chain of the as-cast form III sample and so the chain becomes much more ordered, resulting in the disappearance of the long trans bands and the appearance of the gauche bands.

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Monomer Sequence Distributions in Four-Component Polyesters As Determined by ^{13}C and ^{1}H NMR

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ABSTRACT: Four-component polyesters derived from ethylene glycol, 1,4-butanediol, azelaic acid, and terephthalic acid have been characterized by ^{13}C and ^{1}H NMR at 63 kG. Derived statistical parameters permit comparison of monomer sequence distributions in multicomponent systems and have been applied to the four-component polyester system. Sequence-dependent chemical shift information has been used to determine these parameters in various samples of the four-component polyester. Melt polycondensation gives polymers having random sequence distributions, whereas sequential addition of diacid chlorides to diols in solution gives polymers in which the diacid residues are arranged in long blocked sequences with the diol groups interspersed randomly within. Alternate addition of the diacid chlorides in several steps in solution leads to a slightly nonrandom polymer with an unequal distribution of the diols between the diacid residues.

Polyesters are used in a number of important materials, including fibers, film supports, injection molding resins, adhesives and adhesive primers, transparency supports, photoresists, and a variety of specialty products. Early commercial polyesters were formed by the condensation of a single type of diol and a single type of diacid or were formed from an ω-hydroxy acid.[1] More recently, two or more types of diacid and/or diol have frequently been incorporated into a given polyester to optimize such properties as the glass transition temperature (T_g), melting point (T_m), crystallizability, solubility, modulus, and tensile strength. As a result, methods which can be used to determine monomer composition and monomer sequence distribution in such materials are important.

Alkaline hydrolysis coupled with gas chromatography[2] or liquid chromatography[3] can be used to determine overall monomer compositions in copolyesters, but it reveals nothing about the monomer sequence distribution. Nuclear magnetic resonance (NMR) is an important tool for characterizing copolyesters because it can, in favorable cases, yield information about overall composition and monomer sequence distribution simultaneously. NMR has been used to study various three-component polyester systems[4,5] and has recently been applied to four-component systems.[6]

We describe here the use of a combination of ^{13}C and ^{1}H NMR to determine the composition and sequence distribution in a four-component copolyester composed of terephthalic (T) and azelaic (A) acid residues with ethylene glycol (E) and butanediol (B). The structures of the monomer units are shown in Figure 1. We have derived a set of statistical parameters which can be used to characterize monomer sequence distributions in four-component polyesters.

Experimental Section

Most of the polymers used in this study were produced by two-stage melt polycondensation of the appropriate diols with the dimethyl esters of the appropriate diacids. The monomers used were commercial materials and were used without further purification. The polymers were transesterified in the melt under nitrogen, and then vacuum was applied to distill off methanol

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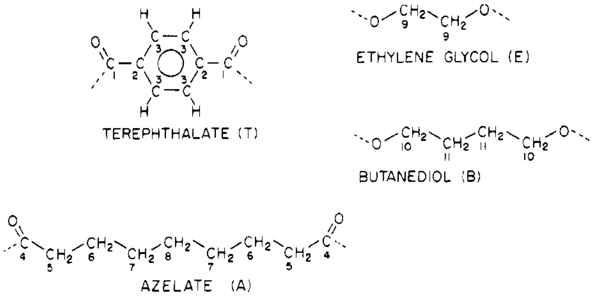

Figure 1. Structures of diols and diacids in four-component polyester PEBTA.

and excess diol to leave high-molecular-weight polymer. The polymer was isolated by cooling the melt to room temperature and then breaking the reaction vessel. Except for those determined with NMR, compositions were determined from the feed ratio of the monomers.

