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Preparation and properties of azobenzene-containing amphiphilic miktoarm star polymers

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Summary

A series of novel miktoarm star polymers composed of a poly(ethylene oxide) (PEO) and two side-chain liquid crystalline azobenzene-containing polymethacrylate (PEO-(PMMAZO)$_2$) were prepared using atom transfer radical polymerization (ATRP). Bifunctional macroinitiator PEO-Br$_2$ was synthesized by condensation reaction in two steps and characterized by ^{1}H NMR, ^{13}C NMR and IR. Kinetic study showed that it was a first order reaction referred to the monomer MMAZO, namely, 6-(4-methoxy-4'-oxy-azobenzene)hexyl methacrylate. The liquid crystalline behaviors of the miktoarm star polymers were studied by differential scanning calorimetry (DSC) and polarized optical microscope (POM). They exhibited smectic and nematic mesophases when Mn was beyond 9.4×10^3 g/mol. The phase transition temperatures of the smectic and nematic phases increased while the melting temperature of PEO decreased with increasing molecular weight of the LC block. Compared with diblock polymer PEO-PMMAZO, the melting temperature of PEO in miktoarm star polymer decreased more rapidly.

Introduction

More and more attention has been attracted to star polymers due to their unique properties, such as low solution viscosity, and potential applications, including using as drug carriers [1-2]. Generally, there are two basic methods for preparing star polymers. One is the so-called "core-first" method in which a multifunctional initiator is used to initiate the polymerization of monomer to form a multiarm star polymer [3-4]. The other is the so-called "arm-first" method in which a number of terminally reactive linear polymers (arms) are anchored through cross-linkable monomers to form a microgel [5-6]. By combining the two methods, miktoarm star polymers, which have also attracted much attention because of their interesting microphase separation properties in solution and solid state [7-8] can be synthesized.

Amphiphilic miktoarm star polymers, which combine hydrophilic and hydrophobic arms, have been a subject of special attention in surface-related applications [9-10]. Among them, star copolymers containing hydrophilic poly(ethylene oxide) (PEO) stand apart because of the nonionic and highly crystalline nature of the hydrophilic PEO blocks [11-12]. As an example, PEO$_{10}$-PS$_{10}$ was synthesized and its lyotropic liquid crystalline structures were investigated in aqueous solutions as well as in water-oil solvent mixtures [13]. Although many studies have been focused on amphiphilic copolymers, there were only few researches on amphiphilic miktoarm star polymers containing crystalline polymer PEO and liquid crystalline polymers. Since crystalline polymer and liquid crystalline polymer are two kinds of ordered polymers, it is interesting to study the influence of the two in a corporate system. Azobenzene-containing liquid crystalline polymers are widely explored due to that azobenzene in the elongated trans form could be converted to the contracted cis form, which is known to destabilize the LC phase and induce a photochemical LC-to-isotropic phase transition [14]. Yue Zhao and co-workers [15-17] reported the synthesis of block copolymers comprising methacrylate-based azobenzene-containing side-chain liquid crystalline polymer. They investigated the dissociation and reformation of azobenzene block copolymer vesicles by light. We have reported the preparation and characterization of miktoarm star polymer carrying one amorphous polystyrene (PS) arm and two liquid crystalline azobenzene-containing polymethacrylate (PMMAZO) arms [18]. And we also have reported the synthesis of PEO diblock copolymers PEO-PMMAZO and their properties [19]. How could the crystallinity of PEO be affected in confinement and the liquid crystalline behavior of PMMAZO be influenced within limit? In addition, block polymers and liquid crystalline polymers are two sorts of the materials, which can self-assemble to various morphologies [20]. The unique molecular design of LC-coil miktoarm star copolymers could potentially lead to different morphologies, liquid crystalline behaviors and self-assembly behaviors as compared with those observed in LC-coil systems. With these in mind, we designed and synthesized a novel amphiphilic heteroarm star polymer containing a coil chain, PEO and two liquid crystalline (LC) chains, liquid crystalline azobenzene-containing polymethacrylate. The phase behaviors of these polymers were investigated primely.

