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Sensitivity of X-ray Data to Sequence Distribution for Liquid Crystalline Copolyesters

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ABSTRACT: The sensitivity of X-ray diffraction data to monomer sequence distribution has been investigated for liquid crystalline aromatic copolyesters prepared from 4-hydroxybenzoic acid, 2,6-dihydroxynaphthalene, and terephthalic acid. The meridional intensity maxima in the fiber diagrams are aperiodic, and their positions are reproduced by calculating the theoretical diffraction patterns of copolymer chains, averaged over all possible monomer sequences. The monomer sequence distribution was varied from totally random to highly blocky by variation of the neighbor probabilities in the copolymer chains. For each of three monomer compositions it was found that the best agreement between the observed and calculated meridional data is obtained for completely random sequences and that all but minimal blockiness can be ruled out. Thus it appears that X-ray methods can be used to investigate the monomer sequence distribution of these relatively stiff copolymer chains and hence can provide information not currently available by more usual analytical techniques.

Introduction

In recent years a number of thermotropic copolyesters with the mesogenic groups in the main chain have been reported in the literature (for a review see ref 1). These materials are of commercial interest in that they can be processed from the melt as self-reinforcing plastics or as high-strength fibers: the latter can have properties that approach those of Kevlar 49.[2,3] Interest is growing in the structure/property relationships of these copolymers, and other laboratories have published the results of investigations on their morphology and thermal properties.[4-7] In this laboratory we are using X-ray methods to determine the structure at the molecular level, and we have shown that, for two sets of wholly aromatic copolyesters, the fiber patterns are consistent with completely random monomer sequences.[8,9] The present paper describes further work on one of these copolymers, that prepared from 4-hydroxybenzoic acid (HBA), 2,6-dihydroxynaphthalene (DHN), and terephthalic acid (TPA), in order to investigate the sensitivity of the X-ray data to deviations from randomness, i.e., blockiness, in the monomer sequence.

The X-ray fiber diagrams of the copolymers of HBA/DHN/TPA (molar ratios: 60/20/20, 50/25/25, and 40/30/30) are shown in Figure 1. Schematics of the same X-ray patterns are shown in Figure 2. These data are characterized by strong diffuse scattering on the equator and some relatively sharp meridional maxima. In addition, within the diffuse intensity there are two sharp equatorial reflections at d = 4.43 and 2.57 Å and one off-equatorial reflection at d = 3.26 Å for all three compositions (see Figure 2). These data indicate a structure comprised of highly oriented chains that are poorly packed in the lateral direction, except that the equatorial and off-equatorial Bragg reflections point to the presence of some three-dimensional order. A very interesting aspect of the X-ray data is that the meridional maxima are aperiodic and vary in their positions with the monomer ratio. In particular, the intense doublet in the d = 3.5–3.0-Å region becomes more separated as the HBA content decreases. This feature is inconsistent with extensive block copolymer character and the data were analyzed in terms of copolymer chains of random sequence. As a consequence of the 1,4-phenylene and 2,6-naphthylene linkages, the chains necessarily have relatively stiff, extended conformations. The meridional intensity is due to the projection of the chain onto the fiber axis, which will be approximately independent of conformation (i.e., of the torsional rotations about the aromatic–ester linkages). Initially the chains were modeled as linear arrays of points separated by the appropriate monomer lengths. It was shown that the positions of the meridional maxima are reproduced very accurately by a model with completely random monomer sequence.[8]

Although the point residue approximations give good agreement for the positions of the intensity maxima, the relative intensities could not be compared because the model did not allow for interferences between the scattering of the atoms of the individual residues. In later work, the calculations were extended to an atomic model for the chain and were shown to predict not only the positions of the maxima but also the relative intensities following refinement of the average orientation of the residues with respect to the fiber axis.[10] Figure 3 shows a comparison of the observed and calculated intensities for the doublet at d = 3.5–3.0 Å. The same methods have been applied to copolymers of HBA and 2-hydroxy-6-

