2006, **25**, 766–774.
103 C. Kim, H. Kim and K. Park, *J. Organomet. Chem.*, 2003, **667**, 96–102.
104 M. M. Kose, G. Yesilbag and A. Sanyal, *Org. Lett.*, 2008, **10**, 2353–2356.
105 M. Tonga, N. Cengiz, M. M. Kose, T. Dede and A. Sanyal, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 410–416.
106 A. Vieyres, T. Lam, R. Gillet, G. Franc, A. Castonguay and A. Kakkar, *Chem. Commun.*, 2010, **46**, 1875–1877.
107 N. W. Polaske, D. V. McGrath and J. R. McElhanon, *Macromolecules*, 2010, **43**, 1270–1276.
108 A. A. Kavitha and N. K. Singha, *ACS Appl. Mater. Interfaces*, 2009, **1**, 1427–1436.
109 H. L. Wei, Z. Yang, L. M. Zheng and Y. M. Shen, *Polymer*, 2009, **50**, 2836–2840.
110 S. A. Canary and M. P. Stevens, *J. Polym. Sci., Part A: Polym. Chem.*, 1992, **30**, 1755–1760.
111 E. Goiti, M. B. Huglin and J. M. Rego, *Eur. Polym. J.*, 2004, **40**, 219–226.
112 C. Gousse and A. Gandini, *Polym. Bull.*, 1998, **40**, 389–394.
113 F. Ghezzo, D. R. Smith, T. N. Starr, T. Perram, A. F. Starr, T. K. Darlington, R. K. Baldwin and S. J. Oldenburg, *J. Compos. Mater.*, 2010, **44**, 1587–1603.
114 K. Inoue, M. Yamashiro and M. Iji, *J. Appl. Polym. Sci.*, 2009, **112**, 876–885.
115 B. J. Adzima, H. A. Aguirre, C. J. Kloxin, T. F. Scott and C. N. Bowman, *Macromolecules*, 2008, **41**, 9112–9117.
116 T. Nemoto and G.-i. Konishi, *Polym. J.*, 2008, **40**, 651–656.
117 H. Laita, S. Boufi and A. Gandini, *Eur. Polym. J.*, 1997, **33**, 1203–1211.
118 C. Gousse, A. Gandini and P. Hodge, *Macromolecules*, 1998, **31**, 314–321.
119 S. Magana, A. Zerroukhi, C. Jegat and N. Mignard, *React. Funct. Polym.*, 2010, **70**, 442–448.
120 Y. L. Liu, C. Y. Hsieh and Y. W. Chen, *Polymer*, 2006, **47**, 2581–2586.
121 Y. Imai, H. Itoh, K. Naka and Y. Chujo, *Macromolecules*, 2000, **33**, 4343–4346.
122 A. A. Kavitha and N. K. Singha, *Macromolecules*, 2010, **43**, 3193–3205.
123 R. Gheneim, C. Perez-Berumen and A. Gandini, *Macromolecules*, 2002, **35**, 7246–7253.
124 M. Watanabe and N. Yoshie, *Polymer*, 2006, **47**, 4946–4952.
125 Z. W. Shi, W. Liang, J. D. Luo, S. Huang, B. M. Polishak, X. S. Li, T. R. Younkin, B. A. Block and A. K. Y. Jen, *Chem. Mater.*, 2010, **22**, 5601–5608.
126 Q. A. Tian, M. Z. Rong, M. Q. Zhang and Y. C. Yuan, *Polym. Int.*, 2010, **59**, 1339–1345.
127 J. Canadell, H. Fischer, G. De With and R. A. T. M. van Benthem, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 3456–3467.
128 B. J. Adzima, C. J. Kloxin and C. N. Bowman, *Adv. Mater.*, 2010, **22**, 2784–2787.
129 A. M. Peterson, R. E. Jensen and G. R. Palmese, *ACS Appl. Mater. Interfaces*, 2010, **2**, 1141–1149.
130 K. Ishida and N. Yoshie, *Macromol. Biosci.*, 2008, **8**, 916–922.
131 A. Amalin Kavitha and N. K. Singha, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 4441–4449.
132 Y.-L. Liu and Y.-W. Chen, *Macromol. Chem. Phys.*, 2007, **208**, 224–232.
133 W. H. Heath, F. Palmieri, J. R. Adams, B. K. Long, J. Chute, T. W. Holcombe, S. Zieren, M. J. Truitt, J. L. White and C. G. Willson, *Macromolecules*, 2008, **41**, 719–726.
