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Study on Synthesis of Star-Shaped Poly(ethylene oxide) by Atom Transfer Radical Polymerization

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Star-shaped poly(ethylene oxide) (PEO) was prepared by atom transfer radical polymerization (ATRP) with a 2-bromoisobutyryl PEO ester as a macroinitiator. Divinylbenzene (DVB) and ethylene glycol dimethacrylate were employed as the coupling reagents. Several factors pertinent to star polymer formation are: type of coupling reagents and solvents, feed ratio of DVB to the macroinitiator, and reaction time. These were studied and used to optimize the star formation process. The optimum yield of star polymer was ca. 90–98%.

Keywords star polymer, synthesis, atom transfer radical polymerization (ATRP), poly(ethylene oxide) (PEO)

Introduction

As new polymer materials star polymers have attracted much interest due to their unique properties and important applications (1–3), the synthesis of star polymers from vinyl monomers with living anionic polymerization, cationic polymerization, and ring-opening metathesis polymerizations has been extensively investigated (4–6). Generally, there are two basic methods for preparing star polymers. One is the so-called "core-first" method of which a multifunctional initiator is used to initiate the polymerization of monomer to form a multi-arm star polymer (7–10). The other is the so-called "arm-first" method. A terminally reactive linear polymer initiates the polymerization of a cross-linkable monomer to form a microgel, from which a number of arms are anchored (4, 11–13). Recently, controlled/"living" radical polymerization has been used to prepare various well-defined polymers and complex architectures (14). One such method is atom transfer radical polymerization (ATRP) (15). ATRP is a convenient method for the preparation of star copolymers where a transition metal compound acts as a carrier of a halogen atom in a reversible redox process.

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Poly(ethylene oxide) (PEO) star polymers are regarded as a particularly promising class of materials, since they represent variable building blocks for structured polymer networks, e.g., hydrogels (16) or amphiphilic network systems (17). Due to the excellent biocompatibility of PEO, both the star precursors and the resulting networks are of interest for biomedical and pharmaceutical applications. Star-shaped PEO was prepared by anionic ring-opening polymerization of ethylene epoxy with multi-alcohol or hydroxyl-functionalized dendrimer as the initiators (18, 19). Recently, Chen et al. (20) reported the synthesis of star-shaped PEO by ATRP. However, the efficiency of the initiator is not high enough, which will affect the purity of the resulting star polymer. Thus, further study on the condition of the synthesis of star-shaped PEO is necessary.

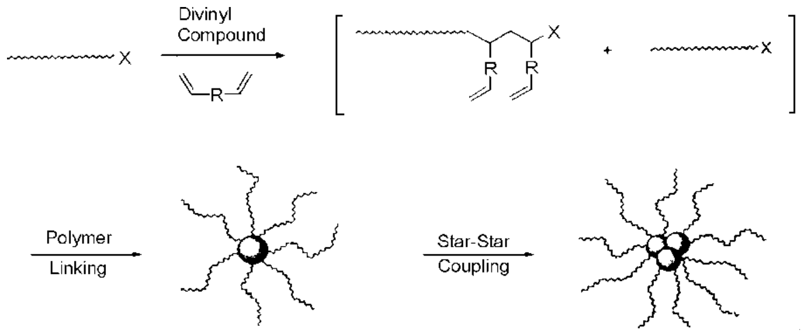
Here, we report the synthesis of star-shaped PEO by ATRP and the study on several factors pertinent to star polymer formation, in order to obtain the purer star-shaped PEO polymer. The synthesis route is shown in Scheme 1. Monmethoxyl PEO 5000 ($M_{n,NMR} = 5300\,g\,mol^{-1}$) was applied as the precusor of macroinitiator. It reacted with 2-bromoisobutyryl bromide to introduce an active species for ATRP. Initially, a few units of the divinyl coupling reagents were added to the PEO macroinitiator chain ends to form short block copolymers. The block copolymers containing the divinyl units then started to react with each other to form crosslinked cores, and this led to the formation of PEO star polymers. Finally, star-star coupling could occur, leading to the formation of high molecular weight PEO stars.

