

# Liquid crystal polymers: 21. Thermotropic properties and crystallization-induced reactions of aromatic copolyesters

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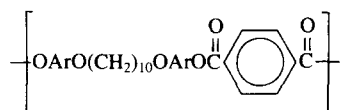
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A series of copolyesters containing both mesogenic and non-mesogenic aromatic ester units connected by a flexible spacer were prepared and characterized for their liquid crystalline properties. Samples containing 75 mole percent mesogenic units were heated at temperatures either below or above their melting points to determine if the initially random copolyester could be reorganized to a blocky structure by the process referred to in earlier studies as a 'crystallization-induced reaction'. This type of reorganization was observed to occur in both the solid state and liquid crystalline state for these copolyesters.

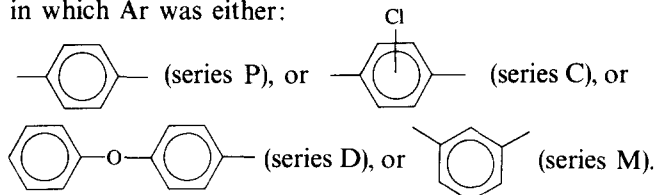
(Keywords: liquid crystalline polymers; crystallization induced reactions; polyesters; thermotropic properties)

## INTRODUCTION

In a previous report, we described the preparation and properties of a family of polyesters based on four different, but closely related, aromatic ester triads, each with a decamethylene spacer in its repeating units, as follows<sup>1</sup>:



in which Ar was either:

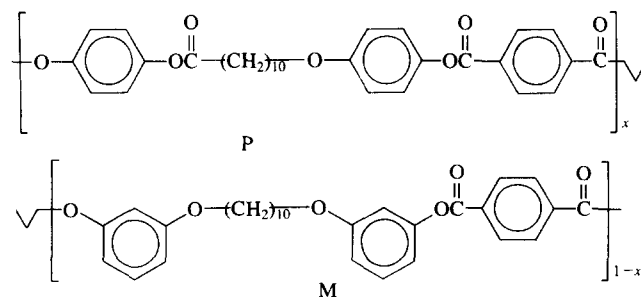


The first three homopolymers were thermotropic, and each formed a nematic phase above its melting point. The last homopolymer, as expected from the non-linear structure of its repeating unit, was not thermotropic. Of the first three, the P series of polymers had the highest melting and isotropization temperatures, presumably because of the symmetry and linearity of its repeating units in comparison to those of the C and D series.

The present investigation was directed at three goals: (1) evaluating the use of 'solid-state' reaction methods for the preparation of high molecular weight copolymers with P and M repeating units, (2) determining the effect of the non-mesogenic M units on the thermotropic properties of copolymers containing principally the mesogenic P units, and (3) investigating the thermal reorganization of these copolymers from random to blocky structures by a process termed the 'crystallization-induced reaction', CIR, which has been applied for this purpose to a wide variety of copolyesters in this laboratory<sup>2,3</sup>.

## RESULTS AND DISCUSSION

In our previous investigations of the homopolymers shown above, we found that the simplest procedure for preparing relatively high molecular weight polyesters was to first react an acid chloride monomer with a phenol monomer in the melt under a nitrogen gas flow to remove the hydrogen chloride formed, then cool and grind the resulting polymer, and in a second step complete the polymerization reaction at a temperature just below its melting point. This type of 'solid-state' polymerization reaction is often used for the preparation of high molecular weight polyesters. However, in our attempts to prepare higher molecular weight copolyesters in this manner, very erratic results were obtained, and as often as not the final polymer had a lower molecular weight than the intermediate polymer. Indeed, while higher molecular weights could be achieved occasionally, in most cases after the solid-state reaction, the inherent viscosities of the final copolymers were the same (approximately 0.5–0.6 dl/g) regardless of either the viscosities of the initial copolymer (either higher or lower), or of the conditions of the second stage reaction, or of the type of ester-interchange catalyst used. Hence, the initial copolymers that were used in the CIR studies were those obtained directly by the first stage, melt polymerization only, and the data for the samples so prepared are collected in *Table 1*. The structures of these copolyesters are as follows:



$x = 1.0, 0.8, 0.75, 0.6, 0.5, 0$

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**Table 1** Thermal properties of polyesters and copolyesters with P and M units

Composition, unit mole fractions			Transition temperatures (°C) <sup>b</sup>			
P	M	$\eta_{inh}^a$ dl/g	Heating cycle		Cooling cycle	
			$T_m$	$T_i$	$T_c$	$T_d$
1.0	0	0.79	265	321	229	309
0.80	0.20	0.67	238	274	208	270
0.75	0.25	0.90	233	265	217	267
0.60	0.40	1.0	230	242 <sup>c</sup>	215	— <sup>d</sup>
0.50	0.50	0.67	212	— <sup>d</sup>	170	— <sup>d</sup>
0	1.0	0.21	108	— <sup>d</sup>	— <sup>d</sup>	— <sup>d</sup>

<sup>a</sup> Inherent viscosity of solutions in *p*-chlorophenol at a concentration of 0.2 g/dl at  $45 \pm 0.3^\circ\text{C}$

<sup>b</sup> Temperature of endothermic or exothermic peaks in d.s.c. thermograms for heating or cooling cycles, respectively; abbreviations:  $T_m$  melting peak,  $T_i$  isotropization peak,  $T_c$  recrystallization peak,  $T_d$  deisotropization peak

<sup>c</sup> Estimated by observation on hot stage of a polarizing microscope; no peak in thermogram

<sup>d</sup> No peak in thermogram

### Thermal transitions of copolyesters

As expected the copolyesters showed regular decreases in all of their transition temperatures with decreasing P unit content, including their temperatures of melting,  $T_m$ , isotropization,  $T_i$ , deisotropization,  $T_d$ , and recrystallization,  $T_c$ , in Table 1. The copolymer containing 60 mole percent of the mesogenic P unit was observed to form a barely visible nematic phase on melting on the hot stage of a polarizing microscope, as shown in the photomicrograph in Figure 1, but no clear  $T_i$  endotherm was found in its d.s.c. endotherm (see Figure 3). Even for the copolymer containing 75 mole percent P units, the nematic phase which formed on melting contained many dark regions, as seen in Figure 1. We believe that this type of mesogenic/non-mesogenic copolymer can form a two-phase melt, which contains both liquid crystalline and isotropic regions in equilibrium, and the relative amounts of bright and dark regions (and the birefringence intensities) are an indication of the 'degree of liquid crystallinity' (that is, the fractional amount of liquid crystalline phase) of the thermotropic melt, as suggested in our previous report<sup>4</sup>.

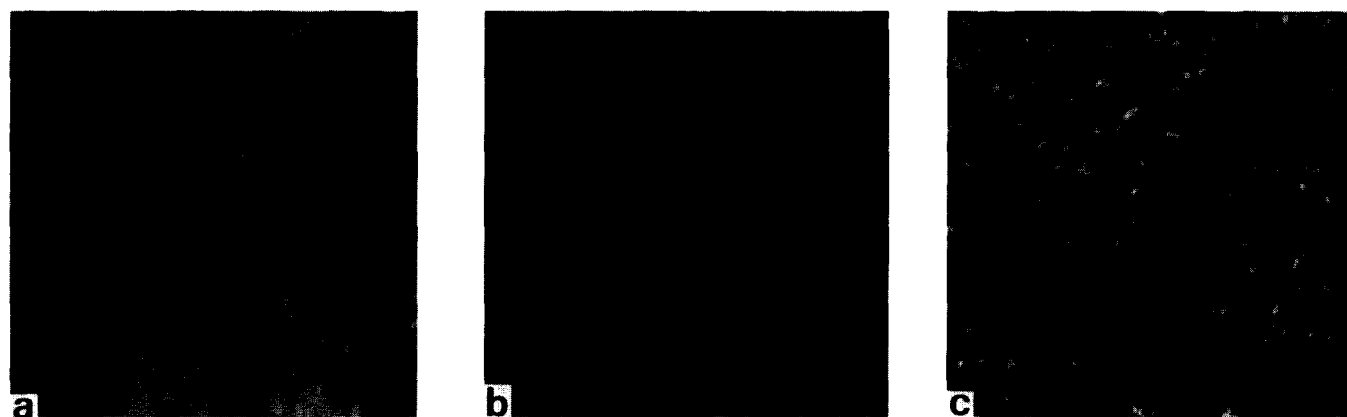
The solubilities of these copolymers increased with decreasing P unit contents, as would be expected on the basis of their decreased degrees of crystallinity and the

