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SET-LRP synthesis of novel polyallene-based well-defined amphiphilic graft copolymers in acetone

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A series of polyallene-based well-defined amphiphilic graft copolymers consisting of hydrophobic poly(6-methyl-1,2-heptadiene-4-ol) (PMHDO) backbone and hydrophilic poly(2-(dimethylamino)ethyl acrylate) (PDMAEA) side chains, was synthesized by the combination of living coordination polymerization and single-electron transfer living radical polymerization (SET-LRP). A double-bond-containing PMHDO backbone with pendant hydroxyls was prepared *via* $[(\eta^3\text{-allyl})NiOCOCF_3]_2$-initiated living coordination polymerization of a hydroxyl-containing allene derivative, 6-methyl-1,2-heptadiene-4-ol (MHDO). The pendant hydroxyls in the homopolymer were then treated with 2-chloropropionyl chloride to provide the PMHDO-Cl macroinitiator. Finally, the target PMHDO-*g*-PDMAEA well-defined graft copolymers were constructed through the grafting-from technique *via* SET-LRP of 2-(dimethylamino)ethyl acrylate (DMAEA) in acetone, a nonpolar solvent, initiated by the macroinitiator using CuCl/Me_6TREN as catalytic system. The narrow molecular weight distributions ($M_w/M_n \leq 1.18$) and kinetics experiment showed the controllability of SET-LRP graft copolymerization of DMAEA. The critical micelle concentrations (*cmc*) of PMHDO-*g*-PDMAEA amphiphilic graft copolymers in aqueous solution were determined by fluorescence probe technique and the dependence of *cmc* on pH or salinity were also investigated. Micellar morphologies were visualized using transmission electron microscopy.

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Introduction

As it is well-known, allene derivatives possess cumulated double bonds so that they can be regarded as the isomers of propargyl ether derivatives. They have been utilized for sigmatropic rearrangements as well as for cyclization reactions in organic synthesis. Allene derivatives are also attractive monomers to produce reactive polymers bearing *exo*-methylene moieties directly attached to the polymeric backbone or internal double bonds in the main chain by vinyl polymerization of either part of cumulated double bonds. The polymerized products of allene derivatives, polyallenes, have been used as attractive synthetic precursors for the versatile materials including various kinds of functional groups because of the versatility of addition reactions of double bonds.[1]

Polyallenes can be obtained by different polymerization approaches including radical, cationic, coordination, and zwitterionic polymerization, *etc.*[2] While using radical or cationic polymerization, the controlled synthesis of polyallenes (*i.e.* the control of structure, molecular weight and molecular weight distribution, end functionalization, and block copolymerization, *etc.*) was extremely difficult. For solving these problems, Endo *et al.* developed the Ni-catalyzed living coordination polymerization technique of allene derivatives, which could afford the well-defined polymers in high yields using $[(\eta^3\text{-allyl})NiOCOCF_3]_2$ as initiator.[3–6] With the advent of this living coordination polymerization, block copolymers of different allene derivatives have been prepared by using two stages of monomer feeding due to the stability of the living π-allylnickel end group.[7] Moreover, some functionalized polyallenes were developed by the direct living coordination polymerization of allene derivatives containing hydroxyl[8] or chiral functionality.[9] The copolymers of allene derivatives with butadiene, isocyano monomers or PEG were also reported.[10–12] Recently, Li and his co-workers synthesized some functional polyethylenes with unimodal molecular weight distributions *via* the copolymerization of ethylene and substituted allenes using bis(β-enaminoketonato) titanium catalysts.[13] However, well-defined polyallene-based copolymers prepared from vinyl monomers cannot be obtained by this kind of Ni-catalyzed living polymerization because of the different polymerization mechanism.

Therefore, our group has been developing various strategies for the preparation of well-defined copolymers of allene derivatives and vinyl monomers. As we know, graft copolymers have more complicated and confined structures,[14,15] which may provide more parameters to control the polymers'

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properties and further design new nano-materials. Nevertheless, the synthesis of well-defined graft copolymers with controlled molecular weight and narrow molecular weight distribution is much more difficult than that of linear block copolymers. With the development of reversible deactivation radical polymerization (RDRP) in past decades, such as nitroxide-mediated polymerization (NMP),[16,17] atom transfer radical polymerization (ATRP),[18–23] single-electron transfer living radical polymerization (SET-LRP),[24–32] and reversible addition–fragmentation chain transfer (RAFT) polymerization,[33–38] diverse well-defined copolymers with different topological structures have been prepared. Generally, three strategies of grafting-through, grafting-onto, and grafting-from, can be employed to synthesize the graft copolymers.[39] The grafting-through strategy is to prepare the graft copolymers *via* the polymerization of macromonomers with a polymerizable end group, which seems to be not an easy task because only copolymers with very low molecular weights can be obtained while using living polymerization.[40,41] The grafting-onto technique is to graft the as-prepared side chains onto the backbone by a coupling reaction, normally with insufficient grafting efficiency.[42] Recently, some coupling reactions with high specificity and nearly quantitative yields, such as click chemistry,[43] thiol–ene reactions,[44,45] atom transfer nitroxide radical coupling (ATNRC) chemistry,[35] and others[46] have been used for preparing well-defined graft copolymers, which successfully overcame the trouble of insufficient grafting efficiency. The grafting-from method utilized the pendant initiating groups on the backbone to initiate the polymerization of another monomer to form side chains.[47] The recent boom of RDRP techniques, have rendered this means more prevailing.[16,21,48–51]

In our early work, we utilized the graft-from technique to synthesize hydrophobic graft copolymers consisting of polyallene backbone *via* the combination of Ni-catalyzed living coordination polymerization and ATRP.[52–54] Afterwards, we have been focusing on the synthesis and micellization properties of polyallene-based amphiphilic graft copolymers. The self-assembly behavior of amphiphilic copolymers has received a great deal of attention due to their special physicochemical properties and micellar morphologies, which result in potential applications in many fields including solubilizers,[55] drug delivery,[56,57] catalysis,[58] and microelectronics.[59] In 2009, we reported a polyallene-based amphiphilic graft copolymer containing hydrophilic PEG side chains synthesized by the grafting-onto method, whose grafting density was below 40%, and its diverse self-assembled nanostructure with the changing of experiment parameters.[60] In this work, we reported the synthesis of a series of polyallene-based amphiphilic graft copolymers bearing hydrophilic poly(2-(dimethylamino)ethyl acrylate) (PDMAEA) side chains with high grafting densities (>80%) *via* the grafting-from technique as shown in Scheme 1. The critical micelle concentrations (*cmc*) and micellar morphologies of these amphiphilic copolymers in aqueous media were explored by fluorescence spectroscopy and transmission electron microscopy (TEM).