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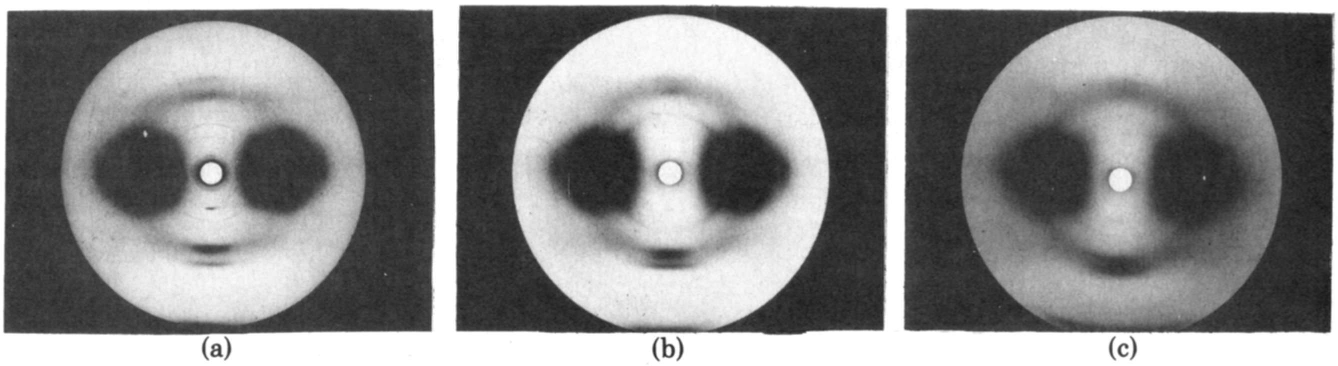


Figure 1. X-ray diffraction fiber diagrams of HBA/DHN/TPA copolymers: (a) 60/20/20; (b) 50/25/25; (c) 40/30/30. The fibers are tilted slightly with respect to the chain axis.

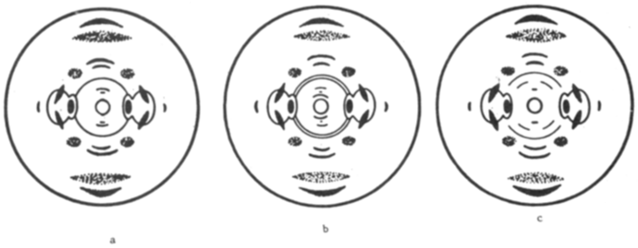


Figure 2. Schematics of the X-ray fiber diagrams of the HBA/DHN/TPA copolymers shown in Figure 1. The molar compositions are (a) 60/20/20, (b) 50/25/25, and (c) 40/30/30.

naphthoic acid (HNA) with similarly satisfactory results for both the point and atomic models for completely random chains.[9,11]

The good agreement for the completely random sequences leads naturally to the question of how sensitive are the X-ray data to deviations from a totally random distribution. Sequence distribution can be expected to be a determinant of the properties and, in addition, it has been suggested that transesterification in the melt may lead to the development of blocky structure in this kind of copolymer.[12] At present there is no analytical information regarding the sequence distribution. For example. NMR techniques are difficult to apply because of very low solubility and the similarity of the monomers. In this paper the effect of nonrandom monomer sequences on the X-ray data is investigated, and it is shown that blockiness can be detected at relatively small deviations from a fully random structure.

Experimental Methods

The methods used to acquire the X-ray data have been described previously.[8] The original X-ray fiber diagrams for the three HBA/DHN/TPA monomer ratios, 60/20/20, 50/25/25, and 40/30/30, are shown in Figure 1, and schematics that show the detail lost during reproduction are presented in Figure 2.

Calculations of the theoretical meridional scattering followed the methods described by Blackwell et al.[13] The meridional intensity distribution, $I(Z)$, for atomic models of the copolymer chains is given by

$$I(Z) = \sum_U \sum_V Q_{UV}(z_l) F_{UV}(Z) \exp(2\pi i Z z_l) \qquad (1)$$

where Z is the coordinate in reciprocal space in the direction corresponding to the fiber axis, and $Q_{UV}(z_l)$ is the value of the autocorrelation function at z_l in real space and defines the probability of finding residues U and V separated by z_l along the chain axis, i.e., residue U at the origin and residue V at z_l. $F_{UV}(Z)$, the Fourier transform of the convolution of residue U with residue V, is defined by

$$F_{UV}(Z) = \sum_U \sum_V f_{U,j} f_{V,k} \exp[2\pi i Z(z_{U,j} - z_{V,k})] \qquad (2)$$

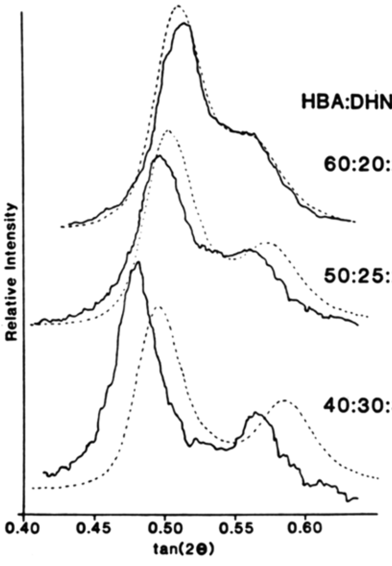


Figure 3. Meridional intensity distribution in the 3.5–3.0-Å region for HBA/DHN/TPA copolymers of three different compositions: 60/20/20, 50/25/25, and 40/30/30. Optical densitometer scans are drawn as solid lines. The dashed lines show the intensity calculated with the refined atomic models (see ref 10).

