

# Sequence Distribution, Thermal Properties, and Crystallization Studies of Poly(trimethylene terephthalate-co-1,4-cyclohexylene dimethylene terephthalate) Copolyesters

Jian Yang,<sup>1</sup> Wengang Li,<sup>2</sup> Aifang Yu,<sup>2</sup> Peng Xi,<sup>2</sup> Xiang'an Huang,<sup>2</sup> Suming Li<sup>1,3</sup>

<sup>1</sup>Department of Material Science, Fudan University, Shanghai 200443, China

<sup>2</sup>State Key Laboratory for Modification of Chemical Fibers and Polymer Materials, Donghua University, Shanghai 200051, China

<sup>3</sup>Max Mousseron Institute on Biomolecules, University Montpellier I, 34060 Montpellier, France

Received 9 July 2008; accepted 5 September 2008

DOI 10.1002/app.29340

Published online 3 December 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** A series of novel poly(trimethylene terephthalate-co-1,4-cyclohexylene dimethylene terephthalate) (PTCT) with various compositions were synthesized by melt polycondensation of 1,3-propanediol, 1,4-cyclohexanedimethanol and dimethyl terephthalate. The resulting copolyesters were characterized using <sup>13</sup>C and <sup>1</sup>H nuclear magnetic resonance. The average length of both trimethylene terephthalate (TT) and cyclohexylene dimethylene terephthalate (CT) sequences varies from 1 to 10, and the chain structure is statistically random. The crystallization was investigated using wide angle X-ray diffractometer (WAXD) and differential scanning calorimeter. The WAXD patterns can be divided in two groups according to the

composition: copolyesters with less than 35 mol % CT content exhibit PTT-type lattice, and those with CT unit content higher than 42 mol % crystallize with the PCT-type lattice. The crystallizability of CT sequence is higher than that of TT sequence. Thermodynamic analysis shows that the comonomer is excluded from the PTT-type or PCT-type crystal of the copolyesters. The thermal decomposition temperature of copolyesters increases with increasing CT content, and their thermal stability is improved as compared to that of PTT. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 2751–2760, 2009

**Key words:** polyester; thermal properties; crystallization

## INTRODUCTION

Among the linear aromatic polyesters, poly(trimethylene terephthalate) (PTT) has attracted much attention because of its outstanding properties, such as elastic recovery and inherent stain resistance.<sup>1–3</sup> PTT is a typical semicrystalline polymer, with higher crystallization rate and lower glass transition temperature ( $T_g$ ) than poly(ethylene terephthalate). However, the high chain mobility in amorphous regions of PTT results in decrease in stiffness.

Copolymerization with third constitutional comonomers is an approach frequently used to obtain novel linear thermoplastic polyesters with modified properties. It was reported that cyclic aliphatic diols such as 1,4-cyclohexane dimethanol (CHDM) can impart rigidity to polyester chains.<sup>4</sup> Improved thermal stability and mechanical performance of many copolyesters<sup>5–7</sup> with cyclohexylene ring in the backbone have also been attributed to the rigidity of the ring and its influence on chain mobility. Poly(1,4-

cyclohexylene dimethylene terephthalate) (PCT) derived from CHDM and dimethylene terephthalate (DMT), for example, presents low  $T_g$  (60–90°C) and high melting temperature ( $T_m = 278–318°C$ ), which depend on the trans diol content.<sup>8</sup>

The ever-growing applications of copolyesters of the poly(methylene terephthalate) series have given a strong impulse to studies on the chemical structure and physical properties of these materials. In fact, the crystallinity and crystallization rate are mainly dependent on the chemical structure, including chemical composition, sequence distribution, etc. Okui and coworkers<sup>9,10</sup> found that the crystallization behavior of random copolymers of ethylene terephthalate with 1,4-cyclohexylene dimethylene terephthalate (PETCT) is largely influenced by the copolymer sequence distribution.  $T_m$  depression and cocrystallization have also been observed. It is well known that the crystallizability of copolyesters decreases as the content of minor component increases. Copolymers often become totally amorphous with intermediate compositions.

Cocrystallization can be termed as isodimorphic and isomorphic crystallization according to the crystallization mechanism. In the case of isodimorphism,

Correspondence to: S. Li (lisuming@univ-montp1.fr).

the copolymer crystallizes into the crystal structure of one component and changes over to the crystal structure of the other component at an intermediate composition. A melting temperature minimum (eutectic  $T_m$ ) can be observed. Isodimorphism has been reported for most crystallizable copolyesters, such as PETCT, poly(ethylene terephthalate-*co*-trimethylene terephthalate),<sup>11,12</sup> poly(butylene terephthalate-*co*-cyclohexylene dimethylene terephthalate),<sup>8</sup> poly(butylene-*co*-1,3-cyclopentylene dimethylene terephthalate),<sup>4</sup> poly(propylene terephthalate/2,6-naphthalate),<sup>13</sup> poly(hexa-methylene terephthalate-*co*-hexamethylene 2,6-naphthalate) (P(HT-*co*-HN)),<sup>14</sup> poly(trimethylene/butylene terephthalate),<sup>15</sup> etc. However, copolyesters derived from DMT, CHDM, and 1,3-propanediol (PDO) have not been studied so far.

Considering the similar chemical structures of the crystallizable PTT and PCT homopolymers, it can be expected that poly(trimethylene terephthalate-*co*-1,4-cyclohexylene dimethylene terephthalate) (PTCT) exhibit cocrystallization. In this work, a series of novel copolyesters were prepared by copolymerizing DMT and diols with varying feed ratios of 1,3-propanediol (PDO) and CHDM, respectively. The chemical composition, sequence distribution, crystallization, and thermal properties of these copolyesters were studied by means of NMR, WAXD, DSC, and TGA.

## EXPERIMENTAL

### Materials

PDO, CHDM with trans/cis isomer ratio of 70/30, and DMT were obtained from Degussa (Dusseldorf, Germany), Eastman Chemical (Kingsport, TN), and from Yizheng Chemical Fibers (Yizheng, China), respectively. Zinc acetate, potassium titanate oxalate, and antimony oxide ( $\text{Sb}_2\text{O}_3$ ) of analytical grade were used as catalyst of polycondensation. Phenol and 1,1,2,2-tetrachloroethane of analytical grade were used without purification for intrinsic viscosity measurements.