Experimental

Materials

Monmethoxyl PEO ($M_n = 5000$, Alfa) was dried by azeotropic distillation with toluene before use. Traces of residual toluene were removed under vacuum. Triethylamine (TEA) was refluxed with *p*-toluenesulfonyl chloride and then distilled. The resulting amine free TEA was stored over CaH_2. Before use, it was refluxed and distilled again.

4-(Dimethylamino)pyridine (DMAP) (Aldrich, 98%) was recrystallized from toluene. Methylene dichloride (CH_2Cl_2) (Shanghai Chemical Reagents Co., A. R. grade) was shaken with portions of concentrated sulfuric acid until the acid layer remained colorless, then washed with water, aqueous 5% sodium bicarbonate solution and with water again, and finally distilled from calcium hydroxide. Chlorobenzene (C_6H_6Cl),



Scheme 1. Synthesis of star PEO polymer.

benzene, anisole, O-xylene (Shanghai Chemical Reagents Co., A. R. grade) were purified by washing with concentrated sulfuric acid to remove residual thiophenes, followed by washing twice with water, once with 5% sodium carbonate solution, and again with water before being dried with anhydrous calcium chloride, Divinylbenzene (Aldrich, 80%, mixture of isomers) and ethylene glycol dimethacrylate (Aldrich, 98%) were distilled under reduced pressure and stored at −20°C. 2-bromoisobutyryl bromide (Aldrich, 98%), CuBr (Adrich, 99.99%), 2.2′-dipyridine (dipy) (Acros, 99%). Other reagents were all commercial products and used without further purification.

Methods

The ^{1}H-NMR spectra were recorded at 25°C on a INOVA-400 NMR spectrometer with chloroform-*d* as a solvent and with tetramethylsilane (TMS) as an internal standard. The number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) were measured on a water 1515 gel permeation chromatography (GPC) instrument with a set of HT3, HT4, and HT5, μ-Styragel columns with THF as an eluent (1.0 ml/min) at 35°C. Calibration was made with standard polystyrene (PS). Monomer conversions were determined from the concentration of the residual monomer on a Shimadzu GC-14 gas chromatograph equipped with a J&W Scientific 30 m DB-WAX column and a flame ionization detector with helium as the carrier gas.

Synthesis of PEO-Br Macroinitiator

A 250 ml three-neck round-bottom flask equipped with condenser, dropping funnel, gas inlet/outlet, and a magnetic stirrer was charged with DMAP (0.915 g, 7.5 mmol), PEO (25 g, 5 mmol), TEA (0.505 g, 5.0 mmol) and dry methylene dichloride (120 ml). After cooling to 0°C, 2.875 g (12.5 mmol) of 2-bromoisobutyryl bromide in 20 ml of CH_2Cl_2 was added to the formed yellow dispersion dropwise during 1 h under dry nitrogen; subsequently, the temperature was allowed to rise to room temperature. The reaction was continued under stirring for 18 h. The solution was filtered, half of the solvent was evaporated, and the PEO-Br macroinitiator was precipitated in cold diethyl ether. After dissolution in absolute ethanol, the solution was stored overnight to recrystallize. The macroinitiator was filtered, washed with cold diethyl ether, and dried in vacuum.

Synthesis of Star Polymers Using Macroinitiators

In a typical experiment, a dry glass tube with a magnetic stirrer was charged with CuBr (14.3 mg, 0.1 mmol), PEO macroinitiator (500 mg, 0.1 mmol), DVB (0.14 ml, 1 mmol), bipy (47 mg, 0.3 mmol), and o-xylene (0.14 ml). The glass tube was degassed by three freeze-pump-thaw cycles, sealed under vacuum, and then immersed in an oil bath thermostated at 110°C. After 24 h, the glass tube was taken out and broken. The sample was dissolved in THF, precipitated in petroleum ether after being passed through an alumina column to remove the copper complexes, and dried in a vacuum oven overnight at room temperature. The conversion of polymerization was determined by gravimetry.

