

Sequence Length Determination in Poly(ethylene terephthalate)–Bisphenol-A Polycarbonate Random Copolymers by Application of Selective Degradation

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ABSTRACT: Poly(ethylene terephthalate) (PET) and bisphenol-A polycarbonate (PC) are melt-mixed in equimolar ratios under various conditions to get a series of PET–PC copolymers. Samples from each copolymer are characterized by differential scanning calorimetry, ¹H and ¹³C nuclear magnetic resonance (NMR), size exclusion chromatography (SEC), and polarizing light microscopy. The lengths of the PET sequences are determined in different copolymer samples by NMR sequential analysis before and after removal of the PC segments by selective degradation. In the former case, rather unusual results are obtained, suggesting predominant alternating order of single PET and PC repeating units. After selective elimination of the PC units, however, the NMR techniques show evidence of consecutively bonded dyads or triads of PET and PC units, which corresponds to the theoretical values in random copolymers obeying the statistics of Bernoulli. Considering the ¹H-NMR and SEC results after selective elimination of the PC sequences, a possible structure of the residual PET containing segments is proposed for the first time. It is concluded that in the PET/PC copolymers studied, when sequence distribution approaches the random one, determination of the PET block lengths after elimination of the PC sequences is more reliable as compared to the cases when selective degradation is not applied. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 429–440, 1998

Key words: polymer blends; transesterification; poly(ethylene terephthalate); polycarbonate; nuclear magnetic resonance; size exclusion chromatography

INTRODUCTION

It has been known for a long time that polymers obtained by both polymerization and polyconden-

sation could be mixed to the advantage and optimization of the properties.¹ Recently, there has been considerable scientific and industrial interest in blending of condensation homopolymers. In some of these blends, transreactions can easily occur during melt processing with a great effect on the compatibility and mechanical properties. As the transreactions advance, blends convert first to block copolymers with a decreasing length of the sequences to give finally random copolymers.² This concept is not new and has been

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proven in numerous homopolymer blends.³⁻⁸ Intensive research in this area has shown that the control of transreactions can provide a new method for preparation of copolymers within the processing equipment. Such copolymers are expected to have wider variation in microstructure and properties than copolymers prepared directly from monomers.¹

Blends comprising poly(ethylene terephthalate) (PET) and bisphenol-A polycarbonate (PC) have received special attention because of their potential industrial application. Both homopolymers are widely used as engineering plastics. In particular, PC has high impact strength, and PET displays an excellent solvent resistance. The reactive blending of PET and PC has already proved to be a successful and inexpensive route for producing new polymers with modified or even improved properties.^{9,10} In principle, it is possible to prepare different materials simply by changing the weight fractions of PET and PC or the reaction conditions of melt-mixing. For instance, PET-PC block copolymers are obtained that are useful as compatibilizers in PET-PC blends¹¹ and also poly(ether ester) random copolymers with properties enhanced or intermediate as compared to those of the pure components.¹²

In the study of transesterification reactions in a molten blend of condensation polymers, it is often important to know whether the resulting product is a block copolymer, a random copolymer, or still a mechanical mixture of the starting homopolymers. To that purpose, the following analytic techniques are most frequently used in the PET-PC or similar systems: differential scanning calorimetry (DSC)²⁻⁵, ¹H and ¹³C nuclear magnetic resonance (NMR),^{6-8,10,13-16} chromatographic methods,^{10,17} and selective degradation of the PC segments with subsequent determination of viscosity.¹⁸ The process of PET-PC copolymer preparation has been carried out in different ways, with^{7,9,10,12,18} or without^{2-5,8,13,14,16} effective mixing of the molten homopolymer blend.

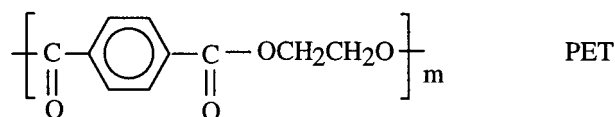
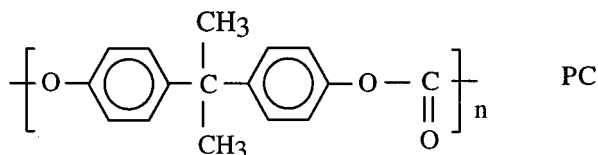
The purpose of this study is to characterize the sequence lengths in PET-PC copolymers obtained via transesterification, employing a combination of all of the above techniques, that is, DSC, followed by PC units selective degradation, calculation of the lengths of the PET sequences based on NMR data, and size exclusion chromatography (SEC) of the selectively degraded PET-PC copolymer. By means of polarizing light microscopy (PLM) an attempt is also made to evaluate the

role of effective mass transfer in the molten homopolymer blend for the obtaining of amorphous copolymers with a more or less random sequence distribution.

EXPERIMENTAL

Materials

The polymers used were commercial PC (Macrolon, weight-average molecular weight $\bar{M}_w = 28,000$) with a glass transition temperature T_g of 150°C and PET (Yambolen, viscosity-average molecular weight $\bar{M}_v = 21,000$ determined at 25°C in a phenol-tetrachloroethane mixture (60:40 by weight, as indicated by Devaux et al.¹⁹) with a melting temperature T_m of 260°C and $T_g = 70^\circ\text{C}$). Both products were supplied in the form of pellets. The chemical structures of the homopolymers employed are as follows.



