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Synthesis of functionalized poly(ethylene oxide) macromonomers

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Abstract

Functionalized poly(ethylene oxide) (PEO) macromonomers (α-tertiary amino and ω-methacryloyl groups) were prepared by ring-opening polymerization of living PEO anions using 2-[2-(*N*,*N*-dimethylamino)-ethoxy]ethanol potassium alkoxides as an initiator with glycidyl methacrylate. Terminal double bond functionality was controlled in the range of 1–1.5 per molecule in toluene as the hydrocarbon solvent. However, gelation was observed upon such ring-opening polymerization system in tetrahydrofuran solvent. These macromonomers can be applied for the synthesis of peripheral functionalized stars and polymer brushes as the starting materials. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: PEO macromonomer; Ring-opening polymerization; Terminal amino group

1. Introduction

Star-branched or radial polymers have the structure of linked polymers with a core of small molecular mass. Interests in star polymers arise from their compactness and from their enhanced segment density. Homopolymerizations of macromonomers provide regular multibranched polymers with a branch density, as it is called ‘polymer brushes’. Such polymer brushes show the formation of lyotropic phases due to the overcrowded bulky side chains. Star polymers are usually prepared by coupling of anionic living polymers with multifunctional electrophilic coupling agents. In general, it is difficult to extend the arm numbers of the stars with such coupling agents. At present, the most convenient way to prepare star polymers possessing more than 10 arms is the copolymerization of monocarbanionic chains with divinylbenzene (DVB) [1–3]. However, this copolymerization sometimes led to gelation, and the stars obtained showed a broad molecular weight distribution.

More recently, we have established a novel architecture for polyisoprene (PI) stars by means of organized polymerization in micelles [4]. In free radical copolymerization of vinylbenzyl-terminated PI macromonomers with DVB, the primary copolymer radicals composed of PI and a few sequence units of DVB (resembling the structure of block copolymer) may be produced in the initial stage. Such primary copolymer radicals formed micelles in a selective solvent such as aliphatic hydrocarbon at more than the critical micelle concentration. In this organized assembly, the star polymers were formed by copolymerization of PI macromonomers with DVB.

We also investigated in detail the structural ordering of such stars by means of small-angle X-ray scattering (SAXS) [5]. PI stars (arm number $n >$ ca. 90) formed a body-centred cubic (bcc) structure near the overlap threshold (C^*). This structure changed to a mixed lattice of bcc and face-centred cubic (fcc) structures with increasing polymer concentration. It is interesting to study the peripheral charge effect of stars on the lattice formation in solution. Therefore, we prepared the functionalized star-shaped PI possessing peripheral amino groups [6]. Subsequently, positive charges were introduced to such peripheral tertiary amino groups by quaternization reaction. However, the solubility of these stars in organic solvents decreased extensively due to hydrophilic ionic groups [7]. In order to study the peripheral charge effects of stars on the lattice formation, it is necessary to prepare the functionalized amphiphilic (or water-soluble) star-shaped polymers.

In this article, we mention the synthesis of functionalized poly(ethylene oxide) (PEO) macromonomer having terminal tertiary amino groups.

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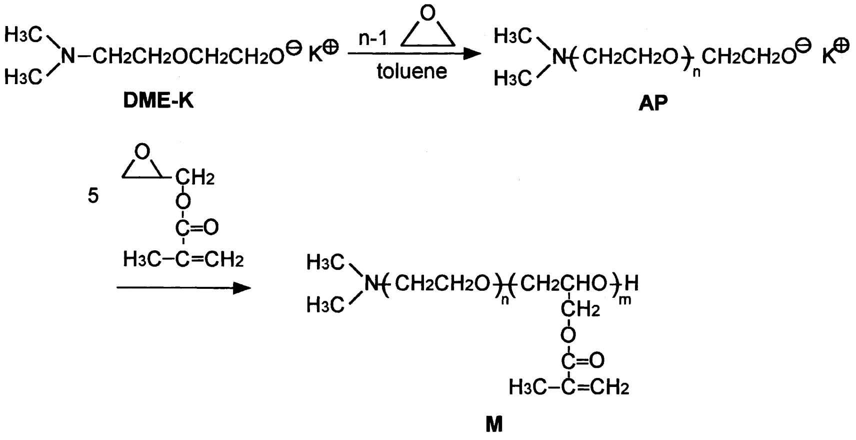

Scheme 1.

