Copolymers of 2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene with Styrene and Methyl Methacrylate: Synthesis, Monomer Reactivity Ratios, Thermal Properties, and Liquid Crystalline Behavior

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Received 20 October 2004; accepted 19 January 2005
DOI: 10.1002/pola.20742
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Copolymers of a liquid crystalline monomer, 2,5-bis[(4-methoxyphenyl)oxycarbonyl]styrene (MPCS), with St and MMA were prepared by free radical polymerization at low conversion in chlorobenzene with 2,2'-azobisisobutyronitrile (AIBN) as initiator. The copolymers of poly(MPCS-co-St) and poly(MPCS-co-MMA) were characterized by $^1$H NMR and GPC. The monomer reactivity ratios were determined by using the extended Kelen–Tudos (EKT) method. Structural parameters of the copolymers were obtained from the possibility statistics and monomer reactivity ratios. The influence of MPCS content in copolymers on the glass transition temperatures of copolymers was investigated by DSC. The thermal stabilities of the two copolymer systems increased with an increase of the molar fraction of MPCS in the copolymers. The liquid crystalline behavior of the copolymers was also investigated using DSC and POM. The results revealed that the copolymers with high MPCS molar contents exhibited liquid crystalline behaviors. © 2005 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 43: 2666–2674, 2005

Keywords: glass transition; liquid crystalline polymer; radical copolymerization; reactivity ratios; thermogravimetric analysis (TGA)

INTRODUCTION

The mesogen-jacketed liquid crystalline polymers (MJLCPs) in which the mesogenic units are laterally attached to the polymer main chain without or with very short spacers have been attracting considerable attention since Zhou et al. first proposed the concept in 1987. Unlike conventional side chain liquid crystalline polymers (SCLCPs) with long spacers, the absence of spacers for MJLCPs leads to semirigid main chain conformations and some properties similar to main chain liquid crystalline polymers (MCLCPs) because of the steric requirement of the side groups and the strong interactions between the side groups and the backbones. Most MCLCPs are synthesized by condensation polymerization, in which it is difficult to control the molecular weight and architecture. In addition, condensation polymerization has strict requirements for polymerization conditions and monomer purity. One of the primary advantages of MJLCPs is that they can be synthesized via chain polymerization as conventional SCLCPs. Because of their unique molecular architecture, many studies related to MJLCPs were made,
including molecular design of novel types of MJLCPs,5–7 synthesis of new rod-coil diblock copolymers8 and its self-assembly behaviors in dilute solution,9,10 synthesis of the hybrid liquid crystalline diblock copolymers,11 and the investigation of morphology and rheology.12

For LC monomers, the polymerization kinetics may be complicated by preordering or self-assembly of monomers.13 Recently, Ober et al.14 investigated the stable free radical polymerization (SFRP) of a MJLCP monomer, 2,5-bis[(4-butylbenzoyl)oxy]styrene (BBOS), and noticed that BBOS polymerized an order of magnitude faster than styrene under identical bulk polymerization conditions. The effects of both electron-withdrawing substituents and liquid crystallinity of BBOS on the polymerization kinetics were reported. To examine the influence of mesogenic units on the reactivity of MJLCP's monomer, the copolymerization reactivity ratios of MJLCP's monomer with other monomers should be investigated.

Moreover, copolymerization is an important and useful way to develop new materials. Copolymerization modulates both the intramolecular and intermolecular forces exercised between like and unlike polymer segments. Therefore, properties such as the glass transition temperature, melt point, solubility, crystallinity, permeability, adhesion, elasticity, and chemical reactivity may be varied within wide limits.15,16 For liquid crystalline copolymer, liquid crystalline behavior is also associated with copolymer composition.17 As one of the most important parameters for the composition equations of copolymers, the reactivity ratios can offer information such as the relative reactivity of monomer pairs, the monomer composition, and distribution in the copolymer.18–21 There was a report22 that preliminarily discussed the effect of composition of 2,5-bis[(4-methoxyphenyl)oxy carbonyl]-styrene, MPCS (one of MJLCP's monomers), on the liquid crystalline behavior of copolymers, but the microstructure of the copolymers was still unknown. To date, no studies on copolymerization reactivity ratios of MJLCP's monomer with other monomers have been reported.

