

# Synthesis and Characterization of Monomer-Casting Polyamide 6/Polymethacrylic Ionomer Blends

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**ABSTRACT:** Monomer-casting polyamide 6 (MCPA6)/polymethacrylic ionomer blends were synthesized by the *in situ* anionic ring-opening polymerization of  $\epsilon$ -caprolactam. The polymethacrylic ionomer used in this study was a copolymer of methyl methacrylate and sodium or zinc methacrylate. Because the polymethacrylic ionomer strongly interacted with polyamide 6 (PA6) chains, it influenced the alignment of the polyamide chains. The change in the degree of the order of hydrogen bonding in MCPA6 caused by the addition of the polymethacrylic ionomer was studied with Fourier transform infrared. The change in the interaction between PA6 chains was studied with rheological measurements. The influence of the polymethacrylic ionomer on the crystallization behavior of MCPA6 was also studied with differential scanning calorimetry. The isothermal crystallization and subsequent melting behavior were investigated at the designated temperature. The commonly used Avrami equation was used to fit the

primary stage of the isothermal crystallization. The Avrami exponent ( $n$ ) values were evaluated to be  $2 < n < 3$  for the neat MCPA6 and MCPA6/polymethacrylic ionomer blends. The polymethacrylic ionomer, acting as a stumbling-block agent in the blends, decelerated the crystallization rate with the half-time of crystallization increasing. The polymethacrylic ionomer made the molecular chains of MCPA6 more difficult to crystallize during the isothermal crystallization process. More less perfect crystals formed in the MCPA6/polymethacrylic ionomer blends because of the interaction between the MCPA6 molecular chains and polymethacrylic ionomer. The crystallinity of the blends was depressed by the addition of the polymethacrylic ionomer. The thermal stability was also studied with thermogravimetric analysis. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2970–2979, 2009

**Key words:** anionic polymerization; blends; crystallization

## INTRODUCTION

Ionomers are metal salts of polymers with unique properties. Commercial ionomers include AClyn Na and Surlyn Na, which are copolymers of ethylene and sodium or zinc acrylate. There are also lots of other kinds of ionomers, such as sulfonated polystyrene and sulfonated poly(ethylene terephthalate). In this study, the ionomer used was a polymethacrylic ionomer, a copolymer of methyl methacrylate and sodium or zinc methacrylate.

Ionomers are well known and are used as crystallization promoters of poly(ethylene terephthalate)<sup>1</sup> or as compatibilizers<sup>2–6</sup> in applications. Ionomers can carry out specific interactions with polyamides. In a polyamide/sulfonated polystyrene system, the formation of an ion-dipole complex between the amide and sulfonate groups has been proved with infrared

spectra,<sup>7</sup> small-angle neutron scattering analysis,<sup>8</sup> and electron paramagnetic resonance.<sup>9</sup> However, polymer blends are most often immiscible because of the small combinatorial entropy of mixing for high-molecular-weight compounds; the miscibility of polyamides and ionomers can be achieved by this intermolecular exothermic interaction.

These specific interactions between polymers and ionomers can lead to an interesting performance of blends.<sup>10–14</sup> In polyamide copolymer/Surlyn ionomer blends, the crystallization process from the molten state of the nylon copolymer can be thwarted with a high concentration of a zinc ionomer.<sup>10</sup>

In this study, we synthesized monomer-casting polyamide 6 (MCPA6)/polymethacrylic ionomer blends by continuous synthesis. The influence of the polymethacrylic ionomer on the degree of the order of hydrogen bonding in MCPA6, the interaction between polyamide 6 (PA6) molecular chains, and the crystallization behavior of MCPA6 were studied with Fourier transform infrared (FTIR), rheological measurements, and differential scanning calorimetry (DSC), respectively. The thermal stability was also

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studied with thermogravimetric analysis (TGA) in this work.

## EXPERIMENTAL

### Materials

$\epsilon$ -Caprolactam (CLA) was obtained from Joint Stock Co. (Grodno, Republic of Belarus). Methyl methacrylate,  $\alpha$ -methacrylic acid, NaOH, ZnO, 2,2'-azobisisobutyronitrile (AIBN; used as an initiator for acrylic polymerization), and *N*-acetylcaprolactam (*N*-COCLA; used as an activator in this work) were purchased from Shanghai Chemical Reagents Co. (Shanghai, China) and used without further treatment.

### Preparation of poly(methyl methacrylate-*co*-methacrylic acid) (PMMA-*co*-MA) in CLA

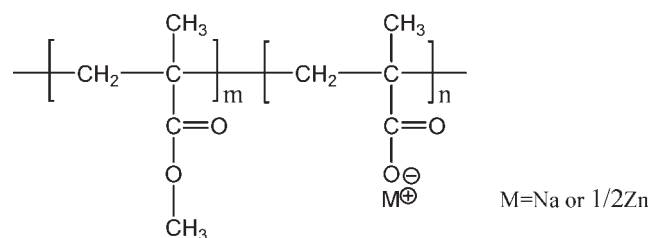
PMMA-*co*-MA was synthesized from methyl methacrylate and methacrylic acid by radical polymerization in CLA. A mixture of MMA (15 g), methacrylic acid (5 g), AIBN (1 g), and CLA (80 g) were placed in a 250-mL glass flask and heated at 80°C for 10 h with tender mechanical stirring. The resulting solution was used to prepare MCPA6/poly(methyl methacrylate) ionomer blends.