Experimental section

Materials

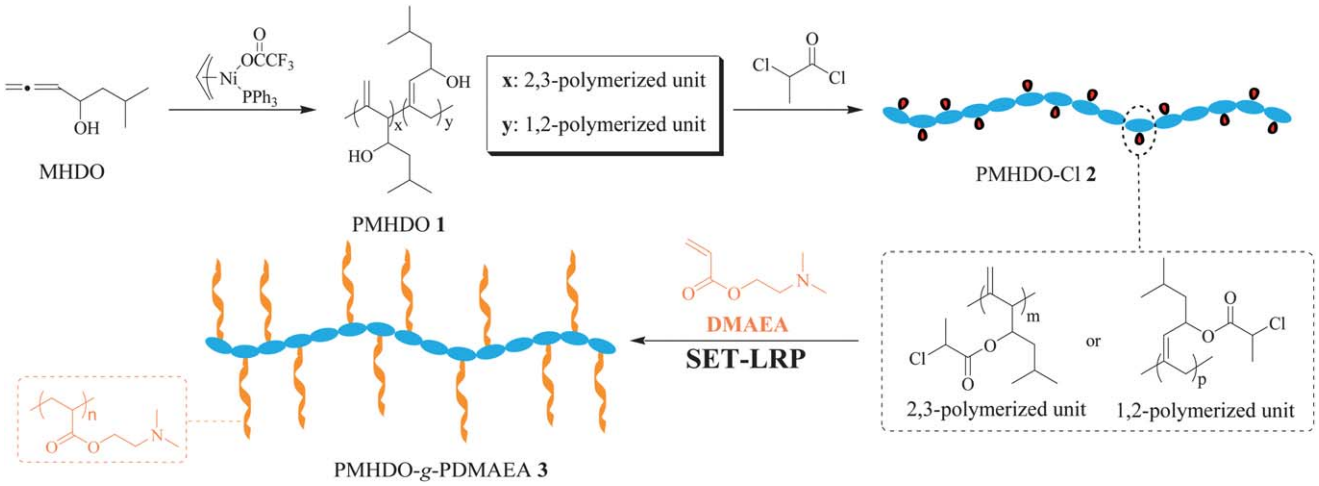
2-(Dimethylamino)ethyl acrylate (DMAEA, Aldrich, 98%) was passed through a basic alumina column and distilled under reduced pressure from CaH_2 prior to use. Copper(I) chloride (CuCl, Aldrich, 99%) was purified by stirring overnight over CH_3CO_2H at room temperature, followed by washing the solid with ethanol, diethyl ether, and acetone prior to drying *in vacuo* at 40 °C. Allyltrifluoroacetate (Aldrich, 98%) was re-distilled prior to use. Triphenyl phosphorate (PPh_3, Acros, 99%) was recrystallized with CH_2Cl_2/hexane. Triethylamine (TEA, Aldrich, 99.5%) was dried over KOH and distilled from CaH_2 under N_2 prior to use. Acetone (Aldrich, 99%) was refluxed with small portions of $KMnO_4$ followed by distilling prior to use. Toluene (Aldrich, 99%) and tetrahydrofuran (THF, Aldrich, 99%) were dried over CaH_2 and distilled from sodium and benzophenone under N_2 prior to use. *N*-Phenyl-1-naphthylamine (PNA, Alfa Aesar, 97%) was purified by recrystallization in ethanol three times. 2-Chloropropionyl chloride (2-CPC, Acros, 95%), 4-(dimethylamino) pyridine (DMAP, Aldrich, 99%), bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$, Aldrich), and tris(aminoethyl) amine (TREN, Aldrich, 96%) were used as received. 6-Methyl-1,2-heptadien-4-ol (MHDO) was synthesized according to previous literature.[61] Tris(2-(dimethylamino)ethyl)-amine (Me_6TREN) was prepared from TREN according to previous literature.[62] Poly(6-methyl-1,2-heptadien-4-ol) (PMHDO **1**, M_n = 5700 g mol^{-1}, M_w/M_n = 1.10) was prepared according to our previous reports.[52–54]

Measurements

FT-IR spectra were recorded on a Nicolet AVATAR-360 FT-IR spectrophotometer with a resolution of 4 cm^{-1}. All ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR analyses were performed on a Varian Mercury 300 spectrometer in $CDCl_3$, TMS (^{1}H NMR) and $CDCl_3$ (^{13}C NMR) were used as internal standards. Chlorine content was determined by the titration with $Hg(NO_3)_2$. Relative molecular weights and molecular weight distributions were measured by conventional gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector, and a set of Waters Styragel columns (HR3 (500–30 000), HR4 (5000–600 000) and HR5 (50 000–4 000 000), 7.8 × 300 mm, particle size: 5 μm). GPC measurements were carried out at 35 °C using THF as eluent with a flow rate of 1.0 mL min^{-1}. The system was calibrated with linear polystyrene standards. Steady-state fluorescent spectra of PNA were measured on a Hitachi F-2700 spectrophotometer with the band width of 5 nm for excitation and emission, the emission intensity at 418 nm was recorded to determine the *cmc* where λ_{ex} was 340 nm. TEM images were obtained by a JEOL JEM-1230 instrument operated at 80 kV.

Esterification of PMHDO homopolymer with 2-CPC

PMHDO **1** homopolymer (M_n = 5700 g mol^{-1}, M_w/M_n = 1.10) was first prepared by living coordination homopolymerization of MHDO in toluene at 50 °C using a feeding ratio



Scheme 1 Synthesis of PMHDO-*g*-PDMAEA well-defined graft copolymer.

of [MHDO] : [Ni(COD)$_2$] : [allyltrifluoroacetate] : [PPh$_3$] = 50 : 1 : 1 : 1 with the similar procedure reported before[52–54] and it was then reacted with 2-chloropropionyl chloride to give the PMHDO-Cl **2** macroinitiator possessing pendent CHCl(CH$_3$)CO RDRP initiating groups.