lowered stability of the crystalline phase. The two homopolymers and all of the copolymers were soluble in either *p*-chlorophenol or trifluoromethanesulphonic acid or pentafluorophenol, but the copolymers could also be dissolved in mixtures of these solvents with chloroform, depending on their compositions. The thermotropic melts of the copolymers containing 75 mole percent of P units or higher, and its homopolymer, showed strong opalescence on stirring, while that with 60 mole percent was weakly opalescent, and the 50 mole percent copolymer showed no stir opalescence<sup>4</sup>. Hence, as suggested above, this property also indicates in a semi-quantitative manner that either the amount or the stability of the liquid crystalline phase is directly related to the mesogenic to non-mesogenic unit ratio in the same manner as are the crystalline properties in a copolymer. Previous experience in this laboratory with a variety of aromatic polyesters suggests that a polymer must contain no less than 50–60 weight percent mesogenic units to be able to form a stable thermotropic mesophase<sup>4,5</sup>.

A more quantitative indication of the 'degree of liquid crystallinity' can be made from the areas of the  $T_i$  endothermic peaks and the  $T_d$  exothermic peaks in their d.s.c. thermograms, which are collected together in Figures 2 and 3. Relative and very approximate estimates of the amount or the order of the nematic phase can be determined from these peak areas, but visual inspection of the thermograms in Figure 1 reveals that even at 80 mole percent P, the copolymer had a much smaller  $T_i$  endotherm compared with that of the homopolymer.

### Crystallization-induced reactions of copolyesters

The ability of semi-crystalline copolyesters to undergo a structural reorganization from random to blocky comonomer sequence distributions, as a result of ester interchange reactions occurring below the melting point of the crystalline phase, has been studied extensively in this laboratory<sup>2,3,6,7</sup>. This process has been termed a 'crystallization-induced reaction', CIR, in our studies. We have recently studied the CIR reorganization in the liquid crystalline phase of the thermotropic copolyesters containing ethylene terephthalate and either *p*-oxybenzoate or *o*-chloro-*p*-oxybenzoate units<sup>3</sup>. However, the data obtained in that investigation were of limited usefulness because of the partial infusibility and insolubility of the reorganized copolymers, which presumably resulted from the formation of extended



**Figure 1** Photomicrographs of polymer sampled in the liquid crystalline state on the hot stage of a polarizing microscope: (a) P homopolymer at  $275^\circ\text{C}$  ( $T_m = 265$ ,  $T_i = 321^\circ\text{C}$ ); (b) 0.75 P copolymer at  $240^\circ\text{C}$  ( $T_m = 233$ ,  $T_i = 265^\circ\text{C}$ ); (c) 0.60 P copolymer at  $230^\circ\text{C}$  ( $T_m = 230$ ,  $T_i = 242^\circ\text{C}$ )

