Crystallization-induced reactions of copolymers: 6. Reorganization of polyesters in the liquid crystal state

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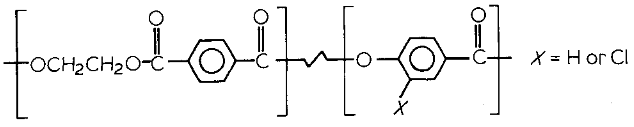
A series of random thermotropic poly(4-oxybenzoate-co-ethylene terephthalate), P(OB/ET), and poly(3-chloro-4-oxybenzoate-co-ethylene terephthalate), P(COB/ET), copolymers were prepared and their thermal properties were determined. The crystallization induced reactions (CIR) of some of these copolymers were investigated in the liquid crystal state. The effects of reaction parameters such as reaction time, temperature, type and amount of catalyst, and molecular weight of the initial sample were examined for yields, compositions, properties and sequence distributions of the reorganized products. The initial liquid crystal copolymers formed a mixture of soluble and insoluble products after the CIR process, and the latter are believed to be multiblock, crystalline oxybenzoate copolymers which are infusible above an average oxybenzoate sequence length of approximately four units.

Keywords Crystallized-induced reactions; liquid crystal copolymers; copolyesters; ester-interchange reorganization; oxygenzoate–terephthalate copolymers

INTRODUCTION

Since the discovery of the crystallization induced reaction, CIR, of isomeric poly(ester acetals) in this laboratory[1], similar phenomena have been observed to occur for random copolyesters of *cis/trans*-1,4-cyclohexylenedimethylene terephthalate[2], poly(ethylene terephthalate-co-2-methylsuccinate)[3] and poly(ethylene terephthalate-co-succinate)[4]. Ester-interchange reorganization reactions of these random copolyesters to more blocky sequences by the CIR process could be achieved simply by heating these polymers below the melting point of the initial copolymer, preferably in the presence of a suitable catalyst. The CIR process results in an increase in degree of crystallinity and melting point by converting the initial random or statistical copolyester to a multiple block copolymer because, as shown in the previous studies, a semicrystalline copolymer will develop an increasingly blocky sequence when its structural units are made to undergo isomerization or interchange reactions in the solid state below the initial polymer melting point. In the CIR process, the non-crystallizable comonomer units adjacent to the crystalline regions are replaced by the crystallizable units through the interchange or isomerization reaction, and the latter then irreversibly crystallize into the crystalline domain, thus increasing the crystalline domain size and thereby the overall degree of crystallinity as well as the sequence length of the crystalline unit. The latter effect, in turn, results in an increase in melting point[2-4].

In the present study two series of random copolyesters were prepared by the insertion of *p*-oxybenzoate units, OB, or 3-chloro-4-oxybenzoate units, COB, into poly(ethylene terephthalate), PET, to prepare copolyesters of the following structure, which were capable of forming liquid crystalline melts, in order to investigate the possibility of carrying out a CIR process in the thermotropic state:



Jackson and Kuhfuss of Tennessee Eastman Company described the preparation and properties of P(OB/ET) copolyesters of this type[6]. The thermotropic behaviour observed was of the nematic type, and the polymers showed the appropriate characteristic optical anisotropy and birefringence. The molecular orientation associated with this thermotropic behaviour could be put to advantage either in the extrusion of fibres or in the injection moulding of plastics from these polymers to give products with an unusually high modulus and tensile strength[7]. Similar products have been obtained from the closely related polyesters based on hydroquinone and terephthalic acid, which were reported on extensively in a series of patents issued to the DuPont Company[8]. In that work they observed that the nematic melt behaviour was retained even when substituents were present on the hydroquinone ring, and the principal effects of the substituent was both to lower the transition temperature for conversion into the anisotropic melt and to increase the solubility of the polymers.

EXPERIMENTAL

Dimethyl terephthalate (Eastman Chem. Co.) was used after double recrystallization from absolute ethanol (mp

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143°C). Ethylene glycol (Aldrich Chemical Co.) was purified by refluxing over sodium under a dry nitrogen atmosphere followed by vacuum distillation. Calcium acetate (certified grade from Fisher Scientific Co.), antimony trioxide (reagent bgrade from Matheson, Coleman and Bell) and sodium acetate (certified grade from Fisher Scientific Co.) were dried in an oven at 190°C overnight and stored in a dessicator. *p*-Toluenesulphonic acid (Eastman Chemical Co.) was used after drying at 80°C at less than 10 mm Hg. Trifluoroacetic acid (Aldrich Chemical Co), phenol (reagent grade from Fisher Scientific Co.), 1,1,2,2-tetrachloroethane (TCE, reagent grade from Fisher Scientific Co.), and 1,1,1,3,3,3-hexafluoro-2-propanol (Eastman Chemical Co.) were used as received without further purification. Diphenyl ether (certified grade from Fisher Scientific Co.) used as a solvent for the solution polymerization of *p*-acetoxybenzoic acid was purified by vacuum distillation. *p*-Acetoxybenzoic acid, mp 187° ~ 187.5°C, was prepared by reacting *p*-hydroxybenzoic acid with acetic anhydride at 60°C in the presence of sulphuric acid catalyst. The product was recrystallized twice from benzene. 3-Chloro-4-acetoxybenzoic acid was prepared in the same manner and recrystallized from an ethanol–water mixture, m.p. 159°C.