This article discusses the copolymerization of MPCS with styrene (St) and methyl methacrylate (MMA) at low conversion and estimates the monomer reactivity ratios. The relationship between the monomer ratio in the feed and that in copolymers was established. Based on reactivity ratios, structural parameters of the copolymers were also obtained. Meanwhile, the effects of monomer composition in copolymers on thermal properties and liquid crystalline behavior were studied.

EXPERIMENTAL

Materials
MMA and St were freed from the inhibitor via passing through a column of silica gel. After drying over calcium hydride, they were distilled under vacuum. 2,2’-Azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. Chlorobenzene was washed with H2SO4, NaHCO3, and distilled water separately, and was distilled from calcium hydride. Monomer 2,5-bis[(4-methoxyphenyl)oxy carbonyl]-styrene (MPCS) was prepared as reported.5

Copolymerization Reaction
Solution copolymerizations (40 wt %) of MPCS with St and MMA, with different feed compositions, were carried out in chlorobenzene at 60 ± 0.5 °C using AIBN as initiator (0.05%, based on the total molar of monomers). Typical procedures of polymerization were as follows. An appropriate amount of AIBN, monomers, and chlorobenzene were mixed in a reaction tube. After three freeze–pump–thaw cycles, the tube was sealed under vacuum and put into a 60 ± 0.5 °C water bath. In most experiments, the copolymerization was terminated before the conversion reached 10%, and in no case did the conversion exceed 15%. After the tube was broken, the mixture was diluted with THF and then poured into a large amount of methanol to precipitate the polymer. The polymers were purified by precipitation in methanol from THF solution three times to eliminate the unreacted monomers completely. After purification, the polymers were dried to a constant weight. The monomer conversions were calculated by gravimetry, and the amounts of monomeric units in the copolymers were determined from 1H NMR spectra.

Measurements
Gel permeation chromatography (GPC) measurements were carried out in THF with a Waters 2410 instrument equipped with a Waters
2410 RI detector and three Waters μ-Styragel columns (10^3, 10^4, and 10^5 Å). The flow rate was 1.0 mL min\(^{-1}\) at 35 °C. The calibration curve was obtained by polystyrene standards. \(^1\)H NMR spectra were obtained with a BRUKER 400 MHz spectrometer at room temperature in dichloromethane-d\(_2\). Differential scanning calorimetry (DSC) examination was carried on a TA DSC Q100 calorimeter at a heating rate of 10 °C min\(^{-1}\) under continuous nitrogen flow. The sample size was about 4 mg, and the data was based on the second heating process. The thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 10 °C min\(^{-1}\) in a nitrogen atmosphere. Polarized optical microscopy (POM) observation was conducted on a Leitz Laborlux 12 microscope with a Leitz 350 hot stage.

RESULTS AND DISCUSSION

Copolymerization

The copolymerizations of MPCS with St and MMA in chlorobenzene were studied with different monomer to monomer ratios in the feed. The constituent monomeric units of the copolymers are as shown in Scheme 1. The conversions of copolymerization were controlled below 10%, and in no case did the conversions exceed 15%. The data of the feed ratios and the characteristics of two series of copolymers are summarized in Table 1.

The \(^1\)H NMR spectra of poly(MPCS-co-St) (PS-5) and poly(MPCS-co-MMA) (PMMA-2) are presented in Figure 1. The composition of copolymers was determined from peak intensities at 8.0–7.2 ppm (middle phenyl ring protons of MPCS) and 7.1–6.0 ppm (side phenyl ring protons of MPCS and phenyl ring protons of St) for the poly(MPCS-co-St) system. For the poly(MPCS-co-MMA) system, the composition of copolymers was determined from peak intensities at 8.0–7.2 ppm (middle phenyl ring protons of MPCS), 7.1–6.0 ppm (side phenyl ring protons of MPCS), and 1.0–0.1 ppm (methyl protons of MMA).\(^{21}\) The results are summarized in Table 1.

Monomer Reactivity Ratios and Copolymer Structures

The monomer reactivity ratios for the copolymerization of MPCS with St and MMA were determined from the monomer feed ratios and the copolymer compositions using linearization methods of Fineman–Ross (F–R),\(^{23}\) rearrange Fineman–Ross (rearrange F–R),\(^{23}\) and Kelen–Tudos (K–T).\(^{24}\)

We noticed that the \(r_{\text{MPCS}} \gg r_{\text{St}}\) (and \(r_{\text{MMA}}\)), so we calculated the reactivity ratios using the extended Kelen–Tudos (EKT) method when the effect of conversion is considered.\(^{18,25}\) In the EKT method, the partial molar conversions for the two comonomers are defined as:

\[
\zeta_2 = W(\mu + X)/\mu + Y
\]

(1)

\[
\zeta_1 = \zeta_2(Y'/X')
\]

(2)

where \(W\) is the weight conversion of polymerization, and \(\mu\) is the ratio of molecular weights of monomer 2 to that of monomer 1, with \(X = F_1/F_2\) and \(Y = f_1/f_2\).

