Syntheses and Characterizations of Poly[2-(dimethylamino)ethyl methacrylate]–Poly(propylene oxide)–Poly[2-(dimethylamino)ethyl methacrylate] ABA Triblock Copolymers

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ABSTRACT: A novel, near-monodisperse, well-defined ABA triblock copolymer, poly[2-(dimethylamino)ethyl methacrylate]-b-poly(propylene oxide)-b-poly[2-(dimethylamino)ethyl methacrylate], was synthesized via oxyanion-initiated polymerization. The initiator was a telechelic-type potassium alcoholate prepared from poly(propylene glycol) and KH in dry tetrahydrofuran. The copolymers produced were characterized by Fourier transform infrared, 1H NMR, and gel permeation chromatography (GPC). GPC and 1H NMR analyses showed that the products obtained were the desired copolymers, with narrow molecular weight distributions (ca. 1.09–1.11) very close to that of the original poly(propylene glycol). 1H NMR, surface tension measurements, and dynamic light scattering all indicated that the triblock copolymer led to interesting aqueous solution behaviors, including temperature-induced micellization and very high surface activity.


Keywords: anionic polymerization; block copolymers; solution properties

INTRODUCTION

Oxyanion-initiated polymerization is an attractive polymerization technique from which well-defined block copolymers or macromonomers with narrow molecular weight distributions can be prepared.1–5 In 1997, Nagasaki and coworkers3,6 reported that 2-(diethylamino)ethyl methacrylate could be polymerized with potassium 4-vinylbenzyl alcoholate as a functional initiator at or above ambient temperature. Such an oxyanionic initiator does not normally lead the polymerization of methacrylate monomers to yield a narrow-distribution polymer. Although the precise mechanism for this polymerization has not yet been established, the polymerization of tertiary amine methacrylates nevertheless produces well-defined macromonomers or block copolymers. Very recently, Armes and coworkers1,5 extended the synthetic method to macromonomers with differ-
rent chemical structures, including other tertiary amine methacrylates such as 2-(dimethylamino)-ethyl methacrylate (DMAEMA), 2-(N-morpholino)-ethyl methacrylate, and 2-(diisopropylamino)-ethyl methacrylate. They also used the reaction to prepare hydrophilic–hydrophilic diblock copolymers of poly(ethylene oxide) (PEO) and poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA). One of the advantages of oxyanion-initiated polymerization is that it does not require such strict experimental conditions as anionic polymerization. Therefore, this living process provides a new approach for the synthesis of block copolymers or macromonomers with controlled molecular weights and molecular weight distributions. Another advantage of the technique is that it facilitates the incorporation of polymer blocks with poly(tertiary amine methacrylates) to give diblock or triblock copolymers. In our lab, we prepared a Y-type PDMAEMA-based macromonomer via oxyanion-initiated polymerization. The functional initiator was dipotassium alcoholate from trimethylolpropane allyl ether and KH in dry tetrahydrofuran (THF). It is well-known that Pluronic block copolymers are commercially available symmetric triblock copolymers with PEO as the hydrophilic end block and poly(propylene oxide) (PPO) as the hydrophobic middle block. Aqueous solutions of PPO, with a degree of polymerization (DP) of 40, exhibit temperature dependence. Below approximately 15 °C, water is a good solvent for PPO, whereas PPO aggregates at higher temperatures. In this article, we report the synthesis of ABA triblock copolymers composed of cationic PDMAEMA (as the outer A blocks) and PPO (as the central B block) via oxyanion-initiated polymerization. DMAEMA monomer can be protonated in an acidic medium. Its homopolymer is a weak polybase that is soluble in neutral or acidic aqueous media. Therefore, DMAEMA polymer can be used as the pH-sensitive component and hydrophilic end blocks, whereas PPO can be used as the hydrophobic moiety in the copolymers. The effects of the temperature on the properties of the ABA triblock copolymer in aqueous solutions, such as the micellization behavior and surface activity, were investigated in detail.