### Preparation of the MCPA6/polymethacrylic ionomer blends

An amount of a PMMA-*co*-MA solution was diluted to the desired concentration with CLA. The resulting mixture was first exposed to a vacuum at 140°C for 20 min to remove water. This was followed by the addition of NaOH (0.5 wt % CLA plus 50 wt % methacrylic acid to neutralize the carboxyl groups) under stirring. The vacuum was maintained for another 20 min to remove water, and then *N*-COCLA (0.5 wt % CLA) was added. Immediately, the mixture was poured into a mold preheated to 180°C. After 10 min, the MCPA6/sodium polymethacrylate ionomer blends were obtained. The MCPA6/zinc polymethacrylate ionomer blends were prepared by a similar method, except for the addition of ZnO and NaOH. First, ZnO (50 wt % methacrylic acid) was added to the PMMA-*co*-MA/CLA mixture to neutralize the carboxyl groups. The vacuum was maintained for another 20 min to remove water, and then NaOH (0.5 wt % CLA) was added. To remove water, the vacuum was maintained for more 20 min. After that, *N*-COCLA (0.5 wt % CLA) was added to carry out the anionic ring-opening polymerization. The final polymethacrylic ionomer used in this study was a copolymer of methyl methacrylate and sodium or zinc methacrylate as follows:

**TABLE I**  
Monomer Conversions of Neat MCPA6, MCPA6Na05, MCPA6Na10, MCPA6Zn05, and MCPA6Zn10

| Sample     | Polymethacrylic ionomer content (wt %) | Conversion (wt %) |
|------------|--|-------------------|
| Neat MCPA6 | —                                      | 96.0              |
| MCPA6Na05  | 0.5                                    | 96.1              |
| MCPA6Na10  | 1.0                                    | 95.0              |
| MCPA6Zn05  | 0.5                                    | 95.5              |
| MCPA6Zn10  | 1.0                                    | 95.3              |



Corresponding to the weight percentage of the polymethacrylic ionomer, the names given to the products are neat MCPA6 (0 wt % polymethacrylic ionomer), MCPA6Na05 (0.5 wt % sodium polymethacrylate ionomer), MCPA6Na10 (1 wt % sodium polymethacrylate ionomer), MCPA6Zn05 (0.5 wt % zinc polymethacrylate ionomer), and MCPA6Zn10 (1 wt % zinc polymethacrylate ionomer). The monomer conversion was measured by a comparison of the sample weight before and after extraction of the unreacted monomer with water, as shown in Table I. It was evident that the polymethacrylic ionomer content had almost no influence on the monomer conversion in this study.

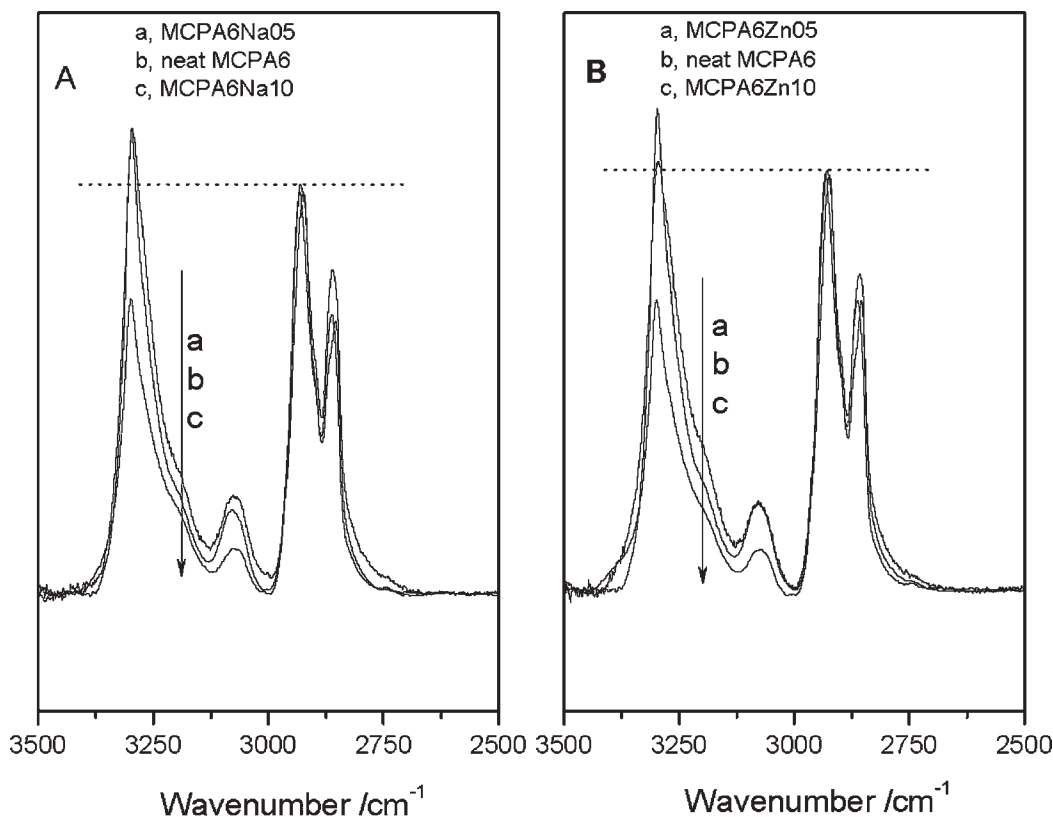
### Characterization

FTIR spectroscopy was carried out on a Nicolet Avatar 360 FTIR spectrometer. Each sample was annealed at 250°C to erase any previous thermal history and naturally cooled to room temperature.

DSC measurements were performed on a Netzsch DSC 200 PC (Bavaria, Germany) in a nitrogen atmosphere at a heating and cooling rate of 10 K/min. Calibration was achieved with indium standard samples. All the measurements were performed from room temperature to 250°C, the samples were held there for 5 min to erase any previous thermal history, and then subsequent cooling and second heating cycles were recorded. The melting enthalpy in the second heating scan was used to measure the degree of crystallization ( $X_c$ ) according to the following equation:

$$X_c = \Delta H_f / F\Delta H_f^* \times 100\% \quad (1)$$

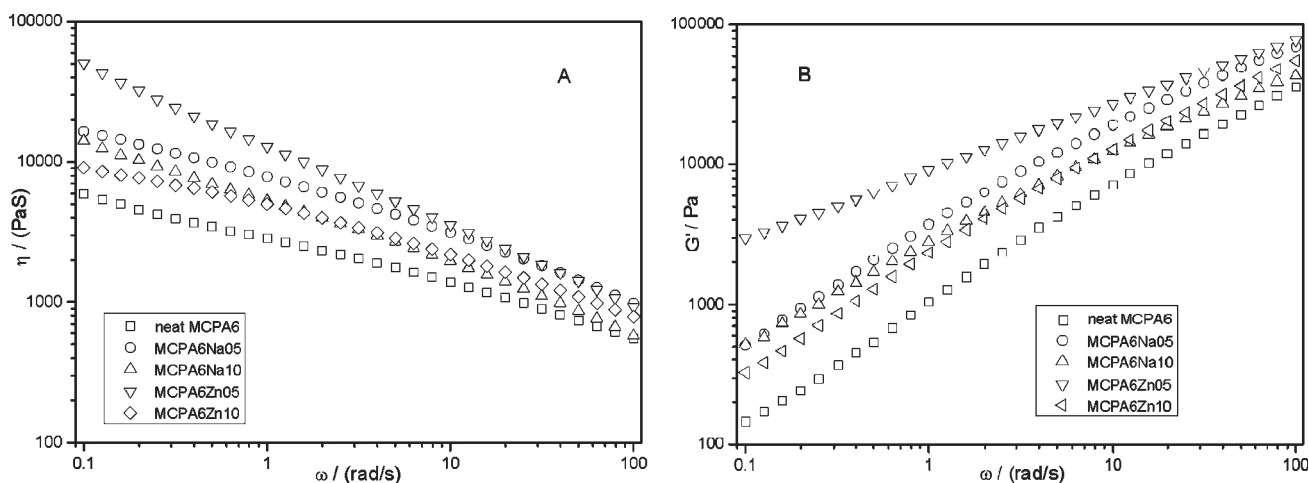
where  $\Delta H_f$  is the melting enthalpy of MCPA6 (or PA6) in the sample,  $F$  is the homopolymer weight



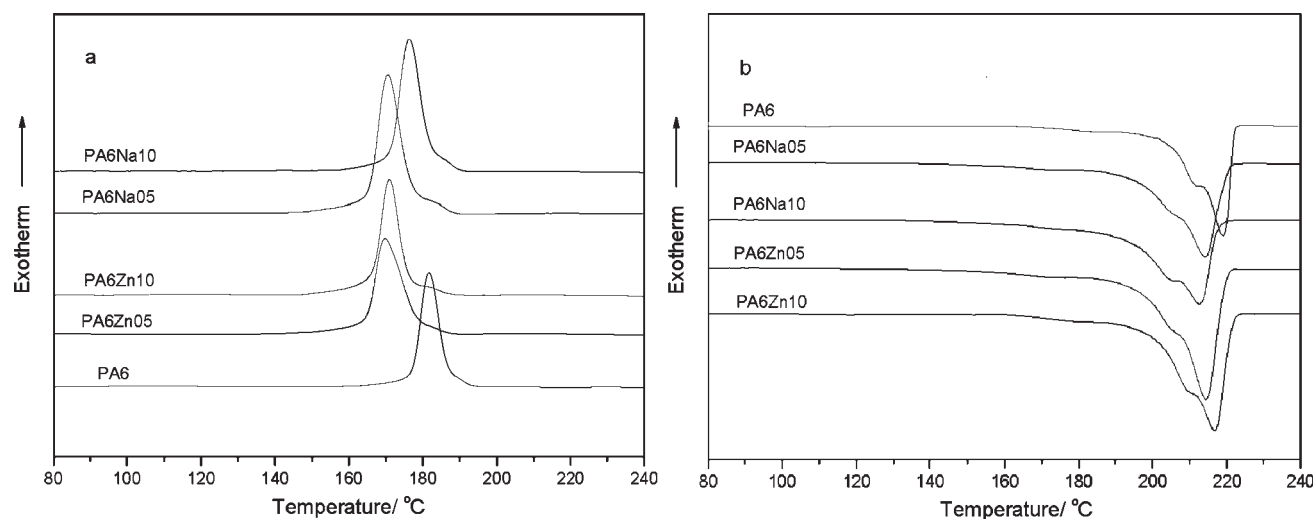
**Figure 1** FTIR spectra of the N—H stretching region of various samples in the range of 3500–2500  $\text{cm}^{-1}$ .

fraction in the blend, and  $\Delta H_f^*$  is the melting enthalpy of the matrix polymer of 100% crystallization ( $\Delta H_f^* = 230 \text{ J/g}^{15}$ ). Moreover, the values of the degree of supercooling ( $\Delta T_d = T_m - T_c$ , where  $T_m$  is the melting point and  $T_c$  is the maximum crystallization temperature), which were indirectly proportional to the rate of crystallization, were used for the examination of the influence of the blend components on the crystallization rate of MCPA6.

Rheological measurements were carried out on an Advanced Rheometric Expansion System (Rheometrics Scientifics, United States) with a parallel-plate fixture (25 mm in diameter). Dynamic frequency sweep experiments were carried out under a nitrogen flow, with the viscosity ( $\eta$ ) and storage modulus ( $G'$ ) measured as functions of the shear rate ( $\omega$ ), which ranged from 0.1 to 100 rad/s, at 230°C. The measurements were made with 1-mm-thick samples and a constant shear amplitude of 5%.



**Figure 2** Viscoelastic properties of various samples at 230°C: (A) plots of  $\log \eta$  versus  $\log \omega$  and (B) plots of  $\log G'$  versus  $\log \omega$ .



**Figure 3** Thermograms of neat MCPA6 and MCPA6Na05, MCPA6Na10, MCPA6Zn05, and MCPA6Zn10 blends: (a) second heating and (b) cooling.

TGA was carried out with an SDT Q600 (TA Instrument Corp., New Castle, DE) at a heating rate of 10°C/min up to 550°C under a nitrogen flow.