A polymer which deviated from a random distribution of monomer sequences (nonrandom sample I) was made by solution-phase block polycondensation in methylene chloride (CH_2Cl_2). Diacid chlorides of terephthalic and azelaic acids were used instead of the dimethyl esters used in the melt polycondensations. The polymerization was carried out by dissolving the two diols (B and E) in chilled methylene chloride and triethylamine. Azeloyl chloride was then added dropwise over 30 min. A slight excess of diols was used so that the resulting azelaic acid blocks were predominantly diol end-capped. When the diacid chloride addition was complete, an additional amount of the diols was added. Terephthaloyl chloride was then added dropwise, thus building up the second block of the copolymer. The polymer was precipitated in methanol, washed, and dried under vacuum.

Another polymer (nonrandom sample II) was made by five alternate additions of azeloyl chloride and terephthaloyl chloride in methylene chloride to a solution of the diols and triethylamine in methylene chloride. After each addition of acid chloride, the reaction was allowed to proceed for 10 min before addition of the other acid chloride. The resulting mixture was neutralized after 1.5 h with hydrochloric acid solution, washed with water, and precipitated in methanol.

Low-field ^{13}C NMR spectra of the polymers were obtained at 20.1 MHz with a Varian CFT-20 spectrometer using 8K data points. The samples contained 25 g/dL polymer in CD_2Cl_2 in 10-mm tubes. Spectra were obtained at ambient temperature (ca. 300 K) with broad-band decoupling to eliminate carbon-proton splitting. A pulse delay of 10 s was used to allow essentially complete relaxation of the carbon nuclei, whose T_1 values are all less than 2 s.[7] The solvent, CD_2Cl_2, also provided an internal deuterium lock signal. Spectra were obtained by summing 4000–10 000 transients prior to Fourier transformation. Exponential broadening was not used. Chemical shifts were determined by referring to the CD_2Cl_2 resonance, assumed to be 53.6 ppm from tetramethylsilane.[8]

High-field ^{13}C and ^{1}H NMR spectra were obtained in CD_2Cl_2 and CF_3COOD, respectively, with a Bruker WH-270 spectrometer using quadrature detection with 16K or 32K data points. Field strength was 63 kG, resulting in 67.9-MHz ^{13}C spectra or 270-MHz ^{1}H spectra.

^{1}H NMR spectra required ~100 transients. Peak assignments in the ^{1}H NMR spectra were confirmed with homonuclear decoupling experiments, carried out by selectively irradiating certain protons while observing the remainder of the spectrum. In the proton spectra, resolution was noticeably better in samples with concentrations of 0.5 g/dL than in those with 1.0 g/dL. Therefore, concentrations were kept low.

The ^{13}C NMR spectra were based upon summation of ~1000 transients prior to Fourier transformation. Care was taken in the carbon spectra used for quantitative work to avoid saturation. However, no correction was made for possible variations of the nuclear Overhauser enhancement from one resonance to the next. The internal consistency of the results suggests that no major errors were introduced, and direct measurements of the nuclear Overhauser enhancements have not shown major deviations.[7]

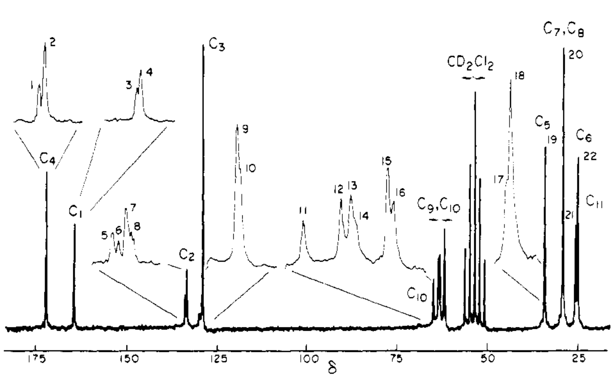

Figure 2. Low-field (20.1 MHz) ^{13}C NMR spectrum of polymer made from 30 mol % butanediol, 70% ethylene glycol, 60% azelaic acid, and 40% terephthalic acid. Concentration is 25 g/dL in deuterated methylene chloride. Spectrum was obtained from an average of 5000 transients obtained with a 45° flip angle and a 10-s delay between pulses. No exponential broadening was used, and the memory size was 8K.

