Preparation and characterization of a novel star ABC triblock copolymer of styrene, ethylene oxide, and methacrylic acid

Zaijun Lu, Sheng Chen, Junlian Huang*

Department of Macromolecular Science, Fudan University, The Open Laboratory of Molecular Engineering of Polymer, Education Ministry of China, Shanghai 200433, China

(Received: January 4, 1999; revised: March 4, 1999)

SUMMARY: The preparation of a star triblock copolymer based on polystyrene, poly(ethylene oxide), and poly(methacrylic acid) blocks (S-St-EO-MAA) is described. The polymer structure was achieved by the following route: the polystyrene macroanion (PSₘ) was formed first by a butyllithium-initiated polymerization of styrene and capping with Michler’s ketone; the resulting N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethanol (TDDM)-terminated polystyrene was further reacted with metal potassium. The oxo-anion initiated the ring-opening polymerization of ethylene oxide, and the desired ABC triblock copolymer was obtained by precipitation polymerization of methacrylic acid (MAA) initiated with a charge transfer complex (CTC) under UV irradiation using benzene as a solvent. The complex is composed of PS-b-PEO with a TDDM end group (PS-b-PEOₘ) and benzophenone (BP).

Introduction

The design and preparation of new well-defined block copolymers with different blocks in structure and polarity represent a molecular level architecture with monomeric building blocks. These model materials have facilitated many studies on polymers, such as microphase separation, the relationship of morphology and composition, unperturbed dimensions, and rheology.

Hadjichristidis et al. have prepared a star triblock copolymer with three different arms, i.e., polystyrene, polybutadiene, and polyisoprene via the successive coupling of the corresponding living macroanions with methyltrichlorosilane in strictly calculated feed ratios. Fujimoto et al. have reported the preparation of a triblock copolymer of poly(dimethylsiloxane), polystyrene, and poly(tert-butyl methacrylate). The synthetic approach involves the reaction of PS Li⁺ with a diphenylethyleneterminated poly(dimethylsiloxane), followed by polymerization of tert-butyl methacrylate with the formed −CH₂C-(Ph₂)Li⁺ group. Quick described a novel strategy to synthesize star triblock copolymers using macromonomers functionalized with 1,1-diphenylethylene groups.

Nevertheless, only a few samples of this kind of special triblock copolymers, such as polystyrene-polybutadiene-poly(methyl methacrylate), polystyrene-poly(ethylene oxide)-poly(e-caprolactone), and others, have been reported because of the difficulties in synthetic technology.

In a previous paper, we described the preparation of a star triblock copolymer with poly(ethylene oxide), polystyrene, and polymethacrylate by combination of anionic and charge transfer polymerizations using p-aminophenol as a parent compound. The weak point of this method is the time-consuming separation procedure of the final copolymer from the mixture.

In the present work this synthetic approach has been improved and applied to prepare a new model star triblock copolymer with different arms, i.e., poly(ethylene oxide), polystyrene and poly(methacrylic acid), in which the last poly(methacrylic acid) block was obtained by precipitation polymerization of methacrylic acid (MAA) initiated with a charge transfer complex (CTC) under UV irradiation using benzene as a solvent. The complex is composed of PS-b-PEO with a TDDM end group (PS-b-PEOₘ) and benzophenone (BP).

Experimental part

Materials

Styrene (St) (Shanghai First Chemical Reagent Factory, China) and ethylene oxide (EO) (Shanghai Gao Qiao Third Chemical Industrial Factory, China) were dried with calcium hydrate and distilled. Methacrylic acid (MAA) (Shanghai Wu Lian Chemical Industrial Factory) was purified by distillation under reduced pressure. Michler’s ketone (MK) (Shanghai Wu Lian Chemical Industrial Factory) was purified by distillation under reduced pressure. Michler’s ketone (MK) was recrystallized twice with ethanol and the m.p. of the purified product is 173–175 °C. Benzophenone (BP) was also purified by recrystallization with ethanol; the m.p. of the recrystallized product is 47–49 °C. All other solvents were purified by standard methods.