## RESULTS AND DISCUSSION

### Strength and degree of the ordering of hydrogen bonds studied by FTIR

Introducing a polymethacrylic ionomer, which also has carbonyl groups and cations, especially  $\text{Zn}^{2+}$ , with a capacity for combination, may influence the alignment of polyamide chains, resulting in a different hydrogen-bonding status. Figure 1 illustrates infrared spectra in the range of 3500–2500  $\text{cm}^{-1}$  for MCPA6/ionomer (0, 0.5, or 1 wt %) at room temperature. The band at about 3300  $\text{cm}^{-1}$  indicates a hydrogen-bonded N—H stretching vibration.<sup>16–18</sup> We can see that the intensity of the band decreases and the width of the band becomes broad. It is well known that the breadth of the band is mainly a reflection of the distribution of hydrogen-bonded groups: the broader the band is, the more disordered the sample is.<sup>17</sup> The widths at half-height of the MCPA6/polymethacrylic ionomer blends are larger than that of the neat MCPA6, and this suggests that the introduction

of the polymethacrylic ionomer increased the distribution of the hydrogen-bonded N—H groups with various strengths and evidently lowered the degree of the order of hydrogen bonding.

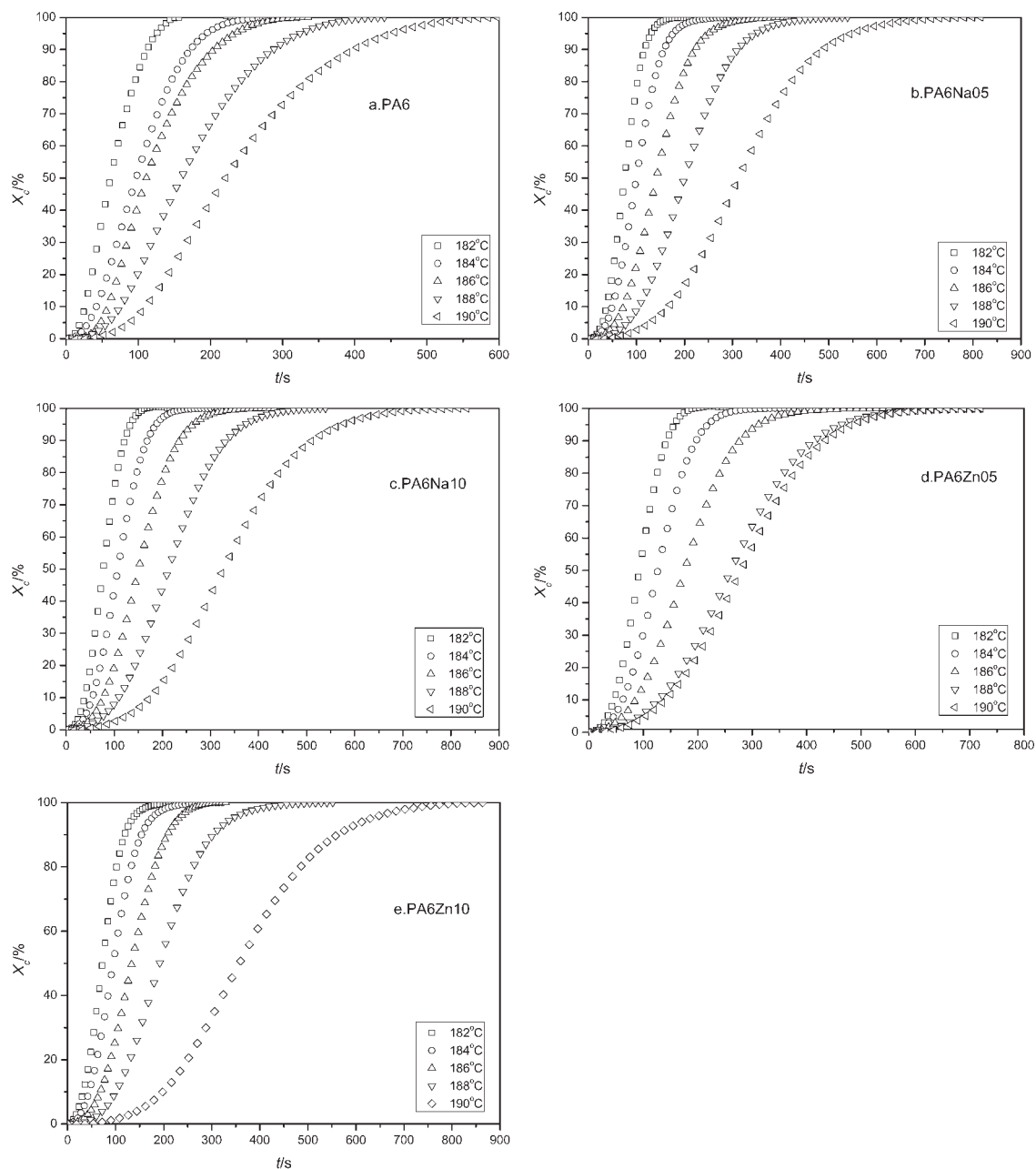
### Rheological behavior

As is well known, the viscoelastic response of melted PA6 is related to the interaction of PA6 chains. The effect of the polymethacrylic ionomer on the hydrogen bonds of MCPA6 can also be verified by the viscoelastic properties, as shown in Figure 2. The addition of the polymethacrylic ionomer resulted in higher  $\eta$  and  $G'$  values in comparison with neat MCPA6. This may be due to the essential formation of a graft copolymer by the formation of an ion-dipole complex between the amide and acrylate groups.<sup>8</sup> The ion-dipole action was stronger than hydrogen bonding, and this enhanced the interaction between PA6 chains and improved  $\eta$  and  $G'$ . It is worth noting that for MCPA6Zn10, the complex viscosity did not reach a plateau value, and it tended to show a leveling-off in  $G'$  at low frequencies.<sup>18</sup> This gel-like characteristic was due to the network structure formed from the zinc