### Synthesis of PTCT copolyesters

PTCT copolyesters were prepared according to the two-step procedure commonly used for polyester synthesis. Predetermined amounts of DMT, CHDM, PDO, and zinc acetate were introduced into a polymerization autoclave equipped with heating, vacuum, and stirring facilities. In the first stage, the reaction mixture was rapidly heated to 170°C under nitrogen atmosphere, then the temperature was slowly increased to 230°C for 2 h, methanol being collected in a condenser. In the second stage, the reaction temperature was raised to 300°C and maintained at 300°C for 1.5 h. Appearance of serious

Weissenberg effect was observed after addition of potassium titanate oxalate and  $\text{Sb}_2\text{O}_3$  used as catalyst of polycondensation. The pressure of the reaction system was then gradually reduced up to below 100 Pa. Finally, the system was returned to atmospheric pressure using nitrogen to prevent oxidation-induced degradation, and the product was recovered for characterization.

### Structural analysis

The intrinsic viscosity was measured at 30°C in a mixed solvent of phenol/1,1,2,2-tetrachloroethane (5/5, w/w) using an Ubbelohde viscometer. The original concentration of polymer solutions was 0.5 g/dL.

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy was realized on a Bruker AV400 NMR spectrometer at ambient temperature, using deuterated trifluoroacetic acid (*d*-TFA,  $\text{CF}_3\text{COOD}$ ) as solvent.  $^1\text{H}$  NMR spectra were obtained with a FID resolution of 0.183 Hz/point, corresponding to a sweep width of 12 kHz. The pulse delay was 2 s.  $^{13}\text{C}$  NMR spectra were registered by using 3 s pulse delay, with a FID resolution of 0.40 Hz/point and a sweep width of 26 kHz for quantitative  $^{13}\text{C}$  NMR measurements because of the difference of spin-lattice relaxation time among various carbons.

X-ray diffractograms were obtained on a D/Max-2550 PC X-ray diffractometer with Ni-filtered Cu/K $\alpha$  radiation ( $\lambda = 0.154$  nm, 40 kV, 300 mA). All the samples were compression-molded into thin films with a hot press at a temperature 20°C above the  $T_m$ , then quenched in ice-water. After drying, the samples were annealed for 30 min at 160°C for WAXD analysis.

### Differential scanning calorimetry

DSC measurements were performed with Mettler Toledo Star DSC instruments. The samples were melted for 5 min at temperature about 30°C above the  $T_m$ , then quenched in ice water. Heating and cooling scans were realized in the temperature range from 0 to 350°C at a scanning rate of 10°C/min under nitrogen atmosphere.  $T_g$  was taken as the onset of the heat capacity increment associated with the transition.  $T_m$ , cold crystallization temperature ( $T_{cc}$ ) and melt crystallization temperature ( $T_{mc}$ ) were determined as the peak value of the endothermic or exothermic peaks on the DSC curves, respectively.

To determine the equilibrium melting temperature ( $T_m^0$ ) of the samples, isothermal crystallization for all the samples was carried out on Perkin-Elmer DSC Pyris-6 equipped with an intercooler system. The samples were first heated to the temperature 30°C above their respective apparent  $T_m$ , held for 5 min to



TABLE I  
Composition, Sequence Distribution, and Randomness of PTCT Copolyesters

Samples	Feed ratio	$[\eta]$ (dL/g)	$X_{CT}$ (%)	$P_{TT}/P_{CT}^a$	$P_{TT}/P_{CT}^b$	$P_{TPT}$ (%)	$P_{TPC}$ (%)	$P_{CPC}$ (%)	$\overline{L}_{nTT}$	$\overline{L}_{nCT}$	R
PTT	100/0	0.88	0	100/0	100/0	–	–	–	–	–	–
PTCT1	90/10	0.68	18	81.8/18.2	78.3/21.7	62.6	31.5	6.0	4.93	1.38	0.93
PTCT2	80/20	0.66	35	65.5/34.5	63.0/37.0	41.2	43.6	15.2	2.89	1.70	0.94
PTCT3	70/30	0.55	49	50.4/49.6	51.0/49.0	25.6	50.8	23.6	2.01	1.93	1.02
PTCT4	60/40	0.81	63	34.6/65.4	35.6/64.4	13.2	44.9	41.9	1.59	2.86	0.98
PTCT5	50/50	0.81	76	22.1/77.9	23.7/76.3	6.5	34.3	59.2	1.38	4.45	0.95
PTCT6	40/60	0.72	91	10.8/89.2	13.3/86.7	3.0	20.7	76.3	1.28	8.36	0.90
PCT	0/100	0.59	100	100/0	100/0	–	–	–	–	–	–

<sup>a</sup> Calculated by <sup>1</sup>H NMR.

<sup>b</sup> Calculated by <sup>13</sup>C NMR.

sequence effects than any other aromatic carbons due to the occurrence of through-space and through-bond interactions between neighboring units. The resonances of CF<sub>3</sub>COOD appear at 110.50–119.03 ppm and at 161.06–162.67 ppm on the <sup>13</sup>C NMR spectra, respectively, (Fig. 2). The quaternary carbon of terephthalate is split into four signals corresponding to four dyads: C<sup>6</sup> for the TPT sequence and C<sup>7</sup> for the CPC sequence are detected at 133.91–133.96 ppm and 134.18–134.23 ppm, respectively, and two additional signals are detected at 133.71–133.78 ppm for the CT side (C<sup>9</sup>) and at 134.37–134.40 ppm for the TT side (C<sup>8</sup>) for the TPC sequence.<sup>8–10,12,18</sup> The three types of dyad, TPT, CPC, and CPT are shown in Figure 2 with T, C, and P representing trimethylene, cyclohexylene dimethylene, and terephthalate,

respectively. Figure 2 also presents the assignments for all the carbon atoms of the copolyesters.