Results and Discussion

Synthesis and Characterization of PEO-Br Macroinitiator and PEO Star Polymers

PEO-Br macroinitiator for ATRP was obtained by the reaction of PEO with 2-bromoisobutyryl bromide according to the literature (21). It was carried out at 0°C in CH_2Cl_2 in the presence of TEA and DMAP in order to avoid cleavage of the polymer chains as found in the case of other derivatizations of PEO (22).

The Br-functionality of the-prepared PEO ($M_{n,GPC} = 9800\,g\,mol^{-1}$, $M_w/M_n = 1.02$) as an isolated macroinitiator was probed by chain extension to a new block of PS or PMMA. Figure 1 displays the overlaid gel permeation chromatography (GPC) traces of the PEO macroinitiator. The relatively clean shift of the GPC traces toward higher molecular weights indicated that most of the PEO chain ends had reactive Br functional groups.

The PEO-Br macroinitiator was then used to initiate a suitable bis-unsaturated monomer (i.e., divinylbenzene) to form PEO star polymers by copper-mediated atom transfer radical polymerization. The reaction was carried out in suitable solution at 110°C. The reaction conditions and resulting PEO star polymers were summarized in Table 1.

The chemical structures of PEO, PEO-Br and the obtained PEO star polymers were characterized by a 400 MHz ^{1}H-NMR spectroscopy. In the ^{1}H-NMR spectrum of PEO (Figure 2a), the $-CH_2-CH_2-O-$ resonance is observed at 3.65 ppm. Figure 2b shows the typical ^{1}H-NMR spectrum of the resulting PEO-Br macroinitiator. The complete substitution of the hydroxyl group of PEO in $CDCl_3$ around 2.45 ppm disappeared after the esterification and two new signals appeared at 4.33 and 1.94 ppm due to the substituted PEO. The peak area ratio of a, b and d is 6 : 2 : 3, which also confirmed the complete esterification. Thus, the obtained PEO-Br macroinitiator is functionalized with a

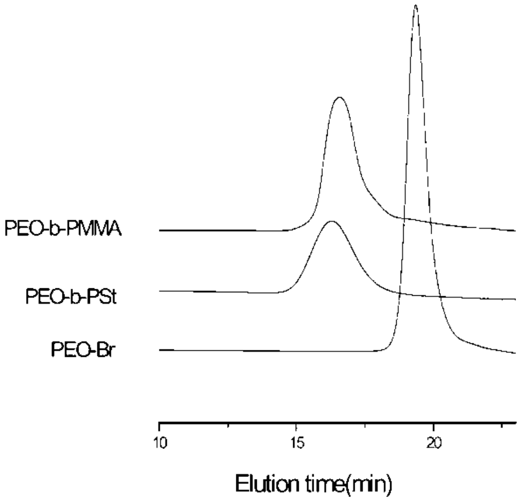


Figure 1. Synthesis of block copolymers with styrene and MMA using preformed PEO as the macroinitiator. $[PEO\text{-}Br]_0 = [CuBr]_0 = [bpy]_0/3 = 0.072\,M$; For styrene: $[styrene]_0 = 7.2\,M$, $T = 110°C$, reaction time = 6 h. For MMA: $[PMMA]_0 = 7.2\,M$, $T = 50°C$, reaction time = 2 h.

Table 1
Coupling reaction conditions and resulting star polymer

PEO star	Coupling reagent	Ratio[a]	Solvent	Time (h)	$M_{n,GPC}$ ($\times 10^{-4}$)	M_w/M_n	Yield[b] (%)	m[c]
S_1	EDGMA	12	Anisole	2				
S_2	DVB	12	Anisole	24	7.15	1.50	87.25	7.94
S_3	DVB	12	Benzene	24	8.02	1.67	86.15	8.91
S_4	DVB	12	Chlorobenzene	24	7.61	1.48	85.28	8.46
S_5	DVB	12	O-xylene	24	5.30	1.12	99.13	5.89
S_6	DVB	15	O-xylene	24	6.12	1.15	99.04	6.8
S_7	DVB	10	O-xylene	24	3.43	1.10	98.19	3.81
S_8	DVB	5	O-xylene	24	2.01	1.08	38.26	2.23
S_9	DVB	15	Anisole	24	7.34	1.42	98.69	8.15
S_{10}	DVB	15	Anisole	1	0.94	1.40	/	1.04
S_{11}	DVB	15	Anisole	5	3.32	1.24	53.16	3.69
S_{12}	DVB	15	Anisole	15	5.01	1.27	76.18	5.57

[a] Ratio: the divinylbenzene to Macroinitiator ratio on the synthesis of PEO star polymers.
[b] Yield: coupling efficiency.
[c] m: is the average number of arms per star polymer, calculated according to Eq. (2).