**TABLE II**  
Characteristic Values of the Crystallization and Melting Behavior of Neat MCPA6, MCPA6Na05, MCPA6Na10, MCPA6Zn05, and MCPA6Zn10

| Sample     | Content (wt %) | $T_{m1}$ (°C) | $T_{m2}$ (°C) | $T_c$ (°C) | $\Delta H_m$ (J/g) <sup>a</sup> | Crystalline degree (%) | $\Delta T_d$ (°C) |
|------------|----------------|---------------|---------------|------------|---------------------------------|------------------------|-------------------|
| Neat MCPA6 | 0              | 211.5         | 218.9         | 181.7      | 44.7                            | 19.4                   | 37.2              |
| MCPA6Na05  | 0.5            | 204.9         | 214.4         | 170.6      | 35.2                            | 15.3                   | 43.8              |
| MCPA6Na10  | 1.0            | 204.7         | 216.5         | 176.3      | 38.0                            | 16.5                   | 40.2              |
| MCPA6Zn05  | 0.5            | 204.9         | 214.1         | 169.8      | 35.3                            | 15.3                   | 44.3              |
| MCPA6Zn10  | 1.0            | 209.5         | 212.6         | 171.0      | 26.8                            | 11.7                   | 41.6              |

<sup>a</sup> Melting enthalpy.



**Figure 4**  $X_c$  versus time  $t$  for the isothermal crystallization of (a) neat MCPA6 and (b) MCPA6Na05, (c) MCPA6Na10, (d) MCPA6Zn05, and (e) MCPA6Zn10 blends at different  $T_c$  values.

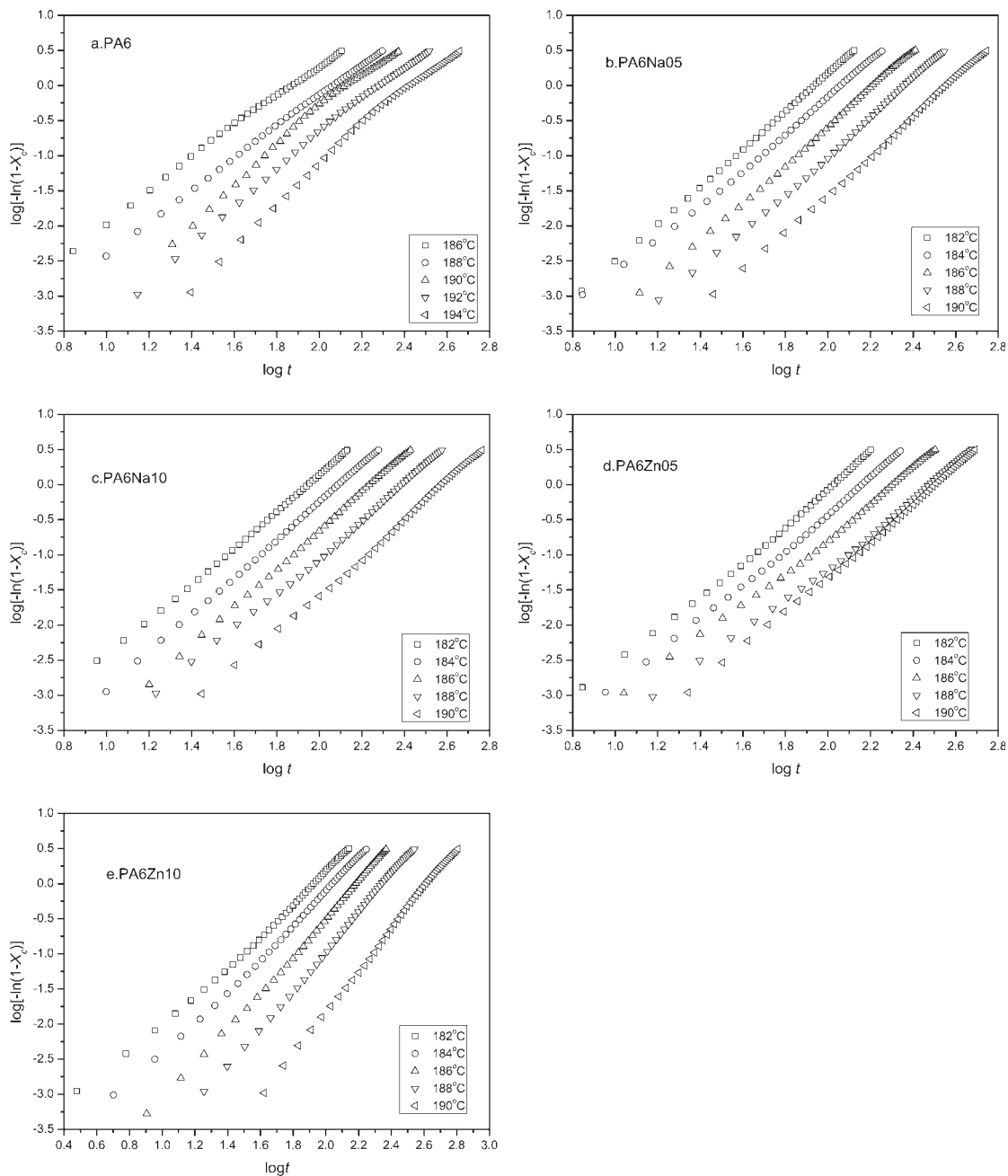
polymethacrylate ionomer and MCPA6 chains with the ion-dipole complex as the crosslinking point.

### Crystallization behavior of the MCPA6/poly-methacrylic ionomer blends

#### Melting and crystallization behavior

The crystallization behavior of the MCPA6/poly-methacrylic ionomer blends was investigated with DSC. The heating and cooling thermograms of neat MCPA6 and MCPA6/poly-methacrylic ionomer blends are compared in Figure 3. The data are summarized in Table II in detail.