The selected regions in the range of 133.0–135.0 ppm belonging to aromatic carbon atoms for all the copolyesters are shown in Figure 3. The relative intensities of C<sup>8</sup> and C<sup>9</sup> signals are almost equal, whereas the intensity of C<sup>6</sup> corresponds to the additional TT molar fraction and that of C<sup>7</sup> to the additional CT molar fraction. Thus, the molar ratio of TT/CT in the copolyesters can be determined from the integrations of C<sup>6</sup>, C<sup>7</sup>, C<sup>8</sup>, and C<sup>9</sup>, according to the following equation:

$$P_{TT}/P_{CT} = \frac{I_6 + (I_8 + I_9)/2}{I_7 + (I_8 + I_9)/2} \quad (3)$$

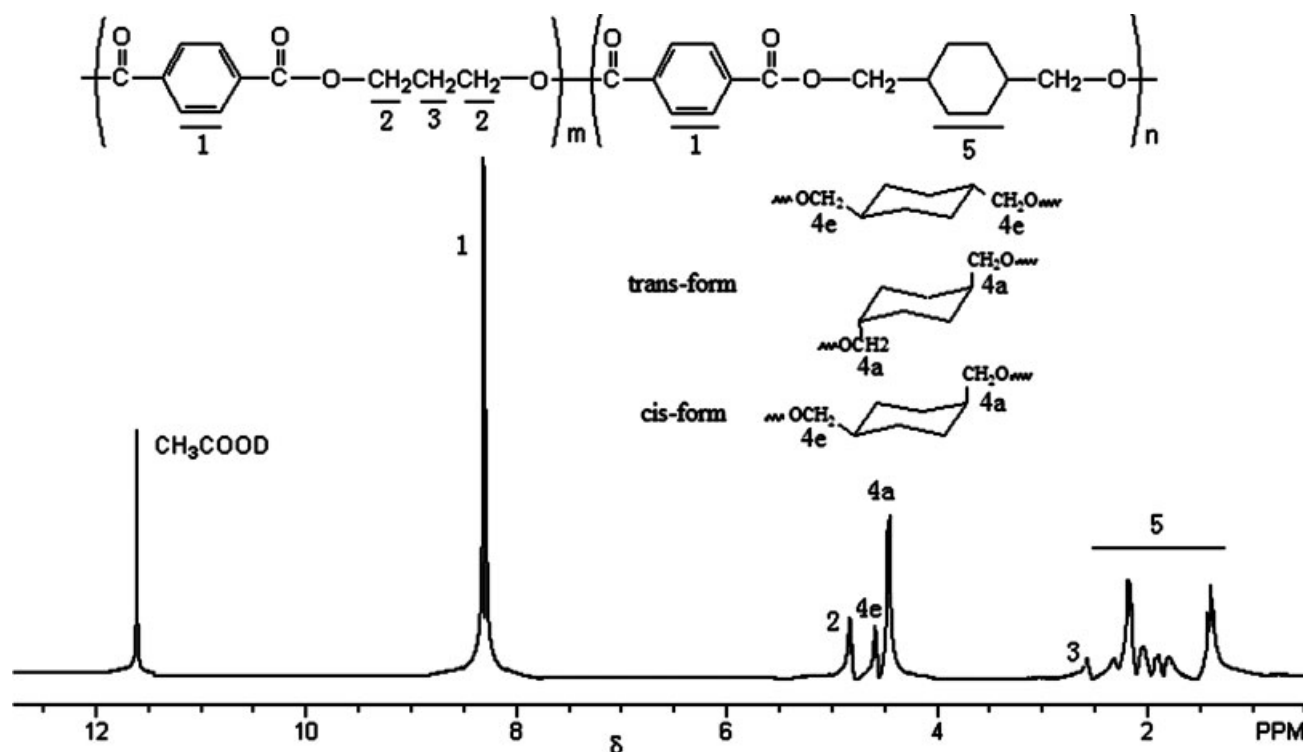
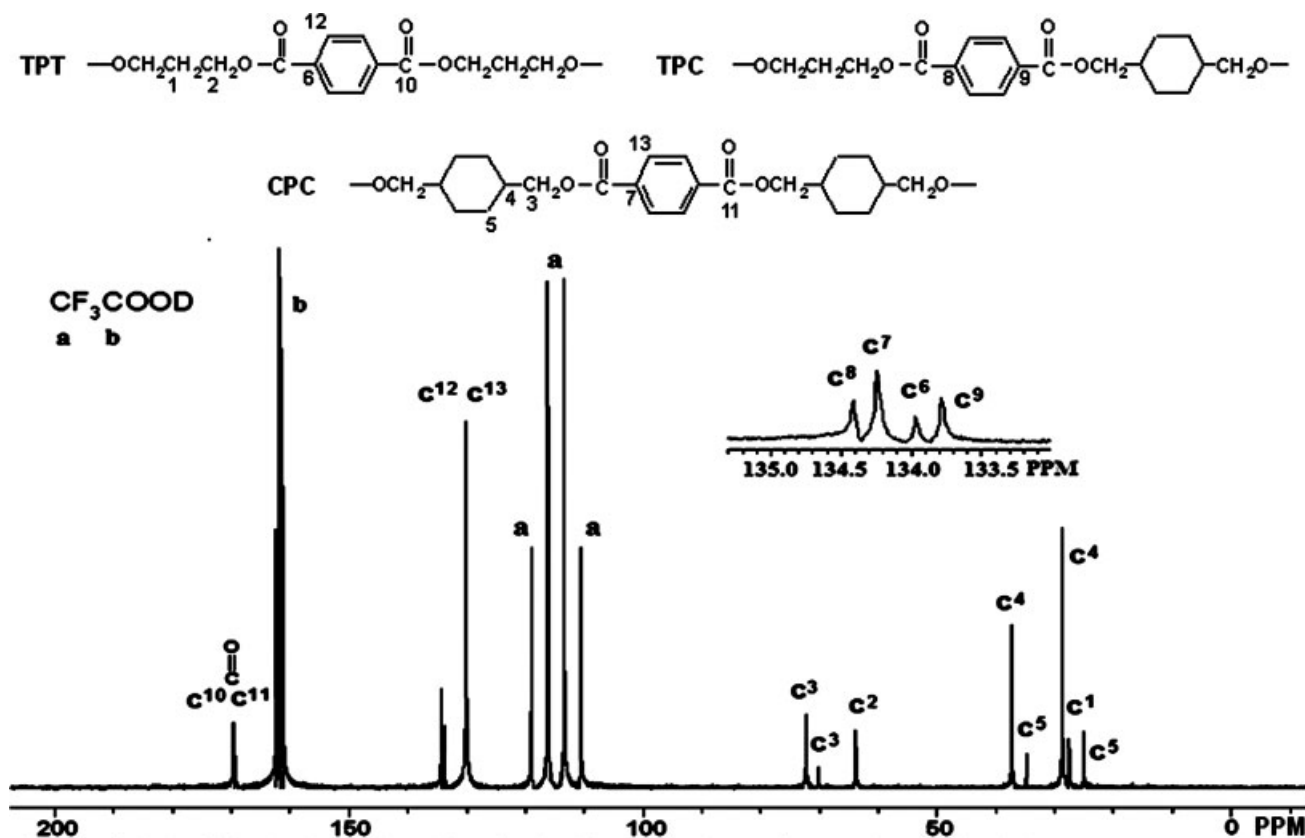


Figure 1 <sup>1</sup>H NMR spectrum of the PTCT5 copolyester.