Polymerizations

Poly(ethylene terephthalate), PET, was prepared by a conventional transesterification method from dimethyl terephthalate (39.5 g) and ethylene glycol (30.1 g) with calcium acetate (0.0637 g) and antimony trioxide (0.0153 g) catalysts. The reactions were conducted at 200°C for 3 h, 220°C for 20 min, and finally 280°C for 10 min, after which the pressure was reduced slowly to 0.5 mm Hg over a period of 15–20 min and maintained for 5 h. The product was dissolved in 400 ml of trifluoroacetic acid. The solution was filtered through a double-thickness of Whatman$^{(R)}$ No. 1 filter paper and the product was collected by precipitation into a 10-fold volume of methanol, filtered, and dried overnight in a vacuum oven at 80°C, then ground on a mortar and pestle with dry ice to pass a 40 mesh sieve. The product yield was 26.7 g (94%), and the d.s.c. melting endotherm occurred at 266°C.

Poly(p-oxybenzoate-co-ethylene terephthalate), P(OB/ET). All copolyesters were prepared by the Kuhfuss and Jackson 'melt blending' method[5,6], in which a mixture of the *p*-acetoxybenzoic acid, PET, and a catalyst were charged into a reaction vessel fitted with a stirrer, nitrogen inlet, condensate collector and vacuum outlet. After removing the adsorbed moisture from the reactants at 100°C and 0.2 mm Hg, the reactor was alternately purged with pre-purified nitrogen and evacuated to approximately 0.2 mm Hg. After the third nitrogen purge, the nitrogen flow was adjusted for approximately 25 cc min^{-1} and the reactor was immersed in a eutectic salt bath of sodium nitrite, sodium nitrate maintained at 275°C. With nitrogen passing through the reaction system and venting through the outlet bubbler, the temperature was maintained at 275°C and atmospheric pressure for 30 min. After the initial polymer fragmentation reaction was completed, the accumulated acetic acid in the collector was removed and the nitrogen purge valve was closed. Vacuum was then slowly applied over a 5 min period, and the polymerization reaction was allowed to occur for 4 h. The contents of the reactor were cooled under a nitrogen atmosphere and approximately a tenfold (v/v) quantity of trifluoroacetic acid was added and allowed to reflux overnight. After cooling to room temperature, the solution was filtered through a double thickness of No. 1 Whatman$^{(R)}$ filter paper into a tenfold (v/v) quantity of vigorously stirred methanol. The precipitate was filtered and vacuum dried at 80°C overnight, and the product was finely ground in a mortar and pestle with dry ice to pass a 40 mesh sieve. Product yields varied widely, continuously decreasing with increasing amounts of the oxybenzoate monomers in the monomer mixture.

POB Homopolymerization[10]. The bulk polymerization procedure for the polymerization of *p*-acetoxybenzoic acid or the chlorine-substituted monomer followed exactly the procedure for the copolymers with the exception that the polymer was refluxed in trifluoroacetic acid for three days to insure the complete removal of any residual monomer and soluble oligomers. Homopolymers were also prepared by a solution polymerization using diphenyl ether as the solvent with the appropriate monomer at a concentration of 20 mole per cent in a procedure identical to that described above. The reaction was allowed to proceed at 250°C under a nitrogen sweep for 4 h, and the unreacted monomer and residual diphenyl ether were removed from the insoluble polymer by Sohxlet extraction with ethanol overnight. The final drying and grinding were as described above.

Crystallization-induced reorganization, CIR

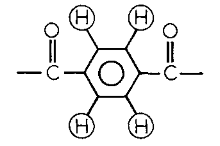
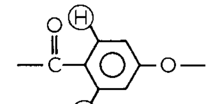
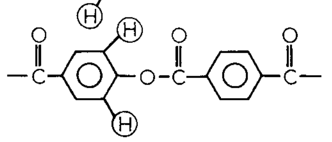
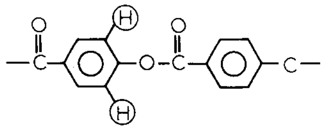
The copolymers prepared and purified by the procedures above were ascertained to be free from residual catalyst[11]. Catalyst reimpregnation of the purified copolyesters for the CIR process was accomplished by dissolving the catalyst in freshly distilled methanol and adding the solution to the polymer powder. Immersion of the sample in an ultrasonic bath aided in the complete wetting of the particles and in gas removal. The sample 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, 1.1 to 1.2 g of copolymer was placed in an 8 inch standard test tube which had been shortened to fit in a centrifuge, and the contents were again ground with a glass rod to a fine powder. The test tube was sealed with a rubber septum, the contents were evacuated to 0.2 mm Hg, the atmosphere was purged with pre-purified nitrogen twice, after which the sample was kept under a slight positive nitrogen pressure. The samples were suspended in the constant temperature bath at the desired reaction temperature for a fixed period of time, the contents of the test tube were again ground up with a glass rod, 30 ml trifluoroacetic acid was added, and the contents were maintained at room temperature for four days. Separation of the soluble and insoluble fractions was accomplished by centrifugation and extraction with fresh solvent. The soluble polymer was collected by precipitation in methanol, filtration and washing with methanol. The insoluble polymer remaining in the test tube was dried under a prepurified nitrogen current, and both products were then dried in an unheated vacuum oven for 24 h.