DSC cooling scans of MCPA6 and MCPA6/poly-methacrylic ionomer blends are shown in Figure 3(a). The crystallization temperature ( $T_c$ ) of the MCPA6/poly-methacrylic ionomer blends decreased to various extents in comparison with neat MCPA6 (174.4°C). The second heating DSC traces are presented in Figure 3(b), in which the peaks around 211 and 218°C can be attributed to the melting peaks of crystals with different crystal perfections;<sup>19–21</sup> this is further discussed in the section on isothermal crystallization kinetic analysis. The melting temperature of the MCPA6/poly-methacrylic ionomer blends was much lower than that of the pure MCPA6. With



**Figure 5** Plots of  $\log\{-\ln[1 - X_c(t)]\}$  versus  $\log t$  for (a) neat MCPA6 and (b) MCPA6Na05, (c) MCPA6Na10, (d) MCPA6Zn05, and (e) MCPA6Zn10 blends after isothermal crystallization at the indicated temperatures.

increasing polymethacrylic ionomer content, there were almost no changes in these two melting peaks and no changes in the crystalline form. Furthermore, Table II shows that the crystalline degree of MCPA6 decreased,  $\Delta T_d$  increased, and the half peak width of the crystalline peaks widened in comparison with those of neat MCPA6; this indicated that the ability to crystallize was baffled by the addition of the polymethacrylic ionomer. This might be due to the influence on the hydrogen bonding between MCPA6 chains. The introduction of the polymethacrylic ionomer increased the distribution of the hydrogen-

bonded N—H groups, as proved by FTIR, and this suggested that there was a stronger interaction between MCPA6 and the polymethacrylic ionomer that limited the mobility of the MCPA6 molecule chains and wrecked the crystallization of MCPA6. Therefore, MCPA6 formed more imperfect crystals. This was in good agreement with the rheological results.

#### Isothermal crystallization kinetic analysis

*Analysis based on the Avrami equation.* To quantitate the influence of the polymethacrylic ionomer on the

crystallization of MCPA6, isothermal crystallization kinetic analysis was studied. Figure 4 shows the relative crystallinity ( $X_t$ ) integrated from exothermal diagrams of the isothermal crystallization analysis as a function of the crystallization time ( $t$ ) for samples MCPA6, MCPA6Na05, MCPA6Na10, MCPA6Zn05, and MCPA6Zn10 at various isothermal  $T_c$  values. In Figure 4(a–e), as  $T_c$  increases, the characteristic sigmoidal isotherms are shifted to the right along the time axis, and this indicates that  $T_c$  is an important influencing factor determining  $t$ . This result indicates a progressively slower crystallization rate as  $T_c$  increases.

If we assume that  $X_t$  increases with  $t$ , the Avrami equation can be used to analyze the isothermal crystallization process of the neat MCPA6 and MCPA6/polymethacrylic ionomer blends as follows:<sup>22,23</sup>

$$1 - X_c(t) = \exp(-Z_t t^n) \quad (2)$$

$$\log[-\ln(1 - X_c(t))] = n \log t + \log Z_t \quad (3)$$

where  $X_c(t)$  is the relative degree of crystallinity at time  $t$ , Avrami exponent  $n$  is a mechanism constant with a value depending on the type of nucleation and the growth dimension, and parameter  $Z_t$  is a growth rate constant involving both nucleation and growth rate parameters.

Plots of  $\log\{-\ln[1 - X_c(t)]\}$  versus  $\log t$  according to eq. (3) are shown in Figure 5. The crystallization process is usually divided into two stages: the primary crystallization stage and the secondary crystallization stage. In Figure 5, we can see that each curve is composed of two linear sections. This fact indicates the existence of secondary crystallization for the neat MCPA6 and MCPA6/polymethacrylic ionomer blends. It is generally believed that secondary crystallization is caused by spherulite impingement in the later stage of the crystallization process.<sup>23–27</sup> Comparing three curves measured at the same temperature, such as  $T_c = 186^\circ\text{C}$ , as shown in Figure 5(a–e), we can see that the times of secondary crystallization for MCPA6Na05 and MCPA6Zn05 were 158 ( $\log t = 2.2$ ) and 199 s ( $\log t = 2.3$ ), respectively, and the times of secondary crystallization for MCPA6Na10 and MCPA6Zn10 were not apparent. These were much longer than that of the neat MCPA6 ( $t = 40$  s,  $\log t = 1.6$ ). This fact indicates that without the intervention of the polymethacrylic ionomer, the nuclei in the neat MCPA6 grew rapidly into spherulites before they impinged against one another. By a stronger interaction with MCPA6, the polymethacrylic ionomer limited the mobility of the MCPA6 molecule chains, caused primary crystallization to be completed later, and wrecked the crystallization of MCPA6.

$n$  and  $Z_t$  can readily be extracted from the Avrami plots in Figure 5. The values of  $n$  and  $Z_t$  of various