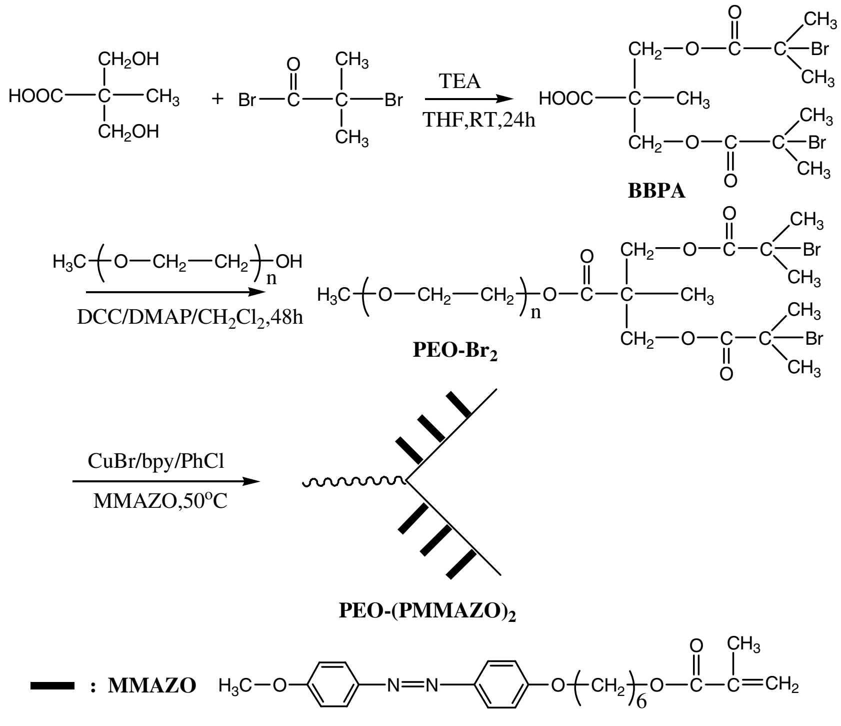
Experimental

Materials

2,2-Bis(hydroxymethyl) propionic acid (BHPA, Acros, 98%) was dried at 50°C before use. 2,2'-Bipyridine (bpy, Aldrich, 99%) was purified by recrystallization from n-hexane. Chloroform was washed with oil of vitriol (15% v/v) three times and then with distilled water until neutralization. After being dried over anhydrous $CaCl_2$, $CHCl_3$ was distilled. Chlorobenzene was purified as $CHCl_3$. Thionyl chloride (Xilong Chemical Reagent Factory, >98%) was distilled before use. Tetrahydrofuran was refluxed with sodium and distilled. Triethylamine was dried with potassium hydroxide, refluxed with p-toluenesulfonyl chloride, and then distilled. Poly(ethylene oxide) (Mn = 5000 g/mol, Mw/Mn = 1.08) was obtained from Acros. Other reagents were purchased from Xilong Chemical Reagent Factory, and used without further purification.

Instruments

Gel permeation chromatography (GPC) analysis was performed on a Waters Liquid Chromatograph system equipped with a Waters 1515 highpressure liquid chromatography pump, a Waters 2414 refractive-index detector, and three Styragel columns (combination of HR-1, HR-3, and HR-4). Linear PS standards were applied as calibration samples. The eluent was THF and the flow rate was 1 mL/min. NMR spectra were recorded on a Bruker DMX400 spectrometer with deuterated chloroform at room temperature. Thermograms were obtained using a Perkin Elmer DSC-7 instrument. Polarized optical microscope analysis was performed on a Leitz Laborlux 12POL microscope with a Leitz 350 hot stage.