Preparation of PS with a Michler’s ketone end group (PSₘ)

The PS macroanion was synthesized by common anionic technology using butyllithium as an initiator at room temperature in cyclohexane; an aliquot of the polymer solution was taken out for gel permeation chromatography (GPC) measurements before the addition of Michler’s ketone.
Preparation of capped PS and its reaction with metal potassium is described in Scheme 1.

A 100 mL ampoule charged with 1.35 g (5.0 \times 10^{-3} \text{ mol}) MK was evacuated, then 58 mL (1.82 \times 10^{-2} \text{ mol/L}) of the above-mentioned living PS macroanion solution was added dropwise at room temperature in 20 min, and the mixture was stirred for 4 h. The capped polymer was precipitated in methanol and purified by repeated dissolution/precipitation with trichloromethane/methanol until no special absorption of the aromatic amine at 310 nm was detected by UV spectroscopy.

Reaction of PS\textsubscript{m} with metal potassium

Into a 100 mL ampoule 1.6 g (2 \times 10^{-4} \text{ mol}) of PS\textsubscript{m}, 20 mL of dried tetrahydrofuran (THF) and 0.3 g (7.7 \times 10^{-3} \text{ mol}) of potassium were introduced. The reactor was degassed three times by a freeze-pump-thaw cycle, then irradiated at 25 °C for 24 h by a 300 W high-pressure mercury lamp (DDZ-300 from the Shanghai Ya Ming Lamp Factory). A cupric sulfate aqueous solution was used as a photofilter to obtain 365 nm monochromatic light. A copper salt precipitated during the polymerization due to the insolubility of the MAA polymer in the benzene solution. Thus the unreacted PS-b-PEO\textsubscript{m} was easily removed due to its solubility in benzene. The crude S-PS-PEO-PMMA was purified by extraction with trichloromethane for 50 h to remove the possibly remaining PS-b-PEO\textsubscript{m} and with water for another 50 h to remove the homopolymer of MAA. The purified product weighed 0.8 g (Scheme 3).

Instruments

IR spectra were recorded on a Perkin-Elmer 983 G spectrometer; \textsuperscript{1}H NMR spectra were obtained by a Bruker MSL-300 spectrometer, trichloromethane and dimethyl sulfoxide-\textit{d} \textsubscript{6} as solvents, and tetramethylsilane as internal standard; UV spectra were taken on a 756 MC UV-Vis spectrophotometer (Shanghai Third Analytical Instrument Factory, China); number-average molecular weight and molecular weight distribution (MWD) were derived with a Shimadzu LC-3A gel permeation chromatograph (GPC), UV detector, \textit{N},\textit{N}-dimethylformamide as solvent and eluent. Monodisperse PS samples were used as standards for calibration.
Results and discussion

Capping reaction of the PS macroanion with Michler’s ketone

The reaction of MK with the PS macroanion was conducted rapidly, the red PS anion was turned into a yellow green as soon as it was added to MK. Fig. 1 shows the UV spectra of the model compound N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane (TDDM) (A), PS (B), and PS_m (C). Comparing with PS and TDDM, the peaks of PS_m at 263 and 271 nm could be attributed to the π→π* transition of the benzene ring and the peak at 310 nm to the n→π* transition of the end group of PS_m. The capping efficiency could also be derived from the UV spectra on the basis of a linear relationship between the concentration of TDDM and its corresponding absorbance at 310 nm in dilute solution. The measured value is as high as 100%.

Characterization of PS-b-PEO_m

Fig. 2 shows the IR spectrum of the block copolymer. The peak at 1108 cm⁻¹ (C=O) attributed to the PEO block and at 3206 (benzene ring C-H) and 1599, 1490, and 1449 cm⁻¹ (benzene ring bend vibration) attributed to the PS block confirmed the formation of PS-b-PEO_m. From the 1H NMR (Fig. 3), the chemical shifts of 1.42 (–CH₂–), 1.84 (–CH – of the benzene ring), 3.64 (–CH₂CH₂O–), and 6.46–7.09 (benzene ring) also established the existence of PS-b-PEO_m. Fig. 4 (A) shows the UV spectrum of the diblock copolymer: the π→π* transition of the benzene ring at 263 and 275 nm and the n→π* transition at 310 nm which is nearly the same as PS_m (B). That means the TDDM functional group is still attached to the block copolymer after the copolymeriza-
Preparation and characterization of a novel star ABC triblock copolymer of styrene, ethylene oxide, and methacrylic acid