PMHDO **1** (0.4425 g, M_n = 5700 g mol^{-1}, M_w/M_n = 1.10, 3.512 mmol –OH groups) and DMAP (0.0470 g, 3.847 mmol) were first added to a 50 mL sealed three-neck flask for degassing and kept under N$_2$. Dry THF (45 mL) and anhydrous TEA (0.65 mL, 4.664 mmol) were charged *via* a gastight syringe. The solution was cooled to 0 °C before adding 2-CPC (0.50 mL, 5.139 mmol) dropwise. The mixture was stirred at 0 °C for 1 hour followed by stirring at room temperature for another 20 hours. The solution was concentrated and precipitated into CH$_3$OH/H$_2$O. After repeated purification by dissolving in THF and precipitating in CH$_3$OH/H$_2$O, 0.6418 g of PMHDO-Cl **2** macroinitiator was obtained after drying *in vacuo* overnight. GPC: M_n = 7500 g mol^{-1}, M_w/M_n = 1.11. FT-IR: ν (cm^{-1}): 2958, 2932, 2871, 1736, 1638, 1468, 1369, 1342, 1162. EA: Cl%: 14.50%. ^{1}H NMR: δ (ppm): 0.92 (6H, CH$_2$CH(C*H*$_3$)$_2$), 1.26–1.78 (3H, C*H*$_2$C*H*(CH$_3$)$_2$ and 3H, CHCl(C*H*$_3$)CO), 2.09–3.70 (2H × *y*, =C–C*H*$_2$ and 1H × *x*, =C–C*H*), 4.34 (1H × *x*, CO$_2$C*H* and 1H, C*H*Cl(CH$_3$)CO), 4.93 (1H × *y*, CO$_2$C*H*), 5.44 (2H × *x*, =C*H*$_2$ and 1H × *y*, =C*H*). ^{13}C NMR: δ (ppm): 22.1, 23.5, 24.8, 40.3, 44.0, 52.7, 71.7, 115.6, 127.3, 129.1, 137.9, 144.6, 169.6.

SET-LRP graft copolymerization of DMAEA in acetone

In a typical procedure, CuCl (21.0 mg, 0.212 mmol) and PMHDO-Cl **2** macroinitiator (M_n = 7500 g mol^{-1}, M_w/M_n = 1.11. Cl% = 14.50%, 0.0523 g, 0.212 mmol RDRP initiating groups) were added to a 25 mL Schlenk flask sealed with a rubber septum for degassing and kept under N$_2$. Freshly distilled acetone (6.0 mL) and DMAEA (6.4 mL, 42.4 mmol) were introduced *via* a gastight syringe. The solution was degassed by three cycles of freezing–pumping–thawing. Finally, Me$_6$TREN (59 μL, 0.217 mmol) was charged *via* a gastight syringe followed by stirring 5 min at room temperature, and the flask was then immersed into an oil bath preset at 40 °C. The polymerization was terminated by immersing the flask into liquid N$_2$ after 4 hours. Monomer conversion was calculated from ^{1}H NMR spectrum of raw sample in CDCl$_3$ by comparing the integration area ratio of **3** unsaturated protons (C*H*$_2$=C*H*) of remaining DMAEA at 6.43, 6.05, and 5.80 ppm to 2 methylene protons of remaining DMAEA monomer and PDMAEA (CO$_2$C*H*$_2$CH$_2$N(CH$_3$)$_2$) at 4.16 ppm. Prior to GPC measurement, the raw sample was diluted in THF and passed through a neutral Al$_2$O$_3$ column to remove residual Cu complex followed by concentration and precipitation in hexane. The crude product was purified by repeated dissolution in THF and precipitation in hexane followed by drying *in vacuo* overnight to afford 0.3016 g of PMHDO-*g*-PDMAEA **3a**, a yellow sticky solid. GPC: M_n = 21 000 g mol^{-1}, M_w/M_n = 1.18. ^{1}H NMR: δ (ppm): 0.89 (6H, CH$_2$CH(C*H*$_3$)$_2$), 1.26–2.21 (3H, C*H*$_2$C*H*(CH$_3$)$_2$ of the backbone, 4H, C*H*(C*H*$_3$)CO, and 3H, C*H*$_2$C*H* of PDMAEA side chains), 2.29 (6H, CO$_2$CH$_2$CH$_2$N(C*H*$_3$)$_2$), 2.57 (2H, CO$_2$CH$_2$C*H*$_2$N(CH$_3$)$_2$), 4.16 (2H, CO$_2$C*H*$_2$CH$_2$N(CH$_3$)$_2$), 5.35 (2H × *x*, =C*H*$_2$ and 1H × *y*, =C*H*).

Determination of critical micelle concentration

PNA was used as a fluorescence probe to measure the *cmc* of PMHDO-*g*-PDMAEA **3** graft copolymer in aqueous solution. Acetone solution of PNA (1 mM) was added to a large amount of water until the concentration of PNA reached 0.002 mM. Next, different amounts of THF solutions of PMHDO-*g*-PDMAEA **3** graft copolymer (2, 0.2 or 0.01 mg mL^{-1}) were added to water containing PNA ([PNA] = 0.002 mM). The concentration of PMHDO-*g*-PDMAEA **3** copolymer ranged from 2 × 10^{-5} g L^{-1} to 0.1 g L^{-1}. All fluorescence spectra were recorded at 25 °C.

TEM images

PMHDO-*g*-PDMAEA **3** graft copolymer was first dissolved in THF (2 mg mL^{-1}) followed by adding deionized water slowly (0.4 mL h^{-1}) to 0.4 mL of THF solution until the desired water content was reached. The solution was sealed with a PTFE plug for equilibration under stirring for another 12 hours. The solution was dialyzed against deionized water with slow stirring for 5

days to remove THF and deionized water was changed twice everyday. For TEM studies, a drop of micellar solution was deposited on an electron microscopy copper grid coated with carbon film and the water evaporated at room temperature.

Results and discussion

Synthesis of PMHDO-Cl 2 macroinitiator

PMHDO **1** homopolymer was first prepared *via* nickel-catalyzed living coordination polymerization of MHDO, a hydroxyl-containing allene derivative, in the presence of PPh_3 at 50 °C using toluene as solvent, detailed characterization can be found in our previous reports.[52–54] This homopolymer showed a unimodal and symmetrical GPC curve with a narrow molecular weight distribution (M_w/M_n = 1.10), which verified successful living coordination polymerization of MHDO monomer. We also estimated from the data of molecular weight (M_n = 5700 g mol^{-1}) that every PMHDO chain possess *ca.* 45 repeating units.