Scheme 1. Synthetic route of precursor PEO-Br_2 and miktoarm star polymer PEO-$(PMMAZO)_2$

Synthesis of 2, 2-Bis(methyl-α-bromoisobutyrate) Propionic acid (BBPA)

The synthetic route was depicted in Scheme 1. In a typical procedure, 2, 2-bis(hydroxymethyl) propionic acid (1.0 g, 7.5×10^{-3} mol), THF (5.0 ml) and freshly distilled triethylamine (2.5 ml, 1.8×10^{-2} mol) were added into a 50 ml flask with a magnetic stirring bar. After the flask was cooled to 0°C, a diluted solution of α-bromoisobutyryl bromide (2.1 ml, 1.6×10^{-2} mol) was added dropwise over 2 h. The reaction mixture was warmed to room temperature and stirred for 24 h. After Nt_3NHBr was filtered off, THF and the excess α-bromoisobutyryl bromide were removed by distillation under reduced pressure. The crude product was separated through a silicon column using a mixture solution v($CHCl_3$):v(acetone) = 10:1 as the eluent. The first ingredient was collected. By removing the solvent with rotate vaporizing apparatus, the product, 2, 2-bis(methyl-α-bromoisobutyrate) propionic acid (BBPA, 2.7 g, 84% yield) was obtained. ^1H NMR δ (ppm): 1.36 [s, 3H, CH_3C], 1.92 [s, 12H, $(CH_3)_2CBr$], 4.43 [m, 4H, CH_2O]. A peak of carboxylic acid was not observed because of its broadness. ^{13}C NMR δ (ppm): 177.7 (*C*OOH), 171.0 (*C*OO), 66.0 (CH_2O), 55.3, 55.2 (*C*Br), 46.5 (*C*–COOH), 30.6 (CH_3–CBr), 17.8 (CH_3–C).

Synthesis of bifunctional macroinitiator PEO-Br$_2$

In a 50 ml flask with a magnetic stirring bar, PEO (Mn = 5000 g/mol, 2.0 g, 0.4 mmol) was dissolved in 9.0 ml of methylene chloride. 4-dimethylaminopyridine (DMAP, 0.29 g, 2.4 mmol) and BBPA (0.87 g, 2 mmol) were added subsequently. After the flask was cooled to 0°C, a diluted solution of N, N'-Dicyclohexyl carbodiimide (DCC, 0.41 g, 2 mmol) was added dropwise over 2 h. The reaction mixture was warmed to room temperature and stirred for 48 h. After filtration, the crude product was precipitated into diethyl ether and collected by vacuum filtration. After redissolving the solid in CH_2Cl_2, the precipitation cycle was repeated two more times followed by recrystallizing in ethanol. The solid product was dried in a vacuum oven at 40°C for 24 h to obtain the macroinitiator PEO-Br$_2$ (1.8 g, 85% yield). ^{1}H NMR δ (ppm): 1.34 [CH_3C]; 1.91 [$(CH_3)_2CBr$]; 3.38 [-OCH_3]; 3.64 [-OCH_2CH_2O-]; 4.32-4.42 [$COOCH_2$].

Polymerization Procedures of Miktoarm Star Polymers (PEO-(PMMAZO)$_2$)

The monomer MMAZO, namely, 6-(4-methoxy-4'-oxy-azobenzene)hexyl methacrylate, was synthesized using the documented procedure [21]. Y-shaped block copolymers (PEO-(PMMAZO)$_2$) were then obtained via atom transfer radical polymerization (ATRP). Typical procedure was as follows. Each of predetermined six glass tubes was charged with PEO-Br$_2$ macroinitiator (53.2 mg, 0.01 mmol), MMAZO (158.4 mg, 0.4 mmol), bpy (9.4 mg, 0.06 mmol), CuBr (2.9 mg, 0.02 mmol) and PhCl (633.6 mg). After three freeze-pump-thaw cycles, the tubes were sealed under vacuum. After thawing, the tubes were immersed into an oil bath thermostated at 50°C, removed at timed intervals, broken open, withdrawn to measure conversion by ^{1}H NMR and injected into GPC. The polymer solution was diluted in THF, passed through a column of neutral alumina, and precipitated in methanol, which was a good solvent for PEO.