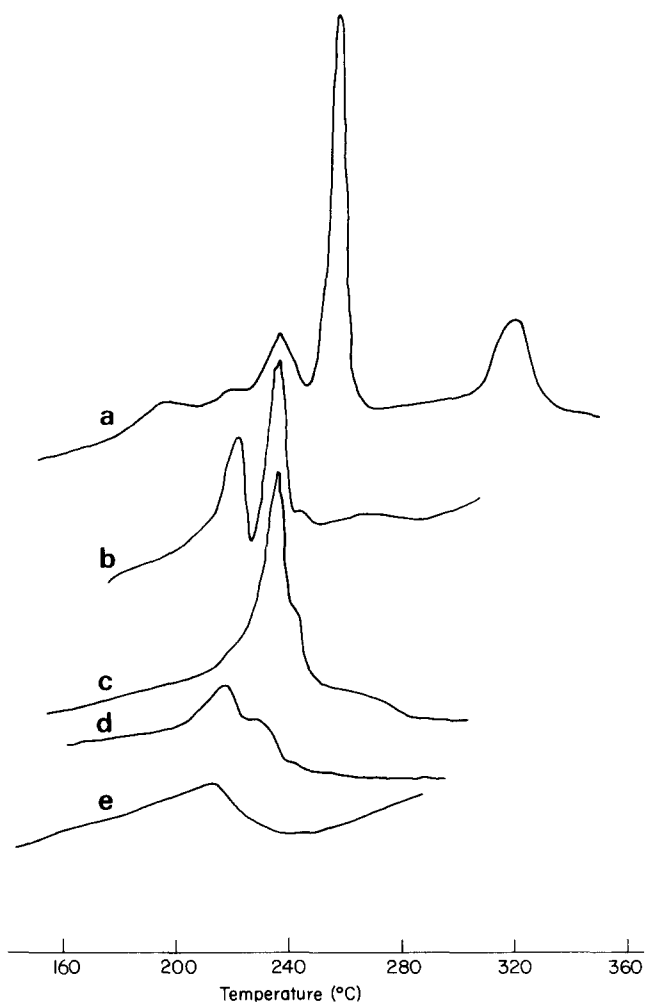


Figure 2 First heating cycle of d.s.c. thermograms: (a) P homopolymer; and copolymers containing (b) 80 mole percent; (c) 75 mole percent; (d) 60 mole percent, and (e) 50 mole percent of P units

blocks of the *p*-oxybenzoate units because their homopolymers are insoluble and infusible. It was expected that the successful application of the CIR process to the present copolymers in their liquid crystalline state would be more apparent because the P homopolymer is fusible and has an observable  $T_i$ , so the effect of such a reorganization should be directly observable from changes in the  $T_m$ ,  $T_i$ ,  $T_d$  and  $T_c$  thermal transitions, as well as in the measured  $\Delta H$  and  $\Delta S$  values of these transitions, all of which should increase with increased blockiness<sup>2,6,7</sup>.

The copolymer containing 75 mole percent of P units was chosen for this study, and four different ester interchange catalysts were first evaluated for their efficacy in promoting a CIR process, including sodium acetate, antimony oxide, toluenesulphonic acid and calcium acetate. Of these, only sodium acetate was found to be effective. Even with this catalyst, however, the results obtained were highly variable and difficult to reproduce, both because of variations in the molecular weights before and after the thermal treatments, and variations in the crystalline and liquid crystalline properties from sample to sample.

The data and d.s.c. thermograms (cooling cycle only) for the best case observed for the reorganization of the copolyester containing 75 mole percent of P units are shown in Table 2 and Figure 4. In the table, the transition temperatures and thermodynamic data for the deisotrop-

ization temperature are compared for the initial copolymer and for samples of this copolymer after heat treatments at 240°C for 24 h both with and without the ester interchange catalyst. At this reaction temperature and time, no significant amount of interchange should occur in the absence of a catalyst; that is, the CIR process should not take place.

It was observed in these studies that the cooling cycles of the thermograms were much more reproducible than the heating cycles, so the former were used to follow the effects of the CIR process in Figure 4 and to calculate the  $\Delta H$  and  $\Delta S$  values for the isotropic-to-nematic transitions,  $T_d$ , in Table 2. The increases observed as a result of the CIR process were as follows: for the copolymer melting point,  $T_m$ , a 24°C increase; for the isotropization or clearing temperature,  $T_i$ , a 32°C increase; for the deisotropization temperature,  $T_d$ , a 39°C increase; for the recrystallization temperature, a 23°C increase. Substantial increases in both  $\Delta H_d$  and  $\Delta S_d$  for the formation of the nematic phase are also readily seen in Figure 4 and confirmed by the data in Table 2. All of these changes suggest that the reorganized copolymers had more ordered structures presumably because of increased blockiness of the P units, which form the crystalline and liquid crystalline phases<sup>2,3</sup>.

In other attempts to carry out the CIR process in this study, the results were less clear. In Table 3 are collected data for the effects of heat treatments on another sample of this copolymer containing 75 mole percent P units with sodium acetate catalyst both below (at 210°C) and above (at 240°C and 260°C) the melting point of the copolyester for 24 h. At 280°C the polymers became insoluble and discoloured, apparently because of crosslinking and degradation reactions.