In the current work, PDMAEA side chains were chosen for the construction of polyallene-based amphiphilic graft copolymers *via* the grafting-from strategy while DMAEA monomer was generally polymerized *via* RDRP. Therefore, the pendant hydroxyls in PMHDO **1** homopolymer needed to be converted to RDRP initiating groups because they obviously could not initiate RDRP of DMAEA. This homopolymer was then treated with 2-chloropropionyl chloride in order to transform the pendant hydroxyls into $CHCl(CH_3)CO$ RDRP initiating groups. The esterified product was characterized by ^1H NMR, ^{13}C NMR, FT-IR, and element analysis. The content of Cl was found to turn from 0% before the reaction with 2-CPC to 14.50% after the reaction, which demonstrated the successful introduction of Cl element. The strong stretching peak of pendant hydroxyls around 3403 cm^{-1} in FT-IR spectrum before the reaction became very weaker and a new strong peak originated from the carbonyls appeared at 1736 cm^{-1} after the reaction. Fig. 1A shows the ^1H NMR spectrum of PMNDO-Cl **2** and the corresponding peak assignments. All signals of the MHDO repeating unit were observed such as the broad peak at around 5.44 ppm belonging to the protons of the double bond. The integration area of the peak at 4.34 ppm apparently increased due to the introduction of $CHCl(CH_3)CO$ groups. Moreover, a new signal corresponding to carbonyl appeared at 169.6 ppm in ^{13}C NMR spectrum after the esterification, this indicating the existence of $CHCl(CH_3)CO$ groups. So, we can make sure of the successful linking of $CHCl(CH_3)CO$ RDRP initiation groups onto the PMHDO backbone. The molecular weight of the esterified product (7500 g mol^{-1}) was a little higher than that of the homopolymer (5700 g mol^{-1}) because of the new grafted $CHCl(CH_3)CO$ groups. The unimodal and symmetrical GPC after the reaction with a low polydispersity of 1.11 witnessed the keeping of the carbon–hydrogen backbone during the esterification. The approximate grafting efficiency of RDRP initiating groups was calculated to be 82% from the result of Cl content (14.50%) according to the same method in our previous papers.[52–54] All above-mentioned results confirmed the successful synthesis of polyallene-based PMHDO-Cl **2** macroinitiator bearing 37 (= 45 × 82%) $CHCl(CH_3)CO$ RDRP initiating groups.

Clarification of the mechanism of RDRP performed in acetone

In the current case, RDRP graft copolymerization of DMAEA was initiated by the pendant $CHCl(CH_3)CO$ initiating groups of PMHDO-Cl **2** macroinitiator in acetone using $CuCl/Me_6TREN$ as catalytic system. We first assumed the mechanism of this RDRP was that of ATRP since that SET-LRP has been reported to be generally performed in polar solvents including DMF, alcohol, and H_2O or mixed solvents containing polar solvents.[24,25,27,63–65] However, we observed obvious black Cu(0) sedimentation at the bottom of the flask containing acetone solution of CuCl and Me_6TREN (6 mL acetone + 21.0 mg CuCl + 59 μL Me_6TREN) as shown in inset A of Fig. 2; here acetone is apparently a kind of nonpolar solvent. This phenomenon inspired our curiosity and we also prepared another mixture of acetone (6 mL), $CuCl_2$

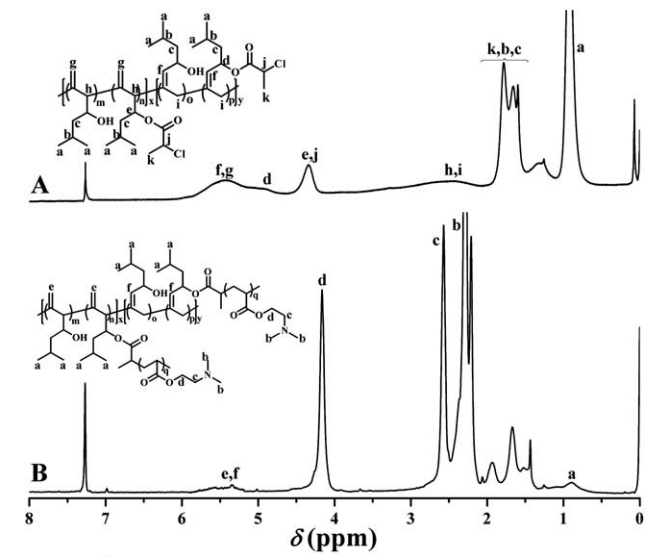


Fig. 1 ^1H NMR spectra of PMHDO-Cl **2** macroinitiator (A) and PMHDO-*g*-PDMAEA **3** graft copolymer (B) in $CDCl_3$.

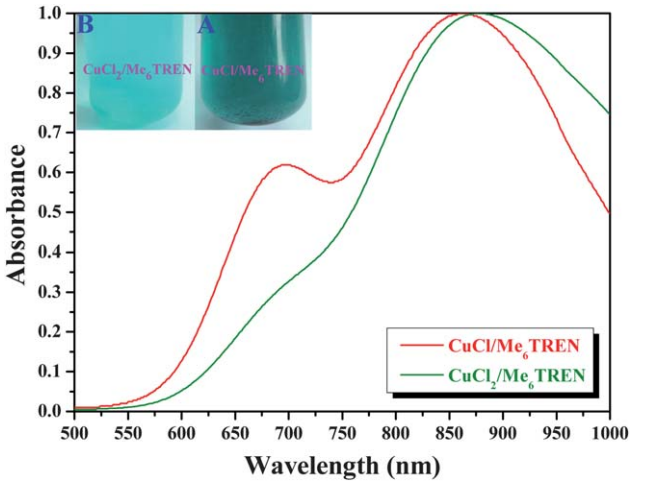


Fig. 2 UV-vis spectra of acetone solutions containing $CuCl/Me_6TREN$ and $CuCl_2/Me_6TREN$.

(28.5 mg), and Me_6TREN (59 μL). This solution was homogeneous without any black sedimentation at the bottom of the flask (inset B of Fig. 2). The maximum wavelength of UV absorption of the solution containing CuCl was found to be located at 861 nm (Fig. 2) similar to the absorption of the Cu(II) complex. Now, it is clear that acetone, a nonpolar solvent, can mediate the disproportionation process of Cu(I) into Cu(0) and Cu(II), this result is same as the reports by Percec *et al.*,[31,66–68] which also revealed the disproportionation of Cu^IX in acetone and the following SET-LRP in acetone. This disproportionation may be caused by trace water in commercial acetone.

The sedimentation of Cu(0) in the solution containing CuCl/Me_6TREN almost disappeared in 3 minutes and the solution turned into homogeneous after PMHDO-Cl **2** macroinitiator was added. The color of the solution turned blue same as that of the solution containing $CuCl_2$/Me_6TREN. While PMHDO-Cl was added, Cu(0) and Cu(II) turned into soluble Cu(I) through reversible activation and deactivation steps; on the other hand, Cu(I) generated *in situ* was disproportioned into Cu(0) and Cu(II) again. Thus, the 'visible' agglomeration of Cu(0) disappeared and turned into 'atomic' Cu(0) or 'invisible' Cu(0) colloids because that *in situ*-generated Cu(0) was consumed in the activation step at the rate that rivalled that of agglomeration.[24,26,69] Thus, it can be concluded that the mechanism of this RDRP is that of SET-LRP.