Results and discussion

Synthesis of bifunctional macroinitiator PEO-Br$_2$

In this work, the bifunctional macroinitiator PEO-Br$_2$ was synthesized by using N, N'-Dicyclohexyl carbodiimide (DCC) as the efficient condensation agent with two steps. Formerly, the preparation of PEO-Br$_2$ included three steps [22-23], the synthesis of 2, 2-bis(methyl-α-bromoisopropyl) propionic acid BPPA, the synthesis of 2, 2-bis(methyl-α-bromoisopropyl) propionyl chloride (BPPC), by reacting BPPA with PCl_5 at room temperature [22] or $SOCl_2$ at refluxing temperature [23], and the synthesis of PEO-Br$_2$. Since BPPC was a viscous liquid with high boiling point and easy to react with the moisture in the air, purification of BBPC turned to be difficult. By employing DCC, the reaction became smoother. The pure BBPA was obtained by passing through a silicon column using a mixture solution v($CHCl_3$):v(acetone) = 10:1 as the eluent. The experiment was carried out at room temperature and less smelly. To obtain the aimed product, excess α-bromoisobutyryl bromide and DCC were used. Figure 1 shows the ^{1}H NMR spectrum of PEO-Br$_2$. As can be seen, the new signals at 1.91 ppm of $(CH_3)_2CBr$ (peak d) and 4.32–4.42 ppm of OCH_2 of PEO and $COOCH_2$ (peaks c and e) indicated the successful preparation of PEO-Br$_2$. In Figures 2 and 3 the IR spectra of PEO and PEO-Br$_2$ demonstrated the same result. The peak at 3474 cm^{-1}

(Figure 2) attributed to the –OH of PEO disappeared. Meanwhile, the characteristic absorb peak of ester group at 1738 cm^{-1} was observed in Figure 3, revealing that PEO had been converted to PEO-Br_2.

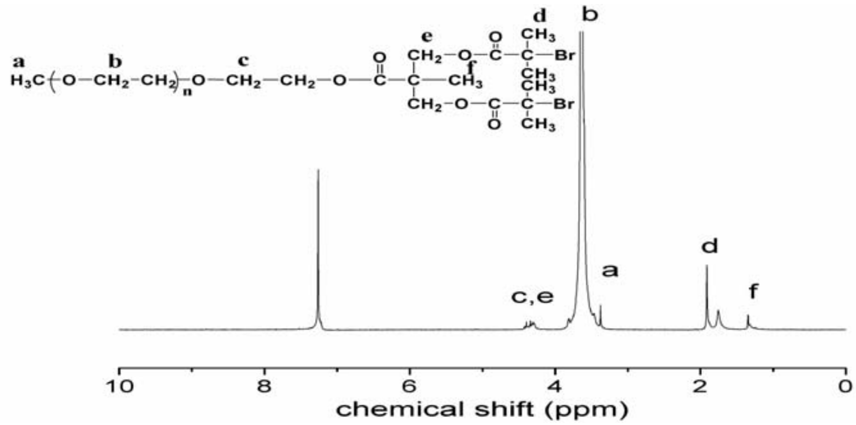


Figure 1. ^1H NMR spectrum ($CDCl_3$: 400 MHz) of PEO-Br_2

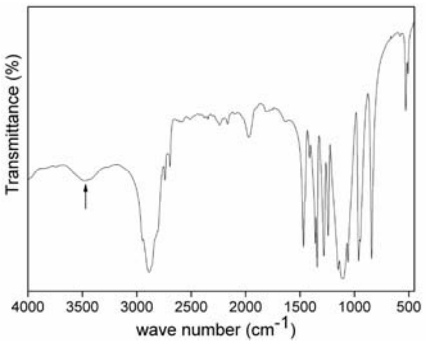


Figure 2. IR spectrum of PEO

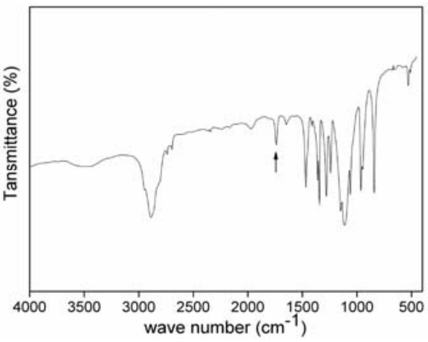


Figure 3. IR spectrum of PEO-Br_2

Polymerization Procedures of Miktoarm Star Polymers (PEO-(PMMAZO)$_2$)

Amphiphilic miktoarm star polymers, (PEO-(PMMAZO)$_2$, were synthesized via atom transfer radical polymerization (ATRP) in CuBr/bpy catalyst system. Figure 4 shows the dependence of monomer conversion on reaction time. The first-order kinetic plot indicated that the number of active species was constant and the termination reactions were not significant. As in all other radical polymerization oxygen can adversely affect the polymerization. Therefore, the critical step in successful polymerization was the removal of any dissolved oxygen via freeze-pump-thaw cycle. Purity of the liquid crystalline monomer MMAZO was also found to be an important factor for narrow polydispersity of the obtained polymers. Hence, MMZAO monomer was purified by column chromatography. However, it was noticeable that an “induction” period of approximately 35 min was observed in the polymerization. This induction period is often seen and is not yet fully understood, but may be due to residual oxygen [24] or other impurity in the system.