134 J. A. Syrett, G. Mantovani, W. R. S. Barton, D. Price and D. M. Haddleton, *Polym. Chem.*, 2010, **1**, 102–106.

135 X. X. Chen, M. A. Dam, K. Ono, A. Mal, H. B. Shen, S. R. Nutt, K. Sheran and F. Wudl, *Science*, 2002, **295**, 1698–1702.
136 H.-L. Wei, Z. Yang, Y. Chen, H.-J. Chu, J. Zhu and Z.-C. Li, *Eur. Polym. J.*, 2010, **46**, 1032–1039.
137 H.-L. Wei, Z. Yang, L.-M. Zheng and Y.-M. Shen, *Polymer*, 2009, **50**, 2836–2840.
138 H.-L. Wei, Z. Yang, H.-J. Chu, J. Zhu, Z.-C. Li and J.-S. Cui, *Polymer*, 2010, **51**, 1694–1702.
139 A. J. Inglis, L. Nebhani, O. Altintas, F. G. Schmidt and C. Barner-Kowollik, *Macromolecules*, 2010, **43**, 5515–5520.
140 J. A. Syrett, C. R. Becer and D. M. Haddleton, *Polym. Chem.*, 2010, **1**, 978–987.
141 Y. Zhang, A. A. Broekhuis and F. Picchioni, *Macromolecules*, 2009, **42**, 1906–1912.
142 A. M. Peterson, R. E. Jensen and G. R. Palmese, *ACS Appl. Mater. Interfaces*, 2010, **2**, 1141–1149.
143 A. Gandini, D. Coelho and A. J. D. Silvestre, *Eur. Polym. J.*, 2008, **44**, 4029–4036.
144 A. Gandini, A. J. D. Silvestre and D. Coelho, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 2053–2056.
145 X. X. Chen, F. Wudl, A. K. Mal, H. B. Shen and S. R. Nutt, *Macromolecules*, 2003, **36**, 1802–1807.
146 Y. L. Liu and C. Y. Hsieh, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 905–913.
147 B. Gotsmann, U. Duerig, J. Frommer and C. J. Hawker, *Adv. Funct. Mater.*, 2006, **16**, 1499–1505.
148 J. S. Park, K. Takahashi, Z. H. Guo, Y. Wang, E. Bolanos, C. Hamann-Schaffner, E. Murphy, F. Wudl and H. T. Hahn, *J. Compos. Mater.*, 2008, **42**, 2869–2881.
149 A. S. Jones, J. D. Rule, J. S. Moore, S. R. White and N. R. Sottos, *Chem. Mater.*, 2006, **18**, 1312–1317.
150 J. D. Rule, E. N. Brown, N. R. Sottos, S. R. White and J. S. Moore, *Adv. Mater.*, 2005, **17**, 205.
151 J. W. C. Pang and I. P. Bond, *Compos. Sci. Technol.*, 2005, **65**, 1791–1799.
152 E. N. Brown, S. R. White and N. R. Sottos, *J. Mater. Sci.*, 2004, **39**, 1703–1710.
153 E. B. Murphy, E. Bolanos, C. Schaffner-Hamann, F. Wudl, S. R. Nutt and M. L. Auad, *Macromolecules*, 2008, **41**, 5203–5209.
154 J. P. Kennedy and K. F. Castner, *J. Polym. Sci., Part A: Polym. Chem.*, 1979, **17**, 2055–2070.
155 J. P. Kennedy and K. F. Castner, *J. Polym. Sci., Part A: Polym. Chem.*, 1979, **17**, 2039–2054.
156 J. R. Jones, C. L. Liotta, D. M. Collard and D. A. Schiraldi, *Macromolecules*, 1999, **32**, 5786–5792.
157 S. D. Bergman and F. Wudl, *J. Mater. Chem.*, 2008, **18**, 41–62.
158 R. P. Wool, *Adv. Polym. Sci.*, 2008, **4**, 400–418.
159 D. Y. Wu, S. Meure and D. Solomon, *Prog. Polym. Sci.*, 2008, **33**, 479–522.
160 S. Burattini, B. W. Greenland, D. Chappell, H. M. Colquhoun and W. Hayes, *Chem. Soc. Rev.*, 2010, **39**, 1973–1985.