Polymer characterization

Inherent viscosity. The inherent viscosity, η_{inh}, and the intrinsic viscosity, $[\eta]$, were determined using 1 g dl^{-1} solutions of the copolymers in 60/40 (v/v) phenol/TCE solvent mixture. All measurements were made using an Ubbelohde type viscometer in a constant temperature bath maintained at 25° ±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^{-1}. The parameters investigated were the glass transition, T_g, the polymer melting temperatures, T_m, the reversible crystal–crystal (c–c) transition temperature, T_x,[10] and the recrystallization temperatures, T_c. T_c was defined as the extrapolated point of the departure of the exotherm from the baseline, while T_m and T_x were reported as the extrapolated return to baseline of the endotherm. T_g was calculated as the average of the extrapolated onset of departure and extrapolated return to baseline temperatures.

Copolymer analyses. Proton n.m.r. analysis was used to determine the compositions of the copolymers prepared from the OB monomer while n.m.r. and chlorine analyses were used for the COB copolymers. Solutions for n.m.r. analyses were prepared by dissolving 0.15 g of the OB copolymers in 0.75 ml of trifluoroacetic acid. A Perkin-Elmer model R32 (90 MHz) spectrometer operated at 35°C was used, and the average of five integrations of each of the resulting peaks was taken to calculate the mole fractions of each monomer unit. The following assignments for various protons in the OB copolymers were made in which the values of the chemical shifts are relative to tetramethylsilane as the standard:

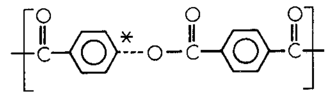
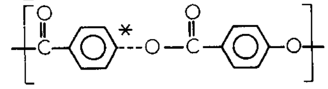
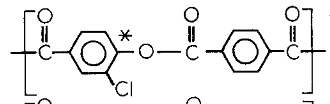
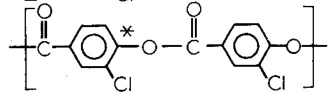
Designation	Structural unit	Chemical shift (ppm)
A'		7.8
A''		7.95 and 8.05 (doublet)
B'		6.95 and 7.05 (doublet)
B''		7.05 and 7.15 (doublet)
C	$—OCH_2CH_2O—$	4.5

The copolymer composition was calculated by the following equation:

$$X_{OB}=\frac{2B}{2A-C}$$

where X_{OB} is the mole fraction of *p*-oxybenzoate units in the copolymer; $A=A'+A''$, and $B=B'+B''$. A typical proton n.m.r. spectrum of a copolymer prepared from a mixture of 60 mole % PET and 40 mole % *p*-acetoxybenzoic acid is shown in *Figure 1*. According to the analysis described above, this copolymer contained 52 mole % *p*-oxybenzoate units.

Sequence distribution. In order to determine sequence distributions by C-13 n.m.r. analysis, a 45/55/5 mixture (v/v/v) of chloroform-d/1,1,1,3,3,3-hexafluoror-i-propanol/tetramethylsilane was used to prepare a solution of 0.6 g of polymer in 1.25 ml of solvent for the analyses. The sequence distributions of the comonomer units in the soluble polymers of the as-prepared and reorganized copolymers were obtained with a Varian Model CFT-20 spectrometer using the following C-13 n.m.r. assignments and equations[12]:

P(OB/ET) copolymers		Chemical shift (ppm)
A dyad		156.3
B dyad		158.2
P(COB/ET) copolymers		
A dyad		152.2
B dyad		152.9

and:

$$\alpha(X_{OB})=\frac{B}{A+B}$$

$$\alpha^0(X_{OB})=\frac{X_{OB}}{X_{OB}+2(1-X_{OB})}$$

$$\Psi(X_{OB})=\frac{\alpha(X_{OB})-\alpha^0(X_{OB})}{1-\alpha^0(X_{OB})}$$

where $\alpha(X_{OB})$ is the fraction of OB (or COB units) which are connected directly to another OB (or COB) unit in a

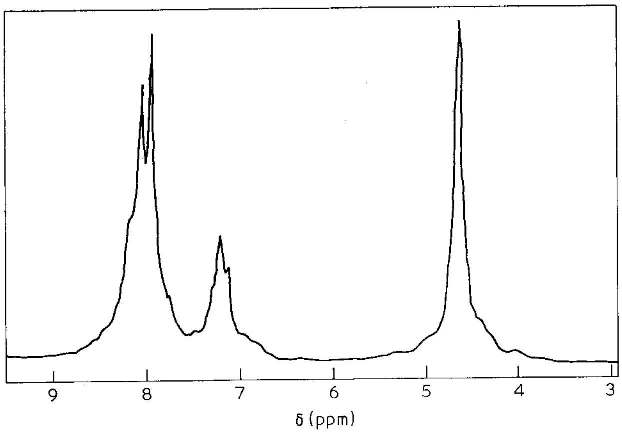


Figure 1 90 MHz H-n.m.r. spectrum of the P(OB/ET) copolyester prepared from a 60/40 mixture of PET and *p*-acetoxybenzoic acid