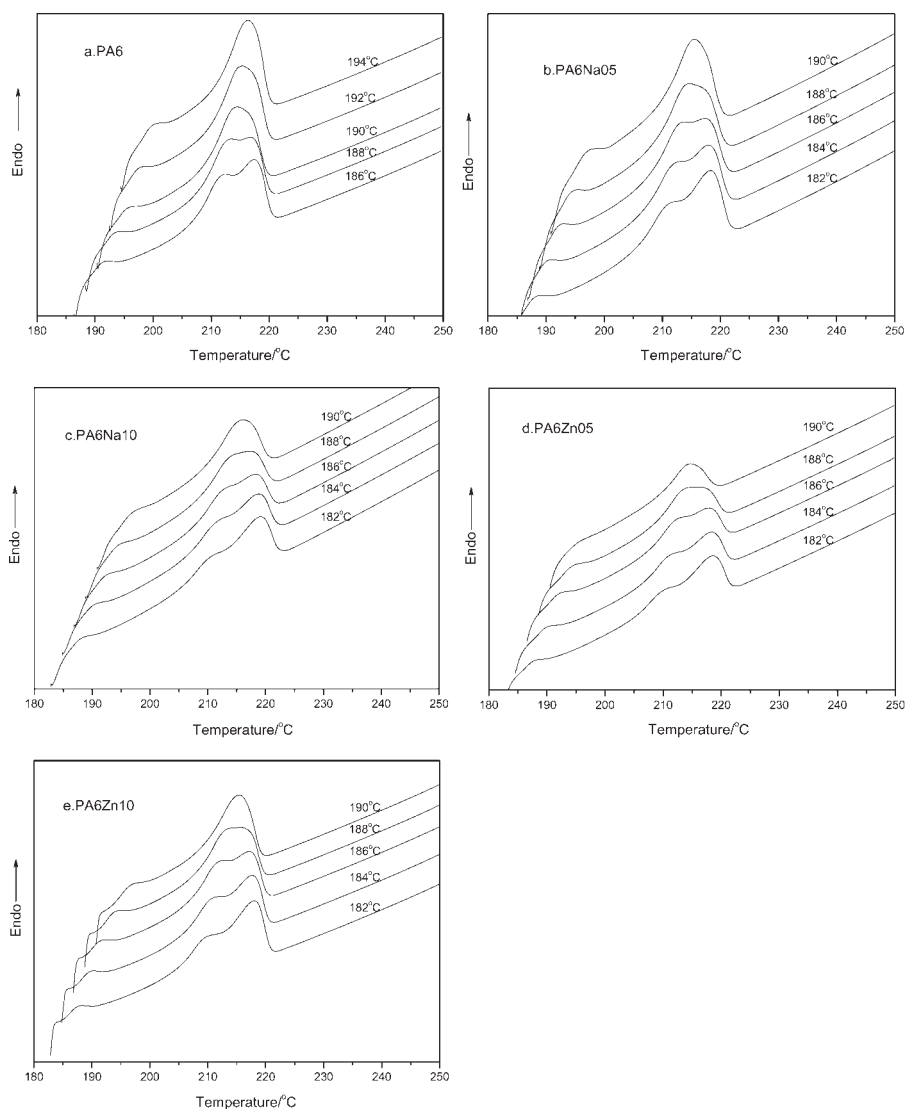
**TABLE III**  
Kinetic Parameters of Isothermal Crystallization for Various Samples

| Sample    | $T_c$ ( $^\circ\text{C}$ ) | $n$   | $Z_t \times 10^7$ | $t_{1/2}$ (s) |
|-----------|----------------------------|-------|-------------------|---------------|
| MCPA6     | 186                        | 2.2   | 716               | 61.5          |
|           | 188                        | 2.2   | 518               | 97.0          |
|           | 190                        | 2.5   | 40.5              | 111.4         |
|           | 192                        | 2.5   | 24.9              | 160.0         |
|           | 194                        | 2.6   | 4.24              | 221.0         |
| MCPA6Na05 | 182                        | 2.6   | 61.1              | 75.5          |
|           | 184                        | 2.6   | 50.8              | 100.0         |
|           | 186                        | 2.7   | 9.26              | 142.2         |
|           | 188                        | 2.7   | 3.53              | 200.1         |
|           | 190                        | 2.8   | 0.809             | 313.1         |
| MCPA6Na10 | 182                        | 2.6   | 99.0              | 77.5          |
|           | 184                        | 2.7   | 24.3              | 107.6         |
|           | 186                        | 2.7   | 7.71              | 150.7         |
|           | 188                        | 2.7   | 5.72              | 213.0         |
| MCPA6Zn05 | 190                        | 2.7   | 1.04              | 327.4         |
|           | 182                        | 2.4   | 68.5              | 93.0          |
|           | 184                        | 2.4   | 37.7              | 126.8         |
|           | 186                        | 2.5   | 25.5              | 175.9         |
|           | 188                        | 2.6   | 11.4              | 216.8         |
| MCPA6Zn10 | 190                        | 2.6   | 3.37              | 218.1         |
|           | 182                        | 2.2   | 595               | 72.5          |
|           | 184                        | 2.4   | 143               | 95.4          |
|           | 186                        | 2.6   | 17.2              | 134.0         |
|           | 188                        | 2.8   | 3.22              | 192.5         |
| 190       | 3.0                        | 0.190 | 357.6             |               |

samples are listed in Table III. In this work, the values of  $n$  are between 2 and 3 for the neat MCPA6, MCPA6Na05, MCPA6Na10, MCPA6Zn05, and MCPA6Zn10. It may be an average value of various nucleation types and growth dimensions occurring simultaneously in the crystallization process. At  $T_c = 186^\circ\text{C}$  (Table III), the  $n$  values slightly increased with the addition of the polymethacrylic ionomer in the primary crystallization stage. For neat MCPA6 without any heterogeneous nucleus, the nucleation type should be predominantly homogeneous, and the growth dimensions should be predominantly two-dimensional. For the MCPA6/polymethacrylic ionomer blends with the heterogeneous nucleus polymethacrylic ionomer, the nucleation type should mostly be heterogeneous, and the growth dimension should mostly be a two-dimensional space extension.

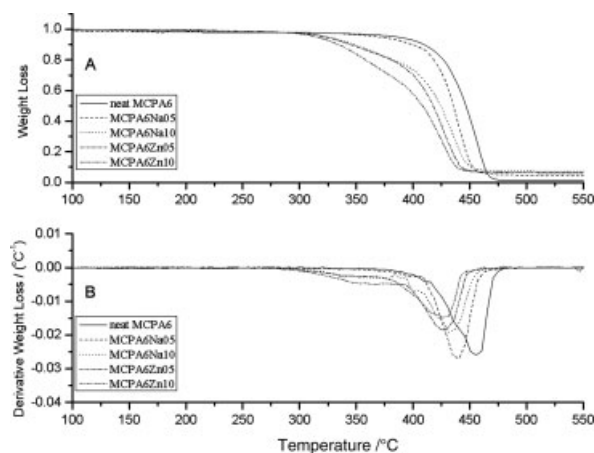
The crystallization rate parameter ( $Z_t$ ) values of the neat MCPA6 and MCPA6/polymethacrylic ionomer blends are also listed in Table III. At  $T_c = 186^\circ\text{C}$ ,  $Z_t$  for the polymethacrylic ionomer blends decreased by about 30–100 times with respect to that for the neat MCPA6. These facts indicate that the polymethacrylic ionomer prominently reduced the crystallization rate.