2. Experimental

2.1. Synthesis of funtionalized PEO macromonomers

2-[2-(*N*,*N*-dimethylamino)ethoxy]ethanol potassium alkoxide (DME-K) as an anionic initiator was synthesized by the reaction of corresponding alcohol with potassium metal in toluene. The synthetic route of functionalized PEO macromonomers is shown in Scheme 1. Functionalized PEO macromonomers were prepared by living anionic polymerization technique under high vacuum using the break-seal method. Ethylene oxide (EO; 3 M Steri-EO Gas) and glycidyl methacrylate were dried over calcium hydride and then distilled under vacuum. Toluene was dried over sodium metal and then purified with butyllithium under vacuum. Tetrahydrofuran (THF) was purified with α-methylstyrene tetramer sodium under vacuum. First, PEO anions (AP) were prepared by anionic polymerization of EO initiated by DME-K in toluene at 20°C for 140 h, then rising the temperature up to 60°C for 100 h.

Synthesis of functionalized PEO macromonomers was followed by two methods: (1) such PEO anions were quenched with a small amount of glycidyl methacrylate (fivefold amount with respect to PEO anion ends) in toluene at 60°C; (2) after evaporating toluene from PEO solution, PEO anions were quenched with glycidyl methacrylate in THF at 40 or 60°C. After reaction, the resulting solution was poured into a large excess of hexane. Such product was purified by reprecipitation from benzene solution with hexane.

2.2. Characterization

The number-average molecular weight ($\bar{M}_n$) of the PEO precursor was determined by vapour pressure osmometer (VPO) on a Corona NA 117 in benzene. The polydispersity ($\bar{M}_w/\bar{M}_n$) was determined by gel permeation chromatography (GPC; Tosoh high-speed liquid chromatograph HLC-8020) with chloroform as the eluent at 38°C, two TSK gel columns, GMH_{XL} and $G2000H_{XL}$, in series and a flow rate of 1.0 ml min^{-1}.

The methacryloyl groups of PEO macromonomers were

Table 1
Reaction conditions and results of functionalized PEO macromonomers (PEO anions were quenched with a small amount of glycidyl methacrylate, fivefold amount with respect to PEO anion ends)

Expt. No.	PEO precursor		Solvent	Temperature (°C)	Time (h)	Functionality[c] (number per molecule)
	$\bar{M}_n$[a]	$\bar{M}_w/\bar{M}_n$[b]				
M11	3200	1.08	Toluene	60	20	1.10
M12					40	1.23
M13					71	1.52
M21	2600	1.12	THF	40	3	0.79
M22					29	0.59
M23					59	–[d]
M31	3400	1.09	THF	60	5	0.94
M32					10	0.76

[c] Determined by ^1H NMR in $CDCl_3$.

[a] Determined by VPO in benzene.

[b] Determined by GPC.

[d] Observed gelation.