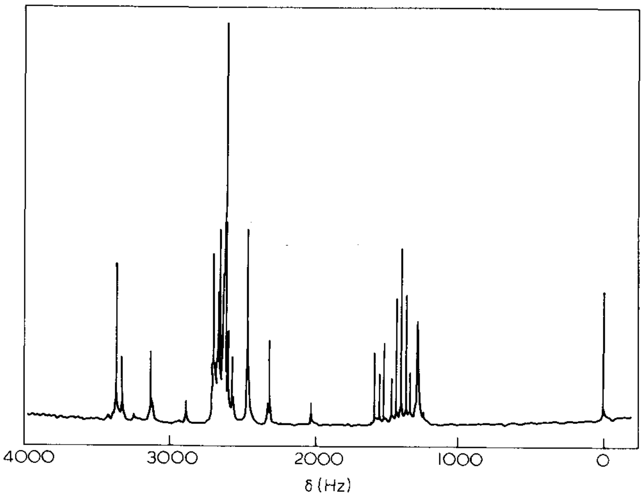


Figure 2 ^{13}C-n.m.r. 4 kHz spectrum of P(OB/ET) copolyester

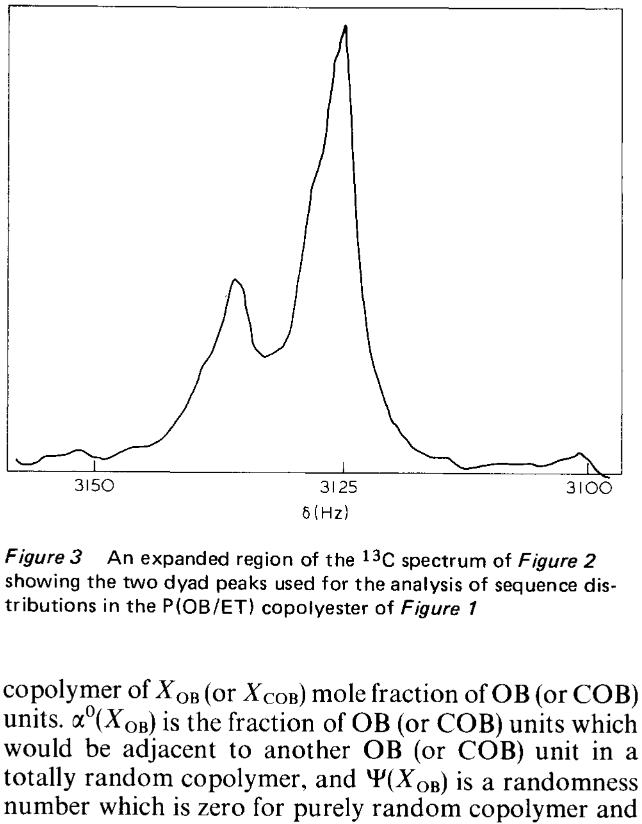


Figure 3 An expanded region of the ^{13}C spectrum of *Figure 2* showing the two dyad peaks used for the analysis of sequence distributions in the P(OB/ET) copolyester of *Figure 1*

copolymer of X_{OB} (or X_{COB}) mole fraction of OB (or COB) units. $\alpha^0(X_{OB})$ is the fraction of OB (or COB) units which would be adjacent to another OB (or COB) unit in a totally random copolymer, and $\Psi(X_{OB})$ is a randomness number which is zero for purely random copolymer and one for purely block copolymer. A 4 kHz spectrum of the P(OB/PET) copolymer is shown in *Figure 2*, and an expanded 50 Hz spectrum of the two peaks used for this analysis is shown in *Figure 3*.

Wide angle X-ray diffraction. Samples were prepared by pressing 0.3 g of polymer in a die measuring 8 mm in diameter and 0.8 mm in thickness. The temperature of the press was adjusted to 100°C for soluble polymers and 200°C for insoluble copolymers and for the oxybenzoate homopolymers. The die was inserted in the press, and the pressure was raised to 1100 psi. The heater was then shut off and the sample was allowed to cool. After the temperature had reached 80°C the samples were removed and enclosed between two pieces of cellophane tape. The samples were exposed to the X-ray beam for 12 h with a sample-to-film-distance of 5 cm.

Optical characterization. A microscope (Leitz, Ortholux) fitted with cross-polarizing filters and programmable hot-stage (Metler's FP-2) was used to observe the birefringence behaviour of the polymers. Slides of the samples were prepared by pre-melting 1–3 mg of polymer between a clean slide and coverslip on a hotplate. Contact time was kept to a minimum to avoid polymer degradation. Observations were made at a hot-stage temperature of 300°C, 120°C and at room temperature.