Then:

\[
Z = \log(1 - \zeta_1)/\log(1 - \zeta_2)
\]

(3)

With the \(Z\) factor, \(\eta\) and \(\xi\) are equal to \(G/(\alpha + H)\) and \(H/(\alpha + H)\), respectively, where \(G\) and \(H\) are defined as \((Y - 1)/Z\) and \(Y/Z^2\), respectively.
The EKT plot of the poly(MPCS-co-MMA) system is presented in Figure 2, and the results are shown in Table 2. For comparison sake, of the reactivity ratios of the monomers with St and MMA in the Polymer Handbook,\textsuperscript{26} there were few greater than those of MPCS with St and MMA. Agron et al.\textsuperscript{27} reported that the reactivity ratios of MMA (M\textsubscript{1}) and 2,5-dichloro styrene (M\textsubscript{2}) were 0.44 and 2.25, respectively. Katz\textsuperscript{28} reported the reactivity ratios of styrene (M\textsubscript{1}) and 9-vinylphenanthrene (M\textsubscript{2}) were 0.58 and 2.36, respectively. The fact that reactivity ratios of M\textsubscript{2} in the above systems are higher than St and MMA is similar to our results. The molecular structure of 2,5-dichloro styrene (M\textsubscript{2}) is similar to MPCS if we take MPCS as styrene substituted by two [(4-methoxy)phenyl]oxycarbonyl groups at the ortho and meta positions, respectively. The reactivity ratio of styrenic monomer is affected by the distance of the substituent to the vinyl double bond, the size of the substituent, and the number of unshared electron pairs in the substituent.\textsuperscript{29,30} Though MPCS has a large substituent, MPCS is more reactive than St and MMA. It is likely that the presence of the electron-withdrawing effect of ester groups and conjugate effect\textsuperscript{28,30} contribute to the high reactivity of MPCS. From Table 2, the r\textsubscript{1}r\textsubscript{2} products for our two systems are greater than unity. It is generally believed that r\textsubscript{1}r\textsubscript{2} = 1 represents the upper limit for proper copolymerization. The value of r\textsubscript{1}r\textsubscript{2} > 1 may be plausible for polarity and bulky groups of MPCS in our systems.\textsuperscript{31,32} Considering the above effect, our reactivity ratios should be taken as apparent reactivity ratios. It is worth noting that there are many systems in the literature, including free radical copolymerizations, that contradict the belief that r\textsubscript{1}r\textsubscript{2} = 1 represents the upper limit for proper copolymerization.\textsuperscript{26,31}

For the poly(MPCS-co-St) system, the reactivity ratio of MPCS (r\textsubscript{MPCS} = 4.15) is greater than 1, and the reactivity ratio of St (r\textsubscript{St} = 0.44) is less than 1. The reactivity ratios suggest that the growing radicals with MPCS ends are added

### Table 1. Summary of Molecular Weights, Polydispeisities, and Composition of the Poly(MPCS-co-St) System and Poly(MPCS-co-MMA) System\textsuperscript{a}