Preparation of PET-PC Copolymer Samples

The starting homopolymers were dried overnight in vacuum at 100°C and used without further purification. Their reactive melt mixing was performed in a round-bottom, four-neck flask equipped with a stirrer, inert gas inlets and outlets, and a thermometer measuring the temperature of the melt. The reaction vessel was thermostated at 280°C. First the PET homopolymer (50 mmol) was charged and allowed to melt completely while stirring in an inert atmosphere. An equimolar amount of PC was then added within a period of 30 min under moderate agitation. In some samples, 0.5% by weight (based on both blend components) of tetrabutyl titanate [Ti(OBu)₄] were introduced as a transesterification catalyst, leaving out of account the trace amounts

of the PET polymerization catalytic system possibly contained in this homopolymer that also promotes transesterification. Samples were taken from the reaction mixture at different stages of copolymer formation and further subjected to DSC. Each PET-PC copolymer was separated from the reaction mixture in two different manners. The first set of samples was obtained by dissolution of each crude reaction product in CHCl_3 , elimination of minor amounts of (up to 2 wt %) insoluble products representing aromatic polyesters or carbonized residues, and evaporation of CHCl_3 . For the second set, the filtered chloroform solutions of the copolymers were precipitated with methanol and dried in vacuum at room temperature. Before being analyzed by various analytical techniques, some of the samples were annealed at 235°C for 24 h. To that purpose, about 0.5 g of the respective copolymer were placed in a glass ampoule, sealed in an inert atmosphere, and thermostated, with the temperature being controlled with an accuracy of $\pm 0.5^\circ\text{C}$.

Selective Degradation of PC Sequences

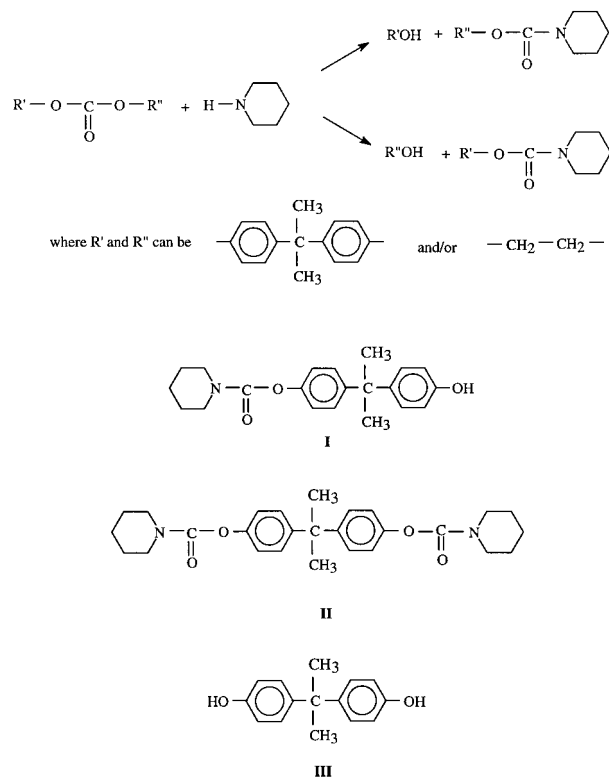
This procedure was performed as previously described.^{10,18} The PC blocks are selectively attacked and removed from the copolymers as low-molecular-weight compounds by reacting the transesterified samples with a CH_2Cl_2 solution of piperidine according to Scheme 1. This process was carried out at room temperature for 3 h. The low-molecular-weight products of PC degradation are 2-(4-hydroxyphenyl)-2-(4'-piperidinocarbonyloxyphenyl)propane (I), 2,2-bis(4-piperidinocarbonyloxyphenyl)propane (II), and bisphenol-A (III)¹⁸. It is worth mentioning here that the method of this selective aminolysis leaves the PET blocks unchanged and does not create additional bonds between them.¹⁸

Measurements

DSC traces were obtained in a Mettler TA 3000 instrument at $10^\circ\text{C}/\text{min}$ heating rate scanning the sample from room temperature up to 280°C . Sample weights were in the 10–20 mg range.

The NMR spectra were recorded in CDCl_3 on a Bruker spectrometer operating at 300 MHz for ^1H - and at 75 MHz for the ^{13}C -NMR measurements. Tetramethylsilane was employed as the internal standard.

Molecular weight distributions (MWDs) were



Scheme 1

studied by SEC on samples dissolved in a 90:10 v/v mixture of tetrahydrofuran and hexafluoroisopropanol (HFIP) and eluted with the same solvent mixture at 1.0 mL/min. A set of Ultrastyrigel columns (10^3 , 10^5 , and 10^6 Å) operating at room temperature and ultraviolet detection were applied.

Polarizing light microscopy studies were performed in a Zeiss-Axiophot light microscope equipped with a heating stage Linkam 400.

RESULTS AND DISCUSSION

It is generally accepted that in blends of condensation homopolymers, the occurrence of transreactions leads to the formation of block copolymers. With the progress of these transreactions, the block lengths gradually decrease, attaining a final state in which the different repeating units are joined in a random order, obeying in binary systems the statistics of Bernoulli.^{20,21} Previous studies on binary blends of polycondensates^{2–5} have shown that even if one or both of the starting

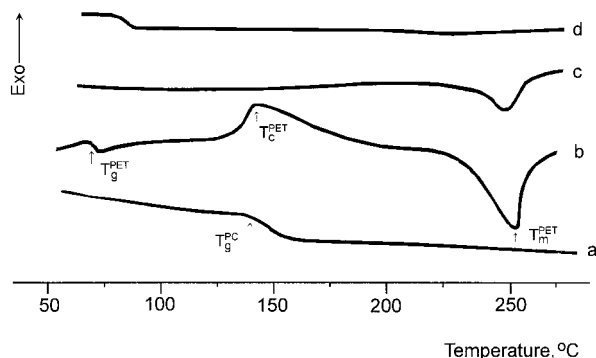


Figure 1 DSC curves of a PET–PC mechanical blend annealed directly in the DSC apparatus for 45 min at 280°C (curve c) and 180 min at 280°C (curve d). Curves a and b characterize the PC and PET homopolymers, respectively.

homopolymers are crystallizable, at higher degrees of transreaction completion, the system becomes amorphous, that is, the copolymer chains obtained are unable to fully contribute to the three-dimensional periodicity of a crystal lattice.