RESULTS AND DISCUSSION

The thermal properties of the copolyesters containing ET and either OB or COB units are presented in *Table 1*[9]. The compositions of the copolymers as determined by either proton n.m.r. analysis for the P(ET/OB) samples or by chlorine analysis for the P(ET/COB) samples were always lower in oxybenzoate unit content than the calculated amount based on monomer composition in the polymerization reactions. The reason for this discrepancy appears to be twofold, either: (1) a loss of the *p*-acetoxybenzoic acid monomer by hydrolysis and sublimation or (2) homopolymerization of this monomer to form an insoluble, infusible polymer, and some insoluble product was always obtained even from polymerization reactions containing only small amounts of this monomer. Others have also reported the formation of a two phase product in this insertion reaction[13].

The thermal properties of the copolymers in *Table 1* agree with those reported by Kuhfuss and Jackson[6] and by Balakrishnan and coworkers[14]. As the content of the oxybenzoate units increased, crystalline transitions could be clearly observed in the d.s.c. endotherms for the OB but not the COB copolyesters containing 40 mole % or more of these units. However, both types of copolymers were birefringent in the melt above 200°C which was indicative of the presence of anisotropic liquid crystal melts[6], although the birefringence intensities of the COB copolymers were much weaker than those of the comparable OB copolymers. As Jackson and Kuhfuss have described, polymerization reaction mixtures containing 50 mole per cent or more of the *p*-acetoxybenzoic acid monomer became turbid during

Table 1 Transition temperatures of OB and COB copolymers of PET

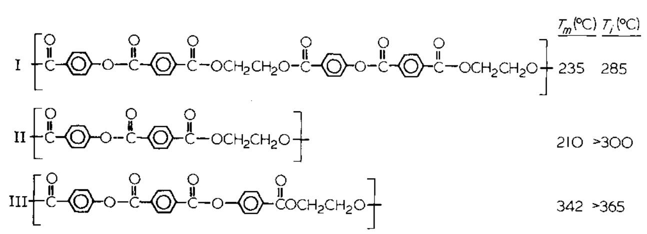
Monomer substituent, *X*	OB or COB amount (mole %)	T_m (°C) by d.s.c.	Temp. range of nematic state (°C)[a]
H	19	224	–[b]
	46	215	220–>350
	48	230	220–>350
	65	290	310–>350
	80 (insol.)[c]	338 (c-c)	–[d]
Cl	35	too broad	180– 240
	50	too broad	190– 240
	53	120–190	190– 260
	60 (insol.)[c]	391 (c-c)	–[d]
	66 (insol.)[c]	378 (c-c)	–[d]

[a] Visually observed on the hot stage of a polarizing microscope with an upper temperature limit of 350°C
[b] No birefringence observed
[c] Insoluble, infusible polymer which shows only an apparent crystal–crystal (c-c) transition
[d] Sample was birefringent up to 350°C but did not flow

polymerization[6], which is another indication that thermotropic liquid crystal melts were formed from these compositions.

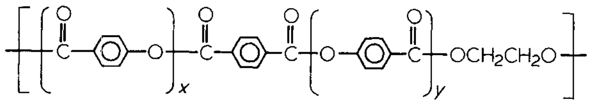
According to the results of the wide angle X-ray diffraction analysis, WAX, of the copolymers, compositions containing as low as 30 mole % OB units destroyed most of the PET crystallinity, and samples with approximately 50 mole % OB units exhibited X-ray diffraction patterns typical of those of the crystalline POB homopolymer. The degree of crystallinity of these copolymers were, as expected, much lower than that of the homopolymers, but the copolymer diffraction pattern contained the first of several large spacings normally observed for the homopolymer. Superimposed upon these spacings was the characteristic amorphous halo typical of a polymer of low degree of crystallinity.

An interesting comparison can be made of the melting, T_m, and clearing, T_i, transitions of these copolymers with closely related homopolymers recently prepared in this laboratory having the following structures[9,15,16]:



All three of these homopolymers contain repeating units which correspond to those which are expected to be formed in a random copolymer of OB and ET units. The melting point of Polymer I was close to that observed for the P(OB/ET) sample containing 48 mole % of OB units, but the latter copolymer remained liquid crystalline up to at least 350°C, while Polymer I was observed to undergo a transition from the nematic to the isotropic melt state, the clearing temperature T_i, at 285°C, which suggests that the copolymer had long blocks of mesogenic units, as expected. Polymer III contains the type of unit which should be present in a P(OB/ET) copolymer containing predominantly OB units, and its thermal properties are similar to those of the random copolyester containing 0.65 mole % OB units in *Table 1*.

The thermal analysis results combined with those for the sequence distributions of both the as-prepared and reorganized P(OB/ET) copolymers indicate that the liquid crystal regions of these polymers are most likely composed of mesogenic blocks having sequences of oxybenzoate units of varying length connected to a terephthalate unit as represented by the following structure:



in which x and y vary from 0 to 3 and $x+y=3$. Units in which x or $y>3$ most likely have very high melting points and associate into infusible, insoluble crystalline domains[10,16].