**EXPERIMENTAL**

**Materials**

KH and DMAEMA were purchased from Aldrich. DMAEMA was passed through an activated basic alumina column and distilled immediately in vacuo before use. THF (Shanghai Chemical Reagent Co., China) was dried with sodium wire for 3 days and subsequently refluxed in the presence of sodium wire for 3 days before use. Poly(propylene glycol) (Shanghai Chemical Reagent) was heated at 140 °C for 4 h with a rotary vacuum distillator for the removal of trace water before use. Gel permeation chromatography (GPC) analysis for poly(propylene glycol) gave a number-average molecular weight ($M_n$) of 2.1 × 10^2 and a molecular weight distribution [weight-average molecular weight/number-average molecular weight ($M_w/M_n$)] of 1.09. In this article, we use the abbreviation PPO to identify both this poly(propylene glycol) oligomer and the PPO segment in the copolymers, unless otherwise stated.

**Block Copolymer Synthesis**

All glassware was heated at 140 °C overnight and allowed to cool in a drybox before use. A telechelic potassium alcoholate of PPO was prepared according to the literature. The polymerization reactor was a 100-mL, round-bottom flask fitted with a rubber septum. The septum was used for injection of the solvent and monomers. Two syringe needles were fixed for the nitrogen inlet and outlet or the addition of the monomer. A typical polymerization procedure for a PDMAEMA–PPO–PDMAEMA triblock copolymer was as follows. In a preweighed flask with a magnetic bar, dry THF (25 mL) and KH (0.21 g, 1.80 mmol) were added as a 35 wt % dispersion in mineral oil under a purge of nitrogen at room temperature. The THF was removed with a needle. After the KH was washed and dried with nitrogen, PPO (1.75 g, ca. 0.88 mmol) was added via a syringe. The polymerization proceeded at either 30 or 50 °C for 0.5–1 h to yield the oligomeric potassium alcoholate shown in Figure 1. DMAEMA monomer (3.45 g, 0.022 mol) was then added to the flask by a syringe. The polymerization proceeded at either 30 or 50 °C for 1–2 h before being quenched with methanol. The solvent was removed with a rotary vacuum distillator. The copolymer was purified by repeated precipitation into cold n-hexane for the removal of unreacted PPO and monomer, followed by separation and drying in a vacuum oven at 40 °C for 3 days.

**Fourier Transform Infrared (FTIR) Spectroscopy**

The IR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer, and the samples were
prepared by the casting of the sample solution onto a piece of aluminum foil.

**GPC Measurements**

Molecular weight distributions were determined with a gel permeation chromatograph (HP-1100 instrument) equipped with a Zorbax HV1618 column connected to a refractive-index detector (G 1362A) and a UV detector (G 1315A). Calibration was carried out with polystyrene standards. THF was used as an eluent at a flow rate of 10 mL min$^{-1}$.

**NMR Spectroscopy**

The composition and $M_n$ for each copolymer was determined by 400-MHz $^1$H NMR (INVOA-400). In addition, $^1$H NMR measurements were also carried out for the investigation of the pH/temperature-induced solution behavior. The copolymer (14 mg) was dissolved in D$_2$O (0.5 mL). Sodium 4,4-dimethyl-4-silapentanesulfonate was used as an internal standard.

**Surface Tension**

Surface tension measurements were carried out with a JYW-200A automatic surface tensiometer equipped with an electrical torsion balance and a platinum ring (Chengde Experimental Instrument Co., China). The triblock copolymers were dissolved in a dilute hydrochloric acid solution at pH 6.2. A series of aqueous copolymer solutions of different concentrations were prepared by the dilution of the original solution with HCl at the same pH. All measurements were carried out at room temperature (20 °C), and the obtained values were checked periodically through measurement of the surface tension of deionized water (72–73 mN m$^{-1}$ at 20 °C).

**Micelle Size and Size Distribution**

The average copolymer micelle size and size distribution data were obtained with a dynamic light scattering (DLS) apparatus (Malvern Autosizer 4700) equipped with a 100-mW argon laser beam operating at a wavelength of 514.5 nm at 25 °C. The intensity of the scattered light was detected at 90° to the incident beam unless otherwise stated. The data were fitted with monomodal cumulant analysis. All measurements were carried out in 4.9 g/L solutions. The polydispersity is a model-independent estimate of the width of the size distribution, which is equal to the normalized second moment from a cumulant analysis of the scattered light autocorrelation function. For relatively narrow size distributions, the polydispersity may be equated to the variance of the distribution.