The block copolymer PS-b-PEO is really formed by a ring-opening polymerization of EO which is initiated by the PS<sub>m</sub> oxo-anion. The initiating efficiency measured by gravimetric methods was about 70%. Fig. 5 shows the GPC data. In comparison with PS<sub>m</sub> (A) (M<sub>n</sub> 8000, M<sub>n</sub>/M<sub>n</sub> 1.21), the peak (B) with molecular weight 15000 and M<sub>n</sub>/M<sub>n</sub> 1.26 supplied a direct evidence for the occurrence of the block copolymer.

**Determination of S-PS-PEO-PMAA**

As Scheme 3 describes, the TDDM is located on the connection point between PS and PEO blocks, and there are two N,N-dimethylaniline groups, or in other words, four methyl groups in TDDM that can constitute the CTC with BP under UV irradiation. Ledwith<sup>13</sup> has successfully prepared block copolymers with different chain structure by...
controlling the feed ratio of ternary amine and BP. In order to obtain the desired copolymer of S-PS-PEO-
PMAA, the used feed ratio of PS-b-PEO₉₆ vs. BP was
fixed at 1:1 (mol/mol). In the preparation of the last
block PMAA, benzene was used as a solvent, and the pro-
duct was precipitated from the solution. The unreacted
PS-b-PEO₉₆, BP, and MAA were soluble and remained in
the benzene solution. Thus the isolation and purification
of S-PS-PEO-PMAA was a very simple procedure.

Fig. 6 indicates the IR spectrum of the final copolymer,
the appearance of peaks at 1715 (−C=O) and 3448 cm⁻¹

Fig. 4. UV spectra of PS-b-PEO₉₆ (A) and PS₉₆ (B); solvent:
benzene, concentration of (A) and (B): 2.42×10⁻⁵ and
3.35×10⁻⁵ mol/L, respectively

Fig. 5. GPC measurement of PS₉₆ (A), PS-b-PEO₉₆ (B), and S-
PS-PEO-PMAA (C)

Fig. 6. IR spectrum of S-PS-PEO-PMAA
Preparation and characterization of a novel star ABC triblock copolymer of styrene, ethylene oxide, and methacrylic acid

(—OH of carboxyl) beside the characteristic peaks for PEO and PS blocks confirms the PMAA block formation. The proton chemical shifts of 12.3 (—OH of carboxyl) and 0.9–1.1 ppm (—CH₃) in the NMR spectrum (Fig. 7) beside the protons signals of PEO and PS also shows the existence of the PMAA block.

As it is well known the hydrodynamic volumes of star block copolymers are quite different from the linear PS standards, especially when the polarity and the structure of the copolymer blocks are sharply different from each other. Thus the GPC results for S-PS-PEO-PMAA using PS as standard samples are unreliable. Nevertheless, the GPC diagram (Fig. 5(C)) could still give the following information: (1) only one peak with a corresponding molecular weight 54000 appeared, that means no other copolymers with multi-blocks of MAA were formed; (2) the molecular weight distribution of the copolymer is 1.4, which is rather narrow, indicating that only one methyl group of TDDM can constitute a CTC with BP under UV irradiation and then initiate the polymerization of MAA. If more than one methyl group would constitute the CTC with BP, multi-blocks of MAA would be formed in the copolymer, and peaks with different molecular weights or with much wider molecular weight distribution should appear.

In order to confirm the reliability of the above-mentioned conclusions, a set of comparing experiments using the small molecules TDDM and BP with different ratios as a binary system to initiate the polymerization of MAA was carried out. Tab. 1 summarizes the experimental results. When the mole ratio of TDDM vs. BP was 1:1, a single peak with molecular weight 20000 and $M_w/M_n$ 1.5 appeared in the GPC diagram, and the conversion of monomeric MAA was about 14.1%; when the mole ratio was turned to 1:2, there appeared a shoulder peak with a corresponding molecular weight 11000 and $M_w/M_n$ 1.7 beside the main peak with a corresponding molecular weight 19000 and $M_w/M_n$ 2.0, and the conversion increased to 23.8%. That means, in this case more monomer participated in the reaction due to the more radical species formed, so the conversion increased and two peaks appeared. If the ratio was turned to 1:3 and 1:4, no new peaks could be detected and the conversion of MAA was nearly the same as for the ratio of 1:2; that means, in our experimental conditions only two methyl groups could attend the reaction no matter how many times the BP content was increased. Thus it can be concluded that when the feed ratio of PS-b-PEOₘ vs. BP was 1:1 (mol/mol), only one methyl of the TDDDM end group of PS-b-