where the subscripts U,j and V,k designate the jth atom in residue U and the kth atom in residue V, respectively, when both residues are located at the chain origin. The corresponding atomic scattering factors are represented by $f_{U,j}$ and $f_{V,k}$.

In a completely random copolymer, where all monomer combinations are equally possible, $Q_{UV}(z_l)$ is given by

$$Q_{UV}(z_l) = \sum_n \prod_m q_m \qquad (3)$$

The summation is over all n monomer sequences that start with residue U and end with residue V and have a length z_l, and is the sum of the products of the mole fraction q_m of the components of the individual sequences. For a nonrandom sequence, eq 3 must be modified to include the (apparent) reactivity ratios of the monomers, r_m, which modulate the neighbor probabilities. r_m is the reactivity of the $(m-1)$th monomer, i.e., the penultimate monomer in the sequence, toward the following mth monomer species. [N.B.: Since r_m needs to be defined for every pair of consecutive residues, $r_1 = 1$ because the probability of a given monomer being at the origin of the chain is identical with its mole fraction.] For convenience $Q_{UV}(z_l)$ is divided into components for first, second, third, etc. nearest neighbors, $Q_{UV}(z_l,N)$, where N is the number of the neighbor. $Q_{UV}(z_l,N)$ is then defined by

$$Q_{UV}(z_l,N) = q_V \sum_n \prod_m r_m q_m \Big/ \sum_t \sum_n \prod_m r_m q_m \qquad (4)$$

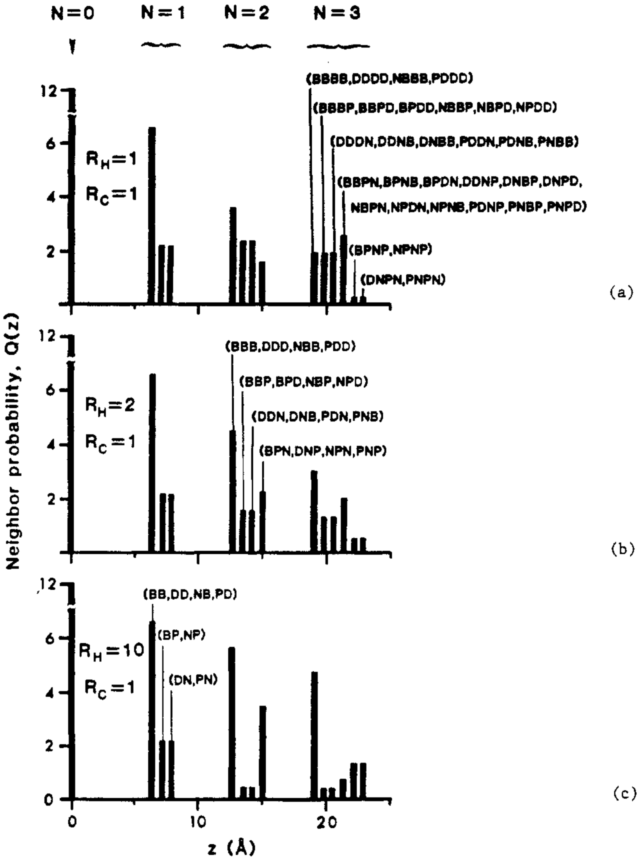
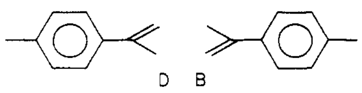


Figure 4. Autocorrelation function $Q(z)$ plotted against z out to the third-nearest-neighbor terms for the 60/20/20 composition HBA/DHN/TPA copolymers with degrees of $(B)_n$ and $(NP)_n$ blockiness: (a) $R_H = 1$, i.e., random sequence; (b) $R_H = 2$; (c) $R_H = 10$. The individual dimer, trimer, and tetramer components to the $Q(z)$ terms are indicated. To conserve space these are shown only once, but this information is transferable to the other plots. Note, however, that the weightings of each component to a particular term vary with R_H. For clarity, the plots shown here are for the untilted residue lengths since some overlap occurs when the refined residue lengths are used. These data are for chains of 12 monomers.

where q_V is the mole fraction of residue V, and the outer summation in the denominator is over all t sequences of $N + 1$ monomers starting with residue U and terminating with residue V. In the present example of the HBA/DHN/TPA terpolymer, only eight of the possible sixteen UV dimer combinations are chemically feasible, and $r_m = 0$ for the remainder.