<table>
<thead>
<tr>
<th>Sample</th>
<th>M\textsubscript{MPCS}\textsuperscript{b}</th>
<th>m\textsubscript{MPCS}\textsuperscript{c}</th>
<th>Conv. (%)</th>
<th>M\textsubscript{n} × 10\textsuperscript{-4}\textsuperscript{d}</th>
<th>PDI\textsuperscript{d}</th>
<th>T\textsubscript{g} (\textdegree C)\textsuperscript{e}</th>
<th>Liquid crystallinity\textsuperscript{f}</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) poly(MPCS-co-St)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PS-1</td>
<td>0.099</td>
<td>0.218</td>
<td>5.4</td>
<td>12.4</td>
<td>1.70</td>
<td>118.2</td>
<td>No</td>
</tr>
<tr>
<td>PS-2</td>
<td>0.199</td>
<td>0.416</td>
<td>6.9</td>
<td>18.0</td>
<td>1.54</td>
<td>125.7</td>
<td>No</td>
</tr>
<tr>
<td>PS-3</td>
<td>0.302</td>
<td>0.567</td>
<td>6.9</td>
<td>16.9</td>
<td>1.66</td>
<td>129.0</td>
<td>No</td>
</tr>
<tr>
<td>PS-4</td>
<td>0.391</td>
<td>0.678</td>
<td>8.1</td>
<td>14.8</td>
<td>1.70</td>
<td>128.9</td>
<td>No</td>
</tr>
<tr>
<td>PS-5</td>
<td>0.597</td>
<td>0.839</td>
<td>8.4</td>
<td>19.3</td>
<td>1.65</td>
<td>133.3</td>
<td>No</td>
</tr>
<tr>
<td>PS-6</td>
<td>0.699</td>
<td>0.893</td>
<td>13.1</td>
<td>24.6</td>
<td>1.47</td>
<td>125.3</td>
<td>Yes</td>
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<tr>
<td>PS-7</td>
<td>0.801</td>
<td>0.940</td>
<td>9.9</td>
<td>20.8</td>
<td>1.60</td>
<td>123.4</td>
<td>Yes</td>
</tr>
<tr>
<td>(b) poly(MPCS-co-MMA)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMMA-1</td>
<td>0.099</td>
<td>0.214</td>
<td>10.9</td>
<td>20.7</td>
<td>1.48</td>
<td>134.6</td>
<td>No</td>
</tr>
<tr>
<td>PMMA-2</td>
<td>0.200</td>
<td>0.417</td>
<td>13.8</td>
<td>22.9</td>
<td>1.47</td>
<td>138.6</td>
<td>No</td>
</tr>
<tr>
<td>PMMA-3</td>
<td>0.299</td>
<td>0.587</td>
<td>13.9</td>
<td>24.0</td>
<td>1.47</td>
<td>139.3</td>
<td>No</td>
</tr>
<tr>
<td>PMMA-4</td>
<td>0.392</td>
<td>0.648</td>
<td>9.3</td>
<td>21.6</td>
<td>1.53</td>
<td>138.7</td>
<td>No</td>
</tr>
<tr>
<td>PMMA-5</td>
<td>0.600</td>
<td>0.844</td>
<td>14.9</td>
<td>21.4</td>
<td>1.58</td>
<td>137.2</td>
<td>Yes</td>
</tr>
<tr>
<td>PMMA-6</td>
<td>0.691</td>
<td>0.891</td>
<td>9.1</td>
<td>20.0</td>
<td>1.61</td>
<td>131.3</td>
<td>Yes</td>
</tr>
<tr>
<td>PMMA-7</td>
<td>0.804</td>
<td>0.942</td>
<td>13.0</td>
<td>21.4</td>
<td>1.60</td>
<td>129.1</td>
<td>Yes</td>
</tr>
<tr>
<td>PMPCS</td>
<td>–</td>
<td>–</td>
<td>80.3</td>
<td>20.7</td>
<td>1.63</td>
<td>122.9</td>
<td>Yes</td>
</tr>
<tr>
<td>PS</td>
<td>–</td>
<td>–</td>
<td>15.0</td>
<td>7.46</td>
<td>1.23</td>
<td>107.4</td>
<td>No</td>
</tr>
<tr>
<td>PMMA</td>
<td>–</td>
<td>–</td>
<td>40.0</td>
<td>14.8</td>
<td>1.64</td>
<td>129.2</td>
<td>Yes</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Polymerization conditions: chlorobenzene solution (40 wt %); temperature: 60 ± 0.5 \textdegree C; initiator: AIBN (0.05\%, based on total molar of monomers).

\textsuperscript{b} The molar fraction of MPCS at feed.

\textsuperscript{c} The molar fraction of MPCS in copolymer, obtained from \textsuperscript{1}H NMR spectra.

\textsuperscript{d} Obtained from GPC, PS as standard.

\textsuperscript{e} Obtained from DSC.