Results

Analysis of ^{13}C NMR Spectra. The 20.1-MHz ^{13}C NMR spectrum of a PEBTA sample is shown in Figure 2. It exhibits at least 20 resolvable nonsolvent resonances. Since there are only 11 chemically distinct types of carbon atoms in PEBTA, the additional resonances must arise from sequence-dependent chemical shifts. However, in making initial peak assignments, we did not attempt to account for sequence-dependent effects. Peaks 1–4 were assigned to the carbonyl carbons of azelate and terephthalate units, based on their large downfield chemical shifts.[8] Peaks 5–8 were assigned to the nonprotonated aromatic carbon in the terephthalate unit, T, based upon intensity and chemical shift considerations. Peaks 9 and 10 were assigned to the protonated aromatic carbons. The peaks in the region 60–65 ppm (peaks 11–16) arose from carbons directly bonded to oxygen. These included the α carbon of 1,4-butanediol and the ethylene glycol carbons. The remaining upfield peaks (peaks 17–22) were assigned to methylene carbons and included the β carbons of butanediol and the four types of methylene carbons in the azelate unit.

To make more detailed chemical assignments, we examined a series of three-component copolyesters in which either one diol (B or E) or one diacid (A or T) was omitted. The 20.1-MHz ^{13}C NMR spectra of three such copolymers are shown in Figure 3. From Figure 3b, the spectrum of PBEA, we can see that the carbonyl peak at 173.3 ppm comes from the azelate group; consequently, the carbonyl peak at 165.7 ppm in Figure 2 must be due to the terephthalate unit. Similarly, the spectrum of PBAT in Figure 3a shows that the methylene peaks at 65.1 and 63.8 ppm are due to the α carbons of butanediol. Thus we make the assignment of the peaks at 63.2 and 61.9 ppm in Figure 2 to ethylene glycol. Finally, the peak at 25.6 ppm was assigned to the β-methylene carbon of butanediol, based upon comparison of spectra a and c in Figure 3.

At 67.9 MHz there is even more detail in the ^{13}C NMR spectrum (Figure 4). Of particular interest is the fact that ethylene glycol gives rise to four separate resonances, indicating that the chemical shift of its methylene carbons is simultaneously influenced by the nature of both diacids adjacent to the diol and not merely by the diacid to which the observed methylene is attached. This allows us to determine the relative proportions of all the ethylene glycol centered triads from the ^{13}C NMR spectrum of the polymer. The chemical shift of the α-methylene carbon in butanediol is influenced by the nature of the nearest diacid

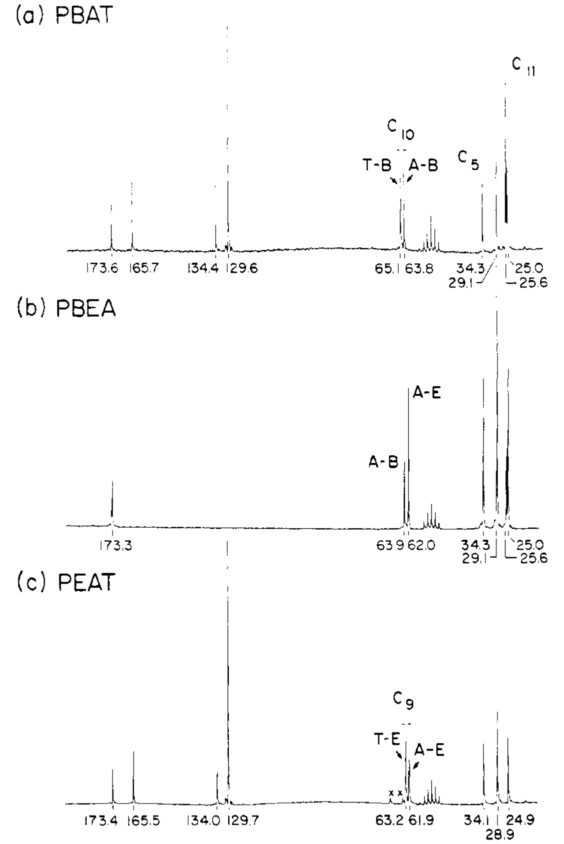

Figure 3. Low-field (20.1 MHz) ^{13}C NMR spectra of three-component polyesters with the following compositions: PBAT, butanediol with 40 mol % azelaic acid and 60% terephthalic acid; PBEA, 30 mol % butanediol and 70% ethylene glycol with azelaic acid; PEAT, ethylene glycol with 40% azelaic acid and 60% terephthalic acid.