Figure 4a shows the autocorrelation function $Q(z)$ $[=\sum Q_{UV}(z)]$ for the completely random 60/20/20 copolymer, out to the third-nearest-neighbor terms. The individual $Q_{UV}(z)$ components are each identified. For convenience, DHN and TPA are further abbreviated to N and P; HBA is designated B or D, depending on the sense of the residue:



Atomic models for the individual residues were based on standard bond lengths and angles and are consistent with the structures of low molecular weight model compounds (see ref 10). The residue lengths for B (or D), N, and P were taken as 6.35, 7.85, and 7.15 Å, respectively, and the residues were tilted with respect to the chain axis by 5° for B and D, 25° for N, and 10° for P, based on refinement to improve the match of observed and calculated intensities.[10] This tilting converts the residue lengths to 6.33, 7.11, and 7.04 Å, respectively. The origin of each residue was set at the ester oxygen. Hence in Figure 4a it can be seen, for example, that B–B, D–D, N–B, and P–D first nearest neighbors occur at the same z.

Table I

HBA/DHN/TPA: 60/20/20 (R_C = 1.0)

R_H	d spacings, Å							
100	7.36	6.18	4.79	3.52	3.17	2.84	2.11	2.03
10	7.47	6.18	4.79	3.51	3.17	2.84	2.11	2.03
5		6.21		3.45	3.18	2.85	2.10	
4		6.21		3.43	3.18	2.87	2.09	
3		6.25			3.18	2.90	2.08	
2		6.29		3.21			2.08	
1.75		6.29		3.24			2.08	
1.5		6.33		3.26			2.08	
1.4		6.33		3.27			2.08	
1.3		6.33		3.28	3.08		2.07	
1.2	7.05	6.33		3.28	3.07		2.07	
1.1	7.05	6.33		3.29	3.07		2.07	
1.0	7.05	6.37		3.29	3.06		2.07	
obsd	~6.8	6.05		3.31	2.98		2.01	

The effect on $Q(z)$ of varying the reactivity ratios for the 60/20/20 composition is shown in Figure 4b,c. These data are derived for a model containing blocks of $(B)_n$ and $(NP)_n$ sequences derived by setting the appropriate reactivity ratios (r_{BB}, r_{DD}, r_{NP}, and r_{PN}) equal to 2 and 10, respectively, with all other allowed reactivities set at 1. (r_{XY} is the reactivity of residue X toward the following residue Y.) Since the reactivity ratios leading to homopolymer blocks, r_{BB}, r_{DD}, r_{NP}, and r_{PN}, were taken as equal, they will be grouped as R_H. The example with R_H reactivities of 10 leads to a very blocky polymer: the peaks in $Q(z)$ for BBBB, DDDD, NPNP, and PNPN predominate, and those for other quadruplets are weak. Where the same reactivities are reduced to $R_H = 2$, $Q(z)$ is intermediate between that for $R_H = 10$ and completely random ($R_H = 1$) copolymer.

The intensity along the meridian has been calculated by using eq 1 for all three monomer ratios for different combinations of reactivity ratios. The results presented here are for copolymers in which the R_H reactivities are varied from 1 to 100, with all other allowed reactivities at 1. This leads to a progressive formation of $(B)_n$ and $(NP)_n$ blocks. Results are also included for the reverse example in which the reactivities for the cross reactions, r_{BP}, r_{DN}, r_{NB}, and r_{PD} (collectively designated as R_C), are varied from 1 to 100 while the other (R_H) reactivities are set at 1. This leads to the progressive formation of alternating $(BPDN)_n$ blocks. The calculations are for a Gaussian distribution of chain lengths centered at 12 monomers, with $\sigma = 1.33$. The effect of limited chain length is included by multiplying $Q(z)$ by a triangular function. The length of 12 monomers corresponds to a persistence length rather than the degree of polymerization, which is believed to be in the range of 150.[14] The use of different average chain lengths has also been explored, and this has an effect only in the widths of some of the calculated peaks but not on their position. We have found that a chain length of 12 monomers gives a reasonable qualitative fit between the observed and calculated data. Previous work on copoly(HBA/HNA) showed that chain lengths of 9–13 residues gave good agreement for the peak widths, depending on the monomer ratio.[11]