Construction of PMHDO-*g*-PDMAEA graft copolymer

PMHDO-*g*-PDMAEA **3** graft copolymers were synthesized by SET-LRP of DMAEA initiated by PMHDO-Cl **2** macroinitiator *via* the grafting-from strategy. SET-LRP is a relatively new RDRP method developed by Percec *et al.* to quickly synthesize well-defined polymers with ultrahigh molecular weights and narrow molecular weight distributions at ambient and subambient temperature.[24–27,69–72] This kind of RDRP is on the basis of the catalysis by Cu(0) powder or Cu(0) wire in conjunction with a suitable combination of ligand and solvent so that this process is relatively simple and versatile. SET-LRP has emerged as a powerful tool for the rapid synthesis of various polymers with excellent control of molecular weight, molecular weight distribution, perfect chain end fidelity, and ultrahigh molecular weight.[24–32,69–72] Here, SET-LRP of DMAEA was conducted in acetone at 40 °C using CuCl/Me_6TREN as catalytic system as listed in Table 1. All graft copolymers' molecular weights were much higher than that of the macroinitiator, this indicating the occurrence of SET-LRP of DMAEA. The molecular weights increased with the extending of polymerization time, which was in consistent with the characteristic of SET-LRP.[27] In the present work, a high feeding ratio of DMAEA monomer to the initiating group (200 : 1) and a low conversion of monomer (<18%) were employed to suppress the intermolecular coupling reactions,[21] therefore all copolymers showed unimodal and symmetrical GPC curves (Fig. 3) with narrow molecular weight distributions ($M_w/M_n \leq 1.18$), which illustrated that intermolecular coupling could be neglected.[21]

The resulting graft copolymer was characterized by ^{1}H NMR presented in Fig. 1B and all typical signals of the corresponding protons of PMHDO backbone and PDMAEA side chains were visible in the spectrum. The peaks at 2.57 and 4.16 ppm originated from the 4 protons of $CO_2CH_2CH_2N(CH_3)_2$ of the PDMAEA side chains. The signal of the double bond still appeared 5.35 ppm, which evidenced that PMHDO backbone kept inert during SET-LRP of DMAEA. Furthermore, kinetics plot of $\ln([M]_0/[M])$ *versus* time drawn in Fig. 4A from the data of conversions of DMAEA listed in Table 1 shows a linear dependence of $\ln([M]_0/[M])$ on the time. This linear relationship confirmed that the apparent polymerization rate was first order with respect to the concentration of DMAEA, which meant a constant number of propagating species during SET-LRP of DMAEA. The good control of this graft polymerization was also proved by the linear increasing of M_n with the conversion of DMAEA monomer and low molecular weight distributions throughout the whole polymerization process (Fig. 4B). On the

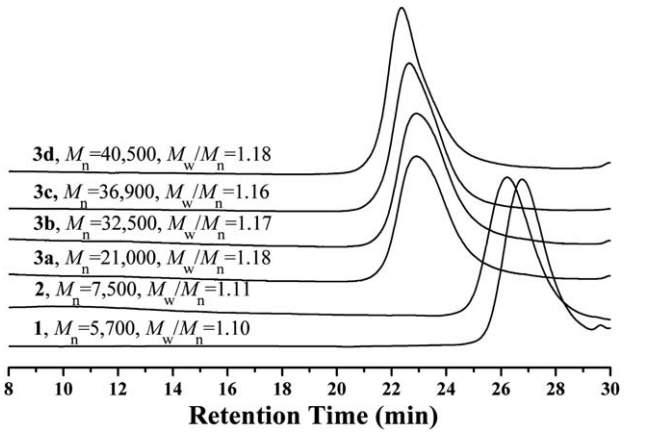


Fig. 3 GPC traces of PMHDO **1**, PMHDO-Cl **2**, and PMHDO-*g*-PDMAEA **3** graft copolymers in THF.

Table 1 Synthesis of PMHDO-*g*-PDMAEA amphiphilic graft copolymers[a]

Copolymer	Time (h)	Conv.[b] (%)	M_n[c] (g mol^{-1})	M_w/M_n[c]	*cmc*[d] (g L^{-1})
3a	4.0	5.33	21 000	1.18	5.40×10^{-3}
3b	8.0	11.36	32 500	1.17	6.42×10^{-3}
3c	12.0	14.09	36 900	1.16	7.00×10^{-3}
3d	16.0	17.28	40 500	1.18	11.80×10^{-3}

[a] Initiated by PMHDO-Cl **2** (M_n = 7500 g mol^{-1}, M_w/M_n = 1.11, density of grafted SET-LRP initiating group: 82%) at 40 °C, solvent : acetone, [DMAEA] : [Cl group] : [CuCl] : [Me_6TREN] = 200 : 1 : 1 : 1. [b] Obtained from ^{1}H NMR. [c] Measured by GPC in THF at 35 °C. [d] Determined by fluorescence spectroscopy using PNA as probe at 25 °C.

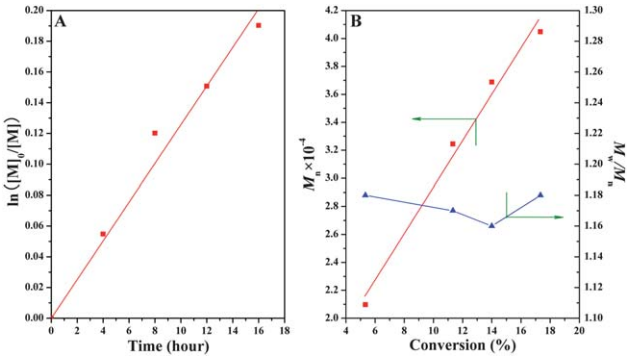


Fig. 4 (A) Kinetic plot for SET-LRP of DMAEA at 40 °C initiated by PMHDO-Cl **2** macroinitiator and (B) dependence of M_n and M_w/M_n on conversion of DMAEA.

other hand, the conversion of the monomer was relatively low due to the polymeric structure of the macroinitiator, which was similar to a previous report.[73] All these phenomena obviously accorded with the characteristic of SET-LRP.[27] From the aforementioned results, we can conclude that PMHDO-*g*-PDMAEA **3** well-defined graft copolymers were successfully synthesized through SET-LRP of DMAEA *via* the grafting-from strategy.