ω-α-bromoisobutyryl group. Comparing the integral ratio of signals (a) and (c), molecular weight of PEO-Br was estimated to be 5500 g mol^{-1}, different from the value 9800 g mol^{-1} measured by GPC (GPC results: PEO-Br : $M_n = 9800$ g mol^{-1}, $M_w/M_n = 1.02$). This discrepancy may be attributed to its hydrodynamic behavior in THF solution. The molecular weight of PEO-Br macroinitiator is a little bigger than the molecular weight of PEO estimated by ^{1}H-NMR ($M_n = 5300$ g mol^{-1}), which showed that no cleavage of the polymer chains occurred during the esterification as reported in the literature (22).

The ^{1}H-NMR spectrum of PEO star polymer (Figure 2c) shows the broad peaks in the region of 5.0–7.3 ppm with low intensity corresponding to the protons of PDVB, which demonstrate the formation of PDVB microgel (11). The peaks at 3.65 ppm are assigned to the protons of $-CH_2-CH_2-O$ in PEO arms. These data illustrate the presence of PDVB microgel and PEO arms in the PEO star polymer. The weight fractions of PEO in PEO star polymers were evaluated by means of ^{1}H-NMR spectroscopy from the integral ratio of the signals originated from the PEO arms at 3.4–3.8 ppm (signal (c), 4H, $-CH_2-CH_2-O$] and the PDVB microgel region (5.0–7.3 ppm) [signal (e), 4H, Ph] according to the following equation:

$$\text{PEO\%} = (I_c \times 44/4)/[I_c \times 44/4 + I_e \times 130/4] \quad (1)$$

where I_c and I_e are the integral of the signals c and e; 44 and 130 are the molar masses of $-CH_2-CH_2-O$ repeat unit in PEO segment and DVB, respectively.

Then according to the following equation, we can estimate the arm numbers:

$$m = (M_{w,\text{PEOstar}} \times \text{PEO\%})/(M_{\text{NMR,PEO}} \times \text{PDI}_{\text{GPC}}) \quad (2)$$