Results and Discussion

Figure 5 shows the meridional transforms for the 60/20/20 composition calculated for different degrees of homopolymer blockiness. The blockiness was achieved by

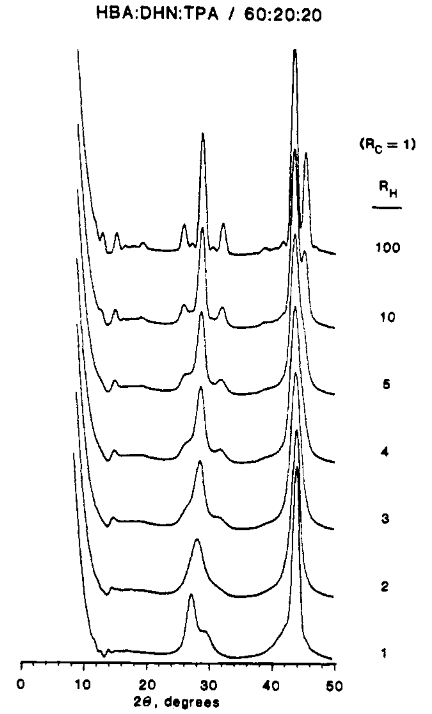


Figure 5. Theoretical meridional intensities for atomic models for the 60/20/20 HBA/DHN/TPA copolymer chains containing different degrees of $(B)_n$ and $(NP)_n$ blockiness: R_H = 100 to R_H = 1.

varying R_H between 1 (totally random) and 100 (highly blocky). The positions of the maxima in these transforms are listed in Table I, where they are compared with the observed meridional *d* spacings. In comparing the observed and calculated data the most significant results are for the three strong intensities observed at *d* = 3.31, 2.98, and 2.0 Å. It can be seen that the last of these *d* spacings is not very sensitive to blockiness, and hence the critical test is how well the calculations reproduce the 3-Å doublet.

Table II
HBA/DHN/TPA: 50/25/25 (R_C = 1.0)

R_H	*d* spacings, Å				
2.0	7.19	6.33	3.27	2.93	2.06
1.75	7.15	6.37	3.30	2.94	2.06
1.5	7.15	6.37	3.32	3.00	2.06
1.4	7.10	6.37	3.32	3.00	2.06
1.3	7.10	6.41	3.34	3.00	2.06
1.2	7.10	6.41	3.34	3.00	2.06
1.1	7.10	6.41	3.34	3.00	2.06
1.0	7.10	6.41	3.34	3.00	2.06
obsd	6.98	~5.9	3.38	2.97	2.02

At R_H = 100 the calculated transform is that for a very blocky copolymer; i.e., it is the diffraction pattern of poly(HBA) and poly(DHN–TBA) superimposed in the correct composition ratio. Poly(HBA) gives peaks at orders of 6.33 Å; poly(DHN–TPA) has peaks at orders of 14.15 Å. The peak widths depend on the chain length, in this case an average of 12 residues. At R_H = 10 and 5, the transforms are similar but the peak widths increase as the average block length falls below 12 residues. Below R_H = 5 the blocky character becomes less obvious. In the 3-Å region, the peaks at 3.75 and 3.17 Å predicted for the blocks begin to merge, and at R_H = 1 these become a doublet that matches the observed data. It can be seen in Figure 5, however, that the agreement for $R_H \geq 2$ is poor. The doublet at 3–3.5 Å does not occur whereas extra peaks are predicted. Hence blocky copolymers with $R_H \geq 2$ can be ruled out as incompatible with the meridional X-ray data.

Figure 6a shows the equivalent data for R_H = 2.0–1.0 for the 60/20/20 composition. It can be seen that the 3-Å doublet begins to be resolved at R_H = 1.4 but the positions of the maxima and especially the separation between them do not match those observed (within experimental error) until R_H = 1.2. The best agreement in terms of doublet