DSC Studies

The DSC traces shown in Figure 1 corroborate this effect in the particular case of PET–PC copolymer obtained by annealing of an equimolar mechanical blend directly in the DSC apparatus.³ After 45 min of such annealing at 280°C (curve c in Fig. 1), the sample still displays some crystallinity that completely disappears after 180 min annealing time (Fig. 1, curve d). The same result was obtained for a much shorter annealing time of 80 min at 280°C when 0.5 wt % of $\text{Ti}(\text{OBu})_4$ were introduced into the mechanical blend (the respective curve is not displayed). Anyway, the DSC traces demonstrated that a 180-min annealing in the DSC apparatus at 280°C produces an amorphous copolymer (as revealed by DSC). Its inability to crystallize could be attributed to the fact that effective transreactions at the above conditions decrease the lengths of the PET blocks to sequences comprising, in average, less than 5 residues, which, as previously indicated,³ would not be enough to form lamellae. It should be mentioned here that the T_g of 82°C registered for the amorphous copolymer obtained without melt mixing (Fig. 1, curve d) is much closer to that of PET than to T_g^{PC} .

The effective mass transfer during the copoly-

mer formation and the degree of phase separation in the PET–PC system to be studied by DSC is also very important, as can be concluded from Figure 2. There, the DSC traces are shown of PET–PC copolymers prepared under different conditions. Curve a characterizes a copolymer obtained after an 80-min melt mixing at 280°C in the presence of transesterification catalyst. The curve does not reveal any melting endotherms, and the T_g registered was 108°C. The next two curves were taken with one and the same sample prepared by 180-min noncatalyzed reactive blending at 280°C, with the copolymer being separated by solvent evaporation (curve b) or precipitation (curve c). The small but detectable crystallizability in curve b is much better revealed in curve c. That is, in the present case, precipitation obviously (and at the same time rather unexpectedly) favors the phase separation, so it was possible to resolve in curve c a melting endotherm at about 120°C and even a T_g at 60°C. When additionally annealed without stirring at 235°C for 24 h (curve d), both samples b and c showed similar and completely amorphous structure with a single T_g at 110°C. Therefore, in the present case, annealing a PET–PC copolymer at a temperature 15–20°C below the T_m of the neat PET results in further copolymer amorphization rather than in restoration of its crystallizability, as found in previous communications.^{3,4} Another important observation is that the DSC traces of a PET–PC amorphous copolymer prepared by melt mixing at 280°C reveal a T_g being significantly higher than that of a similar copolymer obtained by simple annealing of a mechanical mixture at the same temperature and time duration (compare Fig. 1, curve d and Fig. 2, curve b). The effect of the effective mixing upon the formation of amorphous PET–PC copolymers was further studied in the present work by means of PLM.

NMR Studies

Amorphization of the PET–PC copolymer as revealed by DSC cannot be considered a direct proof of randomization. Theoretically, even a block copolymer containing long PET sequences might be found unable to crystallize, owing to various reasons, such as hampered copolymer crystallization due to the presence of degradation products and improper crystallization time during the DSC scanning.

The NMR technique remains the most powerful

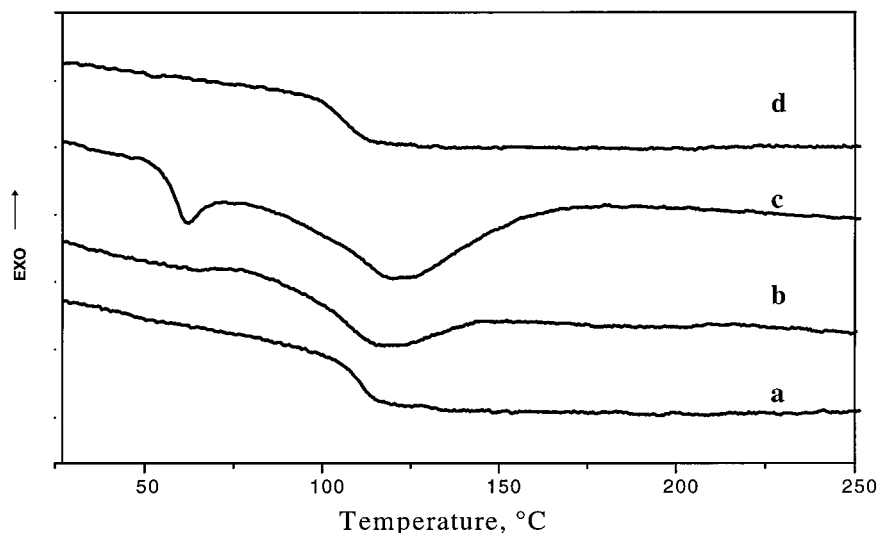


Figure 2 DSC curves (first scans) characterizing differently prepared PET-PC copolymers: (a) melt-mixed for 80 min at 280°C, with additional $\text{Ti}(\text{OBu})_4$; (b) melt-mixed for 180 min at 280°C, with no additional catalyst and the copolymer isolated by solvent evaporation; (c) the same as in (b) but with the copolymer isolated by coagulation; (d) obtained from both samples (b) and (c) after additional annealing of each of them without stirring for 24 h at 235°C.