**Figure 2**  $^{13}\text{C}$  NMR spectrum of the PTCT4 copolyester with the expanded chemical shifts of aromatic alkyl carbon atoms ranging from 133.0 to 135.0 ppm.

where  $P_{\text{TT}}$  and  $P_{\text{CT}}$  represent the proportions of TT and CT units,  $I_6$ ,  $I_7$ ,  $I_8$ ,  $I_9$  corresponding to the integral intensities of  $\text{C}^6$ ,  $\text{C}^7$ ,  $\text{C}^8$ , and  $\text{C}^9$  in  $^{13}\text{C}$  NMR, respectively. The calculated results are in good agreement with those derived from  $^1\text{H}$  NMR, as shown in Table I. The molar fractions of three dyad sequences TPT, TPC, and CPC can be calculated by the following equations:

$$P_{\text{TPT}} = \frac{I_6}{I_6 + I_7 + I_8 + I_9} \quad (4)$$

$$P_{\text{TPC}} = \frac{I_8 + I_9}{I_6 + I_7 + I_8 + I_9} \quad (5)$$

$$P_{\text{CPC}} = \frac{I_7}{I_6 + I_7 + I_8 + I_9} \quad (6)$$

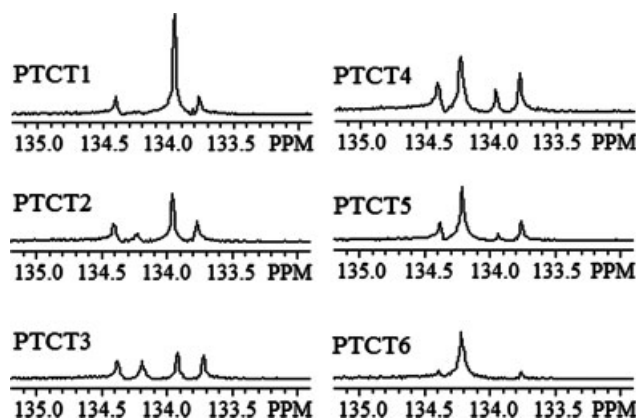
where  $P_{\text{TPT}}$ ,  $P_{\text{TPC}}$  and  $P_{\text{CPC}}$  correspond to the proportions of TPT, TPC, and CPC sequences, respectively. The number-average sequence length of TT and CT units ( $\overline{L}_{n\text{TT}}$  and  $\overline{L}_{n\text{CT}}$ , respectively) and the degree of randomness ( $R$ ) are obtained using the following equations:

$$\overline{L}_{n\text{TT}} = 2P_{\text{TT}}/P_{\text{TPC}} \quad (7)$$

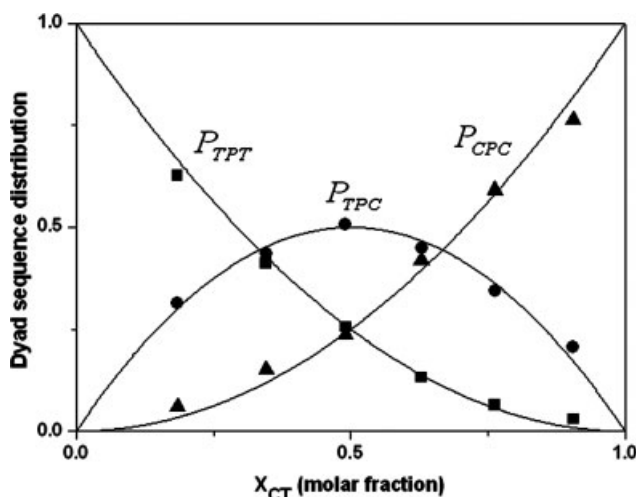
$$\overline{L}_{n\text{CT}} = 2P_{\text{CT}}/P_{\text{TPC}} \quad (8)$$

$$R = P_{\text{TPC}}/2 \times P_{\text{TT}} \times P_{\text{CT}} \quad (9)$$

Table I shows the number-average sequence lengths and degree of randomness. The value of  $R$  ranges from 0.93 to 1.02, i.e., very close to the value of 1, which is characteristic of totally random copolymers.



**Figure 3** Expanded  $^{13}\text{C}$  NMR spectra of the PTCT copolyesters with chemical shifts of aromatic alkyl carbon atoms ranging from 133.0 to 135.0 ppm.



**Figure 4** Dyad sequence distribution as a function of copolymer composition. The solid lines represent the distribution calculated by Bernoullian statistics.

R becomes close to 1 with intermediate comonomer content. On the other hand, if the sequences of the copolymers are statistically random, the dyad sequence percentage can be described by Bernoullian statistics as given in the equations below:

$$P_{TPT} = (1 - X_{CT})^2 \quad (10)$$

$$P_{TPC} = 2X_{CT}(1 - X_{CT}) \quad (11)$$

$$P_{CPC} = X_{CT}^2 \quad (12)$$

The results derived from Bernoullian statistical model are plotted in Figure 4 as a function of the molar fraction of CT moieties, in comparison with experimental data. It appears that the experimentally determined number-average sequence lengths are in all cases in accordance with those predicted on the basis of ideal copolycondensation statistics with randomness equal to 1. Thus, it can be concluded that the distribution of TT and CT units is statistically random along the copolyester chains.

