Synthesis and Characterization of a Diblock Copolymer of Methyl Methacrylate and Vinyl Acetate by Successive Photo-Induced Charge Transfer Polymerization Using Ethanolamine as the Parent Compound

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Introduction

Much research has been performed about polymer blends composed of PMMA and PVAc. Crispim et al.[1] investigated the influence of solvent and temperature on the miscibility of PMMA/PVAc blends using differential scanning calorimetry (DSC) and viscometry and found the miscibility being dependent on both solvent and temperature.

The phase behavior of PMMA/PVAc blends including phase separation and phase transition was studied by many researchers in detail. Kaminska et al.[2] studied the thermal and photochemical stability of PMMA/PVAc blends and revealed that PVAc acts as a stabilizer with respect to thermal and photochemical degradation when the processes take place in air. Especially in the field of phase separation, much attention has been focused on PMMA/PVAc blends because they have lower critical solution temperature (LCST) phase diagrams similar to the blends of polystyrene/poly(methyl vinyl ether). This means that this kind of blends is homogeneous and miscible at low temperature and immiscible at high temperature. The effect of the block or graft copolymer as the compatibilizer on the corresponding blend pairs with an upper critical solution temperature (UCST) phase diagram has been widely investigated, including polystyrene-block-polybutadiene (PS-b-PB)[3,4] and polystyrene-block-poly(methyl phenyl siloxane) (PS-b-PMPS) systems.[5] However, the system with LCST phase diagram...
has been barely studied due to the difficulty of synthesizing the corresponding block copolymers.

Recently, some researchers reported the preparation of graft copolymer of PMMA and PVAc via radical[11] and anionic[12] polymerization. To synthesize block copolymers, anionic polymerization is a common method, but it is only suitable for certain monomers with low polarity, such as styrene, isoprene and others, and is unsuitable for monomers, such as vinyl acetate, vinyl ketone and so on. Thus it is impossible to synthesize block copolymers of PMMA and PVAc by the simple anionic polymerization technique.

In this Communication, a novel strategy is reported to synthesize the diblock copolymers PMMA-b-PVAc and PMMA-b-PVA under mild condition. First, ethanolamine-benzophenone is used as the binary initiation system to initiate the polymerization of methyl methacrylate (MMA) under UV irradiation, and then the PMMA prepolymer containing an imine end group and benzophenone constitutes the binary system again to initiate the polymerization of vinyl acetate (VAc) under UV irradiation. Diblock copolymer PMMA-b-PVAc can be transformed into PMMA-b-PVA by selective, complete hydrolysis of the PVAc blocks using sodium ethoxide as the catalyst.

Experimental Part

Materials
Ethanolamine (Shanghai Third Reagent Factory, China) was dried with Linde 4 Å molecular sieve, followed by distillation under reduced pressure to collect the fraction of 72°C/12 mmHg. Benzophenone (BP) (Beijing Chemical Factory, China) was re-crystallized twice from ethanol. Monomers MMA and VAc, and all the solvents were purified by standard methods[13].

Preparation of the PMMA Prepolymer
Homopolymerization of MMA was initiated by a binary system composed of ethanolamine and BP (Scheme 1).

To a 100 mL ampoule containing 0.0182 g BP (1.0 × 10⁻⁴ mol) in 5 mL THF, 0.0061 g ethanolamine (1.0 × 10⁻⁴ mol) and 5 mL MMA were charged. Next, the ampoule was degassed performing three freeze-thaw-cycles at −196°C. The sealed ampoule was irradiated with a 300 W high-pressure mercury lamp (GGZ-300 manufactured by Shanghai Ya Ming Lamp Factory, China) under an N₂ atmosphere for 24 h at 25°C. A cupric sulfate aqueous solution was used as the photo-filter to obtain 365 nm monochromatic light. The PMMA prepolymer was precipitated by methanol and purified by dissolution/precipitation with chloroform/methanol. Yield: 62.5%.

\[ \text{1H NMR: } \delta = 0.87, 1.01 \text{ and } 1.22 \text{ (−CH₃ for syndiotactic, heterotactic and isotactic configuration, respectively), 1.84 (−CH₂−) and 3.60 (−OCH₃).} \]

\[ \text{FTIR (film): } 1731 \text{ cm}^{-1} \text{ (C=O).} \]

Preparation of the Block Copolymer of PMMA and PVAc
The polymerization of VAc is performed using a binary initiation system containing the PMMA prepolymer with imine end group and BP (Scheme 2).

