Synthesis of a novel diblock copolymer of isoprene and methacrylic acid

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(Received: February 25, 1998; revised: June 29, 1998)

SUMMARY: A new diblock copolymer of isoprene (I) and methacrylic acid (MAA) was prepared by combination of an anionic mechanism with a charge transfer complex mechanism. In the first step, the polyisoprene (PI) macroanion formed by initiation with butyllithium was capped by \( p \)-dimethylaminobenzaldehyde (capped polyisoprene = PI\textsubscript{d}); a dimeric coupling product was not detected. Then the binary system constituting of PI\textsubscript{d} and benzophenone was used to initiate the polymerization of MAA under UV irradiation. The resulting diblock copolymer (PI-b-PMAA) was characterized by IR, NMR and gel permeation chromatography (GPC) in detail.

Introduction

Block copolymers containing acrylic or methacrylic acid segments, such as PS-b-PMAA, are very interesting polymeric systems which were widely used in studies of blend miscibility\textsuperscript{1)} , self-assembly\textsuperscript{2, 3)}, drug delivery vehicles, etc. However, it is difficult to synthesize them by sequential anionic polymerization because of the occurrence of chain transfer and termination caused by the active hydrogen of the carboxyl groups.

The common way to cope with the problem of a direct synthesis of block copolymers containing acidic blocks is to prepare first the poly(alkyl acrylate) block, such as poly(tert-butyl acrylate), by anionic polymerization, and then the poly(alkyl acrylate) is hydrolyzed to the corresponding acid in the presence of an acid catalyst\textsuperscript{4)}. Recently Guegan\textsuperscript{5)} reported that poly(methacrylic acid) can also be obtained by the transformation of poly(tert-butyl methacrylate) into poly(methacrylic anhydride) via thermal treatment and following hydrolysis.

A new methodology to combine anionic polymerization and charge transfer polymerization was developed by us and some unique block copolymers, such as poly(ethylene oxide) (PEO)-\textit{block}-polystyrene\textsuperscript{5)}, PEO-b-PMAA\textsuperscript{6)}, and PEO-\textit{block}-polyacrylonitrile\textsuperscript{7)} were prepared.

In this presentation we report the direct synthesis of the diblock copolymer of isoprene and methacrylic acid (PI-b-PMAA) via a binary initiation system composed of a capped PI macroanion with \( N,N \)-dimethylaniline end-groups and benzophenone under UV irradiation.

Experimental part

Materials

Isoprene (I) and cyclohexane were dried by calcium hydride and then distilled under nitrogen before use. Butyllithium (BuLi) was prepared by reacting lithium ribbon with butyl chloride in cyclohexane according to the literature\textsuperscript{8)}. \( p \)-Dimethylaminobenzaldehyde (DMAB) (Shanghai Reagent Factory) and benzophenone (BP) (Beijing Chemical Factory) was purified by recrystallization from ethanol. Methacrylic acid and benzene were purified by distillation.

Anionic polymerization of isoprene

The polymerization of isoprene was performed with BuLi in cyclohexane at 65°C for 9 h by a standard procedure\textsuperscript{9)}, an aliquot of the polymer solution was taken for GPC measurements before the addition of DMAB, and the remaining polymer solution was used for the subsequent reaction.

Functionalization reaction of the polyisoprene macroanion by capping with DMAB

A 200 mL ampoule containing 0.304 g of DMAB (2.04 \( \times \) \( 10^{-3} \) mol) was degassed by three cycles of pumping and pressurizing of nitrogen with a purity of 99.99% to atmospheric pressure. 100 mL of the above-mentioned living polymer solution (1.46 \( \times \) \( 10^{-2} \) mol/L) was added dropwise at room temperature in 10 min, and the mixture was allowed to stand for 4 h. The capped polymer was precipitated in methanol and purified by repeated dissolution/precipitation with trichloromethane/methanol to remove unreacted DMAB.

Scheme 1:

\[
\begin{align*}
\text{BuLi} & \rightarrow \text{BuLi}_2 \rightarrow \text{BuLi}_3 \rightarrow \text{BuLi}_4 \\
\text{DMAB} & \rightarrow \text{DMAB}_2 \rightarrow \text{DMAB}_3 \rightarrow \text{DMAB}_4
\end{align*}
\]

Photoinduced charge transfer polymerization of methacrylic acid

A 100 mL ampoule containing MAA (5 ml), benzene (5 ml), 0.01 g BP (5.5 \( \times \) \( 10^{-3} \) mol) and 0.35 g of PI\textsubscript{d} (5 \( \times \) \( 10^{-5} \) mol) was degassed three times by freeze-pump-thaw cycles, then
the mixture was irradiated at 25°C for 24 h with a 300 W high-pressure mercury lamp (DDZ-300, from Shanghai Ya Ming Lamp Factory). A cupric sulfate aqueous solution was used as a photofilter to obtain 365 nm monochromatic light. The block copolymerization is a precipitation polymerization, so the unreacted PI left in the benzene solution could easily be removed by filtration. The precipitated product was dissolved in N,N-dimethylformamide and precipitated in ether. Then the crude product was extracted with water for 50 h to remove homopolymeric PMAA and with ether for another 50 h to remove possibly left PI; however, no PI was detected in this case. The weight fraction of homopolymeric PMAA was about 30% of the total MAA monomer weight. The purified product was dried under vacuum at 40°C to constant weight (2.06 g).