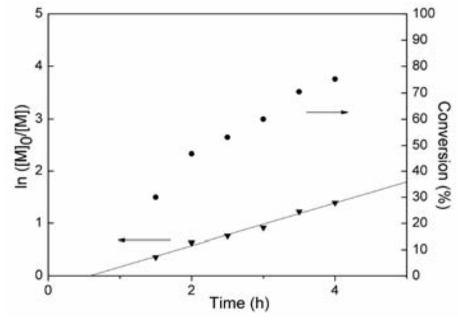


Figure 4. Semilogarithmic kinetic plot of monomer conversion versus reaction time ($[PEO\text{-}Br_2]$:[CuBr]:[bpy]: [monomer] = 1:2:6:40 in chlorobenzene (1.000 g of monomer in 4.000 g of chlorobenzene) at 50°C

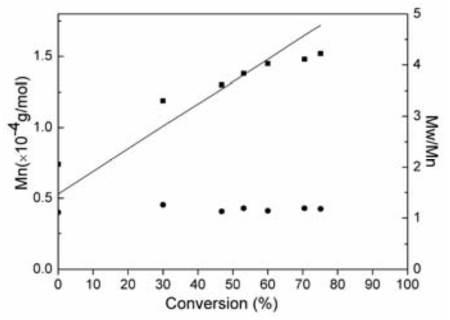


Figure 5. Evolution of Mn and polydispersities with monomer conversion. Mn was based on GPC. The line is the theoretical Mn vs conversion

As can be seen from Figure 5, Mn increased with conversion and the polydispersities were narrow (<1.3) with very little changes, revealing that the synthesis of miktoarm star polymers ($PEO\text{-}(PMMAZO)_2$ was a living polymerization.

Table 1. Molecular weight and ^1H NMR data of miktoarm star polymers

Time (h)	Conversion(%)^a	Mn^b($\times10^{-4}$)	Mn^c($\times10^{-4}$)	Mn/Mw^b
0	0	0.74	0.53	1.11
1.5	30.0	1.19	1.01	1.26
2.0	46.8	1.30	1.27	1.13
2.5	53.1	1.38	1.37	1.19
3.0	60.0	1.45	1.48	1.14
3.5	70.5	1.48	1.65	1.19
4.0	75.1	1.52	1.72	1.18

[a] Calculated according to Eq.1

$$\text{Conv.}(\%) = 1 - [2\,(I_{5.6} + I_{6.1}) / I_{7.9}] \times 100\% \qquad (\mathbf{1})$$

where $I_{5.6}$, $I_{6.1}$, $I_{7.9}$ are the integral areas of $-C(CH_3)=CH_2$, aryl protons, respectively.

[b] Given by GPC calibrated by PS standard.

[c] Theoretical molecular weight, calculated according to Eq. 2

$$Mn = 5324 + 396\times 40 \times \text{Conv.} \qquad (\mathbf{2})$$

where 5324 is the molecular weight of macroinitiator, $PEO\text{-}Br_2$; 396 is the molecular weight of monomer; 40 is the ratio of monomer to macroinitiator

Comparing Mn measured by GPC with the theoretical one (Table 1 and Figure 5), we noticed that Mn was slightly higher than the theoretical one at the beginning of the reaction. There were three factors which might lead to this result. Firstly, Mn of $PEO\text{-}Br_2$ based on GPC was higher than the exact value (Table 1), probably due to the systematic error. Secondly, a certain amount of initiator was lost through primary radical-primary radical reactions, reducing the initiator efficiency, which could be concluded from the evolution of molecular weight with time (Figure 6). Finally, compared with propagation, initiation rate was slow. Similar phenomenon was observed in other reports [25]. On the other hand, Mn was lower than the theoretical

one at the final period. This might be due to the lower hydrodynamic volumes of star-branched polymers than linear analogues of the same molecular weight [3]. It also provided a proof that the well-defined miktoarm star polymer was obtained.
Figure 6 shows the GPC curves of the obtained PEO-$(PMMAZO)_2$ heteroarm star polymers. The results were summarized in Table 1.