161 T. D. Kim, J. D. Luo, Y. Q. Tian, J. W. Ka, N. M. Tucker, M. Haller, J. W. Kang and A. K. Y. Jen, *Macromolecules*, 2006, **39**, 1676–1680.
162 Z. W. Shi, J. D. Luo, S. Huang, Y. J. Cheng, T. D. Kim, B. M. Polishak, X. H. Zhou, Y. Q. Tian, S. H. Jang, D. B. Knorr, R. M. Overney, T. R. Younkin and A. K. Y. Jen, *Macromolecules*, 2009, **42**, 2438–2445.
163 B. Gacal, H. Akat, D. K. Balta, N. Arsu and Y. Yagci, *Macromolecules*, 2008, **41**, 2401–2405.
164 A. S. Hoffman and P. S. Stayton, *Macromol. Symp.*, 2004, **207**, 139–152.
165 R. Duncan, *Nat. Rev. Drug Discovery*, 2003, **2**, 347–360.
166 F. M. Veronese, *Biomaterials*, 2001, **22**, 405–417.
167 S. H. Weisbrod and A. Marx, *Chem. Commun.*, 2008, 5675–5685.
168 D. Graham and A. Enright, *Curr. Org. Synth.*, 2006, **3**, 9–17.
169 F. Buller, L. Mannocci, Y. X. Zhang, C. E. Dumelin, J. Scheuermann and D. Neri, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 5926–5931.
170 K. W. Hill, J. Taunton-Rigby, J. D. Carter, E. Kropp, K. Vagle, W. Pieken, D. P. C. McGee, G. M. Husar, M. Leuck, D. J. Anziano and D. P. Sebesta, *J. Org. Chem.*, 2001, **66**, 5352–5358.
171 G. M. Husar, D. J. Anziano, M. Leuck and D. P. Sebesta, *Nucleosides, Nucleotides Nucleic Acids*, 2001, **20**, 559–566.
172 D. Graham, L. Fruk and W. E. Smith, *Analyst*, 2003, **128**, 692–699.
173 L. Fruk, A. Grondin, W. E. Smith and D. Graham, *Chem. Commun.*, 2002, 2100–2101.
174 V. Borsenberger and S. Howorka, *Nucleic Acids Res.*, 2009, **37**, 1477–1485.
175 R. Tona and R. Haner, *Chem. Commun.*, 2004, 1908–1909.
176 R. Tona and R. Haner, *Bioconjugate Chem.*, 2005, **16**, 837–842.
177 D. Graham, A. Grondin, C. McHugh, L. Fruk and W. E. Smith, *Tetrahedron Lett.*, 2002, **43**, 4785–4788.
178 A. Okamoto, T. Taiji, K. Tainaka and I. Saito, *Bioorg. Med. Chem. Lett.*, 2002, **12**, 1895–1896.
179 K. Stevens and A. Madder, *Nucleosides, Nucleotides Nucleic Acids*, 2007, **26**, 1359–1362.
180 E. Anderson and D. Picken, *Nucleosides, Nucleotides Nucleic Acids*, 2005, **24**, 761–765.
181 B. Seelig and A. Jaschke, *Tetrahedron Lett.*, 1997, **38**, 7729–7732.
182 M. Proupin-Perez, R. Cosstick, L. M. Liz-Marzan, V. Salgueirino-Maceira and M. Brust, *Nucleosides, Nucleotides Nucleic Acids*, 2005, **24**, 1075–1079.
183 X. L. Sun, L. C. Yang and E. L. Chaikof, *Tetrahedron Lett.*, 2008, **49**, 2510–2513.
184 H. A. Latham-Timmons, A. Wolter, J. S. Roach, R. Giare and M. Leuck, *Nucleosides, Nucleotides Nucleic Acids*, 2003, **22**, 1495–1497.
185 C. Heise and F. F. Bier, *Top. Curr. Chem.*, 2005, **261**, 1–25.
186 M. Abramov, G. Schepers, A. Van Aerschot, P. Van Hummelen and P. Herdewijn, *Biosens. Bioelectron.*, 2008, **23**, 1728–1732.
187 R. Schlapak, P. Pammer, D. Armitage, R. Zhu, P. Hinterdorfer, M. Vaupel, T. Fruhwirth and S. Howorka, *Langmuir*, 2006, **22**, 277–285.