Self-assembly of PMHDO-*g*-PDMAEA graft copolymer in aqueous solution

PDMAEA is a biocompatible weak polybase ($pK_b \sim 6.5$)[74] and can switch from hydrophobic to hydrophilic with decreasing pH, as its tertiary amine can be quaternized at low pH, or in the presence of compounds such as methyl chloride or dimethyl sulfate.[75] So we can deduce that the PMHDO-*g*-PDMAEA **3** graft copolymer can form micelles with hydrophobic PMHDO as the core and hydrophilic DMAEA side chains as the shell in acidic solution.[76] The critical micelle concentrations of copolymers in an aqueous phase were determined by fluorescence technique using PNA as probe. Provided the fact that PNA bears high fluorescence activity in nonpolar environments and its fluorescence can be easily quenched by polar solvents such as water, so PNA is a better fluorescence probe than pyrene in terms of reproducibility.[77] Fluorescence emission spectra of PNA in an aqueous solution of PMHDO-*g*-PDMAEA **3c** graft copolymer with different concentrations are shown in the inset of Fig. 5 and the relationship of the fluorescence intensity ratio (I/I_0) of PNA as a function of the concentration of copolymer **3c** is plotted in Fig. 5. The values of I/I_0 increased sharply when the concentration of copolymer **3c** exceeded a certain value, which evidenced the incorporation of PNA probe into the hydrophobic core of micelles. Thus, *cmc* of copolymer **3c** with a value of 7.00×10^{-3} g L^{-1} was determined to be the intersection of two straight lines. As summarized in Table 1, prolonging the length of hydrophilic PDMAEA side chains made *cmc* values raise from 5.40×10^{-3} g L^{-1} to 11.80×10^{-3} g L^{-1}.

Ion strength has been reported to be an important factor of influencing the *cmc* of amphiphilic copolymer.[78] Therefore, the salt effect on the self-assembly behavior of PMHDO-*g*-PDMAEA amphiphilic graft copolymer was first examined by fluorescence

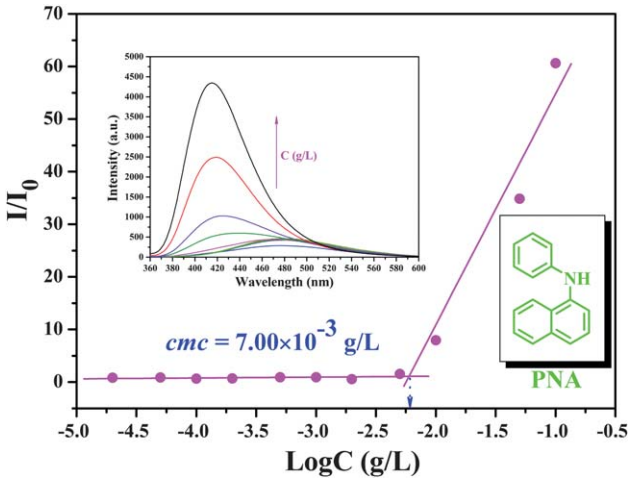


Fig. 5 Dependence of fluorescence intensity ratio I/I_0 of PNA fluorescence emission spectra on the concentration of PMHDO-*g*-PDMAEA **3c** graft copolymer.

probe technology in brine. Fig. 6A shows the relationship between the *cmc* of copolymer **3c** and the concentration of NaCl and it was found that the values of *cmc* increased with the raising of the concentration of NaCl. This can be explained that the salting-in effect made the solubility of PMHDO backbones ascend, this leading to the rising of *cmc* value. We also measured *cmc* of copolymer **3c** at different pHs to check the dependence of *cmc* on pH. We found from Fig. 6B that the values of *cmc* of copolymer **3c** decreased with the lifting of pH value. When pH value was increased, lower quaternization degree of PDMAEA segment resulted in the lower hydrophilicity of PDMAEA side chain, *i.e.* the decreasing of *cmc* value.

The micellar structures formed from PMHDO-*g*-PDMAEA **3a** amphiphilic graft polymers were visualized by TEM as shown in Fig. 7. This copolymer formed spindles (Fig. 7A) in pure water, and these micelles were transformed into spheres with a diameter around 150–200 nm (Fig. 7B) in brine ([NaCl] = 0.05 mol L^{-1}). This phenomenon can be explained in that Na^+ could screen the repulsion among hydrophilic PDMAEA segments, so the hydrophobic PMHDO segments were easier to aggregate to form big micelles.[79]

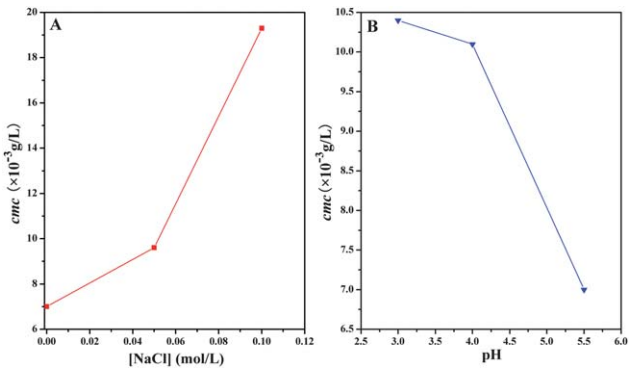


Fig. 6 Influence of salinity (A) and pH value (B) on *cmc* of PMHDO-*g*-PDMAEA **3c** graft copolymer.

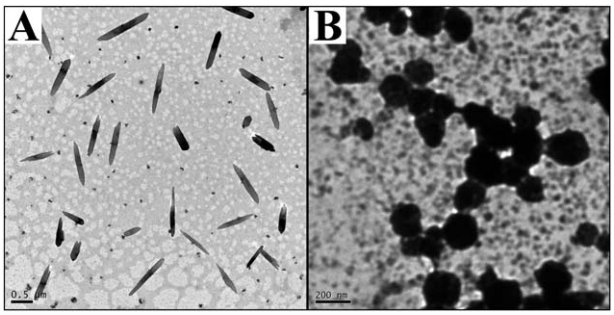


Fig. 7 TEM images of micelles formed by PMHDO-*g*-PDMAEA **3a** graft copolymer in pure water (A) and brine (B, [NaCl] = 0.05 mol L^{-1}), initial copolymer concentration in THF: 2 mg mL^{-1}, water content: 50%.

Conclusion

We have successfully synthesized a series of well-defined amphiphilic PMHDO-*g*-PDMAEA graft copolymers bearing hydrophilic PDMAEA side chains *via* sequential living coordination polymerization and SET-LRP and all obtained graft copolymers possessed narrow molecular weight distributions ($M_w/M_n \leq 1.18$). By using a very common nonpolar solvent, acetone, we employed the "graft-from" strategy to graft PDMAEA side chains from polyallene-based backbone. The syntheses of the backbone and side chain were both controllable. Surprisingly, the mechanism of graft copolymerization of DMAEA was proved to be that of SET-LRP even in a nonpolar solvent. Critical micelle concentrations of PMHDO-*g*-PDMAEA amphiphilic graft copolymers were dependent on the length of hydrophilic PDMAEA side chains and influenced by salinity or pH. Moreover, these graft copolymers aggregated to form various micelles in different environments. They may find potential applications in nanotechnologies, such as serving as templates to fabricate nano-composites.