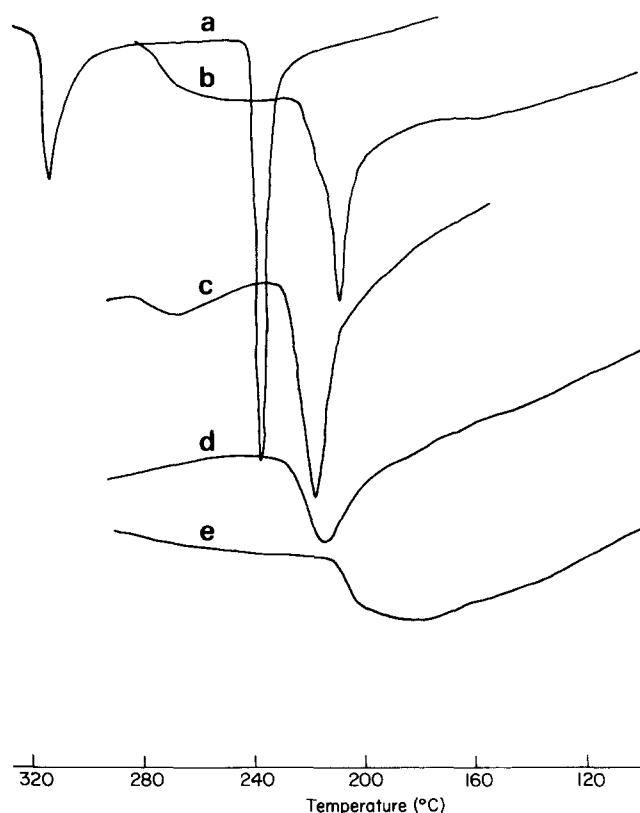


Figure 3 First cooling cycle of d.s.c. thermograms: (a) P homopolymer; and copolymers containing (b) 80 mole percent; (c) 75 mole percent; (d) 60 mole percent, and (e) 50 mole percent P units

**Table 2** CIR reorganization of the copolymer containing 75 mole percent P units

Copolymer sample	$\eta_{inh}^a$ (dl/g)	Transition temperatures, °C <sup>a</sup>				Cooling cycle	
		Heating cycle		Cooling cycle		$\Delta H_d^c$ (kcal/m)	$\Delta S_d^c$ (cal/m°C)
		$T_m$	$T_i$	$T_c$	$T_d$		
Initial	0.28	230	270	207	241	0.15	0.29
Heated with catalyst <sup>b</sup>	0.31	254	302	230	280	0.97	1.8
Heated without catalyst <sup>b</sup>	0.43	230	270	192	248	0.18	0.34

<sup>a</sup> See footnotes *a* and *b* in Table 1<sup>b</sup> Heated at 240°C for 24 h with or without 5 weight percent sodium acetate catalyst<sup>c</sup> Calculated from the areas of the deisotropization exotherms**Table 3** Effect of CIR reaction temperature on properties of copolymer containing 75 mole percent P units<sup>a</sup>

Reaction temp. (°C)	$\eta_{inh}^b$ (dl/g)	Transition temperatures (°C) <sup>b</sup>				Cooling cycle		
		Heating cycle		Range	Cooling cycle		$\Delta H_d$ (kcal/m)	$\Delta S_d$ (cal/m°C)
		$T_m$	$T_i$	$T_i$	$T_c$	$T_d$		
— <sup>d</sup>	0.28	230	264	242–282	200	237	0.64	1.3
210	0.78	233	278	249–299	220	262	0.81	1.5
240	0.45	234	280	246–305	212	260	0.94	1.8
260	0.61	233	273	243–300	210	254	0.63	1.2

<sup>a</sup> After 24 h reaction time with 5 mole percent sodium acetate catalyst<sup>b</sup> See footnotes *a* and *b* in Table 1<sup>c</sup> Initial copolymer sample<sup>d</sup> Temperature interval from start to finish of  $T_i$  peak

It can be seen from these data that the  $T_i$ ,  $T_c$  and  $T_d$  transitions were increased in all cases, but the  $T_m$  transition was not. However, all of these samples as well as those in Tables 1 and 2, both before and after the heat treatments, had multiple melting peaks in their d.s.c. endotherms, as seen in Figure 2 and as is often the case for polyesters. In contrast, the cooling curves of Figure 3 showed only single recrystallization peaks, so the  $T_d$  and  $T_c$  data for the cooling cycle, and the  $T_i$  values for the heating cycle, are believed to be more meaningful than those for  $T_m$ .