**RESULTS AND DISCUSSION**

**Preparation of the Triblock Copolymers**

PDMAEMA–PPO–PDMAEMA triblock copolymers were synthesized by oxyanion-initiated polymerization. DMAEMA monomer was polymer-
ized with the potassium alcoholate of poly(propylene glycol) as a macroinitiator. Nagasaki and coworkers\textsuperscript{3,6} reported the polymerization of both 2-(trialkylsiloxy)ethyl methacrylates and 2-(diethylamino)ethyl methacrylate with various potassium alcoholates as initiators. They proposed that the electron-donor atom in these monomers increased the nucleophilicity of the alkoxide ion by chelation of the alkali metal cation.

We attempted to synthesize the triblock polymers by a similar method. Because there are two hydroxyl groups in the ends of the PPO oligomer, they are able to react with KH to form dipotassium alcoholate salt and then initiate the polymerization of DMAEMA. In the first step (shown in Fig. 1), the reaction temperature of PPO and KH to form the alcoholate salt was chosen to be 0 or 30 °C. The polymerization of DMAEMA proceeded at 30 or 50 °C. In this study, \( ^1 \)H NMR spectroscopy was used for the determination of the relative composition of the PPO and PDMAEMA blocks. The \( ^1 \)H NMR signals due to the three methoxy protons (\( \text{CH}_3\text{O} \) and \( \text{CH}_2\text{O} \)) of PPO are clearly visible at \( \delta = 3.4-3.5 \) ppm and \( \delta = 3.7-3.8 \) ppm. A comparison of the peak integrals obtained for these signals with those associated with the DMAEMA block at \( \delta = 2.2-2.3 \) ppm (due to the six dimethylamino protons) allowed \( M_n \) to be calculated. As derived by \( ^1 \)H NMR, these molecular weight were in reasonable agreement with those expected from the corresponding monomer/initiator ratios. The compositions, molecular weights, and molecular weight distributions are summarized in Table 1.

\[ ^1 \text{H NMR analyses indicated that there was no significant difference in molecular weights between copolymers DP20-1 and DP07-2, which were prepared at 30 °C in the first step and polymerized at 50 or 30 °C in the second step. The } M_w/M_n \text{ values of the copolymers measured by GPC were 1.09--1.11, very close to that of the original PPO. These results indicated that the triblock copolymers had narrow molecular weight distributions. However, the molecular weights of these copolymers were higher than those expected from the calculation based on the monomer/initiator ratio, suggesting that fractional initiator efficiency was less than unity. When the temperature was lowered to 0 °C in the first step, better agreement with the theoretical molecular weight was achieved.} \]

Figure 2 shows the GPC profile of the original poly(propylene glycol) oligomer and the resulting triblock copolymer (DP07-2). Neither PPO nor the monomer were detected in the lower molecular weight region, suggesting that all of the PPO chains had reacted with DMAEMA monomer and that the triblock copolymer had a unimodal molecular weight distribution similar to that of PPO.

Table 1. Compositions, Molecular Weights, and Molecular Weight Distributions of a Series of PDMAEMA–PPO–PDMAEMA Triblock Copolymers Prepared via Oxyanion-Initiated Polymerization

<table>
<thead>
<tr>
<th>Run</th>
<th>[DMAEMA]/[PPO] (Molar Ratio)</th>
<th>Alcoholate Temperature (°C)a</th>
<th>Polymerization Temperature (°C)</th>
<th>Time (h)b</th>
<th>( M_n )</th>
<th>( M_w/M_n )</th>
<th>Theoretical</th>
<th>NMRc</th>
<th>GPC</th>
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<tr>
<td>DP20-1</td>
<td>25/1</td>
<td>30</td>
<td>50</td>
<td>2</td>
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<td>7600</td>
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<tr>
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<td>25/1</td>
<td>30</td>
<td>50</td>
<td>2</td>
<td>6125</td>
<td>6750</td>
<td>1.09</td>
<td></td>
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<tr>
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<td>30</td>
<td>2</td>
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<td>6660</td>
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<td>6236</td>
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a Reaction temperature in the process of forming potassium alcoholate.
b Reaction time of polymerization for DMAEMA.
c The experimental values were determined by \( ^1 \)H NMR spectroscopy.