Crystallization-induced reorganizations

The reorganization of semi-crystalline copolyesters from random to block copolymers at elevated temperatures below the melting points has been verified for several types of copolyesters in previous reports from the laboratory[2-4]. Indeed, one of the first examples of this type of process for forming non-statistical, multiblock copolyesters may have been in the work of Gilkey and Caldwell in 1959 who observed the formation of block copolyesters and even homopolymers when they attempted to prepare copolymers from mixtures of *m*- and *p*-acetoxybenzoic acid by a high temperature, melt polymerization reaction[17]. They attributed the blockiness to a difference in the reactivity of the two monomers, but a CIR process may well have occurred under their reaction conditions.

It was of interest in the present investigations to determine whether an effectively irreversible CIR reorganization could occur above the melting point in the liquid crystalline melt as well as below it, and such a process was observed to occur, but at a very slow rate. Several investigations involving studies of temperature effects and catalyst types and amounts on the CIR rate were carried out on the P(OB/ET) copolymer of *Table 1* having 46 mole % OB units.

The melting point for this copolymer was 215°C, and at 230°C in the presence of an added ester interchange catalyst, *p*-toluenesulphonic acid (TSA), the initially soluble sample formed an insoluble-infusible fraction, which, by d.s.c. analysis, had only an endotherm at 345°C characteristic of the crystal–crystal transition reported for POB[10,18].

The wide angle X-ray diffraction pattern of the insoluble fraction was also very similar to that of POB observed by Economy and coworkers[10,18]. At this reaction temperature, and OB composition, only 10% by weight of the product was present in the insoluble fraction after two weeks of reaction time, but for a copolymer with 58 mole per cent OB units heated at 325°C, an insoluble fraction representing 20% by weight of the product was formed after only 10 h of heating. However, degradation reactions may well have occurred in the latter case as indicated by the formation of small amounts of vinyl groups in the products from ^{13}C n.m.r. and i.r. analyses[19,20].

In both cases described above, the remaining soluble fractions of the copolyesters had decreased OB unit contents, as expected, and shorter number average sequence lengths, $\bar{L}_n$, of the OB unit blocks; $\bar{L}_n$ decreased from 1.46 to 1.33 for the 46 mole % copolymer and from 1.84 to 1.69 for the 58 mole % copolymer. These results suggest that the CIR process occurs primarily on the sections of the copolymer molecules with longer blocks of OB units to form the infusible crystalline domains, as would be expected.

The addition of an ester interchange catalyst greatly facilitated the CIR process, but at high OB contents the reorganization reaction to form an insoluble polymer phase could occur even in the absence of catalyst. Recent results from another laboratory indicate that such was not the case for a copolymer containing only 30 mole % OB units[21], but that copolymer may have had only a very low degree of liquid crystallinity, if any.

CIR of poly(3-chloroxybenzoate-co-ethylene terephthalate), P(COB/ET)

Because of the insoluble, infusible character of the reorganized, presumably multi-block copolymer formed by the CIR process, it was not possible to carry out a quantitative analysis of its composition. Because of their

Table 2 Rate of CIR reorganization of a P(COB/ET) copolymer at 249°C[a]

Reaction time	Soluble polymer (wt. %)	COB content (mole %)		Soluble polymer				Insoluble polymer T_x, (°C)[b]
		Sol. poly.	Insol. poly.	α^0	α	ψ	$\bar{L}_n$	
0	100	53	–	0.36	0.35	–0.021	1.6	–
15 min	>99	52	–	0.35	0.30	–0.070	1.5	–
30 min	>99	52	–	0.35	0.29	–0.085	1.5	–
1 h	97	51	–	0.34	0.32	–0.027	1.5	–
3 h	93	50	58	0.33	0.31	–0.035	1.5	368
17 h	88	49	66	0.33	0.28	–0.066	1.4	380
24 h	85	48	66	0.32	0.31	–0.010	1.4	376

[a] 1.48 wt % TSA catalyst added to sample

[b] Crystal-crystal interchange endotherm in d.s.c. thermogram

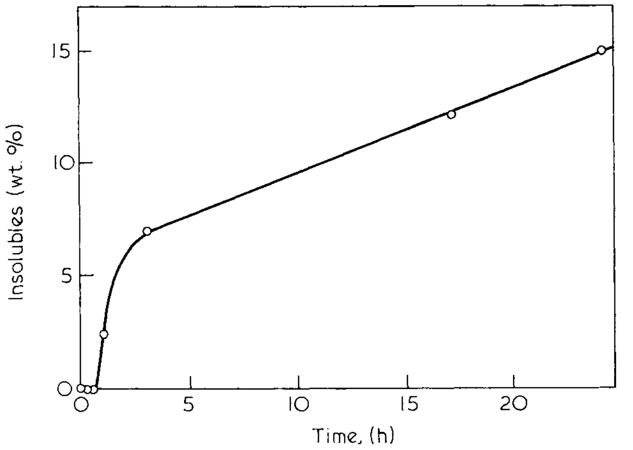


Figure 4 Rate of insoluble polymer formation by the CIR process of the P(COB/ET) copolymer of *Table 2*