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Notes and references

1 M. P. McGrath, E. D. Sall and S. J. Tremont, *Chem. Rev.*, 1995, **95**, 381–389.
2 T. Endo and I. Tomita, *Prog. Polym. Sci.*, 1997, **22**, 565–600.
3 I. Tomita, Y. Kondo, K. Takagi and T. Endo, *Macromolecules*, 1994, **27**, 4413–4414.
4 K. Takagi, I. Tomita and T. Endo, *Macromolecules*, 1997, **30**, 7386–7390.
5 K. Takagi, I. Tomita and T. Endo., *Macromolecules*, 1998, **31**, 6741–6747.
6 K. Mochizuki and I. Tomita, *Macromolecules*, 2006, **39**, 7474–7478.
7 K. Takagi, I. Tomita and T. Endo, *Chem. Commun.*, 1998, 681–682.
8 M. Taguchi, I. Tomita and T. Endo, *Angew. Chem., Int. Ed.*, 2000, **39**, 3667–3669.
9 M. Kyohei and I. Tomita, *Macromolecules*, 2006, **39**, 6336–6340.
10 M. Taguchi, I. Tomita, Y. Yoshida and T. Endo, *J. Polym. Sci., Part A: Polym. Chem.*, 1999, **37**, 3916–3921.
11 I. Tomita, M. Taguchi, K. Takagi and T. Endo, *J. Polym. Sci., Part A: Polym. Chem.*, 1997, **35**, 431–437.
12 M. Taguchi, I. Tomita, Y. Yoshida and T. Endo, *J. Polym. Sci., Part A: Polym. Chem.*, 2001, **39**, 495–499.
13 M. Hong, B. X. Li and Y. S. Li, *Chin. J. Polym. Sci.*, 2011, **29**, 692–698.
14 S. Forster and T. Plantenberg, *Angew. Chem., Int. Ed.*, 2002, **41**, 688–714.
15 G. Riess, *Prog. Polym. Sci.*, 2003, **28**, 1107–1170.
16 I. In, Y. H. La, S. M. Park, P. F. Nealey and P. Gopalan, *Langmuir*, 2006, **22**, 7855–7860.
17 C. Cheng, K. Qi, E. Khoshdel and K. L. Wooley, *J. Am. Chem. Soc.*, 2006, **128**, 6808–6809.
18 J. S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc.*, 1995, **117**, 5614–5615.
19 V. Percec and B. Barboiu, *Macromolecules*, 1995, **28**, 7970–7972.
20 M. Kato, M. Kamigaito, M. Sawamoto and T. Higashimura, *Macromolecules*, 1995, **28**, 1721–1723.
21 G. L. Cheng, A. Boker, M. F. Zhang, G. Krausch and A. H. E. Muller, *Macromolecules*, 2001, **34**, 6883–6888.
22 Y. Q. Zhang, Z. Shen, D. Yang, C. Feng, J. H. Hu, G. L. Lu and X. Y. Huang, *Macromolecules*, 2010, **43**, 117–125.
23 T. Cai, W. J. Yang, K.-G. Neoh and E. T. Kang, *Polym. Chem.*, 2012, **3**, 1061–1068.
24 V. Percec, A. V. Popov, E. Ramirez-Castillo, M. Monteiro, B. Barboiu, O. Weichold, A. D. Asandei and C. M. Mitchell, *J. Am. Chem. Soc.*, 2002, **124**, 4940–4941.
25 V. Percec, T. Guliashvili, J. S. Ladislaw, A. Wistrand, A. Stjerndahl, M. J. Sienkowska, M. J. Monteiro and S. Sahoo, *J. Am. Chem. Soc.*, 2006, **128**, 14156–14165.
26 N. H. Nguyen, B. M. Rosen, G. Lligadas and V. Percec, *Macromolecules*, 2009, **42**, 2379–2386.
27 B. M. Rosen and V. Percec, *Chem. Rev.*, 2009, **109**, 5069–5119.
28 M. W. Jones, M. I. Gibson, G. Mantovani and D. M. Haddleton, *Polym. Chem.*, 2011, **2**, 572–574.
29 N. H. Nguyen, J. Kulis, H. J. Sun, Z. F. Jia, B. Beusekom, M. E. Levere, D. A. Wilson, M. J. Monteiro and V. Percec, *Polym. Chem.*, 2013, **4**, 144–155.
30 M. E. Levere, N. H. Nguyen, H. J. Sun and V. Percec, *Polym. Chem.*, 2013, **4**, 686–694.
31 M. E. Levere, N. H. Nguyen, X. F. Leng and V. Percec, *Polym. Chem.*, 2013, **4**, 1635–1645.
32 N. H. Nguyen, H. J. Sun, M. E. Levere, S. Fleischmann and V. Percec, *Polym. Chem.*, 2013, **4**, 1328–1332.