188 V. Marchan, S. Ortega, D. Pulido, E. Pedroso and A. Grandas, *Nucleic Acids Res.*, 2006, **34**, 1668–1668.
189 V. Steven and D. Graham, *Org. Biomol. Chem.*, 2008, **6**, 3781–3787.
190 K. Lu, Q. P. Duan, L. Ma and D. X. Zhao, *Bioconjugate Chem.*, 2010, **21**, 187–202.
191 C. P. R. Hackenberger and D. Schwarzer, *Angew. Chem., Int. Ed.*, 2008, **47**, 10030–10074.
192 M. Zerial and H. McBride, *Nat. Rev. Mol. Cell Biol.*, 2001, **2**, 107–117.
193 P. C. Lin, D. Weinrich and H. Waldmann, *Macromol. Chem. Phys.*, 2010, **211**, 136–144.
194 J. M. Palomo, *Eur. J. Org. Chem.*, 2010, 6303–6314.
195 M. A. Gauthier and H. A. Klok, *Chem. Commun.*, 2008, 2591–2611.
196 A. D. de Araujo, J. M. Palomo, J. Cramer, M. Kohn, H. Schroder, R. Wacker, C. Niemeyer, K. Alexandrov and H. Waldmann, *Angew. Chem., Int. Ed.*, 2006, **45**, 296–301.
197 A. D. de Araujo, J. M. Palomo, J. Cramer, O. Seitz, K. Alexandrov and H. Waldmann, *Chem.–Eur. J.*, 2006, **12**, 6095–6109.
198 M. N. Yousaf and M. Mrksich, *J. Am. Chem. Soc.*, 1999, **121**, 4286–4287.
199 M. N. Yousaf, E. W. L. Chan and M. Mrksich, *Angew. Chem., Int. Ed.*, 2000, **39**, 1943–1946.
200 E. W. L. Chan, M. N. Yousaf and M. Mrksich, *J. Phys. Chem. A*, 2000, **104**, 9315–9320.
201 M. N. Yousaf, B. T. Houseman and M. Mrksich, *Angew. Chem., Int. Ed.*, 2001, **40**, 1093–1096.
202 M. N. Yousaf, B. T. Houseman and M. Mrksich, *Proc. Natl. Acad. Sci. U. S. A.*, 2001, **98**, 5992–5996.
203 W. S. Yeo, M. N. Yousaf and M. Mrksich, *J. Am. Chem. Soc.*, 2003, **125**, 14994–14995.
204 W. S. Dillmore, M. N. Yousaf and M. Mrksich, *Langmuir*, 2004, **20**, 7223–7231.
205 B. T. Houseman, J. H. Huh, S. J. Kron and M. Mrksich, *Nat. Biotechnol.*, 2002, **20**, 270–274.
206 B. T. Houseman and M. Mrksich, *Trends Biotechnol.*, 2002, **20**, 279–281.
207 G. Mihov, D. Grebel-Koehler, A. Lubbert, G. W. M. Vandermeulen, A. Herrmann, H. A. Klok and K. Mullen, *Bioconjugate Chem.*, 2005, **16**, 283–293.
208 A. Graven and M. Meldal, *J. Chem. Soc., Perkin Trans. 1*, 2001, 3198–3203.
209 A. Doerr, *Nat. Methods*, 2006, **3**, 77–77.
210 Y.-W. Wu, H. Waldmann, R. Reents, F. H. Ebetino, R. S. Goody and K. Alexandrov, *ChemBioChem*, 2006, **7**, 1859–1861.

211 A. D. de Araújo, J. M. Palomo, J. Cramer, M. Köhn, H. Schröder, R. Wacker, C. Niemeyer, K. Alexandrov and H. Waldmann, *Angew. Chem.*, 2006, **118**, 302–307.
212 S. S. van Berkel, A. T. J. Dirks, M. F. Debets, F. L. van Delft, J. J. L. M. Cornelissen, R. J. M. Nolte and F. P. J. T. Rutjes, *ChemBioChem*, 2007, **8**, 1504–1508.
213 V. Pozsgay, N. E. Vieira and A. Yergey, *Org. Lett.*, 2002, **4**, 3191–3194.
214 J. M. Hooker, E. W. Kovacs and M. B. Francis, *J. Am. Chem. Soc.*, 2004, **126**, 3718–3719.
215 U. T. T. Nguyen, J. Cramer, J. Gomis, R. Reents, M. Gutierrez-Rodriguez, R. S. Goody, K. Alexandrov and H. Waldmann, *ChemBioChem*, 2007, **8**, 408–423.