### Waxd analysis

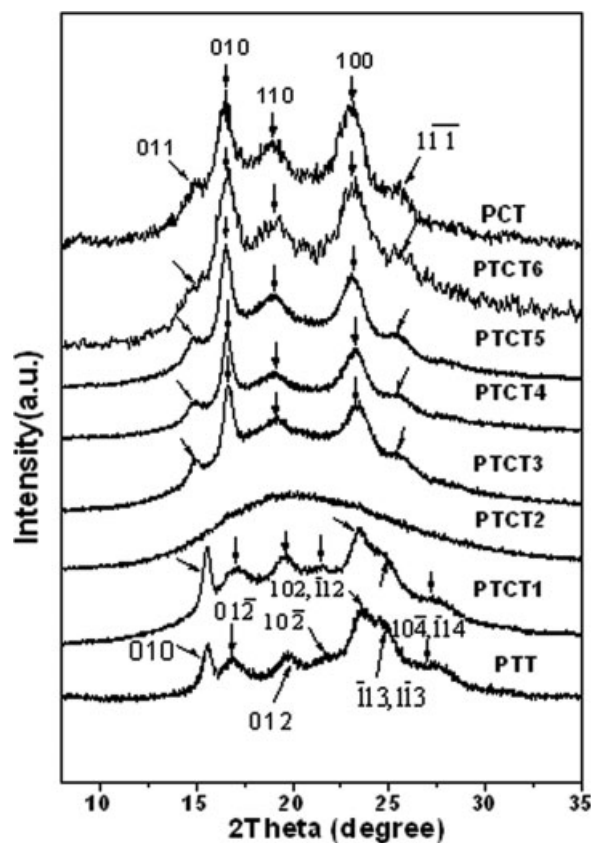
The crystalline structures of the copolyesters were examined by using WAXD to elucidate the phenomenon of crystallization. PTT, PCT, and PTCT copolyesters were subjected to the same thermal treatment before WAXD measurements, i.e., isothermally crystallization for 30 min at 160°C. Diffraction peaks were observed on the spectra of all the samples except that of PTCT2 which appears amorphous (Fig. 5). It has been reported that the crystal unit of PTT is triclinic.<sup>19,20</sup> The crystal unit of PCT is also triclinic, and the diffraction pattern of PCT with

trans/cis isomer ratio above 68/32 is the same as that of pure *trans*-PCT.<sup>21</sup>

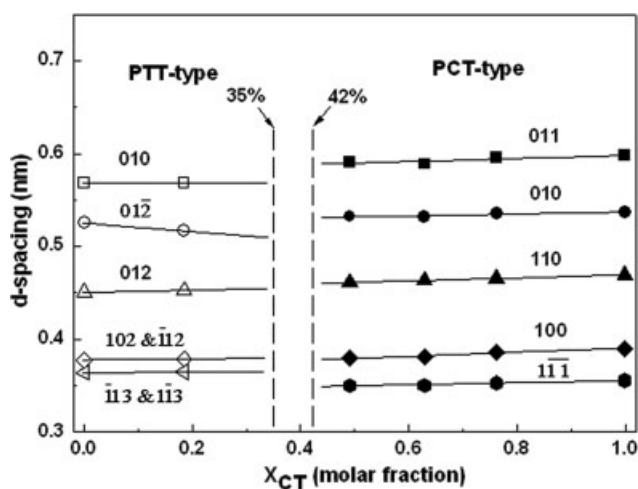
The WAXD patterns can be divided into two groups. PTT homopolymer and copolyesters with less than 35 mol % CT content, i.e., PTCT1 with 18 mol % CT content, present the same WAXD pattern. This finding indicates that the presence of 18 mol % CT content does not alter the crystal structure of the copolymers as compared with that of PTT. In contrast, copolyesters with CT content above 49 mol % exhibit the same WAXD pattern as PCT homopolymer.

Figure 6 presents the variation of *d*-spacing values as a function of copolymer composition. The *d*-spacing of different crystal planes remains almost unchanged in the respective crystal types, only *d*(01 $\bar{2}$ ) spacing slightly declining with increasing CT content. Interestingly, the variation of *d*-spacing with composition shows a break in the region around 35 mol % CT content, indicating that the crystallizable material changed from PTT-type lattice to PCT-type lattice.

Generally, a binary A/B random copolymer can crystallize either in an A-homopolymer or B-homopolymer crystal if both components are crystallizable, depending on the copolymer composition. A



**Figure 5** Wide angle X-ray diffraction profiles of PTT, PCT, and PTCT copolyesters. The indexes of the most intense reflections are reported.



**Figure 6** Changes of  $d$ -spacings for the heat treated samples at 160°C as a function of copolymer composition.

crystal lattice transition occurs at an intermediate composition. The cohesive energy ( $E$ ) corresponding to each component in random copolymers is assumed to be proportional to the copolymer composition.<sup>9</sup> When the cohesive energies for the two components are identical, both components can crystallize separately into different crystal lattices or cocrystallize into a single crystal lattice at a composition given by the following equation.<sup>22</sup>

$$X_A^* = E_B / (E_A + E_B) \quad (13)$$

where  $X_A^*$ ,  $E_A$ , and  $E_B$  represent the eutectic composition and cohesive energy of A or B component, respectively. According to the group contribution method,<sup>23</sup> the cohesive energies of PTT and PCT are 83.0 KJ/mol and 115.3 KJ/mol, respectively. The eutectic composition  $X_{CT}^*$ , where cocrystallization of the two components occurs, is about 42 mol %. In principle, only CT units can crystallize if  $X_{CT}$  is higher than  $X_{CT}^*$ , excluding TT units into noncrystallized regions. If  $X_{CT}$  is lower than  $X_{CT}^*$ , however, only TT units will crystallize.

PTCT2 is intrinsically amorphous despite the fact that the CT content (35 mol %) is lower than  $X_{CT}^*$ , which may be ascribed to the very small number-

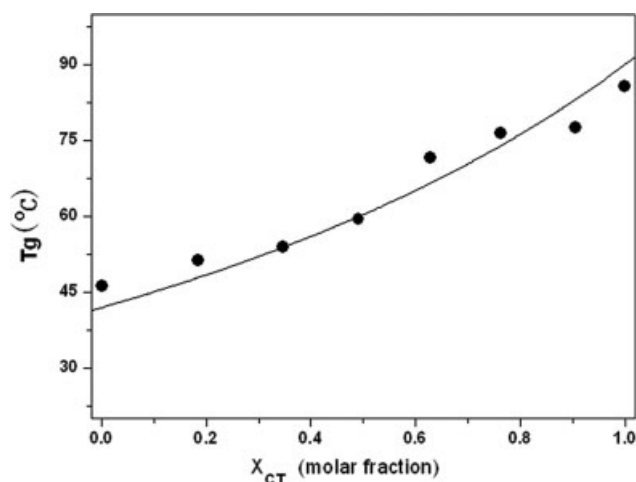
average sequence lengths of TT and CT units, i.e., 2.9 and 1.7, respectively. In fact, Jun et al.<sup>24</sup> reported that an average sequence length higher than three is required to form crystallites. In the cases of PTCT3 and PTCT4, however, the number-average lengths of CT sequences are of 1.9 and 2.9, respectively. Both copolyesters are susceptible to form PCT-type crystallites because of the large molar volume of CT unit. It appears that the crystallizability of CT units is higher than that of TT units. Therefore, the crystallization of PTCT copolyesters is strongly dependent on the chain structure including comonomer distribution or randomness, and TT or CT sequence length.