To a 100 mL ampoule containing 0.8080 g PMMA prepolymer (8.0 × 10⁻⁵ mol, \( M_\alpha = 10 100, M_\alpha/M_\omega = 1.32 \)) and 0.0146 g BP (8.0 × 10⁻⁵ mol), 5 mL THF and 5 mL VAc were introduced. The polymerization procedure is the same as for the preparation of the PMMA prepolymer. The product was precipitated with diethyl ether. The crude product can be purified first by dissolution/precipitation in chloroform/methanol to remove unreacted PMMA prepolymer, and then the copolymer solids are extracted with hot methanol to separate any possible PVAc homopolymer. (There were not even traces of PVAc homopolymer present according to FTIR and GPC analysis.)

Selective Hydrolysis of the PVAc Block
The hydrolysis reaction was carried out in benzene at 70°C for 2 h using 5% ethanolic sodium ethoxide as the catalyst (Scheme 3). The product was precipitated with diethyl ether and extracted with chloroform to remove any possible unhydrolyzed copolymer. (No original copolymer was detected in the chloroform extract by means of FTIR and GPC measurements.)

\[ \text{Scheme 1.} \]

\[ \text{Scheme 2.} \]

\[ \text{Scheme 3.} \]
Kinetic Measurements of CTP

The kinetics of the charge transfer polymerization was investigated using a modified dilatometer that can be evacuated to eliminate the influence of oxygen. The capillary diameter and volume of the dilatometer were calibrated at 25 °C. Conditions were the same as those of the polymerization. The procedure was analogous to that reported in a previous paper.\[14\]

Instruments

FTIR spectra were measured with a Magna-550 spectrometer (film). \(^1\)H NMR spectra were recorded on a Bruker MSL-300 spectrometer with trimethylsilane (TMS) as the internal standard; CDCl\(_3\) and DMSO-\(d_6\) were used as solvents for PMMA-\(b\)-PVAc and PMMA-\(b\)-PVA, respectively. Molecular weight and molecular weight distribution were measured with a Shimadzu LC-3A GPC with a refractive index detector, column length: 1.2 m, filler: crosslinked PS gel (1250 mesh), injection volume: 1.0 mL, solvent and eluent: chloroform, flow rate: 1.0 mL/min, pump pressure: 40 kg/cm\(^2\) (3.99 × 10\(^6\) Pa). The GPC was calibrated with mono-dispersed polystyrene standards.

Results and Discussion

Characterization of PMMA-\(b\)-PVAc

Purified PMMA-\(b\)-PVAc was characterized in detail by means of FTIR and \(^1\)H NMR spectroscopy. Figure 1a shows the IR spectrum revealing a strong band at 1738 cm\(^{-1}\) which can be attributed to the carbonyl group of PMMA and PVAc segments. Figure 2a depicts the \(^1\)H NMR spectrum. Here, all the proton resonance signals of PMMA and PVAc segments, such as 0.89, 1.01 ppm (\(-\text{CH}_3\) for syndiotactic and heterotactic configuration, respectively), 1.84 ppm (\(-\text{C}_2\text{H}_4\)) and 3.60 ppm (\(-\text{OCH}_3\)) for the PMMA segment and 1.84 ppm (\(-\text{CH}_2\text{C}O\)) and 4.88 ppm (\(-\text{CH}\)) for the PVAc segment, are observed. Figure 3 gives the GPC curves of PMMA prepolymer and PMMA-\(b\)-PVAc diblock copolymer. For the former (a), the number-average molecular weight is 10100 and the molecular weight distribution is 1.32; for the latter (b), there is only one peak with a smaller retention volume. Its number-average molecular weight is 34 600 which is much higher than that of the PMMA prepolymer, and the molecular weight distribution of 2.77 is much broader than that of the PMMA prepolymer. This supplies direct evidence for the formation of PMMA-\(b\)-PVAc.