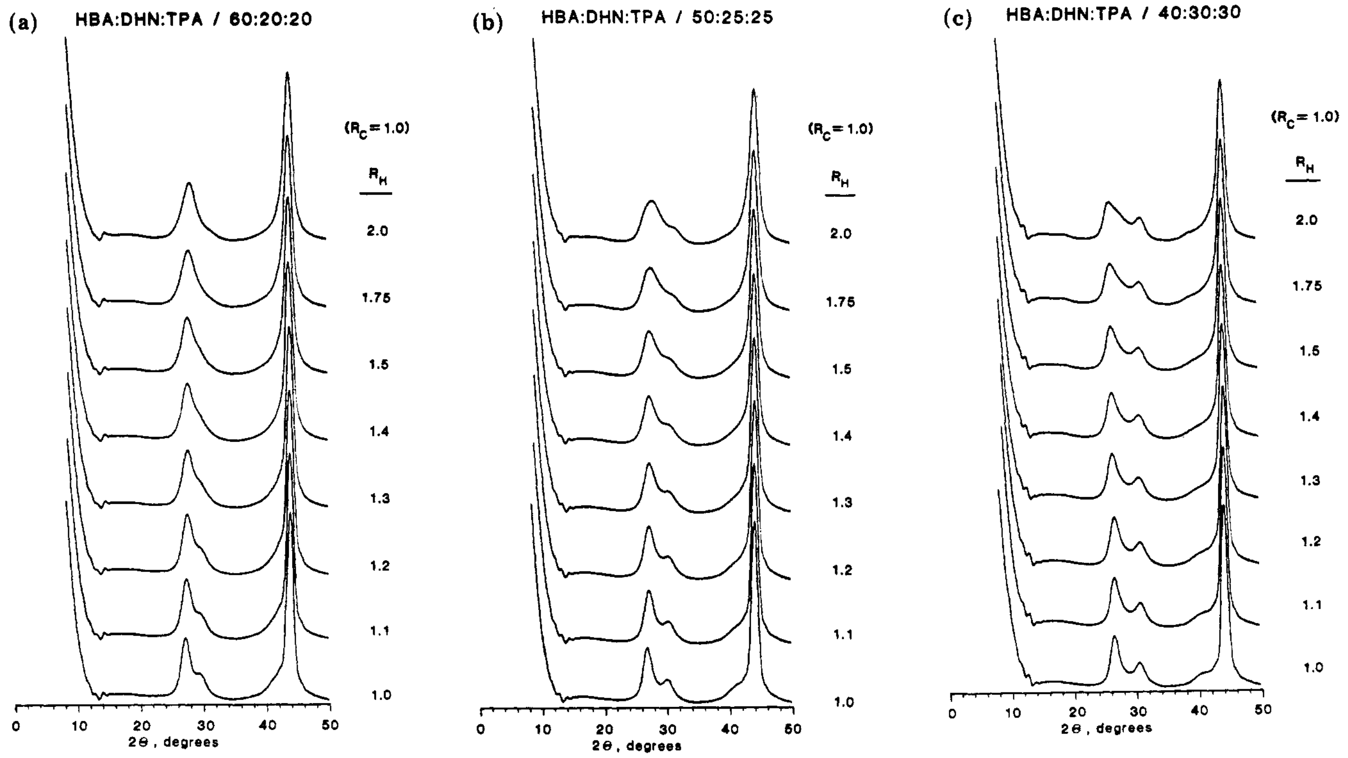


Figure 6. Theoretical meridional intensities for atomic models for the HBA/DHN/TPA copolymer chains containing different degrees of $(B)_n$ and $(NP)_n$ blockiness: R_H = 2.0 to R_H = 1.0. Results are presented for three monomer ratios: (a) 60/20/20, (b) 50/25/25, and (c) 40/30/30.

Table III
HBA/DHN/TPA: 40/30/30 (R_C = 1.0)

R_H	*d* spacings, Å				
2.0	7.20		3.41	2.88	2.05
1.75	7.20	6.41	3.40	2.90	2.05
1.5	7.15	6.45	3.39	2.92	2.05
1.4	7.15	6.45	3.39	2.93	2.05
1.3	7.15	6.45	3.39	2.93	2.05
1.2	7.15	6.45	3.38	2.93	2.05
1.1	7.15	6.45	3.38	2.94	2.05
1.0	7.15	6.45	3.38	2.94	2.05
obsd	6.96		3.48	2.96	2.00

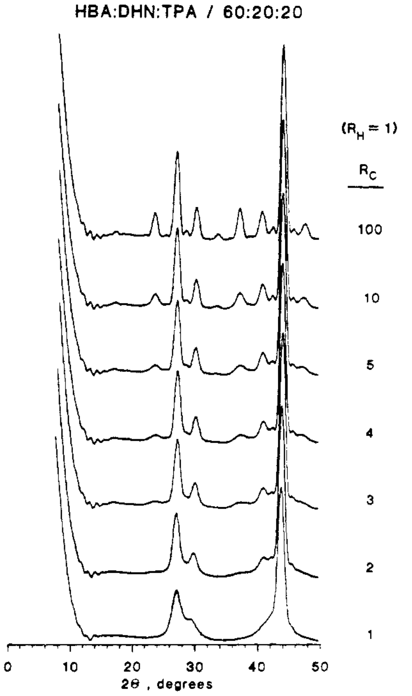


Figure 7. Theoretical meridional intensities for atomic models for the 60/20/20 HBA/DHN/TPA copolymer chains of various degrees of $(\mathrm{BPDN})_n$ blockiness: R_C = 100 to R_C = 1.