![Fig. 7. ¹H NMR spectrum of S-PS-PEO-PMAA](image)

<table>
<thead>
<tr>
<th>Tab. 1. Polymerization of MAA initiated by the small molecules TDDM and BP&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDDM/BP</td>
</tr>
<tr>
<td>mol/mol</td>
</tr>
<tr>
<td>1:1</td>
</tr>
<tr>
<td>1:2</td>
</tr>
<tr>
<td>1:3</td>
</tr>
<tr>
<td>1:4</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> [TDDM]: $5.6 \times 10^{-5}$ mol/L, 6 mL of MAA, 4 mL of benzene, 25°C, 24 h.
PEO\textsubscript{im} constituted the CTC with BP under UV irradiation and then initiated the polymerization of MAA.

The single peak shown in Fig. 5(C) indicated that no coupling product was formed in the radical polymerization of MAA. Kubota\textsuperscript{14)} et al. pointed out that, in the binary initiation system composed of aromatic amine and benzophenone, the aromatic imino radicals are the species which initiates the monomer to polymerize, while the biphenyl methanol radical is stable and serves as a chain terminator. Ranby\textsuperscript{15)} pointed out further that MAA could be grafted on an LDPE film by a living radical polymerization, in which benzophenone was used as an initiator and the forming biphenyl methanol radical as a terminator. This means that the coupling termination does not occur in the presence of biphenyl methanol radicals, which is coincident with our experimental results.

We have also used the NMR technology to measure the molecular weight and the composition of the triblock copolymer via the peak area ratio of the methyl protons of PMMA at 0.9–1.1 ppm vs. the benzene ring protons of PS at 6.42–7.02 ppm. The value is about 3.2:1, so the molecular weight of the PMAA block ($M_{\text{PMAA}} = M_{\text{PS}} \cdot M_{\text{MAA}} \cdot 3.2/M_d$), here $M_{\text{PMAA}}$ and $M_{\text{PS}}$ are the molecular weights of the PMAA and PS blocks, $M_{\text{MAA}}$ and $M_d$ are the formula weights of monomeric MAA and St) is about 21000. The whole polymerization data are listed in Tab. 2.

### Tab. 2. Copolymerization data of S-PS-PEO-PMAA

<table>
<thead>
<tr>
<th>$M_w \times 10^{-4}$</th>
<th>$M_d/M_w$</th>
<th>Conversion</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>PS-b-PEO</td>
<td>S*\textsuperscript{a)}</td>
<td>PS</td>
</tr>
<tr>
<td>0.8</td>
<td>1.5</td>
<td>5.4\textsuperscript{b)}</td>
<td>1.21</td>
</tr>
<tr>
<td>0.8</td>
<td>1.5</td>
<td>3.6\textsuperscript{c)}</td>
<td>(22.2)</td>
</tr>
</tbody>
</table>

\textsuperscript{a)} $S^* = S$-PS-PEO-PMMA.
\textsuperscript{b)} GPC value.
\textsuperscript{c)} NMR value.

Conclusion

A heteroarm star triblock copolymer of styrene, ethylene oxide, and methacrylic acid was successfully synthesized by combination of anionic and photo-induced charge transfer polymerization using N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethanol (TDDM)-terminated polystyrene as an intermediate. The PMAA block was obtained by precipitation polymerization of MAA, which was initiated by a charge transfer complex composed of PS-b-PEO with a TDDM end group and benzophenone under UV irradiation, using benzene as a solvent.

Acknowledgement: We appreciate the financial support from the Natural Science Foundation of China and Doctor Training Foundation of the Education Ministry of China.