\textsuperscript{f} Determined by POM.
to MPCS at a higher rate than to St, and the radicals with St ends are added to MPCS at a higher rate than to St. Therefore, the copolymer chain contains a greater number of MPCS units than in the feeds and probably has some MPCS blocks along the copolymer chain. The value of

Figure 1. $^1$H NMR spectra of (a) PS-5 and (b) PMMA-2 (in CH$_2$Cl$_2$-d$_2$, 400 MHz).
The reactivity ratio $r_{\text{MPCS}} \times r_{\text{St}}$ (close to 2) indicates that the copolymerization is characteristic of nonazeotropic block copolymerization. The monomer units in a polymer chain have a tendency of random distribution. For the poly(MPCS-co-MMA) system, there is a similar situation.

Figure 3 exhibits for both copolymer systems the experimental composition data and the theoretical curves calculated with reactivity ratios using the Mayo and Lewis equation. It is evident that the agreement is satisfactory. Figure 3 suggests that there is greater content of MPCS units in the polymer chain than in the corresponding feed for both the poly(MPCS-co-St) system and the poly(MPCS-co-MMA) system.

From the reactivity ratios of monomers, we determined the “run number,” $R$, defined by Harwood and Ritchey as the average number of monomer alternations per 100 monomeric units in a copolymer chain. The value of $R$ can give us a view of sequence distributions in copolymer chains and help us to estimate the relationship between physical properties of copolymers and their compositions. The value of $R$ can be calculated by reactivity ratios and probability statistics for different monomer feeds. The variation of $R$ with the molar fraction of MPCS in the feed is shown in Figure 4. The maximum value of $R$ is about 43 at $F_{\text{MPCS}} = 0.25$ for the poly(MPCS-co-St) system and the poly(MPCS-co-MMA) system.

To gain further information about the copolymer structure, the formation probabilities of dyad fractions as a function of the molar fraction of monomeric units in the copolymer can be calculated from the monomer feed compositions and reactivity ratios. Figure 5 exhibits the calculated dyad molar fractions as a function of compositions in the copolymers. The concentration of dyads MPCS-MPCS increases with the molar fraction of MPCS in the copolymer.

Table 2. Monomer Reactivity Ratios of MPCS with St and MMA Obtained from EKT Methods

<table>
<thead>
<tr>
<th>Poly(MPCS-co-St)</th>
<th>Method</th>
<th>$r_{\text{MPCS}}$</th>
<th>$r_{\text{St}}$</th>
<th>$r_{\text{MPCS}} \times r_{\text{St}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EKT</td>
<td>4.15</td>
<td>0.44</td>
<td>1.83</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Poly(MPCS-co-MMA)</th>
<th>Method</th>
<th>$r_{\text{MPCS}}$</th>
<th>$r_{\text{MMA}}$</th>
<th>$r_{\text{MPCS}} \times r_{\text{MMA}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EKT</td>
<td>4.20</td>
<td>0.43</td>
<td>1.81</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. EKT plot for poly(MPCS-co-MMA) system.

Figure 3. Composition diagrams of the poly(MPCS-co-St) system and poly(MPCS-co-MMA) system. The lines correspond to the theoretical diagrams calculated from the reactivity ratios obtained from the EKT method.

Figure 4. Variation of the “run number,” $R$, with the feed composition $M_{\text{MPCS}}$ for the poly(MPCS-co-St) system and the poly(MPCS-co-MMA) system calculated from the reactivity ratios obtained from the EKT method.
whereas the concentration of dyads St-St or MMA-MMA decreases. The concentration of dyads MPCS-St (St-MPCS) and MPCS-MMA (MMA-MPCS) exhibit maximum value of about 0.43 at a monomer fraction of 0.50 for the poly(MPCS-co-St) system and the poly(MPCS-co-MMA) system. It is found that the monomer sequences can be regulated by controlling the composition of the monomer in the copolymer.