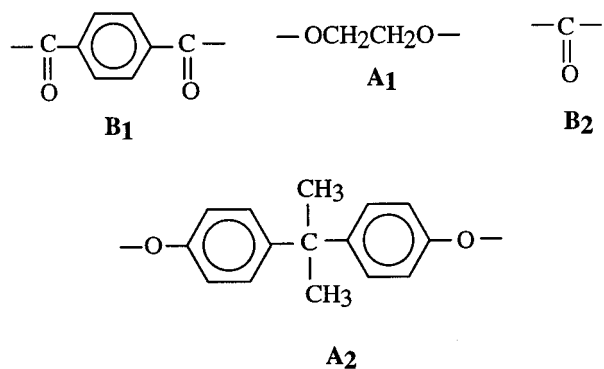
tool for sequential analysis of condensation copolymers. For characterization of our supposedly random PET-PC copolymers, we used the method of Devaux et al.²² based on the earlier works of Guinlock et al.,²³ Kricheldorf,¹⁴ and Yamadera and Murano.²⁰

It was interesting to apply a combination of selective degradation of PC and a subsequent analysis of the remaining PET containing residue by means of NMR in order to compare the results to those derived from the NMR spectra of samples without selective degradation. Amorphous (as revealed by DSC) PET-PC copolymers were only studied obtained from the corresponding neat polymers by melt mixing. These copolymers were completely soluble in chloroform and were isolated by solvent evaporation and/or precipitation with methanol.

Our study was based on the most characteristic range in the ^1H -NMR spectra of the PET-PC copolymers: the signals situated between 8.0 and 8.4 ppm. They belong to the benzene protons of the terephthalic acid residue and are sensitive to the sequence length changes.^{22,23}

In Figure 3, the spectra of an amorphous PET-PC copolymer is depicted (a) before and (b) after selective degradation of the PC units. B_1 and B_2

represent the acidic residues in the system (terephthalic and carbonate, respectively). The ethylene glycol and bisphenol-A moieties are denoted by A_1 and A_2 . The structures of the corresponding fragments are as follows:



From spectrum (b), it becomes evident that the residual product after PC elimination does not comprise PET sequences only; as one might expect, it would have contained then only a singlet at a chemical shift $\delta = 8.06$ ppm, which is not the case. Even though aminolysis affects only the $-\text{OC}(\text{O})\text{O}-$ groups of PC and not the ester groups of any type, the resultant structure after

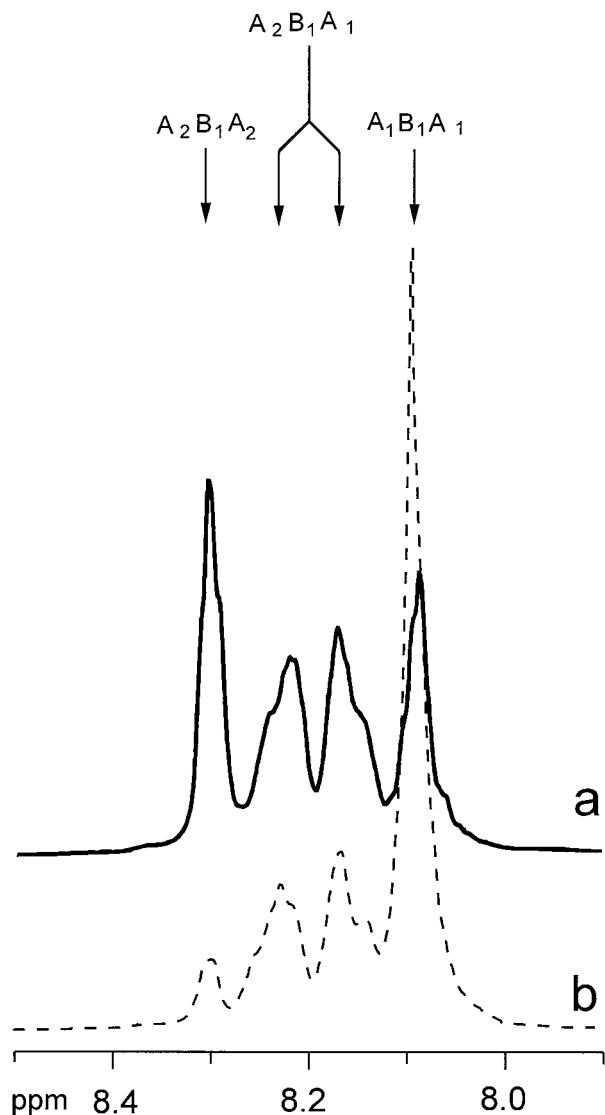


Figure 3 $^1\text{H-NMR}$ spectra of (a) non-degraded and (b) selectively degraded amorphous PET-PC copolymer obtained by melt mixing for 180 min at 280°C .

elimination of the PC repeating units should be rather complex.

Both spectra in Figure 3 represent a superposition of the four signals of an asymmetrically substituted (containing both alkyl and aryl moieties) terephthalic acid residue Alk-Ar (or $A_2B_1A_1$) with the two signals of two symmetric terephthalic acid derivatives Alk-Alk (or $A_1B_1A_1$) at 8.06 ppm and Ar-Ar (or $A_2B_1A_2$) at 8.28 ppm. The former represents a PET unit and the latter represents a unit of an aromatic terephthalic polyester. The relationship between the different

types of terephthalic protons derived from the corresponding peak areas is also worth mentioning. After selective elimination of the PC sequences in all amorphous (as revealed by DSC) PET-PC copolymer samples, the relation of Ar-Ar : Ar-Alk : Alk-Alk = 1 : 6 : 9.