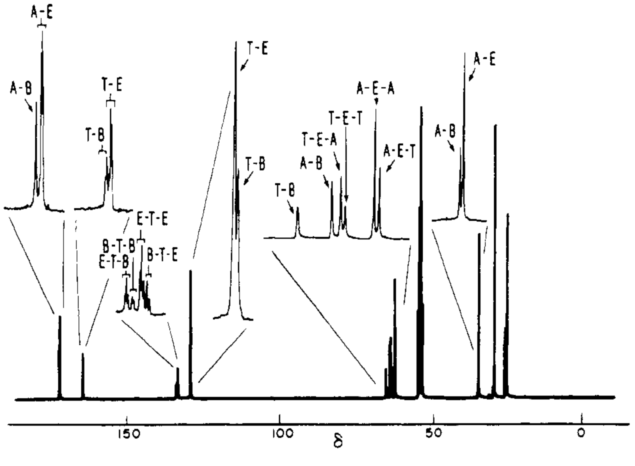

Figure 4. High-field (67.9 MHz) ^{13}C NMR spectrum of the same polymer sample as in Figure 3. Spectrum is from an average of 1000 scans with a 51-s delay and an 80° pulse width in 32K data points. No broadening was used.

to which it is bonded but shows only very slight splitting, not obvious in Figure 4, from the nature of the other diacid. As a result, only compositional dyads can be determined from the butanediol region of the ^{13}C NMR spectrum of PEBTA.

At 67.9 MHz, the spectrum of the nonprotonated ring carbon of the terephthalic acid residue is particularly rich in information. As shown in Figure 5, four regions of peaks can be assigned according to the nature of the diols on either side of the terephthalic acid residue. This means

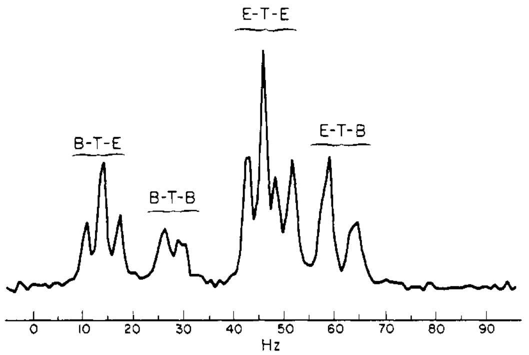

Figure 5. Expansion of the region around 134 ppm for the spectrum of Figure 4. All peaks are assigned to the nonprotonated carbons of the terephthalic acid ring.

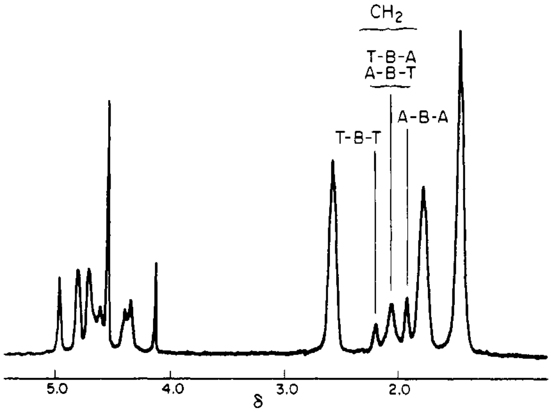

Figure 6. Low-frequency portion of the high-field (270 MHz) ^{1}H NMR spectrum of the polymer described in Figure 3. Concentration is 0.5 g/dL in deuterated trifluoroacetic acid. Spectrum is from an average of 100 transients obtained with a separation of 12 s between pulses of about 60°, stored in 16K data points without exponential broadening.