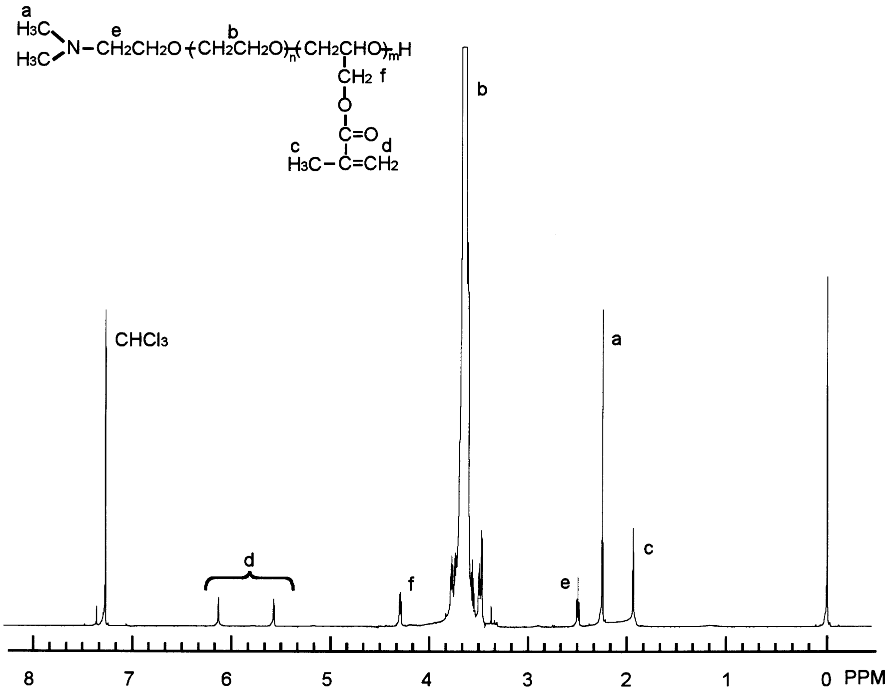

Fig. 1. ^{1}H NMR spectrum of PEO macromonomer M11 in $CDCl_3$.

determined by ^{1}H nuclear magnetic resonance (NMR; 500 MHz, JEOL GSX-500 NMR spectrometer) in $CDCl_3$.

3. Results and discussion

Since simple potassium alkoxides are well known to initiate the living polymerization of EO with a reasonable rate and a good functionality [8–11], we synthesized the potassium alkoxide initiator DME-K having a tertiary amino group. Preliminary experiments toward the polymerization of EO were carried out in toluene, varying the reaction temperature. The monomer conversion was 11% only even after 240 h at 20°C. Therefore, the anionic polymerization was performed under very severe conditions, namely at 20°C for 140 h, then rising the temperature up to 60°C for 100 h as mentioned in the experimental part. As a result, the monomer conversion reached more than ca. 95% under such conditions.

Table 1 lists the reaction conditions and results of functionalized PEO macromonomers. All the GPC profiles for PEO precursors were unimodal. The molecular weight distributions of these products were very narrow ($\bar{M}_w/\bar{M}_n = 1.08$–$1.12$). Each observed value of M_n from VPO measurements was almost identical to the calculated value. It was concluded from these facts that the polymerization of EO initiated by DME-K proceeded via a living anionic mechanism.

The ring-opening polymerizations of functionalized PEO anions with glycidyl methacrylate were carried out in toluene at 60°C, varying the reaction times (see M11–M13 series). Typical ^{1}H NMR spectrum of M11 is shown in Fig. 1. In addition to the signal of the ethylene protons (b: $-CH_2CH_2-$, δ 3.6 ppm) of PEO and methylene protons adjacent to amino group (e: $>NCH_2-$, 2.5 ppm), the spectrum exhibits the expected resonances assignable to methylene protons (d: =CH2, 5.6 and 6.2 ppm), α-substituted methyl protons (c: $-CH_3$, 1.9 ppm) of double bonds, and methyl protons (a: $-CH_3$, 2.3 ppm) of the amino functional initiator. Moreover, the characteristic peak signal of hydroxyl protons (–OH: PEO precursor) at 2.8 ppm disappeared in this spectrum. (It is also a fact that the magnitude of the hydroxyl protons is much too small relative to the protons from the repeating units of the backbone.) The integration ratios of signals a:d or e:d were close to 3:1.1 or 1:1.1, respectively, within experimental error. It is therefore found that the functionality of M11 macromonomer was 1.10 per molecule. These functionalities increase gradually with increasing the reaction temperature in toluene as a reaction medium (see M11–M13). However, the ring-opening rate of glycidyl methacrylate with PEO anion was very slow in such reaction conditions. It is the direct cause that the ring-opening anionic polymerization of glycidyl methacrylate proceeded by essentially secondary alkoxide catalyst as the active species.