However, the interpretation of the results in Table 3, as to the extent of the CIR reorganization, is less certain because the copolyester samples after the heat treatments had substantially higher molecular weights as indicated by their solution viscosities. Furthermore, while  $T_i$ ,  $T_c$  and  $T_d$ , and the thermal stability of the liquid crystalline phase (as indicated by the  $T_i$  peak temperature interval in Table 3), all increased significantly, the  $\Delta H_d$  and  $\Delta S_d$  values did not. Nevertheless, the observed changes in general support the conclusion that CIR reorganization processes occurred both in the solid state, below the melting transition of the copolymer, and in the liquid crystalline state, although the reaction temperature of 260°C was probably too close to the clearing temperature to achieve the maximum effect.

The amount of sodium acetate catalyst which was used to effect the CIR process at 240°C was relatively unimportant, and amounts varying from 2 to 20 weight percent gave essentially the same results in terms of the thermal properties and molecular weights of the final copolymers. On the other hand, the transition temperatures of the reorganized copolyesters increased in a more or less continuous manner for a series of samples heated at 210°C for reaction times of up to approximately 12 h, and

then remained constant, as shown by the data in Table 4. However, this temperature is below the melting point of the copolymer not in the liquid crystalline region.

## EXPERIMENTAL

### Reagents

Calcium acetate (certified grade from Fisher Scientific Company), antimony trioxide (reagent grade from Matheson, Coleman and Bell) and sodium acetate (certified grade from Fisher Scientific Company) were dried in an oven at 190°C overnight and stored in a desiccator. *p*-Toluene sulphonic acid (Eastman Chemical Company) was used after drying at 80°C under vacuum. Trifluoroacetic acid (Aldrich Chemical Company), pentafluorophenol (Aldrich Chemical Company), phenol (reagent grade from Fisher Scientific Company), 1,1,2,2-tetrachloroethane (reagent grade from Fisher Scientific Company) and *p*-chlorophenol (from Aldrich Chemical Company) were used as received without further purification.

### Syntheses of monomers and copolymers

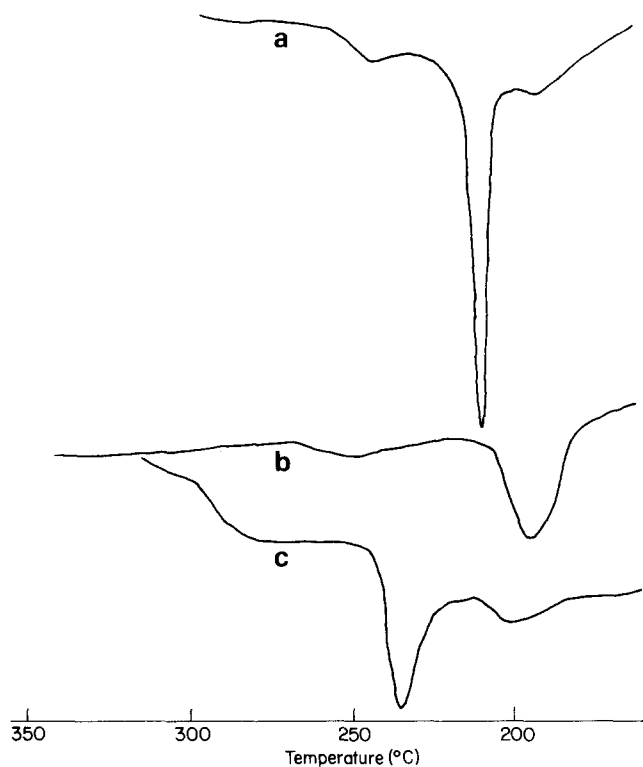
All of the procedures for preparation of the monomers and copolymers were reported earlier<sup>1,5</sup>.