### Thermal properties

The thermal properties derived from the heating and cooling thermograms of the melt-quenched samples at the rate of 10°C/min are listed in Table II. PTT and PCT homopolymers present a  $T_m$  at 229.1 and 293.7°C, respectively.  $T_m$  of PTCT1 is lower than that of PTT, whereas  $T_m$  of the other PTCT copolyesters is lower than that of PCT and higher than that of PTT. The  $\Delta H_m$  of the copolyesters is lower than that of PTT or PCT, with the exception of PTCT6. Commonly, degree of supercooling, the gap between  $T_m$  and  $T_{mc}$ , can represent the crystallization ability of polymers from the melt state. As expected, the gap between  $T_m$  and  $T_{mc}$  increases with  $T_{mc}$  decreasing from PCT to PTCT4. The higher degree of supercooling is characteristic of the decreasing crystallization ability of copolyesters. However, the eutectic  $T_m$  was not detected. In fact, PTCT2 with 35 mol % of CT units presents no crystallization peak even at a heating or cooling rate of 2.5°C/min. In contrast, crystallization is observed for PTCT1 and PTCT3 at a cooling rate of 2.5°C/min or 5°C/min, but not at 10°C/min. Such behavior indicates that the crystallization rate or crystallizability of copolyesters is significantly decreased by the presence of comonomer units randomly distributed along the chains. It is noteworthy that PTCT2 with 35 mol % of CT cannot crystallize under the selected conditions, whereas

**TABLE II**  
Calorimetric and Thermogravimetric Data of PTCT Copolyesters

Samples	$T_g$ (°C)	$T_{cc}$ (°C)	$T_m$ (°C)	$T_{mc}$ (°C)	$\Delta H_m$ (J/g)	$T_{id}$ (°C)	% at $T_{id}$	$T_{max}$ (°C)
PTT	46.2	67.7	229.1	174.7	69.4	371.0	14.0	397.6
PTCT1	51.3	111.2	202.5	—	42.0	374.1	13.7	400.9
PTCT2	53.9	—	—	—	—	376.6	14.8	400.2
PTCT3	59.5	—	—	—	—	379.6	13.5	406.3
PTCT4	71.5	142.2	236.9	160.5	23.7	387.4	18.9	408.3
PTCT5	76.4	137.7	259.5	188.2	29.6	388.3	14.7	415.5
PTCT6	77.5	127.2	277.1	210.7	50.8	390.0	15.8	407.9
PCT	85.7	126.2	293.7	246.2	44.3	390.8	18.1	411.0

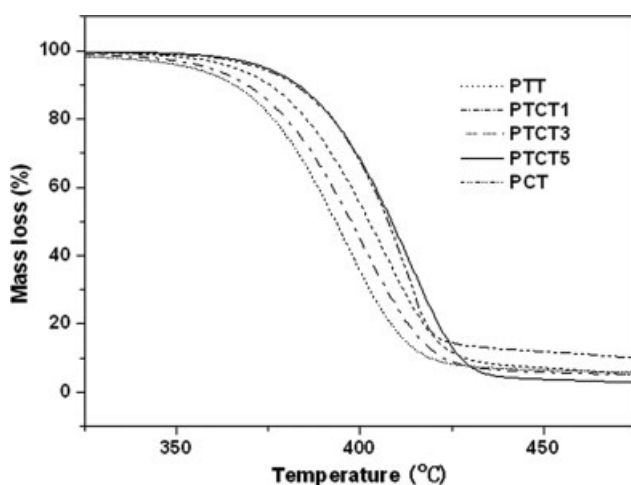


**Figure 7** composition dependence of  $T_g$  for the PTCT copolyesters. The solid line was calculated on the basis of Fox equation.

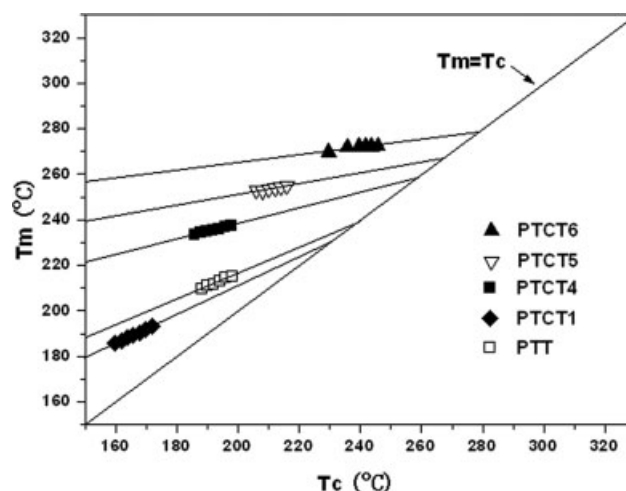
PTCT4 with 37 mol % of TT units is intrinsically semicrystalline. This finding seems to indicate that CT sequences are more susceptible to crystallize than TT ones.

PTT and PCT homopolymers present a glass transition at 46.2 and 85.7°C, respectively. Meanwhile, the  $T_g$ 's of all the copolyesters are also listed in Table II. The  $T_g$ 's of PTCT copolyesters increase with increasing the CT content, which can be assigned to the stiffening effect of the cyclohexylene ring. Figure 7 presents the variation of  $T_g$  as a function of CT content, in comparison with the  $T_g$  values predicted by the Fox equation.<sup>25</sup> A good agreement is observed between the experimental and theoretical data.

Thermogravimetric curves of PTT, PCT, PTCT1, PTCT3, and PTCT5 are shown in Figure 8, and  $T_{id}$ ,  $T_{max}$  and the weight loss percentage at  $T_{id}$  of all the samples are listed in Table II. For PTT, PCT, and



**Figure 8** TGA curves of PTT, PCT, and PTCT copolyesters.



**Figure 9** Hoffman-weeks plots for obtaining the equilibrium melting temperatures of PTT, PTCT copolyesters.

PTCT copolyesters, degradation occurs mostly in the temperature range of 350–450°C. PTT starts to decompose at a temperature of 371.0°C, and PCT at 390.8°C. The thermal decomposition temperature of all the copolyesters increases with increasing CT content, which can be ascribed to the higher thermal stability of cyclohexylene group as compared with that of the trimethylene group. From Figure 8, it is clear that the curves of copolyesters are shifted to higher temperature compared with those of PTT, suggesting that the thermal stability of the copolyesters are better than that of PTT.