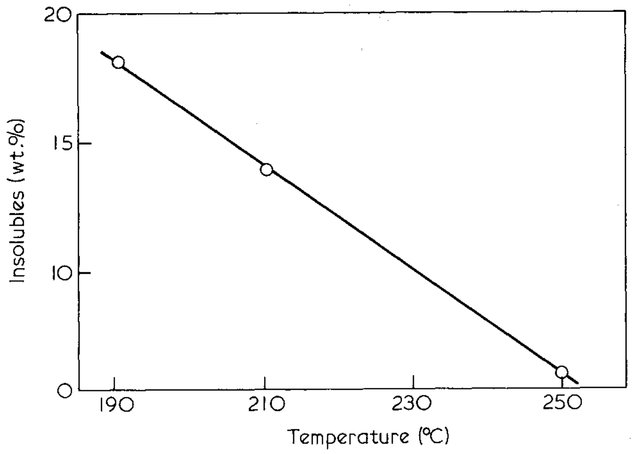


Figure 5 Temperature dependence for formation of the insoluble polymer phase by the CIR process of a P(COB/ET) copolymer, see *Table 3*

lower melting points, a more detailed study was made of the CIR of P(COB/ET) copolyesters, for which the compositions of both fractions could be readily determined by elemental analysis. The results of such a study are given in *Table 2* for the copolymer of *Table 1* containing 53 mole per cent COB units heated at 240°C for varying periods of time up to 24 h. This copolymer was nematic over the temperature range from 190° to 260°C as observed on a polarizing microscope.

As can be seen from the data in *Table 2*, after an induction time of about 15 min, an insoluble product began to form from the initially totally soluble copolymer. This result is consistent with a model involving block sequence domain formation as a result of the CIR process. The insoluble polymer formation proceeded uniformly after the induction time, and the resulting decrease in soluble polymer content reflects the continuous occurrence of a reorganization and crystallization process, the rate of which is illustrated in *Figure 4*. It appears from *Figure 4* that a change in mechanism occurred after approximately 3 h of reaction time. Possibly either a decrease in the amount of endgroups or diffusional limitations of the reactive groups caused a reduced rate of ester interchange reactions and, thus, an overall decrease in the CIR rate[3].

The sequence distribution of the COB units in the copolymer, as indicated by the values for α and ψ in *Table 1*, show that the reactive soluble phase maintained approximately a random or statistical sequence distribution with a gradual decrease in the average sequence length, $\bar{L}_n$, of the COB units, as would be expected from the discussion above for the CIR reorganization of the P(OB/ET) copolymers.

The same copolymer sample was subject to a two-week period of reorganization at a slightly lower temperature, 230°C, in the presence of a greater amount of catalyst, 3.6 wt.% TSA. Under these conditions a product containing approximately 21 wt.% of insoluble polymer ($T_x = 373$°C) was formed which had an X-ray diffraction pattern identical to that of the COB homopolymer. The soluble fraction decreased in COB content from 53 to 43 mole% and was found, by n.m.r. analysis, to have a very low COB–COB dyad content ($\alpha = 0.19$, $\alpha_0 = 0.27$), again indicating a selective removal of the longer blocks initially present in the copolymer due to the CIR process of block extension by an irreversible ester interchange-crystallization sequence.

Reaction temperature

The CIR reorganization reactions were also carried out on this copolymer at various temperatures, and the data given in *Table 3* and *Figure 5* show that the amount of insoluble polymer formation decreased essentially linearly with reaction temperature. This observation leads to the conclusion that crystallization is most likely the rate controlling part of the CIR process because if either the rate of ester interchange or the endgroup diffusion rate

Table 3 Temperature dependence of the CIR reorganization of a P(COB/ET) copolymer^a

Reaction temp. (°C)	Soluble polymer (wt. %)	COB content (mole %)		Soluble polymer			Insoluble polymer
		Sol. poly.	Insol. poly.	α^0	α	ψ	T_x, (°C)
Initial	100	53	–	0.36	0.35	−0.021	–
190	82	49	55	0.33	0.24	−0.13	317
210	86	49	57	0.33	0.25	−0.12	343
240	93	50	58	0.33	0.31	−0.035	368
250	94	50	59	0.33	0.30	−0.043	376

[a] After 3 h reaction time; 5 wt % TSA catalyst added to sample

Table 4 Effect of catalyst type on the CIR reorganization of a P(COB/ET) copolymer at 230°C

Catalyst	Soluble polymer (wt %)	COB content (mole %) soluble polymer	Soluble polymer				Insoluble polymer
			α^0	α	ψ	$\bar{L}_n$	T_x, (°C)
Initial	100	53	0.36	0.35	−0.021	1.6	–
TSA	84	50	0.34	0.26	−0.13	1.4	336
$Ca(OAc)_2$^{b}	94	51	0.34	0.27	−0.12	1.4	395
Sb_2O_3	93	51	0.34	0.25	−0.15	1.4	367

[a] After 3 h reaction time with 5 wt % catalyst added
[b] Calcium acetate

Table 5 Effect of amount of TSA catalyst on the CIR reorganization of a P(COB/ET) copolymer at 190°C^a