The well-known method of Devaux et al.²² was applied to calculate the coefficients x and y , representing the average degree of polymerization of PET and bisphenol-A terephthalate sequences, respectively [also see eq. (2)]. The following relations were used to that purpose:

$$x = \frac{[A_1B_1A_1]}{[A_1B_1A_2]} + 1, \quad y = \frac{[A_2B_1A_2]}{[A_2B_1A_1]} + 1 \quad (1)$$

where $[A_1B_1A_1]$, $[A_1B_1A_2] = [A_2B_1A_1]$ and $[A_2B_1A_2]$ are the concentrations of the corresponding moieties derived from the integral intensities of their $^1\text{H-NMR}$ peaks. As seen from Table I, in all samples where no selective degradation was performed, rather unusual values for x were obtained. They were lower than those of a completely random copolymer, which would normally indicate a trend toward alternating copolymer. The x -values obtained after selective degradation, however, (see the emphasized rows in Table I) are higher than those theoretically calculated for fully random copolymers. We consider them more reliable than the results obtained without degradation because of the following reasons. The degradation procedure eliminates from the system to be studied by NMR not only the PC residues but also all low-molecular-weight side products obtained during the melt mixing and prolonged thermal annealing so that the risk of misinterpretation of the results due to peak overlapping is lower. Furthermore, having in mind the entropic nature of the driving force toward randomization,^{3,4,21} it seems to be very unlikely to reach in a real system and for finite annealing times, the final state of randomization, alternating PET and PC homodyads, not to mention x -values below 2.0.

The same PET-PC samples were studied by $^{13}\text{C-NMR}$. The results are given in Table II. In this table x , y , z , and w are indexes in the following general formula²²:

$$-[(A_1B_1)_x - (A_1B_2)_y] - [(A_2B_1)_z - (A_2B_2)_w] - (2)$$

and are calculated using the following relations:

Table I Average Degree of Polymerization of Ethylene- (x) and Bisphenol-A (y) Terephthalate Segments Derived from $^1\text{H-NMR}$ in Presumably Random PET-PC Copolymers Obtained After Melt Mixing for 180 Min at 280°C

No.	Method of Random Copolymer Separation	Annealing at 235°C for 24 h	Selective Degradation of PC Sequences	x	y
1	Coagulation	No	No	1.72	1.34
2	As for sample 1	No	Yes	2.67	1.23
3	As for sample 1	Yes	No	1.65	1.39
4	As for sample 1	Yes	Yes	2.51	1.17
5	Solvent evaporation of 1	No	No	1.72	1.32
6	As for sample 5	No	Yes	2.66	1.23
7	As for sample 5	Yes	No	1.62	1.44
8	As for sample 5	Yes	Yes	2.50	1.15
9	Theoretical values for random copolymers ²²			2.16	1.87

$$x = \frac{[A_1B_1]}{[A_1B_2]} + 1, \quad y = \frac{[A_1B_2]}{[A_1B_1]} + 1,$$

$$z = \frac{[A_1B_1]}{[A_2B_2]} + 1, \quad w = \frac{[A_2B_2]}{[A_2B_1]} + 1. \quad (3)$$

Again, B_1 and B_2 represent the acidic residues in the system (terephthalic and carbonate, respectively), and the ethylene glycol and bisphenol-A moieties are denoted by A_1 and A_2 . Therefore, $[A_1B_1]$ and $[A_2B_2]$ are the concentrations of pure

PET and PC units, respectively; likewise, $[A_1B_2]$ and $[A_2B_1]$ are the concentrations of the PET-PC transitional structures.

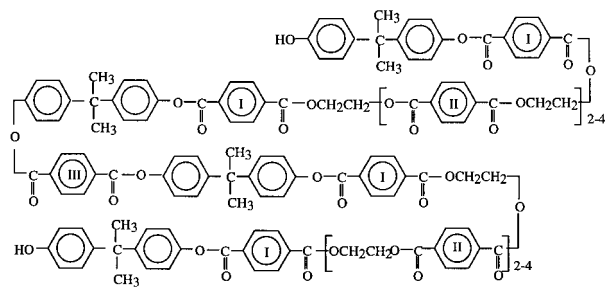
From the above tables, one can see that, as expected, the method of sample separation (coagulation or solvent evaporation) does not affect significantly the PET sequence lengths. The values of the samples with same thermal prehistory determined by the two NMR methods are also close enough. Both NMR techniques applied do not confirm the previously established³ effect of restoration of crystallizable PET sequences upon prolonged annealing of a random PET-PC copolymer. Instead, a further decrease of the PET segments during this annealing is to be supposed. On the other hand, copolymers with fully random sequence distribution (consecutively linked homodyads of PET and PC) were not obtained either. In this respect, our results are in favor of the supposition of Kricheldorf¹⁴ and of Backson et al.,⁸ who pointed out that completely random copolymers could be prepared only in the process of primary polycondensation (starting from monomers, for example, of two diacyl dichlorides and two diols or diphenols) and not by transreactions in binary polyester or polyamide blends.