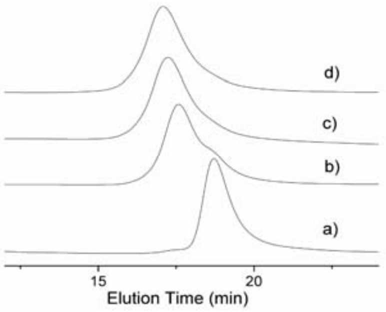


Figure 6. GPC traces of PEO-$(PMMAZO)_2$ heteroarm star polymer formation at various times (under the same conditions as shown in Fig.2): (a) 0 h, (b) 1.5 h, (c) 2.5 h, (d) 4 h

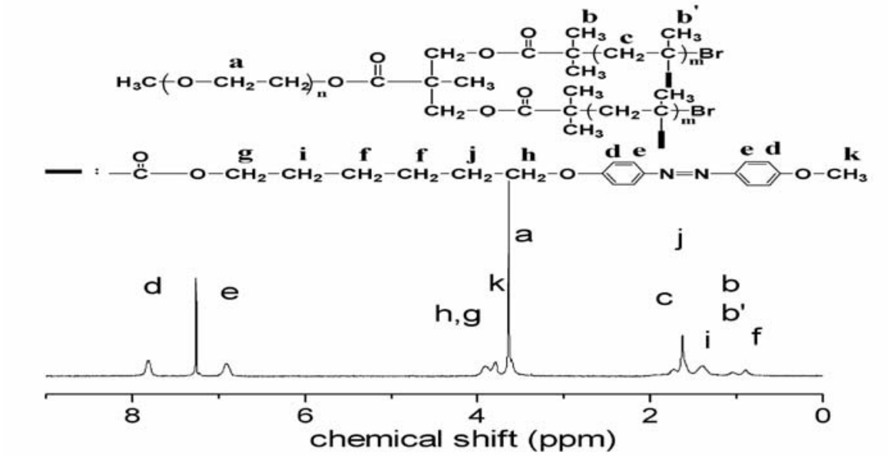


Figure 7. ^{1}H NMR spectrum of miktoarm star polymer S_5 ($M_{n,GPC} = 1.53 \times 10^4$ g/mol) in $CDCl_3$

The chemical structure of the obtained amphiphilic miktoarm star polymer was characterized by 400 MHz ^{1}H NMR spectroscopy. Figure 7 shows the ^{1}H NMR spectrum of the well defined amphiphilic miktoarm star polymer. Characteristic resonance of aromatic protons (peaks d and e) at 7.8 ppm and 6.9 ppm and that of methylene protons in PEO unit (peak a) at 3.6 ppm were present, which convinced the formation of miktoarm star polymer PEO-$(PMMAZO)_2$. Peaks of $C(CH_3)=CH_2$ for monomer MMAZO at 5.6 ppm and 6.1 ppm were not observed, revealing that the polymer so-synthesized didn't contain monomer. Based on this, we could calculate the molecular weight according to Eq. 3

$$Mn = 5324 + 396 \times 450 \times I_d / [4(I_a + I_h + I_g + I_k) - 7I_d] \qquad (\mathbf{3})$$

Where 5324 is the molecular weight of macroinitiator, PEO-Br_2, 396 is the molecular weight of monomer, 450 is the number of methylene protons in PEO, I_a, I_d, I_g, I_h, I_k are the integral areas of methylene protons in PEO, aromatic protons, methylene protons adjacent to ester group, methylene protons adjacent to phenoxy and methoxy group, respectively.