Thus it can be concluded that the diblock copolymer PMMA-\(b\)-PVAc could be successfully synthesized by sequential photo-induced charge transfer polymerization.

Selective Hydrolysis of PMMA-\(b\)-PVAc

Figure 1b shows the FTIR spectrum of a purified sample after hydrolysis of PMMA-\(b\)-PVAc. A new peak at 3441 cm\(^{-1}\) attributable to the hydroxyl group is observed. Figure 2b depicts the respective \(^1\)H NMR spectrum. Here the peak of the PVAc acetyl group at 2.02 ppm disappeared, whereas a new peak at 4.60 ppm can be assigned to the hydroxyl group of PVA. Since the PVAc block of PMMA-\(b\)-PVAc should be selectively hydrolyzed, sodium ethoxide was employed as the catalyst. In order to confirm whether the PMMA block was hydrolyzed simultaneously, a quantitative comparison was conducted utilizing \(^1\)H NMR spectroscopy. The peak of the \(a\)-substituted methyl group (syndiotactic configuration) of the PMMA segment at 0.89 ppm was selected as the internal standard, and the ratios of the integrated areas of the PMMA methoxy group at 3.60 ppm before and after hydrolysis to that of the internal standard were calculated, respectively. It was found that both ratios were nearly equal giving rise to the assumption that the PVAc block only was hydrolyzed. In order to determine whether hydrolysis of the PVAc block was com-
complete, another quantitative comparison was performed by means of $^1H$ NMR spectroscopy. The peak of the α-substituted methyl group (syndiotactic configuration) of the PMMA segment at 0.89 ppm again was selected to be the internal standard, and the ratios of the integrated areas of the PVAc $\text{CH}_1$ group at 4.88 ppm before hydrolysis and the PVA $\text{CH}_1$ group at 3.84 ppm after hydrolysis to that of the internal standard were calculated, respectively. The thus obtained, nearly equal ratios indicated that hydrolysis of the PVAc block was quantitative. We also found no chain cleavage under the given conditions. Hence, diblock copolymer PMMA-$b$-PVAc was completely hydrolyzed using sodium ethoxide as catalyst to give another diblock copolymer: PMMA-$b$-PVA.

Solvent Effects in the Homopolymerization of MMA

Table 1 lists the data of the homopolymerization of MMA. It was found that both the molecular weight of the PMMA prepolymer and the conversion of MMA in THF as the solvent were much higher than those with CH$_3$CN as the solvent under the same polymerization conditions.

<table>
<thead>
<tr>
<th>[Ethanolamine] $10^{-3}$ mol/L</th>
<th>Conversion of MMA (%)</th>
<th>$M_n$</th>
<th>$M_n/M_w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>CH$_3$CN</td>
<td>THF</td>
<td>CH$_3$CN</td>
</tr>
<tr>
<td>4.0</td>
<td>55.1</td>
<td>34.3</td>
<td>26000</td>
</tr>
<tr>
<td>6.0</td>
<td>57.4</td>
<td>36.9</td>
<td>21200</td>
</tr>
<tr>
<td>8.0</td>
<td>59.7</td>
<td>39.2</td>
<td>18400</td>
</tr>
<tr>
<td>10.0</td>
<td>62.5</td>
<td>41.1</td>
<td>16500</td>
</tr>
</tbody>
</table>

Figure 3. GPC traces of PMMA prepolymer (a) and PMMA-$b$-PVAc (b).

Figure 4. Solvent effects in the homopolymerization of MMA; [ethanolamine], [BP] = 1.0 $\times$ 10$^{-2}$ mol/L.