that triad information is available. The additional peaks within each region reflect the distribution of tetrad or pentad sequences. For example, the region from E–T–E traids contains four lines arising from the central terephthalic acid group in the A–E–T–E–A, A–E–T–E–T, T–E–T–E–A, and T–E–T–E–T pentads (Figure 5). Similarly, the region from B–T–E sequences contains three lines, one from the T–B–T–E–T sequence, a line from the overlap of resonances from the T–B–T–E–A and A–B–T–E–T sequences, and a resonance from the A–B–T–E–A sequence. The assignments were confirmed through comparison of spectra in which the proportions of monomer components varied. Information about tetrad and pentad sequences has not been previously available in polyesters.

Closer examination of the assignments in Figure 5 shows that the resonance of the ring proton is sensitive to the nature of the second diol down the chain on the nearest side regardless of whether the first diol is ethylene glycol or butanediol. The nature of the second diol from the far side of the terephthalic acid ring is important only when the first diol is ethylene glycol, however. Thus only two well-resolved signals are observed for the E–T–B sequence whereas four are found for the E–T–E sequence. For the mixed sequence B–T–E the carbon next to the butanediol (resonances on the left) gives rise to three resonances, whereas the carbon next to ethylene glycol (resonances on the right) gives rise to only two.

^{1}H NMR Spectra. Figure 6 shows the 270-MHz ^{1}H NMR spectrum of PEBTA. Only the methylene proton region of the spectrum is shown. The aromatic protons of terephthalic acid give rise to a single peak which occurs well downfield from the methylene protons and which contains no information on sequence distribution. The three resonances centered at δ 2.05 arise from the β-methylene protons of butanediol. The observed differences in chemical shift result from the nature of both adjacent diacid units. As a result, integration of the three β-methylene peaks yields the triad sequence distribution about butanediol. In addition, the peaks at δ 4.4–4.9 can be integrated to yield information about both E-centered and B-centered triads. However, peak overlap makes that integration more difficult than the integration of the β-methylene proton peaks for the butanediol or integration of the ethylene glycol portion of the ^{13}C NMR spectrum of the polymer.

Discussion

Quantitative Comparison of Monomer Sequence Distributions. We need to define simple parameters by which sequence distributions can be characterized, up to the level of information available. Ideally, these parameters will allow comparisons of sequence distributions in polymers having rather different proportions of the various monomer units. These parameters should also be useful in testing various statistical models which might describe the sequence distribution. These statistical models can be used to estimate the relative proportions of various sequences which are too long to be distinguished experimentally.[9,10] In theory, the relative amounts of these longer sequences can be determined only with some direct measurements, but we can reasonably assume that unusual types of long-range order, such as the regular repetition of the same pentad group, are very unlikely to occur in real systems so that the extrapolations can be made.

In our considerations, we assume also that the samples are compositionally homogeneous. This is a reasonable assumption for polyesters, since they are made by polymerizations involving ester–ester interchange reactions. As a result they tend to approach compositional homogeneity as a limit at all conversions. In the Appendix we consider how, in favorable cases, information about sequence distributions can be used to verify that a polymer sample is compositionally homogeneous.

Coleman and Fox[11] have derived a set of statistical parameters describing stereosequence distributions in homopolymers. We will extend their derivation to include monomer sequence distributions in multicomponent polymers and will then apply the resulting formulas to the PEBTA system.