Thermal Properties

The glass transition temperatures ($T_g$'s) of copolymers were determined on TA DSC Q100 with averaged sample size about 4mg. For comparison, homopolymers of PS, PMMA, and PMPCS were also synthesized under the same conditions. The characteristics of the homopolymers are presented in Table 1. Except for PS with appreciably lower molecular weight, there are nearly the same molecular weights for all samples. The samples of the poly(MPCS-co-St) system were heated from 20 °C to 200 °C at a heating rate of 10 °C min$^{-1}$ and cooled from 200 °C to 20 °C to eliminate the influence of thermal history. To avoid the decomposition of PMMA, the samples of poly(MPCS-co-MMA) were heated from 20 °C to 160 °C at a heating rate of 10 °C min$^{-1}$ and cooled from 160 °C to 20 °C. DSC traces of poly(MPCS-co-St) and poly(MPCS-co-MMA) are shown in Figure 6, and the $T_g$ values are listed in Table 1. Each copolymer shows a single glass transition temperature, indicating that the copolymers are homogeneous in the range 10$^{-30}$ nm$^{15}$ With an increase of MPCS content, $T_g$'s of poly(MPCS-co-St) and poly(MPCS-co-MMA) increase at first and then decrease. It must be noted that $T_g$'s of some poly(MPCS-co-St) and poly(MPCS-co-MMA) are higher than those of their corresponding homopolymers. The phenomenon was mentioned in block systems of poly(MPCS-b-PMMA)$^{22}$ and poly(MPCS-b-St)$^{37}$ as surprising results. Our results are similar to those of radical copolymer$^{15,38}$ and polymer blend$^{39}$ systems with hydrogen-bonding interactions. Considering the structure of our copolymers, it is suggested that favorable interactions between MPCS with the bulky group and St or MMA in copolymers may cause a negative volume of mixing or densification. A reduction in the free volume may result

![Figure 5. Dyad molar fractions versus MPCS molar fractions in the polymer chain for the poly(MPCS-co-St) system and the poly(MPCS-co-MMA) system calculated from the reactivity ratios obtained from the EKT method.](image)

![Figure 6. DSC curves of the (a) poly(MPCS-co-St) system and (b) poly(MPCS-co-MMA) system at a heating rate of 10 °C min$^{-1}$.](image)
in a higher \( T_g \). Certainly, there is a lot of work to be done before any reliable conclusion can be made. From Table 1, it can also be observed that \( T_g \)'s of PS-1 and PMMA-1 with small molar fraction of MPCS are about 5 and 10 °C higher than those of PS and PMMA, respectively. It is well known that polymers with high \( T_g \)'s are attractive for industrial polymer science.\(^{15}\)

The thermal stabilities of the copolymers were investigated with TGA in a nitrogen stream. The thermogravimetric curves of the copolymers and corresponding homopolymers are compared in Figure 7. The initial decomposition temperature as well as the temperature at 5.00% weight loss depends on the copolymer composition and shifts toward high temperature with an increase of MPCS content. It must be noted that PMMA has two degradation stages that correspond to the end-chain scission and the random chain-breaking.\(^{40}\) The initial decomposition temperature is improved dramatically when the copolymer contains small MPCS units. It can be seen that the addition of MPCS can depress both the end-chain scission and the random chain-breaking of PMMA.

**Liquid Crystalline Behavior**

The liquid crystalline behavior of all copolymers was studied by POM. The results are summarized in Table 1. It demonstrates that only the copolymers with higher molar content of MPCS exhibit liquid crystalline behaviors. The smallest content of MPCS are 89 and 84% for the poly(MPCS-co-St) system and the poly(MPCS-co-MMA) system, respectively. The birefringence does not disappear until the decomposition temperature. For pure PMPCS, the bulky side groups of MPCS are attached directly to the backbone and force the main chain to take a rod-like conformation.\(^{22,41}\) While MPCS in copolymer is diluted after copolymerization with St and MMA, the main chains of the copolymer become flexible and lose the liquid crystallinity at last.

**CONCLUSIONS**

Copolymers of the poly(MPCS-co-St) system and the poly(MPCS-co-MMA) system were prepared with AIBN as initiator at 60 °C at low conversion. The reactivity ratios of MPCS with St and MMA were determined using linear graphical methods. The data of reactivity ratios indicate that there are greater content of MPCS units in the copolymer than in the feed for both copolymer systems. Structural parameters of the copolymers were obtained from possibility statistics and monomer reactivity ratios. The copolymerizations of MPCS with St and MMA tend to be random in nature, with composition of the copolymer governed essentially by the monomer ratios in the feed. The results of DSC reveal that some copolymers have higher \( T_g \)'s than their corresponding homopolymers have. The TGA studies indicate that the thermal stability of the copolymers increases with an increase of MPCS in the copolymers. The liquid crystalline behavior of the copolymer is found dependent on
the content of MPCS in copolymers. The present work provides useful data for the discovery and application of new materials based on copolymers of MPCS with St and MMA.

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (grant 20134010) and the Science Research Fund of the Chinese Ministry of Education (grant 01001, 104005).

REFERENCES AND NOTES