### Crystallization-induced reorganization, CIR<sup>6-8</sup>

The copolymers prepared and purified were finely ground in a mortar and pestle with dry ice to pass a 40 mesh sieve. Catalyst reimpregnation of the purified copolymers for the CIR process was accomplished by dissolving the catalyst in freshly distilled methanol and adding the solution to the polymer powder. Immersion of the sample in an ultrasonic bath aided in the complete wetting of the particles and in gas removal. The sample

**Table 4** Effect of CIR reaction time on properties of copolymer containing 75 mole percent P units<sup>a</sup>

Reaction temp. (°C)	Conditions time (h)	$\eta_{inh}^b$ (dl/g)	Transition temperatures (°C) <sup>b</sup>					Cooling cycle	
			Heating cycle		Range	Cooling cycle		$\Delta H_d$ (kcal/m)	$\Delta S_d$ (cal/m°C)
			$T_m$	$T_i$	$T_i$	$T_c$	$T_d$		
–	0	0.28	230	264	242–282	197	237	0.64	1.3
210	0.5	0.43	233	270	246–288	205	245	0.53	1.0
–	6	0.54	238	263	245–287	225	256	0.76	1.4
–	12	0.24	233	280	248–299	218	265	0.92	1.7
–	24	0.78	233	278	251–301	216	262	0.81	1.5

<sup>a</sup> Samples contained 20 weight percent sodium acetate catalyst<sup>b</sup> See footnotes a and b in Table 1**Figure 4** First cooling cycles of copolymer containing 75 mole percent of P units: (a) before heat treatment; (b) after 24 h of heating at 240°C without added catalyst; (c) after 24 h heating with 5 weight percent of sodium acetate catalyst added to the sample

dispersion was immersed in an oil bath adjusted to a few degrees lower than the boiling point of the solvent, and a stream of pre-purified nitrogen was passed over the surface of the dispersion. After all of the solvent was evaporated, the sample was dried under vacuum for 24 h. For the CIR process, 0.1–1.0 g of copolymer was placed in a 6-inch standard test tube and the contents were again ground with a glass rod to a fine powder. The test tube was closed with a rubber septum, the contents were evacuated to 0.3 mm Hg, and the atmosphere was purged with pre-purified nitrogen three times, after which the sample was kept under vacuum. The test tubes were suspended in a constant temperature bath at the desired reaction temperature for a fixed period of time, the contents were again ground, then purified by extraction overnight in a Soxhlet apparatus with methanol, and dried in vacuum at 40°C–60°C for 24 h.

#### Polymer characterization

**Inherent viscosity.** The inherent viscosity,  $\eta_{inh}$ , was determined using 0.2 g dl<sup>-1</sup> solutions of the copolymers in

*p*-chlorophenol. All measurements were made using an Ubbelohde type viscometer in a constant temperature bath maintained at 45°C ± 0.03°C.

**Thermal characterization.** A Perkin-Elmer DSC-2 instrument was used to examine the thermal properties of the polymers. The heating and cooling rates were 20°C min<sup>-1</sup>. The parameters investigated were the melting temperatures,  $T_m$ , the clearing or isotropization temperature,  $T_i$ , for the transition from the anisotropic state to isotropic state of the polymers, and the enthalpy and entropy of clearing,  $\Delta H_i$  and  $\Delta S_i$ . A standard sample of tin metal was used for the referent. The assignments for the transition temperatures in the d.s.c. thermograms were confirmed by visual observations of samples to calculate the  $\Delta H_i$  and  $\Delta S_i$  values.

**Optical characterization.** A microscope (Leitz Ortholux) fitted with cross-polarizing filters and fitted with a hot-stage (Metler FP-2) was used to observe the birefringence behaviour of the polymers.

**Copolymer analysis.** Attempts were made to determine copolymer sequence distributions by <sup>13</sup>C n.m.r. and proton n.m.r. analyses on samples dissolved either in a 45/55/5 mixture (w/w/w) of chloroform-*d*/trifluoroacetic acid/tetramethylsilane or in pentafluorophenol. A Varian model CFT-20 spectrometer was used for the <sup>13</sup>C n.m.r. studies and a Bruker WM250 (250 MHz <sup>1</sup>H) spectrometer for the <sup>1</sup>H n.m.r. studies. However, no set of peaks attributable to different dyad structures was found on analysis by <sup>13</sup>C n.m.r. spectroscopy.

#### ACKNOWLEDGEMENT

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