To accelerate the ring-opening rate, such polymerizations were carried out in THF as a polar solvent, varying the reaction temperatures (M21–M23 and M31–M32). The aggregation behaviours were observed during ring-opening polymerizations in all the experimental series. Especially, the polymerization system of M23 led to gelation. Functionalities listed in Table 1 indicate those of soluble parts for

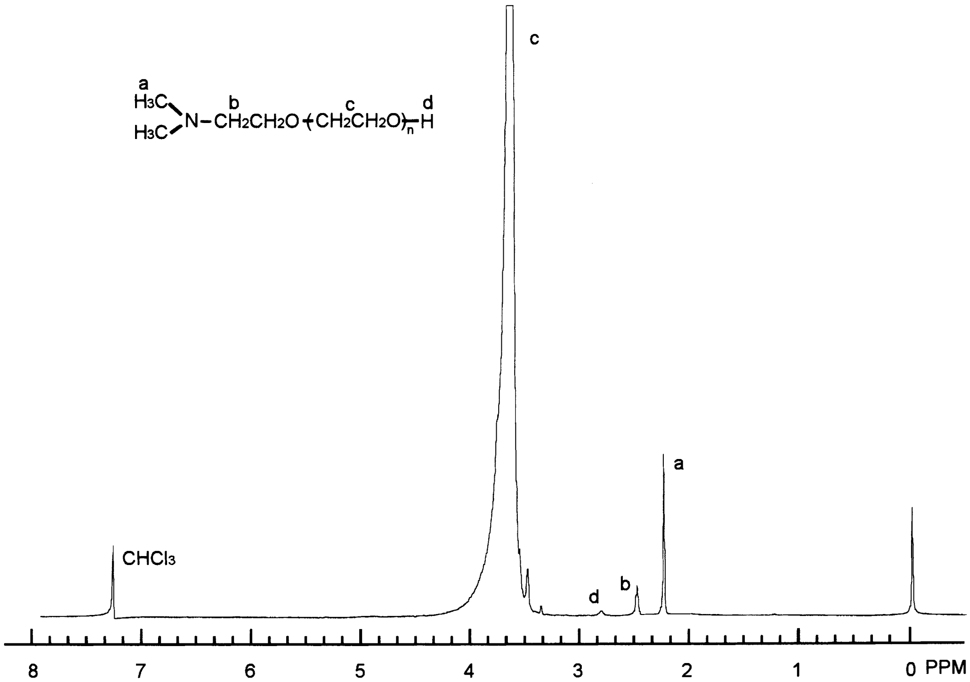

Fig. 2. ^{1}H NMR spectrum of reaction product between α-tertiary amino, ω-hydroxyl PEO precursor and glycidyl methacrylate in THF.

reaction products. Functionalities decrease with increasing the reaction time for both experiments, regardless of the variation of the reaction temperatures. These facts mean the existence of some kinds of side reactions in THF as a polar solvent. Michael addition may be possibly taking place. That is to say, nucleophilic terminal amino groups of PEO macromonomers (M) produced attack to activated carbon–carbon double bonds of α,β-unsaturated carbonyl compounds. In order to recognize the above concept, we carried out the reaction of α-tertiary amino, ω-hydroxyl PEO precursor (PEO anions AP were quenched with water) with glycidyl methacrylate in THF under the same reaction conditions as the experiment M23. ^{1}H NMR spectrum of the reaction product is shown in Fig. 2. As shown by signal assignment of polymer structure, this spectrum is identical to that of PEO precursor. It was concluded that Michael addition did not take place in the process of such macromonomer synthesis.

It may very possibly be produced as other side reactions that potassium alkoxide DME-K not only leads to the ring-opening polymerization of epoxy groups but also adds to double bond of glycidyl methacrylate. In general, alkyl alkoxide cannot initiate methacryloyl groups in hydrocarbon solvent. However, Goode et al. [12] reported that potassium alkoxide led to anionic polymerization of methyl methacrylate in polar solvent such as liquid ammonia. So, we carried out the reaction of the initiator DME-K with glycidyl methacrylate in THF at 40°C. As a result, the reaction system led to macro-gelation after ca. 10 h.

The functionality of PEO macromonomers can be controlled to be about unity in toluene as a non-polar solvent by varying the reaction time. We are investigating to establish a novel architecture of amphiphilic PEO stars having peripheral amino groups by free radical copolymerization of functionalized PEO macromonomer with DVB or ethylene glycol dimethacrylate as the cross-linking reagent in micelles. Current investigations are under way and will be reported in the near future.

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