Figure 2. Typical GPC profiles of (a) a poly(propylene glycol) oligomer (\( M_n = 2.1 \times 10^3 \), \( M_w/M_n = 1.09 \)) and (b) the corresponding PDMAEMA–PPO–PDMAEMA triblock copolymer (DP12-1; \( M_n = 6.7 \times 10^3 \), \( M_w/M_n = 1.11 \)).
FTIR Spectra of PPO and the Copolymer

Figure 3 presents the FTIR spectra of poly(propylene glycol) and the triblock copolymer (DP06-3). With DMAEMA or PPO homopolymer as the reference material, peak assignments were made and are indicated in the figure. The broad band at 3484 cm\(^{-1}\) should be attributed to the O—H stretch of the PPO end group, as shown in Figure 3(a). Its disappearance in Figure 3(b) suggests that the poly(propylene glycol) precursor had reacted with KH to form the potassium alcoholate, which subsequently initiated the polymerization of DMAEMA. A new and strong carbonyl band at 1734 cm\(^{-1}\) is attributed to the DMAEMA residues. Overlapping of the aliphatic CH stretching band of PPO at 2972 cm\(^{-1}\) and of DMAEMA at 2870 cm\(^{-1}\) was also observed. Overall, the IR spectra are consistent with, but do not prove, block copolymer formation.

Effect of Temperature and pH on the Solution Behavior of the Copolymer

Figure 4 depicts a series of \(^1\)H NMR spectra of the copolymer (DP07-2) at various temperatures and pHs. The original \(^1\)H NMR spectrum of the copolymer in D\(_2\)O at 20 °C is shown in Figure 4(a); signals assigned to the PDMAEMA moiety (at \(\delta = 2.3–2.4\) ppm, \(\delta = 2.6–2.7\) ppm, and \(\delta = 4.1–4.2\) ppm) and the PPO moiety (at \(\delta = 3.4–3.5\) ppm and \(\delta = 3.7–3.8\) ppm) are clearly visible. When the solution was heated to 40 °C, the signals assigned to the PPO residues broadened [as shown in Fig. 4(b)] and became much less intense relative to the PDMAEMA signals, suggesting the formation of micelles with hydrophobic PPO cores and hydrophilic PDMAEMA coronas. After the solution cooled to 20 °C, the same \(^1\)H NMR spectrum as that in Figure 4(a) was observed, confirming that copolymer aggregation was reversible. Similar observations were reported by Vamvakaki et al.\(^2\) and Lowe et al.\(^19\) for the micellization of DMAEMA–PEO and DMAEMA–methacrylic acid diblock copolymers, respectively.

To investigate pH-sensitive solution behavior, we recorded \(^1\)H NMR spectra of the same triblock copolymers in D\(_2\)O/DCl at pH 2 and in D\(_2\)O/NaOD at pH 9. The pH-responsive behavior was induced by the adjustment of the solution pH at room temperature, as shown in Figure 4(c,d). Under acidic conditions (pH 2), all signals assigned to PDMAEMA and PPO blocks are sharp and visible. In a comparison with the \(^1\)H NMR spectrum of the copolymer in D\(_2\)O [Fig. 4(a)], we find that the proton peak assigned to the aza-methylene proton of the DMAEMA residues shifts from \(\delta = 2.7\) ppm to \(\delta = 2.9\) ppm and that the proton peak of the six dimethylamino protons shifts from \(\delta = 2.3\) ppm to \(\delta = 3.0\) ppm because of the protonation of tertiary amino groups in PDMAEMA. The triblock copolymer was in its unimer state, and the protonated PDMAEMA blocks behaved as a cationic polyelectrolyte. The fact that PPO signals became less intense at pH 9, but did not disappear, indicates that partially dehydrated micelle cores were formed.
DLS Analysis of the Triblock Copolymer

To further confirm that the obtained copolymer exhibited reversible temperature-induced micellization behavior, we carried out DLS measurements to keep track of the changes in the micellar size with the various temperatures. In this experiment, the concentration of the copolymer (DP07-2) was 4.9 g/L, much higher than the critical...
ical micelle concentration. DLS analysis indicated the formation of near-monodisperse micellar aggregates with a $z$-average diameter of about 20 nm at room temperature (see Fig. 5). As the temperature increased, significant changes in the micelle diameter were observed, from a $z$-average diameter of 16 nm at 25 °C to 70 nm at 33 °C. Under these conditions, the DLS investigation indicated the formation of stable, near-monodisperse micelles. When the temperature increased to 34 °C, the micelle diameter increased to 70 nm, and the aqueous solution became light blue. At 35–36 °C, the micelle size increased to over 200 nm, and the aqueous solution became translucent and milky. More polydisperse micelles and/or macroscopic precipitation was observed beyond 36 °C. After cooling, the aqueous solution returned gradually from translucence to transparency again. This confirmed that such temperature-induced micellization was reversible.