216 R. Rossin, P. Renart Verkerk, S. M. van den Bosch, R. C. M. Vulders, I. Verel, J. Lub and M. S. Robillard, *Angew. Chem., Int. Ed.*, 2010, **49**, 3375–3378.
217 S. S. van Berkel, A. J. Dirks, S. A. Meeuwissen, D. L. L. Pingen, O. C. Boerman, P. Laverman, F. L. van Delft, J. Cornelissen and F. Rutjes, *ChemBioChem*, 2008, **9**, 1805–1815.
218 P. Laverman, S. A. Meeuwissen, S. S. van Berkel, W. J. G. Oyen, F. L. van Delft, F. Rutjes and O. C. Boerman, *Nucl. Med. Biol.*, 2009, **36**, 749–757.
219 M. Wiessler, W. Waldeck, C. Kliem, R. Pipkorn and K. Braun, *Int. J. Med. Sci.*, 2010, **7**, 19–28.
220 R. Pipkorn, W. Waldeck, B. Didinger, M. Koch, G. Mueller, M. Wiessler and K. Braun, *J. Pept. Sci.*, 2009, **15**, 235–241.
221 M. Wiessler, W. Waldeck, R. Pipkorn, C. Kliem, P. Lorenz, H. Fleischhacker, M. Hafner and K. Braun, *Int. J. Med. Sci.*, 2010, **7**, 213–223.
222 J. Schoch, M. Wiessler and A. Jäschke, *J. Am. Chem. Soc.*, 2010, **132**, 8846–8847.
223 N. K. Devaraj, S. Hilderbrand, R. Upadhyay, R. Mazitschek and R. Weissleder, *Angew. Chem., Int. Ed.*, 2010, **49**, 2869–2872.
224 B. T. Houseman and M. Mrksich, *Chem. Biol.*, 2002, **9**, 443–454.
225 J. Zhu, M. D. Ganton, M. A. Kerr and M. S. Workentin, *J. Am. Chem. Soc.*, 2007, **129**, 4904–4905.
226 N. Horan, L. Yan, H. Isobe, G. M. Whitesides and D. Kahne, *Proc. Natl. Acad. Sci. U. S. A.*, 1999, **96**, 11782–11786.
227 A. Berkin, B. Coxon and V. Pozsgay, *Chem.–Eur. J.*, 2002, **8**, 4424–4433.
228 S. J. Park and I. J. Shin, *Angew. Chem., Int. Ed.*, 2002, **41**, 3180–3182.
229 A. Monzo and A. Guttman, *QSAR Comb. Sci.*, 2006, **25**, 1033–1038.
230 K. R. Love and P. H. Seeberger, *Angew. Chem., Int. Ed.*, 2002, **41**, 3583–3586.
231 X. L. Sun, C. L. Stabler, C. S. Cazalis and E. L. Chaikof, *Bioconjugate Chem.*, 2006, **17**, 52–57.
232 M. Shi, J. H. Wosnick, K. Ho, A. Keating and M. S. Shoichet, *Angew. Chem., Int. Ed.*, 2007, **46**, 6126–6131.
233 M. Shi and M. S. Shoichet, *J. Biomater. Sci., Polym. Ed.*, 2008, **19**, 1143–1157.
234 M. Shi, K. Ho, A. Keating and M. S. Shoichet, *Adv. Funct. Mater.*, 2009, **19**, 1689–1696.
235 M. Shi, J. Lu and M. S. Shoichet, *J. Mater. Chem.*, 2009, **19**, 5485–5498.
236 L. Nebhani and C. Barner-Kowollik, *Adv. Mater.*, 2009, **21**, 3442–3468.
237 M. Vargas, R. M. Kriegel, D. M. Collard and D. A. Schiraldi, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 3256–3263.
238 L. Nebhani, D. Schmiedl, L. Barner and C. Barner-Kowollik, *Adv. Funct. Mater.*, 2010, **20**, 2010–2020.
239 X. J. Zhou, Q. Y. Li and C. F. Wu, *Appl. Organomet. Chem.*, 2008, **22**, 78–81.
240 M. T. Beck, G. Mandy, S. Papp and I. Dekany, *Colloid Polym. Sci.*, 2004, **283**, 237–242.
241 C. Menard-Moyon, F. Dumas, E. Doris and C. Mioskowski, *J. Am. Chem. Soc.*, 2006, **128**, 14764–14765.
242 N. Salah, S. S. Habib, Z. H. Khan, S. Al-Hamedi and F. Djouider, *Radiat. Phys. Chem.*, 2009, **78**, 910–913.
243 J. L. Delgado, P. de la Cruz, F. Langa, A. Urbina, J. Casado and J. T. L. Navarrete, *Chem. Commun.*, 2004, 1734–1735.