Comparing the NMR data of PET-PC copolymers before and after aminolysis enabled us to elucidate the sequential ordering in the residual PET containing fragment remaining after PC selective elimination (Scheme 2). We believe that this fragment accurately reflects the PET units sequence in the starting PET-PC copolymer before its selective degradation. Based on the $^1\text{H-NMR}$ data, the model structure in Scheme 2 could

Table II Sequential Analysis for PET-PC Copolymers with Different Thermal Prehistories and Methods of Separation Based on $^{13}\text{C-NMR}$

Sample No.	x	y	z	w
1	1.64	2.55	1.38	3.57
2	2.80	1.56	3.00	1.33
3	1.72	2.45	1.47	3.11
4	2.59	1.63	2.81	1.55
5	1.70	2.42	1.40	3.40
6	2.76	1.57	2.77	1.56
7	1.55	2.82	1.51	2.96
8	2.60	1.62	2.70	1.59
Theoretical value for a random copolymer ²²	2.16	1.87	2.16	1.87

Note: ^{13}C species studied for $[A_1B_1]$ and $[A_2B_1]$: the $\text{C}=\text{O}$ carbon signals of the terephthalic acid residue at 165.6 and 164.3 ppm, respectively. For $[A_2B_2]$ and $[A_2B_1]$: the peak of the H-bonded benzene carbons of the bisphenol-A residue at 121.1 and 120.83 ppm, respectively. Samples are the same as in Table I. Bolded values are for the selectively degraded samples.



Scheme 2

be suggested for the average residual fragment remaining after the PC selective degradation:

The designations I, II, and III are for the Alk–Ar, Alk–Alk, and Ar–Ar terephthalic protons, respectively. According to this theoretical structure, the relation Ar–Ar : Alk–Ar : Alk–Alk = 1 : 4 : 6 (if the average PET sequence is considered to comprise 3 PET units). Comparing it to that practically established, which is 1 : 6 : 9 (or 0.7 : 4.0 : 6.0), it may be concluded that the theoretical value relatively well corresponds to the NMR data. At the same time, it is obvious that the real degraded copolymer would probably contain not only the above theoretical sequence but also various related sequences representing different fragments of the latter containing more asymmetric Alk–Ar moieties and a little longer PET blocks.

SEC Studies

As seen from its theoretical structure, the average residual fragment obtained after selective degradation of the PC units should have a molecular weight between 2500 and 2900, depending on the length (two or three units) of the PET sequences. Therefore, a further evidence in favor or against the structure proposed might be found by SEC investigations of degraded PET–PC copolymers.

In Figure 4 and Table III, all SEC data are summarized about the molecular weights (MW) and molecular weight distributions of the PET–PC copolymers before and after degradation and removal of the PC units. The selective degradation causes a drastic decrease in the molecular weight of the starting samples. In the case of homo-PC (Table III), the average weights of the products of aminolysis are close to that of bisphenol-A, which is one of the low-molecular-weight degradation products. This is an additional indi-

cation that a complete selective degradation of the PC units is carried out.

The MWs as revealed by SEC of all copolymer samples studied are summarized in Table III. The values of a selectively degraded PET–PC random copolymer (prepared by melt mixing of an equimolar PET–PC blend for 180 min at 280°) deserve special attention. They strongly support the proposed hypothetical structure of the residual PET-containing fragment. All degraded PET–PC random copolymers studied by NMR (Tables I and II) reveal similar values, of about 1700–1800 for \bar{M}_n and 2600–3100 for \bar{M}_w ; that is, in all cases, the theoretical MW of 2500–2900 is between the SEC \bar{M}_n and \bar{M}_w . Since these are equivalent polystyrene MWs, one should not look for a complete coincidence between the theoretically calculated and experimentally found SEC MWs. However, the similarity is quite enough to support the structure of the residual PET-containing fragment, as suggested above, on the basis of NMR data (Scheme 2). This fragment contains two sequences of two to three PET repeating units separated by long spacers built up of terephthalic and bisphenol-A moieties and is therefore noncrystallizable. Judging from Table III, melt mixing for 45 min/280°C apparently gives rise to a similar fragment, comprising, however, up to three times longer PET blocks.

PLM Studies

Based on general considerations, the chemical reactions in molten polymer blends should be controlled by the diffusion of the reacting species and their getting in close vicinity so that an effective interaction could take place. This would be true especially when a more or less random copolymer is desired as the main reaction product.

There is no clear distinction in the literature between the properties of PET–PC random copolymers prepared with and without an effective mixing. In this concluding study, we attempted to clarify the role of effective stirring during the PET–PC copolymer preparation. As mentioned above, transreactions leading to a random PET–PC system are accompanied by drastic changes of crystallizability. Since PLM is an useful tool for characterization of crystallizable systems, we performed the following direct observations of the melting: the crystallization cycle in PET–PC samples obtained with and without mixing when annealed at elevated temperatures.

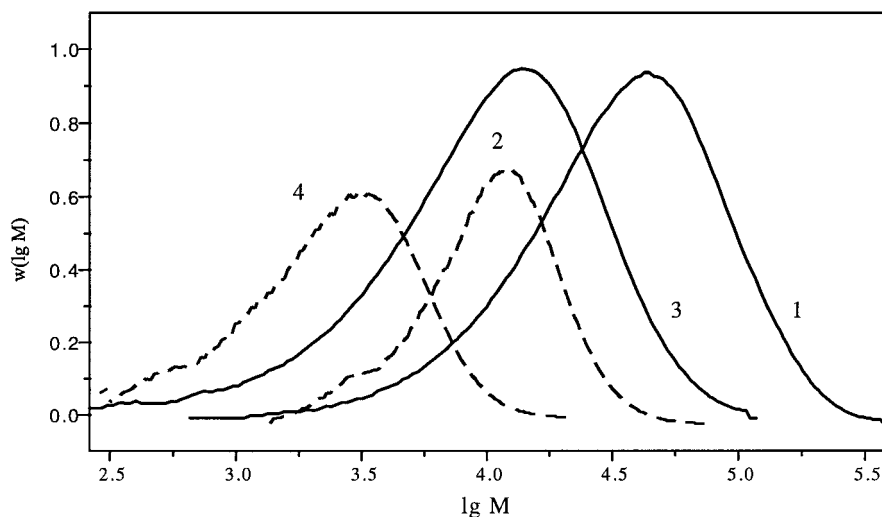


Figure 4 Molecular weight distribution of PET-PC copolymer samples of different block lengths (1) and (3) before and (2) and (4) after PC selective degradation as revealed by SEC. The numbers of the curves correspond to those in Table III.