The  $T_m$  of the isothermally melt-crystallized samples is plotted as a function of the crystallization temperature ( $T_c$ ), as shown in Figure 9. The  $T_m$  values of PTT and PTCT are well fitted by straight regression lines. The intersection of the  $T_m$  versus  $T_c$  plots with the  $T_m = T_c$  line is considered as the equilibrium melting temperature ( $T_m^0$ ) of the samples. The  $T_m^0$  of PTT homopolymer is 239°C, and that of PTCT1 slightly lower (229°C). In contrast, PTCT4, PTCT5, and PTCT6 with higher CT contents present higher  $T_m^0$  values, i.e., 259°C, 268°C, and 279°C, respectively.

### Thermodynamics of copolymer crystallization

A number of theories have been developed to describe the crystallization of copolymers. Two types of model can be distinguished: the comonomer exclusion model<sup>26–28</sup> and the comonomer inclusion model.<sup>29–31</sup> Recently, Windling and Suter<sup>32</sup> proposed a new model for copolymer crystallization which combines the Sanchez-Eby model<sup>31</sup> (a comonomer inclusion model) and the Baur model<sup>28</sup> (a comonomer exclusion model). The Wendling-Suter model is expressed in the following equation by introducing the average defect Gibbs free energy  $\varepsilon$ :



$$\frac{1}{T_m(X_B)} - \frac{1}{T_m^0} = \frac{R}{\Delta H_m^0} \left[ \frac{\varepsilon X_{CB}}{RT} + (1 - X_{CB}) \times \ln \frac{1 - X_{CB}}{1 - X_B} + X_{CB} \ln \frac{X_{CB}}{X_B} + \langle \tilde{\xi} \rangle^{-1} \right] \quad (14)$$

where  $T_m^0$  and  $\Delta H_m^0$  denote the equilibrium melting temperature and the heat of fusion of homopolymer, respectively,  $R$  the gas constant,  $X_B$  the bulk composition of B units in the copolymer,  $X_{CB}$  the concentration of B units in the cocrystal,  $\varepsilon$  the average defect free energy, and  $\langle \tilde{\xi} \rangle$  the average length of the crystallizable copolymer sequences.

In the equilibrium comonomer inclusion, the concentration of B units in the cocrystal is given by<sup>30,31</sup>

$$X_{CB}^{eq} = \frac{X_B e^{-\varepsilon/RT}}{1 - X_B + X_B e^{-\varepsilon/RT}} \quad (15)$$

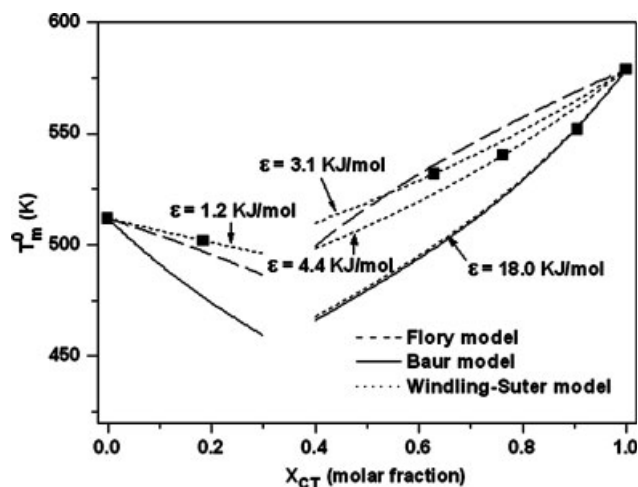
when  $X_{CB}$  in eq. (14) is substituted by eq. (15), eq. (14) is simplified to the following equilibrium inclusion model:

$$\frac{1}{T_m^0} - \frac{1}{T_m(X_B)} = \frac{R}{\Delta H_m^0} [\ln(1 - X_B + X_B e^{-\varepsilon/RT}) - \langle \tilde{\xi} \rangle^{-1}] \quad (16)$$

$$\langle \tilde{\xi} \rangle^{-1} = 2(X_B - X_B e^{-\varepsilon/RT})(1 - X_B + X_B e^{-\varepsilon/RT}) \quad (17)$$

when  $X_{CB} = X_B$  and  $X_{CB} = 0$  ( $\varepsilon \rightarrow \infty$ ), eq. (14) leads to the uniform inclusion model and the exclusion model (the Baur model), respectively.

When the theoretical melting curves of Wendling-Suter equilibrium inclusion model are matched with the  $T_m^0$  of PTCT random copolymers obtained from Hoffman-Weeks plots, the  $\varepsilon/RT$  value is used as an adjustable parameter to determine the average defect free energy. Figure 10 shows comparatively the experimental  $T_m^0$  of PTCT copolyesters with the various models. The  $\Delta H_m^0$  of PTT and PCT homopolymers is 30 KJ/mol<sup>19</sup> and 27.75 KJ/mol,<sup>9,33</sup> and the  $T_m^0$  of PTT and PCT is 239°C and 306°C,<sup>9,33</sup> respectively. The average defect free energies of PTCT copolyesters, calculated from the values of  $\varepsilon/RT_m^0$ , are shown in Figure 10. It is found that the average defect free energy increases from 3.1 to 18.0 KJ/mol with the CT units content from 63 to 91 mol %, indicating that TT units are difficultly incorporated into PCT-type crystal lattice as CT content increases. Moreover, when CT units are incorporated into PTT-type crystal in the case of PTCT1, the defect free energy is 1.2 KJ/mol, which is lower than those of the PCT-type crystals, indicating that the CT unit with larger volume is more easily incorporated into the PTT crystal lattice. This finding is in agreement with results reported by Jeong et al. for random copolymers, such as P(1,4-cyclohexylenedimethylene ter-



**Figure 10** Comparison of the theoretical melting temperature of PTT, PCT, and PTCT copolyesters with the equilibrium melting points experimentally determined. Dashed, solid, and dotted lines represent the Flory model, the Baur model, and the Wendling-Suter equilibrium inclusion model, respectively.

ephthalate-*co*-hexamethylene terephthalate), poly (butylenes 2,6-naphthalate-*co*-1,4-cyclohexylenedimethylene 2,6-naphthalate), and poly(1,4-cyclohexylenedimethylene terephthalate-*co*-1,4-cyclohexylenedimethylene 2,6-naphthalate).<sup>33-35</sup> It is generally expected that the comonomer unit with larger volume is more difficult to incorporate into the crystal lattice with smaller unit cell volume than the opposite case.<sup>29</sup> In this study, however, even though the molar volume of CT is larger than that of TT, the unit cell volume (0.359 nm<sup>3</sup>)<sup>21</sup> of PCT is truly smaller than that (0.479 nm<sup>3</sup>)<sup>36</sup> of PTT, and the CT units of smaller unit cell volume are much more incorporated in the PTT crystal lattice compared with the opposite case. Comparison of the various models shows that Flory model fits the  $T_m^0$  of PTCT1 better than Baur model, whereas Baur model fits well the  $T_m^0$  of PTCT6. Therefore, the PTT-type or PCT-type crystal of the copolyesters with high TT or CT content excludes another minor comonomer according to the comonomer exclusion model.