Another important parameter is the half-time of crystallization ( $t_{1/2}$ ), which is defined as the time



**Figure 6** Melting endotherms of (a) neat MCPA6 and (b) MCPA6Na05, (c) MCPA6Na10, (d) MCPA6Zn05, and (e) MCPA6Zn10 blends recorded at a heating rate of 10°C/min after isothermal crystallization at the specified temperature.

taken from the onset of the relative crystallization until 50% completion. The dependence of  $t_{1/2}$  on  $T_c$  for various samples is also listed in Table III.  $t_{1/2}$  of the neat PA6 increased sharply as  $T_c$  increased from 186 to 194°C, and this indicated that the neat MCPA6 was a thermally activated crystallization polymer. At  $T_c = 186^\circ\text{C}$ ,  $t_{1/2}$  of the polymethacrylic ionomer blends was evidently longer than that of the neat MCPA6. From these results, a clear decrease in the crystallization rate occurred as the polymethacrylic ionomer was added to the MCPA6 matrix. *Melting behavior of the samples annealed at different temperatures.* Figure 6 presents a series of DSC heating thermograms for the neat MCPA6 and MCPA6/polymethacrylic ionomer blends annealed at different  $T_c$ 's. The endotherms of the neat MCPA6 and MCPA6/polymethacrylic ionomer blends exhibit



**Figure 7** (A) TGA and (B) DTG curves of neat MCPA6 and MCPA6Na05, MCPA6Na10, MCPA6Zn05, and MCPA6Zn10 blends.



TABLE IV  
TGA Values for 10, 30, and 50 wt % Losses, Char Yields, and  $T_{\max}$  Values for Neat MCPA6, MCPA6Na05, MCPA6Na10, MCPA6Zn05, and MCPA6Zn10

| Sample     | $T_{10\text{wt}\%}$ (°C) | $T_{30\text{wt}\%}$ (°C) | $T_{50\text{wt}\%}$ (°C) | Char yield (%) | $T_{\max}$   |
|------------|--------------------------|--------------------------|--------------------------|----------------|--------------|
| Neat MCPA6 | 409.4                    | 435.1                    | 446.6                    | 1.2            | 454.3        |
| MCPA6Na05  | 399.1                    | 426.2                    | 435.4                    | 4.7            | 440.1        |
| MCPA6Na10  | 348.4                    | 405.4                    | 424.1                    | 7.2            | 357.3, 435.6 |
| MCPA6Zn05  | 344.5                    | 400.1                    | 417.6                    | 6.6            | 357.6, 426.1 |
| MCPA6Zn10  | 334.0                    | 379.5                    | 408.4                    | 6.4            | 357.5, 426.3 |

$T_{10\text{wt}\%}$  = 10 wt % weight-loss temperature;  $T_{30\text{wt}\%}$  = 30 wt % weight-loss temperature;  $T_{50\text{wt}\%}$  = 50 wt % weight-loss temperature.

two melting peaks when annealed at a temperature below 190°C. Apparently, with  $T_c$  decreasing, the peak at the lower temperature becomes smaller and shifts more sharply to a low temperature than the other peak, which almost does not shift. According to similar explanations for multiple endotherms of PA6,<sup>17–19</sup> these peaks mainly refer to the melting of crystals with different crystal perfections. The cause of the peak at the lower temperature is assumed to be the primary crystal with its perfect form and melting crystallization, whereas the peak at the higher temperature is attributed to the melting of the furthest perfect crystals formed during the melting crystallization. As  $T_c$  increases, the peaks at the lower temperature become smaller, and this indicates that more perfect crystals have formed at a higher  $T_c$ . Furthermore, there is one weak peak around the temperature (ca.  $T_c + 5^\circ\text{C}$ ) for each thermogram. These peaks are named annealing peaks<sup>28,29</sup> and are caused by the melting of the furthest imperfect crystals formed in the rapid-cooling stage.

### Thermal stability

As is known, the addition of metal ions to PA6 influences the thermal stability.<sup>30</sup> Typical TGA weight-loss and derivative thermograms [derivative thermogravimetry (DTG)] for various samples in a nitrogen environment are shown in Figure 7(A,B), respectively. The TGA 10, 30, and 50 wt % loss temperatures, maximum decomposition temperature ( $T_{\max}$ ) values, and char yields are summarized in Table IV. As expected, MCPA6 with the polymethacrylic ionomer had poorer thermal stability than MCPA6, and this probably can be attributed to the fact that the metal ion could act as a catalyzer and result in poorer thermal stability of MCPA6. As shown in Figure 7(A), the zinc polymethacrylate ionomer had a stronger influence than the sodium polymethacrylate ionomer.

### CONCLUSIONS

MCPA6/polymethacrylic ionomer blends were synthesized by *in situ* anionic ring-opening polymerization of CLA. The ionomer used in this study was a copolymer of methyl methacrylate and sodium or zinc methacrylate. The polymethacrylic ionomer had a strong ion-dipole interaction with MCPA6 molecular chains. The influence of this interaction on the degree of the order of hydrogen bonding, rheological properties, and crystallization behavior was studied. The polymethacrylic ionomer increased the distribution of the hydrogen-bonded N–H groups with various strengths and evidently lowered the degree of the order of hydrogen bonding. Rheological measurements showed that the polymethacrylic ionomer enhanced the interaction between MCPA6 chains and improved  $\eta$  and  $G'$ . The influence of the polymethacrylic ionomer on the crystallization behavior of MCPA6 was also proved by the investigation of the isothermal crystallization and melting behavior, which indicated that the polymethacrylic ionomer acted as a stumbling-block agent, and the ability of MCPA6 to crystallize was baffled by the addition of the polymethacrylic ionomer. The polymethacrylic ionomer decelerated the crystallization rate and depressed the crystallinity.

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