Thermotropic Phase Behavior

To investigate the influences of molecular structure on crystallinity of PEO, we synthesized PEO-PMMAZO according to literature [19] as well. The phase behaviors of diblock polymer, PEO-PMMAZO and miktoarm star polymer, PEO-$(PMMAZO)_2$ were characterized by combination techniques consisting of differential scanning calorimetry (DSC) and polarized optical microscopy (POM). To eliminate the effect of thermal history, we pretreated all samples to be used in DSC measurements by heating them from 30°C to 150°C at a rate of 50°C /min, keeping them at 150°C for 3 min and then cooling them to −20°C at 10°C /min. The DSC thermal diagrams were recorded at 10°C /min during the second heating process to 150°C.

Table 2. Characterization data and thermal transition data of the miktoarm star polymers

Polym. No.	Mn^a ($\times10^{-4}$)	Mn^b ($\times10^{-4}$)	Mw/Mn	PEO%^{c}	Phase transitions (°C) and enthalpy changes (J/g)^d
PEO−Br_2	0.73	0.53	1.11	100	K60.4(152.7)I
S_1	0.83	0.77	1.22	68.8	K57.0(77.5)I
S_2	1.13	0.94	1.20	56.4	K48.0(43.7)g64.7S74.6(0.7)N94.8(0.9)I
S_3	1.37	1.45	1.18	36.6	K43.4(24.1)g75.0S86.9(1.5)N114(1.8)I
S_4	1.45	1.85	1.19	28.6	K40.6(1.6)g75.9S88.8(2.3)N119.6(2.8)I
S_5	1.53	2.04	1.18	26.0	K40.9(0.9)g75.3S89.9(2.2)N121.1(2.5)I
S_6	1.81	2.58	1.19	20.5	K40.1(0.1)g74.5S90.6(2.2)N122.7(2.0)I
S_7	1.87	2.80	1.22	18.9	g78.3S94.0(2.5)N130.8(3.2)I
PEO−Br	0.73	0.51	1.10	100	K60.9(154.1)I
B1	1.29	1.23	1.20	41.5	K54.2(79.8)g63.4S76.3(0.5)N99.4(0.3)I
B2	1.40	1.61	1.16	31.7	K51.6(48.0)g73.2S88.6(1.2)N115.5(1.6)I
B3	1.52	1.99	1.19	25.6	K48.0(26.6)g75.2S89.1(1.2)N120.0(1.8)I
B4	1.80	2.43	1.16	21.0	K42.1(8.4)g78.3S93.2(2.0)N125.2(2.3)I

[a] Given by GPC calibrated by PS standard

[b] Calculated by ^{1}H NMR according to Eq.4

$$M_n = M_{n,macroinitiator} + 396 \times 450 \times I_d / [4(I_a + I_h + I_g + I_k) - 7I_d] \qquad (\mathbf{4})$$

Where $M_{n,macroinitiator}$ is the molecular weight of PEO-Br_2 for calculating Mn of miktoarm star polymer and PEO-Br for calculating M_n of diblock polymer respectively. Others were mentioned previously.

[c] Calculated by ^{1}H NMR

[d] S = smectic phase, N = nematic phase, g = glassy phase, K = crystalline phase, I = isotropic phase

The transition temperatures and the corresponding enthalpy changes of all the samples obtained from the second heating were summarized in Table 2. Compared with the linear diblock polymer, the melting temperature of PEO in miktoarm star polymer decreased more rapidly, revealing that PEO was restricted. The PEO chain was inhibited from free stretch due to the AB_2 miktoarm star structure, which reflected the nonlinear structure of the obtained polymer. On the other hand, the phase transition temperatures of $T_{S\text{-}N}$, $T_{N\text{-}I}$ did not change much when PEO content was equivalent in both systems, revealing that PMMAZO chain was affected little in different structures.