## CONCLUSIONS

A series of PTCT copolyesters with different compositions were synthesized by melt copolycondensation of PDO, CHDM, and DMT. The distribution of comonomers along copolymer chains is statistically random, and the number-average sequence length varies from 1 to 10. The randomness becomes close to 1 with intermediate comonomer contents. WAXD analysis indicates that copolyesters with CT contents lower than 35 mol % develop the PTT-type lattice, and copolyesters with CT contents above 42 mol % crystallize with the PCT-type lattice. The

crystallizability of CT units appears higher than that of TT units. PTCT copolyesters are not able to crystallize with intermediate compositions due to short number-average sequence lengths. Thermodynamics analysis also indicated the PTT-type or PCT-type crystals with predominant TT or CT content, which excludes the other minor comonomer from the crystals. Last but not least, thermal gravimetric analysis indicates that the copolyesters present better thermal stability than PTT.

The authors are indebted to the Shanghai Leading Academic Discipline project (No. B113) and to the National Basic Research Program of China (973 Program No. 2007CB935801) for financial support.

## References

1. Chuah, H. H. *Chem Fibers Int* 1996, 46, 424.
2. Brown, H. S.; Chuah, H. H. *Chem Fibers Int* 1997, 1, 72.
3. Ward, I. M.; Wilding, M. A. *J Polym Sci Polym Phys Ed* 1976, 14, 263.
4. Sandhya, T. E.; Ramesh, C.; Sivaram, S. *Macromolecules* 2007, 40, 6906.
5. Sun, Y. M.; Wang, C. S. *Eur Polym J* 1999, 35, 1087.
6. Zhang, Y.; Feng, Z. G.; Feng, Q. L. *Polym Degrad Stab* 2004, 85, 529.
7. Liu, Y.; Ranucci, E.; Lindblad, M. S.; Albertsson, A. C. *J Polym Sci Part A: Polym Chem* 2001, 39, 2508.
8. Sandhya, T. E.; Ramesh, C.; Sivaram, S. *Macromol Symp* 2003, 199, 467.
9. Yoo, H. Y.; Umemoto, S.; Kikutani, T.; Okui, N. *Polymer* 1994, 35, 117.
10. Yoshie, N.; Inoue, Y.; Yoo, H. Y.; Okui, N. *Polymer* 1994, 35, 193.
11. Ko, C. Y.; Chen, M.; Wang, H. C.; Tseng, I. M. *Polymer* 2005, 46, 8752.
12. Shyr, T. W.; Lo, C. M.; Ye, S. R. *Polymer* 2005, 46, 5284.
13. Lorenzetti, C.; Finelli, L.; Lotti, N.; Vannini, M.; Gazzano, M.; Berti, C.; Munari, M. *Polymer* 2005, 46, 4041.
14. Lee, J. H.; Jeong, Y. G.; Lee, S. C.; Min, B. G.; Jo, W. H. *Polymer* 2002, 43, 5263.
15. Kim, J. H.; Park, J. H.; Jang, H. K.; Yoon, J. Y.; Lyoo, W. S. *J Appl Polym Sci* 2003, 90, 2200.
16. Hoffman, J. D.; Weeks, J. J. *J Res Natl Bureau Stand* 1962, 66A, 13.
17. Ou, C. F. *Eur Polym J* 2002, 38, 2405.
18. Matsuda, H.; Nagasaka, B.; Asakura, T. *Polymer* 2003, 44, 4681.
19. Poulin-Dandurand, S.; Perez, S.; Revol, J. F.; Brisse, F. *Polymer* 1979, 20, 419.
20. Wang, B. J.; Li, C. Y.; Hanzlicek, J.; Cheng, S. Z. D.; Geil, P. H.; Grebowicz, J.; Ho, R. M. *Polymer* 2001, 42, 7171.
21. Boye, C. A. *J Polym Sci* 1960, 55, 275.
22. Hachiboshi, M.; Fukuda, T.; Kobayashi, S. *J Macromol Sci Phys* 1960, 35, 94.
23. Van Krevelen, D. W. *Properties of Polymers*; Elsevier: New York, 1990; Chapter 7.
24. Jun, H. W.; Chae, S. H.; Park, S. S.; Myung, H. S.; Im, S. S. *Polymer* 1999, 40, 1473.
25. Fox, G. *Bull Am Phys Soc* 1956, 1, 123.
26. Flory, P. J. *J Chem Phys* 1947, 15, 684.
27. Flory, P. J. *Trans Faraday Soc* 1955, 51, 848.
28. Baur, V. H. *Makromol Chem* 1966, 98, 297.
29. Kamiya, N.; Sakurai, M.; Inoue, Y.; Chujo, R. *Macromolecules* 1991, 24, 3888.
30. Helfand, E.; Lauritzen, J. I. *Macromolecules* 1973, 6, 631.
31. Sanchez, I. C.; Eby, R. K. *Macromolecules* 1975, 8, 638.
32. Windling, J.; Suter, U. W. *Macromolecules* 1998, 31, 2516.
33. Jeong, Y. G.; Jo, W. H.; Lee, S. C. *Macromol Res* 2004, 12, 459.
34. Jeong, Y. G.; Jo, W. H.; Lee, S. C. *Macromolecules* 2003, 36, 4051.
35. Jeong, Y. G.; Jo, W. H.; Lee, S. C. *J Polym Sci Part B: Polym Phys* 2004, 42, 177.
36. Desborough, I. J.; Hall, I. H.; Neisser, J. Z. *Polymer* 1979, 20, 545.