Figure 5 represents a light micrograph of a solution cast film produced from a copolymer obtained by melt mixing (sample 5 in Table I). Inspection at 85°C does not reveal any crystalline entities. Increased temperatures of up to 300°C did not give significant changes of the texture except for the visible signs of sample degradation. This means that PET-PC copolymers obtained by prolonged melt mixing under intensive stirring are most probably amorphous at the above conditions; that is, a complete randomization should

have taken place in such samples. The crystalline phase revealed in the DSC traces (Fig. 2, curve b) cannot be detected by PLM.

Next figures display the changes of the sample texture in a PET-PC homopolymer blend during its transformation into a copolymer without mixing. To that purpose, PET and PC homopolymers were mixed in HFIP, 0.5 wt % of tetrabutyl titanate were added, and a transparent film was prepared after evaporation of the common solvent. The sample was then placed on the heating

Table III Molecular Weights \bar{M}_n and \bar{M}_w and the Polydispersity Ratio \bar{M}_w/\bar{M}_n of PET-PC of Copolymers with Different Thermal Prehistories Before and After PC Selective Degradation

No.	Sample	Melt Mixing at 280°C (min)	Selective Degradation	Molecular Weights from SEC ^a and Polydispersity Ratio		
				\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
1	PET-PC equimolar	45 ^b	No	19690	51332	2.607
2	PET-PC equimolar	45	Yes	5027	8611	1.713
3	PET-PC equimolar	180 ^c	No	10266	28161	2.755
4	PET-PC equimolar	180	Yes	1590	2717	1.709
	Bisphenol-A	—	No	303	312	1.029
	Neat PC	—	No	18567	29800	1.605
	Neat PC	—	Yes	348	361	1.037

^a Equivalent polystyrene MW.

^b Crystallizable (according to DSC) PET-PC copolymer (longer blocks).

^c Noncrystallizable (according to DSC) PET-PC copolymer (shorter blocks).

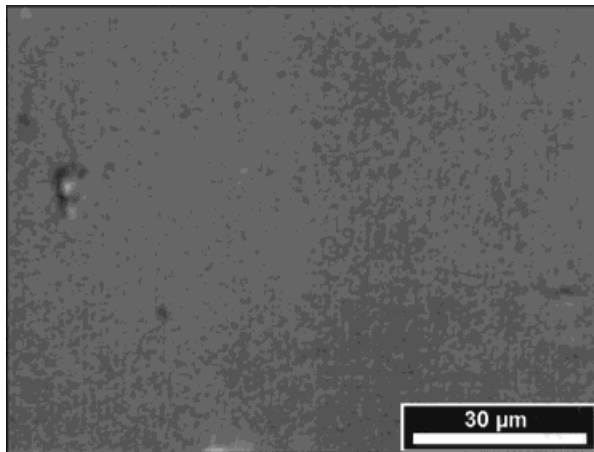


Figure 5 PLM photograph of a copolymer PET-PC sample obtained by melt mixing (sample 5 in Table I). The picture is taken at 85°C, with crossed polars.

stage and observed at temperatures between 25–299°C.

As seen in Figure 6, at room temperature, the crystalline PET phase is well dispersed in the amorphous PC phase, with the texture obtained reminding one of a liquid crystalline system. It is very difficult to define the type of the crystal phase entities. Figure 7(a) shows that short annealing (5 min) of the blend at 299°C did not completely destroy the crystallinity of the sample. This hap-