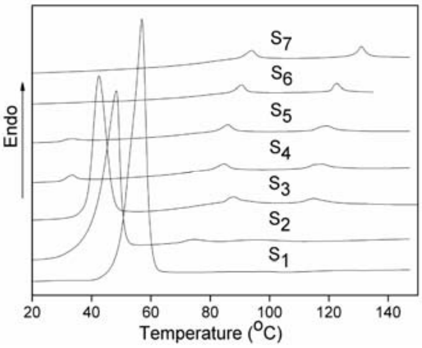


Figure 8. DSC heating curves of some miktoarm star copolymers

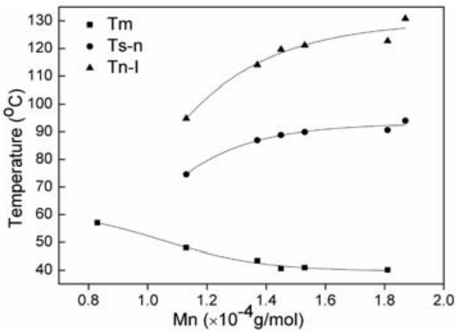
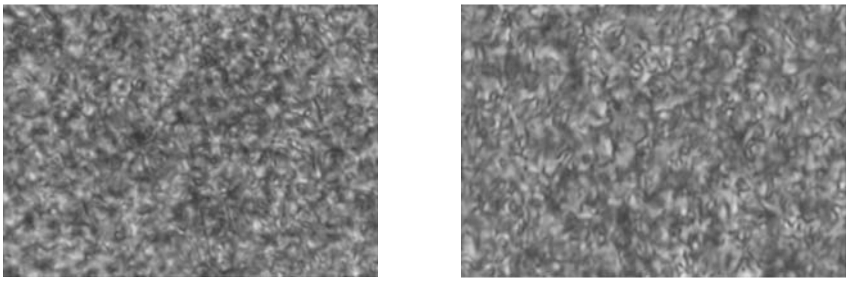


Figure 9. Dependences of T_m, $T_{S\text{-}N}$, and $T_{N\text{-}I}$ on Mn

As can be observed from Figure 8, the miktoarm star polymers PEO-$(PMMAZO)_2$ showed three dominant peaks, which can be assigned to the crystalline phase (K) transition, the smectic phase (S) - nematic phase (N) transition and the nematic phase (N) – isotropic (I) phase transition on second heating except for S_1 and S_7. Figure 9 shows T_m (of PEO segment), $T_{S\text{-}N}$, $T_{N\text{-}I}$ (of PMMAZO segment) as functions of molecular weight. As can be seen, T_m decreased rapidly along with Mn increasing, which revealed that the crystallinity of PEO was drastically affected by the PMMAZO segment. The melting peak even disappeared when Mn reached 1.87×10^4 g/mol (S_7). That was to say, PEO could lose its crystalline ability when the PMMAZO chain was long enough. The phase transition temperatures of $T_{S\text{-}N}$, $T_{N\text{-}I}$ increased remarkably when Mn was below 1.45×10^4 g/mol (Table 2). It was noticeable that $T_{S\text{-}N}$, $T_{N\text{-}I}$ could not be observed when macromolecular weight was low (8.3×10^3 g/mol, S_1). Similar reason could illustrate this phenomenon. When the length of PMMAZO chain was short, it provided little contribution to the character of miktoarm star polymer. Thus we can draw out that PEO and PMMAZO influence each other.



A B

Figure 10. Representative polarized micrograph of the texture of PEO-$(PMMAZO)_2$ (S_7): (A) 129°C; (B) 89°C (magnification: 400 ×)

To study the liquid crystalline behavior of the miktoarm star polymers, polarized optical microscope was used. Figure 10 shows a representative polarized micrograph of the texture of miktoarm star polymer S_7 taken at 129°C and 89°C respectively.

Conclusions

A series of novel miktoarm star polymers, PEO-$(PMMAZO)_2$, were prepared via atom transfer radical polymerization (ATRP) in copper mediated system. Kinetic study showed that molecular weight increased along with conversion and polydispersities were narrow (< 1.3), indicating the good control of the polymerization. DSC study revealed that the miktoarm star polymers exhibited a smectic and a nematic phase when the Mn of miktoarm star polymer was beyond 9.4×10^3 g/mol. The phase transition temperatures of $T_{S\text{-}N}$ and $T_{N\text{-}I}$ increased with increasing molecular weight of miktoarm star polymers, while the melting temperature of PEO decreased. Compared with diblock polymer PEO-PMMAZO, the melting temperature of PEO in miktoarm star polymer decreased more rapidly. Other properties of the novel amphiphilic miktoarm star polymers are in process.

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