Cat. amt. (wt %)	Soluble polymer (wt %)	COB content (mole %)		Soluble polymer				Insoluble polymer
		Sol. poly.	Insol. poly.	α^0	α	ψ	$\bar{L}_n$	T_x, (°C)
Initial	100	54	–	0.37	0.29	−0.12	1.5	–
0	85	51	58	0.34	0.30	−0.064	1.5	376
0.1	85	52	57	0.35	0.30	−0.075	1.5	355
1.0	85	51	57	0.34	0.28	−0.10	1.4	353
10	77	49	49	0.33	0.26	−0.094	1.3	349

[a] After 3 h reaction time

were controlling, the slope of the plot in *Figure 5* should be positive. Of course, the observed overall temperature dependence probably includes a function of the ester interchange kinetics as well as the crystallization kinetics. The linear relationship of *Figure 5* also suggests that there is a limiting temperature, close to 280°C, at which the blocky, crystalline phase will not be formed. This temperature is just above the end of the clearing transition temperature range, which strongly indicates that the CIR process can occur at any temperature within the liquid crystal melt but not in the isotropic melt.

The COB unit compositions of the soluble phase were equal for each of the four temperatures after reaction times of 3 h, while only a slight increase in the COB unit content of the insoluble phase was observed, see *Table 3*. These results again conform to a model in which crystallization is the controlling factor. At the lower reaction temperature, which corresponds to the melting point of the copolymer, crystallization of the newly-formed COB blocks would be more rapid but less perfect, and the expected lower degree of crystal perfection is reflected by the lower amount of COB units in the insoluble phase as well as by the much reduced temperature of the crystalline-crystal interchange transition, T_x. However, at the higher reaction temperature only the more perfect crystalline domains are formed so that the number of domains or nucleii onto which the CIR process can build are reduced. This conclusion is also supported by the decrease in COB dyad content (α) and blockiness (ψ) with increasing reaction temperature.

Catalyst type and amount

In a previous investigation it was found that TSA, antimony trioxide and calcium acetate were all effective ester interchange catalysts for the CIR of poly(ethylene terephthalate-co-succinate)[4], but in the present study TSA was found to be the most effective of the three in terms of the rate of the CIR process, as shown by the data in *Table 4* for the reorganization of the same copolymer at 230°C, although calcium acetate appeared to form a more perfect insoluble polymer phase as indicated by both the ψ and T_x data.

It would be expected that the amount of catalyst should be quite important in controlling the overall CIR rate, even though the rate of crystallization appears to be the more important factor, as discussed above. However, as shown by the data in *Table 5*, which was obtained at the lowest possible temperature for the presence of a liquid crystal phase (190°C), there was no apparent difference in the amount of insoluble polymer formed after 3 h either in the absence of catalyst or at catalyst levels of 0.1 and 1.0 wt.%. Only at the highest level of 10 wt.% was there a significant increase in insoluble polymer formed, but in this case the amount of COB units in the insoluble polymer, and consequently the value of T_x, decreased even

Table 6 Effect of initial molecular weight on the CIR reorganization of a P(COB/ET) copolymer[a]

Polymer sample[b]	$[\eta]$[c]	Soluble polymer (wt %)	COB content (mole %)		Soluble polymer				Insoluble polymer
			Sol. poly.	Insol. poly.	α^0	α	ψ	$\bar{L}_n$	T_x, (°C)
I. Initial	0.11	100	54	–	0.37	0.36	–0.027	1.7	–
Final	0.12	74	49	54	0.32	0.31	–0.020	1.4	305
II. Initial	0.13	100	53	–	0.36	0.33	–0.051	1.6	–
Final	0.15	81	48	54	0.32	0.30	–0.022	1.4	301
III. Initial	0.18	100	53	–	0.36	0.35	–0.021	1.6	–
Final	0.18	82	49	55	0.33	0.24	–0.124	1.3	317

[a] After 3 h reaction time with 5 wt % TSA catalyst added

[b] Initial polymers were taken from the same polymerization reaction mixture after various reaction times: I—after 30 min., II—after 70 min., III—after 300 min

[c] Intrinsic viscosity of initial polymer or of soluble polymer fraction

though the COB content and sequence length of the remaining soluble polymer also decreased. These changes are probably indicative of the occurrence of degradation or chain scission reactions under such conditions and are not related to the CIR process itself. In any case the apparent insensitivity of the CIR rate to the amount of catalyst at the lower levels is again an indication that the process is controlled more by the crystallization rate than by the rate of ester interchange even at this relatively low reaction temperature.

Initial molecular weight

As in previous investigations on the CIR of copolyesters, the rate of reorganization was found to be inversely proportional to the molecular weight of the initial copolymer[3,4]. This effect has been attributed to the decrease in the rate of ester-interchange with decreasing endgroup concentration for higher molecular weight polymers. The results in *Table 6* are consistent with this expectation for the reaction carried out at the minimum temperature, 190°C, and with the other conclusions discussed above for the mechanism of the CIR process.

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