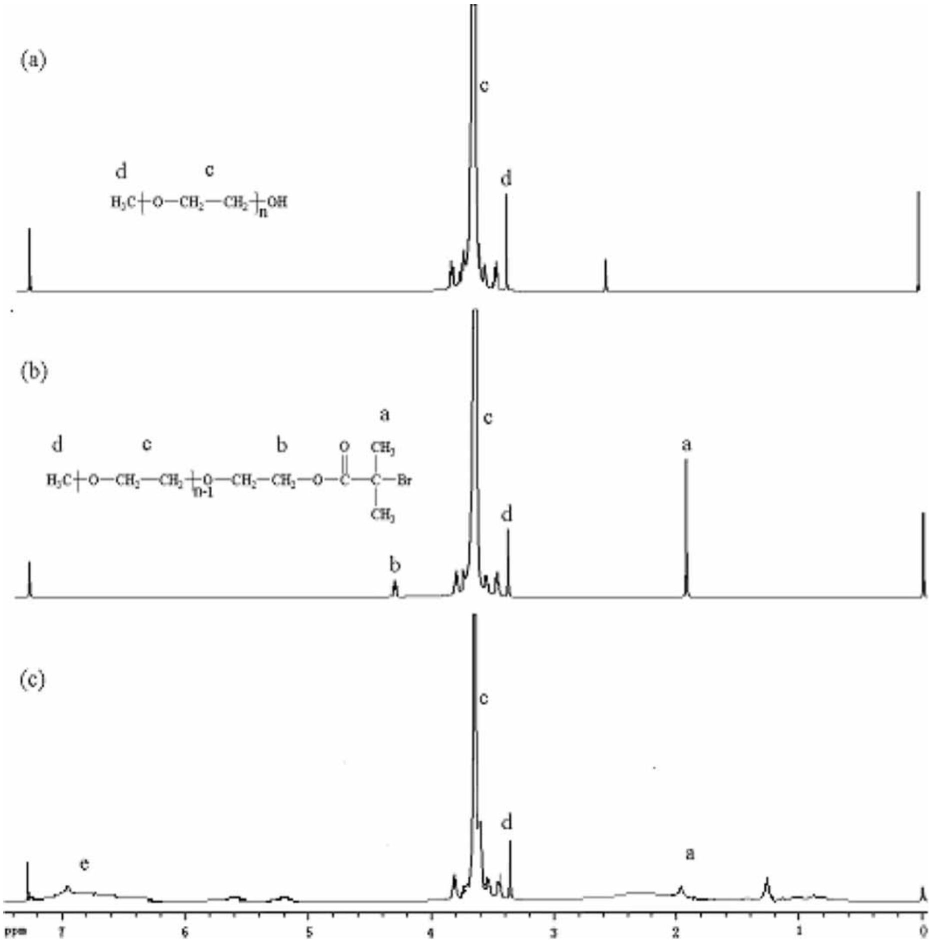


Figure 2. ^{1}H-NMR spectra of (a) PEO, (b) PEO-Br and (c) PEO star polymer.

where $M_{w,PEOstar}$ is the absolute molecular weight of PEO star polymer, measured by GPC with a LS detector.

Effect of the Coupling Reagent

Two commercially available divinyl reagents, divinylbenzene (DVB) and ethylene glycol dimethacrylate (EGDMA), reacted with the PEO macroinitiator by ATRP with CuBr complexed with bipy as the catalyst in o-xylene at 110°C. These two divinyl reagents were chosen so that the effect of the coupling moiety (styrenic and methacrylic) on the star formation can be studied. Under the reaction conditions, DVB led to the formation of a soluble star polymer without gelation after 28 h. In contrast, an insoluble polymer was obtained after 1 h in the presence of EGDMA. These results indicate the importance of choosing an appropriate divinyl coupling reagent. EGDMA used as the coupling reagent led to extensive polymer crosslinking and star-star coupling to form an insoluble gel. DVB has a high affinity to radical addition and a low selfpropagation rate, which favors star formation for PEO macroinitiators under ATRP conditions.

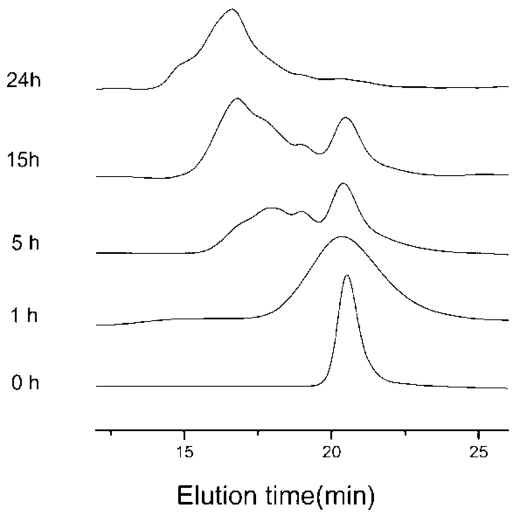


Figure 3. Formation of PEO star polymers in the presence of DVB at various reaction time. $[\text{PEO-Br}]_0 = [\text{CuBr}]_0 = [\text{bpy}]_0/3 = 0.072\,\text{M}$ in anisole. T = 110°C.