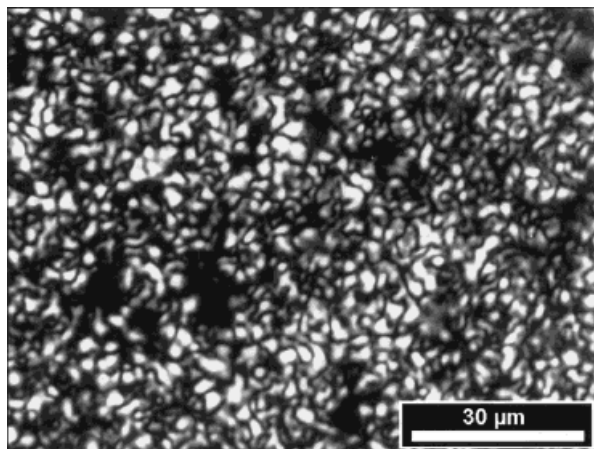
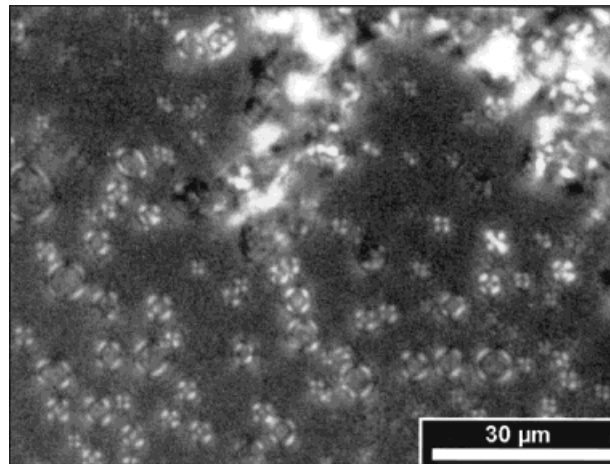
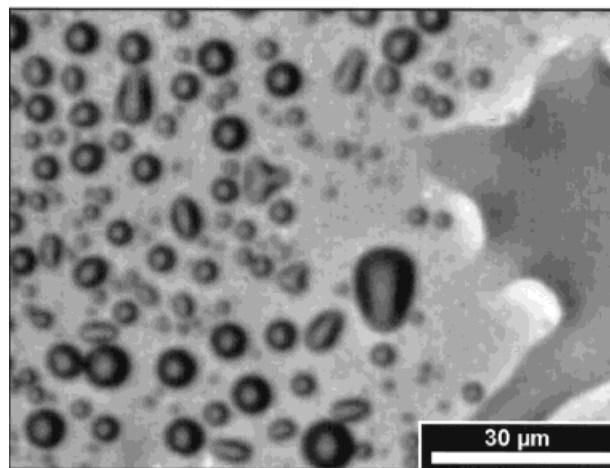


Figure 6 PLM photographs of a PET-PC mechanical mixture containing 0.05 wt % tetrabutyl titanate obtained after evaporation of the common solvent. Conditions were as follows: room temperature; crossed polars.



(a)



(b)

Figure 7 PET-PC blend in Figure 6 and (a) 5 min and (b) 10 min at 299°C. All crossed polars; in (b), λ compensation is applied. The pictures are taken at 299°C.

pens after a 10-min heating [Fig. 7(b)], where isotropic droplets of melted material are clearly observable. The sample was kept for another 20 min at this temperature and cooled down to 235°C. A prolonged (230 min) annealing was then applied that resulted in the texture shown in Figure 8. Further cooling to room temperature did not significantly change the structure of the sample (Fig. 9).

Summarizing the results of the PLM study of the non-stirred PET-PC system, one has to conclude that the equimolar PET-PC mechanical

mixture prepared by dissolution in a common solvent contains finely dispersed ordered domains. A complete melting of the crystalline structures in this blend takes place at unexpectedly high temperatures. Irrespective of the fact that a transesterification catalyst is added and that a prolonged annealing at 235°C is used, upon cooling to room temperatures, the crystalline entities of the PET-PC sample reappear. Therefore, one has to conclude that in this immiscible PET-PC blend where no stirring is applied, transreactions are obviously confined to the interface between the two phases. Obviously, the system does not transform into random (amorphous) copolymer under the conditions employed.

CONCLUSIONS

PET-PC copolymers of nearly random sequence distribution are prepared by mixing of the molten homopolymer blend. DSC and PLM studies demonstrate that the effective mass transfer seems to be of prime importance for the obtaining of amorphous structures with random order of the homopolymer units. Calculation of the sequence lengths in PET-PC copolymers based on NMR data gives more reliable results when applied to samples in which the PC units are selectively removed. Combined NMR and SEC studies of such samples enable determination of the rather complex structure of the average

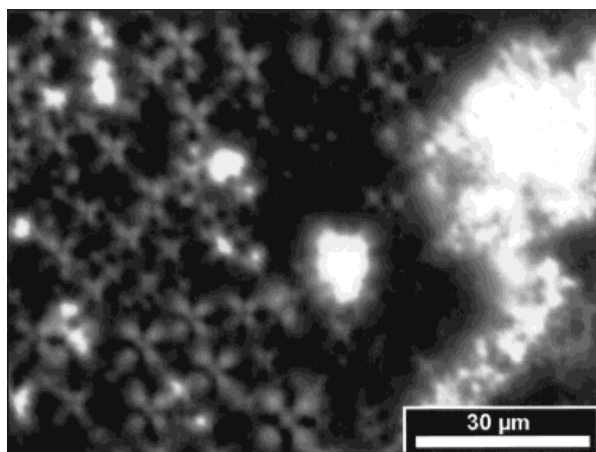


Figure 8 The sample in Figure 7(b) after an additional 20 min annealing at 299°C, cooled to 235°C, and annealed for 130 min more at this temperature. The picture is taken at 235°C, with crossed polars.

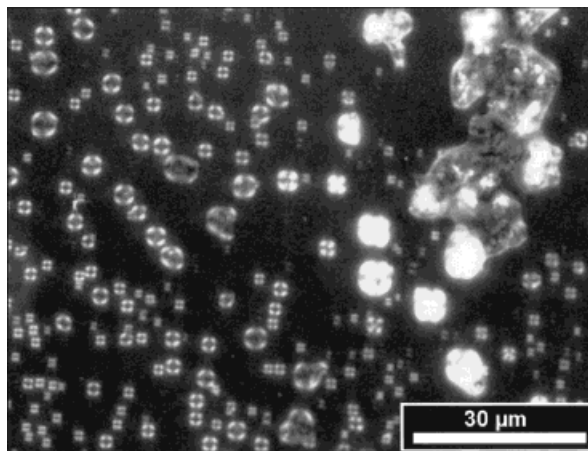


Figure 9 The sample in Figure 8 cooled down to room temperature, with crossed polars.

residual fragment. It accurately reflects the PET units sequence in the starting PET-PC copolymer before its selective degradation.

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