So the molecular weight of the PMMA prepolymer and the conversion of MMA are influenced by solvents.

We think that these phenomena might be caused by chain transfer of the species to the solvent according to the Mayo equation for radical polymerizations\[15\]

$$\frac{1}{X_n} = \left(\frac{1}{X_n}\right)_0 + C_s \frac{[S]}{[M]}$$

where $X_n$ is the degree of polymerization, $(1/X_n)_0$ is the value of $1/X_n$ in the absence of chain transfer agent, [S] and [M] are the concentrations of solvent and monomer. Chain transfer constants $C_s$ of the solvents were determined as the slope of the linear plot of $1/X_n$ vs [S]/[M] with a conversion of MMA lower than 10% (Figure 4); $C_s$ for THF is 21.3 $\times$ 10$^{-4}$ and for CH$_3$CN 53.0 $\times$ 10$^{-4}$. The latter is much higher than the former. Therefore, it is very easy to understand that the molecular weight of the PMMA prepolymer with THF as the solvent should be much higher than that with CH$_3$CN due to the low chain transfer constant of the THF. This is consistent with the experimental results. Since chain transfer to the solvent...
in CH3CN is much easier than that in THF, a large amount of monomer is left in CH3CN which leads to the lower conversion of MMA in CH3CN than in THF.

Solvent Effects in the Block Copolymerization of VAc

The data of the polymerization of VAc are shown in Table 2. Under the same polymerization conditions, only minor differences in the molecular weights of PMMA-b-PVAc and the conversion of VAc are found for THF and CH3CN as the solvent, which is sharply different for the homopolymerization of MMA. In this case, the solvents did not affect the polymerization of VAc.

In order to explain this phenomenon, the chain transfer constants $C_s$ of the two solvents were also determined (Figure 5). The values for THF and CH3CN are 12.9 $\times$ 10^{-4} and 13.2 $\times$ 10^{-4}, respectively. In the range of experimental errors, the difference between them is negligible.

It is well known that imine groups might be enveloped in solvents due to the entanglement of the PMMA prepolymer,[14] leading to a lower photochemical reaction efficiency between imine group and BP, so that the propagation via addition reaction between radical and monomer might be restricted.
Since both THF and CH$_3$CN are good solvents for PMMA, it is probable that the entanglement of the PMMA prepolymer and the envelopment of the imine groups should be similar in both cases. Thus the photochemical reaction environment between PMMA prepolymer and BP should be similar in THF and CH$_3$CN. This explanation could be proved by kinetic measurements both in THF and CH$_3$CN.

Figure 6, Figure 7 and Figure 8 give the relationship between the polymerization rate ($R_p$) of the CTP and the concentrations of ethanolamine (PMMA$_i$), BP and monomer, respectively. When THF is used as the solvent, a normal kinetic expression of the radical polymerization, $R_p \propto$ [ethanolamine]$^{0.49}$[BP]$^{0.50}$[MMA]$^{0.96}$, is obtained for the initiation system consisting of ethanolamine and BP. But when CH$_3$CN is used as the solvent, $R_p \propto$ [Ethanolamine]$^{0.41}$[BP]$^{0.40}$[MMA]$^{0.72}$ which sharply deviates from normal kinetics of a radical polymerization, because of the chain transfer to the solvent. However, for the initiation system composed of PMMA prepolymer and BP, there is only a subtle difference in the kinetics when either THF or CH$_3$CN is used as the solvent. For THF, $R_p \propto$ [PMMA$_i$]$^{0.45}$[BP]$^{0.50}$[VAc]$^{0.74}$ and for CH$_3$CN, $R_p \propto$ [PMMA$_i$]$^{0.43}$[BP]$^{0.44}$[VAc]$^{0.70}$. Thus it can be concluded that the minor effect of the solvents on the polymerization of VAc is attributed to the similar situation of the entanglement of PMMA prepolymer and the envelopment of imine groups both in THF and CH$_3$CN.

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