Effect of Reaction Time

The effect of reaction time on star PEO formation was studied (Figure 3). After 1 h, broad molecular weight distribution without a significant increase in molecular weight was observed, indicating the formation of PEO-DVB block copolymers. Then the DVB units in the block copolymer started to react with each other and formed star polymers. After 15 h, most of the PEO macroinitiators had participated in the star polymer formation. Longer reaction time resulted in an increasing amount of star-star coupling, and slowly decreasing the amount of residual PEO macroinitiator. After 24 h, the

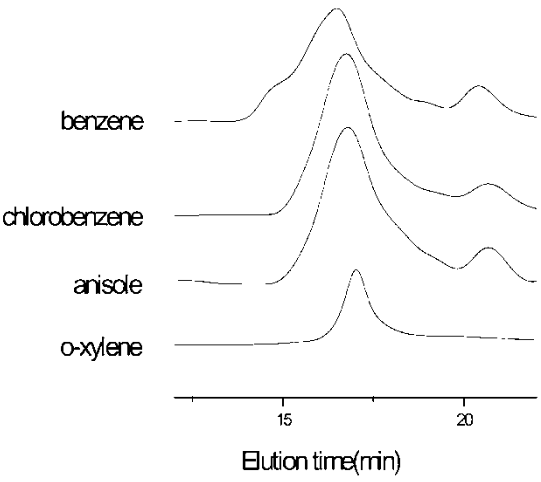


Figure 4. Synthesis of PEO star polymers in the presence of DVB in various solvents. $[\text{PEO-Br}]_0 = [\text{CuBr}]_0 = [\text{bpy}]_0/3 = [\text{DVB}]_0/12 = 0.072\,\text{M}$, T = 110°C, reaction time = 24 h.

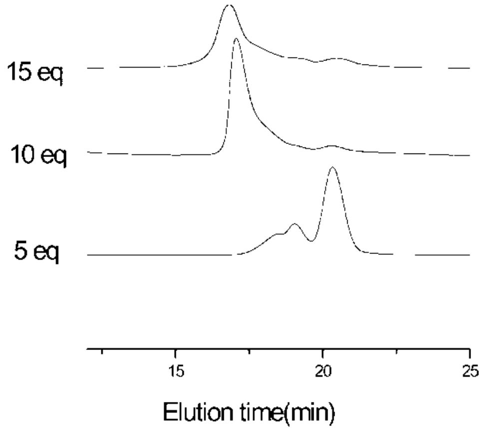


Figure 5. Effect of the divinylbenzene to Macroinitiator ratio on the synthesis of PEO star polymers. $[PEO\text{-}Br]_0 = [CuBr]_0 = [bpy]_0/3 = 0.072\,M$ in o-xylene (x = 5, 10, 15, or 20), T = 110°C, reaction time = 24 h.

shoulder peak of PEO macroinitiator almost disappeared in the GPC trace of the star polymer, indicating the complete star formation.

Effect of Solvent

Solvent influenced the star polymer formation to some extent. Here, we used DVB as the coupling reagent. After the reaction time (24 h), star polymers formed in benzene showed significantly higher molecular weights and broader molecular weight distributions than those obtained in polar solvents (Figure 4). In addition, the reaction in benzene led to higher conversions of DVB and higher degrees of crosslinking indicated by the formation of some insoluble star polymers (gels). These results may show that a nonpolar solvent such as benzene was a relatively poor solvent for the copper(II) complex, whereas a lower concentration of copper(II) complex could lead to a higher concentration of radicals and faster radical termination reactions. Polar solvents, such as chlorobenzene and anisole provided star polymers with similar molecular weight distributions and DVB conversions. O-xylene, used as a solvent afforded star polymers a lower molecular weight distributions and a rather smaller amount of the residual PEO macroinitiator, probably due to the relatively suitable solubility of copper(II) complexes and PEO units in this solvent.

Effect of the Ratio of DVB to Macroinitiator

The effect of the ratio of the DVB to PEO macroinitiator was investigated (Figure 5). It was found that the ratio between 10 and 15 was optimal for the star formation. A lower ratio of the DVB to PEO macroinitiator led to a lower yield of star polymers, while a higher ratio of DVB to PEO (e.g., DVB/PEO 20) led to the formation of an insoluble gel in 5 h without increasing the yield of star polymer markedly.

Conclusions

Star-shaped PEO was prepared by the coupling of PEO macroinitiators in the presence of divinylbenzene by using copper-mediated ATRP. Several factors pertinent to star formation, including the choice of solvent, the ratio of DVB to PEO and the reaction time, were studied.

Acknowledgements

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