separation is for the completely random model, i.e., R_H = 1.0. Parts b and c of Figure 6 show the equivalent data for R_H = 2.0–1.0 for the 50/25/25 and 40/30/30 compositions. The positions of the observed and calculated maxima for these two monomer ratios are given in Tables II and III. As the HBA content is decreased the data get less sensitive to blockiness, but from general appearance of the intensity curves we can rule out $R_H > \sim 1.5$ for 50/25/25 and $R_H > \sim 1.75$ for 40/30/30.

Figures 7 and 8 show data for the 60/20/20 copolymer at the other extreme of blockiness, where the cross reactivities R_C are increased, leading to a preference for B–P–D–N tetramer sequences. Here the transform deviates more slowly from the completely random case but becomes distinguishable from the observed data by R_C = 1.75. This can be readily understood in that there is less obvious difference between the random and repeating tetramer structures than between the random and homopolymer structures. In fact, it can be seen from Figure 7 that when the BPDN sequences predominate ($R_C \geq 3$), maxima occur at d = 3.35 and 2.98 Å (the eighth and ninth orders of the poly(BPDN) repeat of 26.81 Å) but additional peaks (not seen in the X-ray data) are also present at 3.84 and 2.44 Å. In any case, one would anticipate that this second type of blockiness would be less likely to occur than poly(HBA)/poly(DHN–TPA) blockiness. Similar conclusions can be drawn from calculated data for the 50/25/25 and 40/30/30 copolymers at different values of R_C.

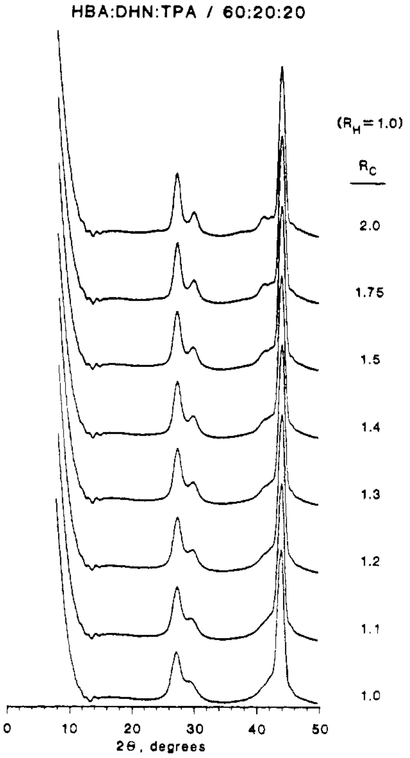


Figure 8. Theoretical meridional intensities for atomic models for 60/20/20 HBA/DHN/TPA copolymer chains of various degrees of $(\mathrm{BPDN})_n$ blockiness: R_C = 2.0 to R_C = 1.0.

Thus it can be seen that these X-ray calculations are highly sensitive to the degree of randomness of the copolymers. As a result one is able to rule out all but minimal blocky character in these copolyesters and propose a completely random monomer sequence. From these results, it appears that X-ray diffraction can be used as a means of investigating sequence distribution in the case of a relatively stiff copolymer where the components have different residue lengths. This cannot be applied, for example, in copolymers of HBA and ethylene terephthalate,[15] because the flexible ethylene units lead to a relatively wide distribution of residue lengths. For the present HBA/DHN/TPA copolymers, however, we can now proceed to consider the three-dimensional packing based on a model for totally random chain sequences and details of this work, now in progress, will be published shortly.