Cho et al. investigated the temperature-induced phase transition of poly[2-(dimethylamino)ethyl methacrylate-co-acrylamide]. They found that when the temperature of a PDMAEMA aqueous solution was raised above 50 °C, the homopolymer precipitated from the solution. This was due to the hydrophobic interaction between 2-(dimethylamino)ethyl groups above the lower critical solution concentration. There were two main factors that influenced the aggregation of the triblock copolymer: (1) the solubility of the PPO block entered into the PPO cores of the micelles. When the solution was cooled, the water solubility of PPO increased. It is obvious that the changes in the micellar size depended on the concentration of the copolymers in aqueous solutions. Further studies regarding this phenomenon will be continued in our lab.

Critical Micelle Concentration of the Triblock Copolymer

In this study, all the triblock copolymers were readily soluble in dilute and aqueous HCl. The aqueous solution was carefully adjusted to the required pH. The surface activity of the copolymer (DP06-3) at the air/water interface was determined from surface tension measurements at pH 6.2. The critical micelle concentration of a copolymer can be obtained by the distinct change in the curve of the surface tension versus the concentration of the copolymer. Figure 6 shows the relationship between the surface tension and the concentration of a triblock copolymer (DP06-3). It indicates that the surface tension decreased rapidly with increasing copolymer concentration up to 0.12 g/L at pH 6.2. Above this concentration, the surface tension remained constant around 41 mN m$^{-1}$. The lowest surface tension achieved was 41 mN m$^{-1}$, which is at least 30 mN m$^{-1}$ lower than that of pure water at the same temperature. These results confirmed that the copolymer contributed to the surface-active properties significantly. These surface tension results imply that such ABA triblock copolymers may condensed onto the original micelles so that free PPO block entered into the PPO cores of the micelles. When the solution was cooled, the water solubility of PPO increased. It is obvious that the changes in the micellar size depended on the concentration of the copolymers in aqueous solutions. Further studies regarding this phenomenon will be continued in our lab.

**Figure 5.** Effect of temperature on the micellar size and polydispersity of a triblock copolymer (DP07-2) in a 4.9 g/L aqueous solution at pH 8.5.

**Figure 6.** Variation of the surface tension with the concentration for a PDMAEMA–PPO–PDMAEMA triblock copolymer (DP06-3) in an aqueous solution at pH 6.2.
have interesting applications as surfactants or emulsifiers.

Our primary studies confirm that novel PDMAEMA–PPO–PDMAEMA triblock copolymers can be synthesized by oxyanion-initiated polymerization. They have reversible pH/temperature-induced micellization behavior and significant surface activity in aqueous solutions. In addition, these copolymers have potential applications as polymeric emulsifiers for the synthesis of polystyrene latex by aqueous emulsion polymerization. The investigation of their use as surfactants in the emulsion polymerization of styrene will be described elsewhere.

CONCLUSIONS

PDMAEMA–PPO–PDMAEMA triblock copolymers were synthesized by the oxyanion-initiated polymerization of DMAEMA monomer with potassium alcoholate as an initiator, which was obtained from the reaction of KH with the two terminal hydroxyl groups of PPO. FTIR and 1H NMR analyses confirmed the structures of the PDMAEMA–PPO–PDMAEMA triblock copolymers. In addition, 1H NMR spectroscopy and GPC measurements were carried out for further determination of the chemical structures, compositions, and molecular weights of the PDMAEMA–PPO–PDMAEMA block copolymers obtained. From the appearance of a narrow unimodal peak with respect to PPO in GPC, we confirmed that the PDMAEMA–PPO–PDMAEMA triblock copolymers were produced without DMAEMA homopolymer or PPO homopolymer impurities. According to NMR and DLS measurements, PDMAEMA–PPO–PDMAEMA triblock copolymer micelles exhibited a z-average diameter of about 20 nm at ambient temperature, whereas the micelle size changed greatly at a higher temperature. Moreover, this temperature-induced micellization was also fully reversible. The critical micelle concentration value determination by surface tensiometry at pH 6 indicated the formation of stable micelles.

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REFERENCES AND NOTES