244 A. Gergely, J. Telegdi, E. Meszaros, Z. Paszti, G. Tarkanyi, F. H. Karman and E. Kalman, *J. Nanosci. Nanotechnol.*, 2007, **7**, 2795–2807.
245 F. Mercuri and A. Sgamellotti, *Phys. Chem. Chem. Phys.*, 2009, **11**, 563–567.
246 M. T. Beck, J. Szepvolgyi, P. Szabo and E. Jakab, *Carbon*, 2001, **39**, 147–149.
247 H. Hayden, Y. K. Gun'ko and T. S. Perova, *Chem. Phys. Lett.*, 2007, **435**, 84–89.
248 L. Zhang, J. Z. Yang, C. L. Edwards, L. B. Alemany, V. N. Khabashesku and A. R. Barron, *Chem. Commun.*, 2005, 3265–3267.
249 X. Lu, F. Tian, N. Q. Wang and Q. N. Zhang, *Org. Lett.*, 2002, **4**, 4313–4315.
250 C.-M. Chang and Y.-L. Liu, *Carbon*, 2009, **47**, 3041–3049.
251 B. Xu, X. S. Wang and Y. Lu, *Appl. Surf. Sci.*, 2006, **253**, 2695–2701.
252 F. M. Fernandes, R. Araujo, M. F. Proenca, C. J. R. Silva and M. C. Paiva, *J. Nanosci. Nanotechnol.*, 2007, **7**, 3514–3518.
253 M. F. Proenca, R. F. Araujo, M. C. Paiva and C. J. R. Silva, *J. Nanosci. Nanotechnol.*, 2009, **9**, 6234–6238.
254 M. C. Paiva, R. M. Novais, R. F. Araujo, K. K. Pederson, M. F. Proença, C. J. R. Silva, C. M. Costa and S. Lanceros-Méndez, *Polym. Compos.*, 2010, **31**, 369–376.
255 S. Munirasu, J. Albuerne, A. Boschetti-de-Fierro and V. Abetz, *Macromol. Rapid Commun.*, 2010, **31**, 574–579.
256 K. I. Guhr, M. D. Greaves and V. M. Rotello, *J. Am. Chem. Soc.*, 1994, **116**, 5997–5998.
257 J. Y. Yao, Z. Xiao, J. X. Zhang, X. B. Yang, L. B. Gan and W. X. Zhang, *Chem. Commun.*, 2009, 401–403.
258 A. Kraus and K. Mullen, *Macromolecules*, 1999, **32**, 4214–4219.
259 L. Nebhani and C. Barner-Kowollik, *Macromol. Rapid Commun.*, 2010, **31**, 1298–1305.
260 Y. Vida, R. Suau, J. Casado, A. Berlin, J. T. L. Navarrete and E. Pérez-Inestrosa, *Macromol. Rapid Commun.*, 2007, **28**, 1345–1349.
261 L. Nebhani, P. Gerstel, P. Atanasova, M. Bruns and C. Barner-Kowollik, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 7090–7095.
262 C. Wendeln, A. Heile, H. F. Arlinghaus and B. J. Ravoo, *Langmuir*, 2010, **26**, 4933–4940.
263 X. F. Liu, M. Zhu, S. H. Chen, M. J. Yuan, Y. B. Guo, Y. L. Song, H. B. Liu and Y. L. Li, *Langmuir*, 2008, **24**, 11967–11974.
264 X. F. Liu, H. B. Liu, W. D. Zhou, H. Y. Zheng, X. D. Yin, Y. L. Li, Y. B. Guo, M. Zhu, C. B. Ouyang, D. B. Zhu and A. D. Xia, *Langmuir*, 2010, **26**, 3179–3185.
265 J. Zhu, A. J. Kell and M. S. Workentin, *Org. Lett.*, 2006, **8**, 4993–4996.
266 K. Adachi, A. K. Achimuthu and Y. Chujo, *Macromolecules*, 2004, **37**, 9793–9797.