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Radiolysis of Resist Polymers. 1. Poly(methyl α-haloacrylates) and Copolymers with Methyl Methacrylate

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ABSTRACT: Methyl α-chloroacrylate (MCA) and methyl α-bromoacrylate (MBA) were copolymerized with methyl methacrylate (MMA) over a broad range of composition. The reactivity ratios for MMA and MCA are 0.36 and 0.26, respectively; they are 0.19 and 0.16 for MMA and MBA copolymerization. The tendency toward alternation of comonomer of methyl α-haloacrylates with MMA decreases in the order Br > Cl > F. The relative reactivities of these monomers toward the MMA radical also decrease in this order. The values of G_s (number of scissions per 100 eV of energy absorbed) for poly(MCA) and poly(MBA) are larger than for PMMA; values of G_r (number of radicals per 100 eV of energy absorbed) are in the range 7–9. All copolymers of MCA have nonzero G_x values (number of cross-links per 100 eV of energy absorbed), but they are soluble in common solvents after γ-radiolysis. Copolymers of MBA and MMA with >7% of the former are insolubilized due to extensive cross-linking by γ-radiolysis. ESR spectra of γ-irradiated homo- and copolymers of MCA and MBA were attributed to $-CH_2\dot{C}(COOMe)CH_2-$, $\cdot C(COOMe)ClCH_2-$, and $\cdot C(COOMe)BrCH_2-$ radicals. GC–MS analysis of the radiolysis products of the MCA homo- and copolymers, together with ESR and radiolysis yields, suggested probable mechanisms for the radiation chemistry. The high radiation sensitivity is attributable to the dissociative electron capture processes. The tendency of the MBA polymers toward cross-linking was postulated to be due to the ease of elimination of HBr giving intermediates for the formation of cross-links and CH_3Br elimination leading to cross-linking directly. The typical PMMA radical was observed for γ-irradiated poly(MMA-*co*-MCA) only when MCA content was ≤20%; it was not detected for γ-irradiated poly(MMA-*co*-MBA) even when MBA was present at 3%. The radiolysis of copolymers of MMA with MCA and MBA is dominated by the α-halogenated monomers.

Introduction

Polymers exhibiting high chain scission susceptibilities to radiation have been investigated as candidates for positive electron-beam (E beam) resists. However, as cross-linking also occurs sometimes, especially at high radiation dose, polymers which undergo scission only in the exclusion of cross-linking are required for resist applications. The relative tendency of the two reaction pathways is usually measured by one of two methods. The first is the determination of scission (cross-linking) yield per 100 eV absorbed, which is G_s (G_x). The second method is the measurement of sensitivity S_s (S_x) of the scission (cross-linking) reactions in C cm^{-2} for a given energy of electron.

Poly(methyl methacrylate) (PMMA) has been demonstrated to be a practical E-beam positive resist by the electronics industry; it is generally regarded as the reference polymer in this application. However, PMMA has only moderate sensitivity to radiation: $G_s = 1.4$, $G_x = 0$, and $S_s \simeq 5 \times 10^{-5}$ C cm^{-2} at 15 keV.[2] Hence, there have been intensive efforts to find polymers and copolymers of greater radiation sensitivity. Several general approaches have emerged.

The first is to take advantage of certain efficient radiolysis processes. An example is the dissociative electron capture. For instance, poly(methyl α-chloroacrylate) (PMCA) has a very high chain scission susceptibility ($G_s = 6.0$)[3]. Other halogen-containing polymers may also exhibit this characteristic. Elements of high atomic numbers are expected to interact with low-energy electrons efficiently. Thus, the incorporation of a few percent of alkali metal in poly(methyl methacrylate-*co*-metal methacrylate)[4] seems to increase G_s values. Polymers which upon radiolysis yield stable products appear to be good candidates for E-beam application. The likely examples are poly(butylene 1-sulfone)[5], poly(methyl isopropenyl ketone)[6], and polyaldehydes.[7,8]

Often times polymers with enhanced G_s also have increased G_x. Thus PMCA tends to cross-link ($G_x = 0.8$)[9] when the electron dose exceeds 6×10^{-4} C cm^{-2}. Copolymerization of such monomers with a non-cross-linking monomer can sometimes alleviate the cross-linking reactions. However, the G_s and G_x values of copolymers are usually not monotonic functions of comonomer composition. For instance, it was found that copolymers of MCA with MMA[10] and MCA with methacrylonitrile[11] and terpolymers of MCA with MMA and hexyl methacrylate[9] of certain compositions have greater G_s values than PMMA and without discernible cross-linking.

Though some of the current researches give results that are quite interesting, they do not contribute toward the understanding of the mechanisms of the chemical processes involved. For instance, if one evaluates a polymer as an E-beam or X-ray resist by the determination of sensitivity and contrast of the material to the radiation of particular energy, the effects of film thickness and surface regularity, of the method of developing, and of back-scattering can influence the overall performance. In the case of comparative study of a family of homopolymers and copolymers, a common developer is needed. The radiolysis products cannot be easily trapped and analyzed and the electron spin resonance (ESR) of the radicals cannot be

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