33 Z. P. Cheng, X. L. Zhu, G. D. Fu, E. T. Kang and K. G. Neoh, *Macromolecules*, 2005, **38**, 7187–7192.
34 G. Moad, E. Rizzardo and S. H. Thang, *Acc. Chem. Res.*, 2008, **41**, 1133–1142.
35 Y. G. Li, Y. Q. Zhang, D. Yang, Y. J. Li, J. H. Hu, C. Feng, S. J. Zhai, G. L. Lu and X. Y. Huang, *Macromolecules*, 2010, **43**, 262–270.
36 Z. F. Jia, C. A. Bell and M. J. Monteiro, *Chem. Commun.*, 2011, **47**, 4165–4167.
37 M. D. Hossain, D. Valade, Z. F. Jia and M. J. Monteiro, *Polym. Chem.*, 2012, **3**, 2986–2995.
38 X. W. Zhang, J. Rieger and B. Charleux, *Polym. Chem.*, 2012, **3**, 1502–1509.
39 M. Zhang, T. Breiner, H. Mori and A. H. E. Muller, *Polymer*, 2003, **44**, 1449–1458.
40 Y. Xia, B. D. Olsen, J. A. Kornfield and R. H. Grubbs, *J. Am. Chem. Soc.*, 2009, **131**, 18525–18532.
41 S. Mougnier, C. Brochon, E. Cloutet, G. Fleury, H. Cramail and G. Hadziioannou, *Macromol. Rapid Commun.*, 2012, **33**, 703–709.
42 A. Deffieux and M. Schappacher, *Macromolecules*, 1999, **32**, 1797–1802.
43 Q. Zhang, S. Slavin, M. W. Jones, A. J. Haddleton and D. M. Haddleton, *Polym. Chem.*, 2012, **3**, 1016–1023.
44 J. W. Chan, B. Yu, C. E. Hoyle and A. B. Lowe, *Chem. Commun.*, 2008, 4959–4961.
45 S. Slavin and D. M. Haddleton, *Soft Matter*, 2012, **8**, 10388–10393.
46 M. W. Jones, G. Mantovani, C. A. Blindauer, S. M. Ryan, X. X. Wang, D. J. Brayden and D. M. Haddleton, *J. Am. Chem. Soc.*, 2012, **134**, 7406–7413.
47 K. L. Beers, S. G. Gaynor, K. Matyjaszewski, S. S. Sheiko and M. Moller, *Macromolecules*, 1998, **31**, 9413–9415.
48 K. Matyjaszewski and J. H. Xia, *Chem. Rev.*, 2001, **101**, 2921–2990.
49 A. Cappelli, M. Paolino, G. Grisci, G. Giuliani, A. Donati, R. Mendichi, A. C. Boccia, F. Samperi, S. Battiato, E. Paccagnini, E. Giacomello, V. Sorrentino, M. Licciardi, G. Giammona and S. Vomero, *Polym. Chem.*, 2011, **2**, 2518–2527.
50 C. Feng, Y. J. Li, D. Yang, J. H. Hu, X. H. Zhang and X. Y. Huang, *Chem. Soc. Rev.*, 2011, **40**, 1282–1295.
51 P. J. Wan, D. S. Tan, Z. S. Li, X. Q. Zhang, J. H. Li and H. Tan, *Chin. J. Polym. Sci.*, 2011, **30**, 190–198.
52 X. H. Zhang, D. Peng, G. L. Lu, L. N. Gu and X. Y. Huang, *J. Polym. Sci., Part A: Polym. Chem.*, 2006, **44**, 6888–6893.
53 X. H. Zhang, Z. Shen, L. T. Li, S. Zhang, G. L. Lu and X. Y. Huang, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 5509–5517.
54 X. H. Zhang, Z. Shen, L. T. Li, G. L. Lu, L. N. Gu and X. Y. Huang, *Polymer*, 2007, **48**, 5507–5513.
55 R. L. Xu, M. A. Winnik, F. R. Hallett, G. Riess and M. D. Croucher, *Macromolecules*, 1991, **24**, 87–93.
56 D. Pan, J. L. Turner and K. L. Wooley, *Chem. Commun.*, 2003, 2400–2401.
57 X. H. Yan, Q. He, K. W. Wang, L. Duan, Y. Cui and J. B. Li, *Angew. Chem., Int. Ed.*, 2007, **46**, 2431–2434.
58 S. B. Clendenning, S. Fournier-Bidoz, A. Pietrangelo, G. C. Yang, S. J. Han, P. M. Brodersen, C. M. Yip, Z. H. Lu, G. A. Ozin and I. Manners, *J. Mater. Chem.*, 2004, **14**, 1686–1690.
59 G. M. Whitesides. and B. Grzybowski, *Science*, 2002, **295**, 2418–2421.
60 X. H. Zhang, Z. Shen, C. Feng, D. Yang, Y. G. Li, J. H. Hu, G. L. Lu and X. Y. Huang, *Macromolecules*, 2009, **42**, 4249–4256.
61 S. Shimizu, T. Sugiura and T. Tsuji, *J. Org. Chem.*, 1985, **50**, 537–539.
62 J. Queffelec, S. G. Gaynor and K. Matyjaszewski, *Macromolecules*, 2000, **33**, 8629–8639.
63 C. Feng, Z. Shen, Y. J. Li, L. N. Gu, Y. Q. Zhang, G. L. Lu and X. Y. Huang, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 1811–1824.
64 S. J. Zhai, B. D. Wang, C. Feng, Y. J. Li, D. Yang, J. H. Hu, G. L. Lu and X. Y. Huang, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 647–655.
65 X. M. Song, Y. Q. Zhang, D. Yang, L. Yuan, J. H. Hu, G. L. Lu and X. Y. Huang, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, **49**, 3328–3337.
66 N. H. Nguyen, B. M. Rosen, X. Jiang, S. Fleischmann and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 5577–5590.
67 B. M. Rosen and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 4950–4964.
68 B. M. Rosen, X. Jiang, C. J. Wilson, N. H. Nguyen, M. J. Monteiro and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 5606–5628.
69 G. Lligadas, B. M. Rosen, C. A. Bell, M. J. Monteiro and V. Percec, *Macromolecules*, 2008, **41**, 8365–8371.
70 G. Lligadas, B. M. Rosen, M. J. Monteiro and V. Percec, *Macromolecules*, 2008, **41**, 8360–8364.
71 N. H. Nguyen, M. E. Levere, J. Kulis, M. J. Monteiro and V. Percec, *Macromolecules*, 2012, **45**, 4606–4622.
72 M. E. Levere, N. H. Nguyen and V. Percec, *Macromolecules*, 2012, **45**, 8267–8272.
73 L. N. Gu, Z. Shen, S. Zhang, G. L. Lu, X. H. Zhang and X. Y. Huang, *Macromolecules*, 2007, **40**, 4486–4493.
74 J. H. Jeong, S. W. Kim and T. G. Park, *Prog. Polym. Sci.*, 2007, **32**, 1239–1274.
75 F. Q. Zeng, Y. Q. Shen and S. P. Zhu, *Macromol. Rapid Commun.*, 2002, **23**, 1113–1117.
76 V. Percec, D. A. Wilson, P. Leowanawat, C. J. Wilson, A. D. Hughes, M. S. Kaucher, D. A. Hammer, D. H. Levine, A. J. Kim, F. S. Bates, K. P. Davis, T. P. Lodge, M. L. Klein, R. H. De Vane, E. Aqad, B. M. Rosen, A. O. Argintaru, M. J. Sienkowska, K. Rissanen, S. Nummelin and J. Ropponen, *Science*, 2010, **328**, 1009–1014.
77 P. S. Xu, H. D. Tang, S. Y. Li, J. Ren, E. van Kirk, W. J. Murdoch, M. Radosz and Y. Q. Shen, *Biomacromolecules*, 2004, **5**, 1736–1744.
78 I. Astafieva, K. Khougaz and A. Eisenberg, *Macromolecules*, 1995, **28**, 7127–7134.
79 Y. Ma, T. Cao and S. E. Webber, *Macromolecules*, 1998, **31**, 1773–1778.