**Measurements**

The number-average molecular weight, \( \bar{M}_n \), and the molecular weight distribution (MWD) of PI, PI\(_d\), and the block copolymer were determined with a Shimadzu LC-3A gel permeation chromatograph, refractive index detector; trichloromethane and DMF were used as solvents and eluents, and monodistribution polystyrene (PS) was used as a standard sample. IR spectra were recorded by a Perkin-Elmer 983 G spectrometer. \(^1\)H NMR was recorded on a Bruker MSL-300 spectrometer, using dimethyl sulfoxide-\(d_6\) as a solvent and tetramethylsilane as internal standard. UV spectra were taken on 756 MC UV-Vis spectrophotometer (Shanghai Third Analytical Instrument Factory, China).

**Results and discussion**

**Capping reaction of the polyisoprene anion with DMAB**

The functionalization reaction of the polyisoprene anion with DMAB was carried out under the condition of an excess of the latter. The reaction was conducted rapidly; the polyisoprene anion with lemon-yellow color was changed into orange instantly as soon as the PI macroanion was dropped on the solid DMAB.

It is well known that, when the molecular weight of the polymer is greater than a certain value, the detection of the end-group of the polymer by common physical means such as IR and NMR is difficult because of its small weight fraction. However, UV spectroscopy which is more sensitive than IR and NMR could be used. Fig. 1 shows the UV spectra of the model compound N,N-dimethylaniline (DMA) (A), PI (B), and PI\(_d\) (C). The maximum absorption peaks of \( \pi \rightarrow \pi^* \) and \( n \rightarrow \pi^* \) for DMA (A) were at 254 and 310 nm, respectively; for PI\(_d\) (C) there were two peaks at 237.5 and 259 nm for \( \pi \rightarrow \pi^* \), and one peak at 311 nm for \( n \rightarrow \pi^* \). Comparing with PI (B) which was formed by direct precipitation in methanol, the peak at 237.5 nm for PI\(_d\) was clearly attributed to the

\[ \pi \rightarrow \pi^* \] of PI main chain. Thus the existence of PI\(_d\) is indisputable.

The capping efficiency of DMAB on the PI macroranions could be also obtained from the UV spectra\(^{10}\) on basis of the linear relationship of DMA concentration and its corresponding absorbance at 310 nm in the dilute solution; the resulting value is 100%.

Fig. 2 shows the GPC curve of PI (A) and PI capped with DMAB (B). Two conclusions could be derived from this: 1. In the capping process the molecular weight and the molecular weight distribution of PI is unchanged, i.e., \( \bar{M}_n = 7000 \) and \( M_w / \bar{M}_n = 1.4 \) for both cases. 2. No dimeric coupling product of the PI macroanion was detected, only one peak appeared in Fig. 2; that is different from the case of the PS macroanion, in which upon capping with DMAB the dimeric product was formed\(^{11}\).

**Preparation of PI-b-PMMA via charge transfer polymerization**

In analogy to a small binary initiation system composed of tertiary amine and BP\(^{12–14}\), PI\(_d\) also constitutes an exciplex with BP by single electron transfer; then the diphenyl methanol radical and the aromatic tertiary amine radical of PI\(_d\) are produced by proton transfer. While the former is stable in our experimental conditions and serves as
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Characterization of the diblock copolymer PI-b-PMAA

The $^1$H NMR spectrum of purified polyisoprene-block-poly(methacrylic acid) is shown in Fig. 3. The observed peaks for the PMAA block, such as 12.3 ppm for the carboxylic proton, 1.02 and 0.93 ppm for the methyl protons, and 4.97 ppm of the vinyl proton, as well as the peak at 1.53 ppm for the cis-H of the PI block methyl group confirm the existence of the objective block copolymer.

Fig. 4 shows the GPC diagram of the block copolymer, in which only one peak appeared. This is a strong evidence which supports that no coupling product was formed in the block copolymerization.
Kubota\textsuperscript{15)} 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 (Scheme 2). Ranby\textsuperscript{13)} pointed out further that MAA could be grafted on an LDPE film by a living radical polymerization, in which benzophenone was used as 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.

$M_c/M_n$ of the diblock copolymer is 1.5, which is nearly the same value as that of PI\textsubscript{b} (1.4). This is another evidence for the existence of a simple diblock copolymer, otherwise the MWD should be broadened due to the formation of a mixture of diblock copolymer and coupling triblock copolymer with double molecular weight.
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Due to the significant different fluid mechanics volume of PI-\textit{b}-PMAA in comparison with common PS standard samples used for GPC, the molecular weight of the diblock copolymer (5.2 \times 10^4) is unreliable. Therefore, NMR was used to measure the molecular weight of the block copolymer. The molecular weight of the first block of PI \textsubscript{d} was derived from GPC, its $M_n$ is 7000 and $M_n/M_w$ is 1.4. Then we used the peak area ratio of the methyl protons of PMAA vs. the proton of the double bond of PI as a measure of the molecular weight for both of them; the value is about 9:1, so the molecular weight of the PMAA block ($M_{\text{PMAA}} = M_n \cdot M\text{MAA} \cdot 9/M_d$) is about 79600 and the total molecular weight of the block copolymer is 86600. The initiation efficiency of PI \textsubscript{d} was obtained by gravimetric methods and UV spectroscopy, both methods are rather coincident, resulting in a value of about 47.6%.

Fig. 5 gives the IR spectra of PI \textsubscript{d} and the block copolymer PI-\textit{b}-PMAA. Comparing with the PI \textsubscript{d} block, a strong band at 1705 cm\textsuperscript{-1} attributed to the carbonyl group and a band at 3221 cm\textsuperscript{-1} attributed to the carboxylic hydroxyl group confirm the existence of the PMAA block.

Acknowledgement: The Natural Science Foundation of China and the Doctor Training Foundation of State Education Commission of China financially supported this work.