Definitions and Postulates. For simplicity, consider for the moment systems composed of only two types of units, A and B. Sequences of A and B units will, by convention,[11] be "read" from right to left. Arbitrary sequences of A and B will be designated as $U^{(n)}$ or $V^{(n)}$, where n is the number of units in the sequence. For example, -A-B-A-A- and -A-B-B-B- are two sequences which could be designated as $U^{(4)}$. The probability for the occurrence of any given sequence, $U^{(n)}$, will be designated $p_n\{U^{(n)}\}$. We normalize all the probabilities for sequences of any given length such that

$$\begin{aligned} \sum_i p_1\{U_i^{(1)}\} &= 1 \\ \sum_i p_2\{U_i^{(2)}\} &= 1 \\ &\vdots \\ \sum_i p_n\{U_i^{(n)}\} &= 1 \end{aligned} \qquad (1)$$

Note that

$$p_1\{A^{(1)}\} = X_A \qquad (2)$$

where X_A is the mole fraction of component A.

Analysis of Sequence Distribution. It is necessary first to consider how many statistical parameters are required to describe the distribution of sequences of length N for a system containing r components. At any given level of sequences we assume that we have complete knowledge of the distribution of all sequences of length $N - 1$ or less. The number of distinguishable sequences of length N will then be denoted as S. We can derive an expression for S as a function of r and N by considering the number of ways in which the letters A, B, ..., r can be arranged in sequences of length N. For example, if $r = 3$ and $N = 2$, we have the following possibilities: A–B, A–C, B–C, B–A, C–A, and C–B. Similarly, if $r = 2$ and $N = 3$ we have A–A–A, A–A–B, A–B–B, B–A–B, A–B–A, and B–B–B. We can continue in this manner, choosing r and N, until we arrive at the following expressions for S:

$$S = \tfrac{1}{2}(r^N + r^{N/2}) \qquad N \text{ even} \qquad (3)$$

$$S = \tfrac{1}{2}(r^N + r^{(N+1)/2}) \qquad N \text{ odd} \qquad (4)$$

Here we assume the chain ends are indistinguishable so that sequences such as A–A–B are equivalent to B–A–A.

The number of parameters required may be reduced for actual systems by chemical prohibitions which eliminate certain types of sequences. For example, in a polyester system the fact that diols cannot be linked to other diols reduces S substantially.

Let us now consider what types of parameters may be useful at the triad level. At first glance we might consider the mean recurrence time for a given component A. The general form for the mean recurrence time can be found in standard references on probability.[12] In terms of our multicomponent copolymer, $\chi(A)$, the mean recurrence time of component A, is given by

$$\chi(A) = \lambda / p\{A\} \qquad (5)$$

where λ is the repeat length between possible sites of A. In a polyester, for example, λ is 2 for the diols. Consequently $\chi(A)$ is not a useful parameter for differentiating between types of sequence distributions because it is defined by composition alone.

An alternative possibility is the average length of blocks of one type of monomer unit, the mean sequence length, $\mu(A)$. It can be shown that

$$\mu(A) = \frac{p_1\{A\}}{p_1\{B\}p_2\{B\text{–}B\}} = \frac{p_1\{A\}}{p_1\{A\} - p_2\{A\text{–}A\}} = \frac{2p_1(A)}{p_2(A\text{–}B)} \qquad (6)$$

Thus the mean sequence length, unlike the mean recurrence time, does contain information about triad sequence distribution.

Another parameter, the persistence ratio, ρ, is related to the mean sequence length[12] and is given by

$$\rho = 2[A][B]/[A\text{–}B] \qquad (7)$$

where [A], [B], and [A–B] are the experimentally determined proportions of each type of unit in the chain. Although it was originally derived for a two-component system (m or r stereochemical configurations), the persistence ratio applies equally well to multicomponent systems, which can be treated as pseudo-two-component systems. It ranges from 0.5 to infinity. Chains which have a random distribution of chemical sequences have a persistence ratio of 1.0. Expected values for Markov chains of various orders exceed 1.0, as has been described by Bovey.[9]

Although either $\mu(A)$ or ρ would be useful parameters to describe triad sequences, there is some ambiguity as to how to apply them to polyesters containing a single diacid and two diols. If a given component is considered to consist of the diacid and one of the two diols, one has a simple two-component polymer. In the most general sense the diacid should also be considered a separate component, however, to allow for the possibility of several different types of diacids. Most of the cases considered up to now have had only one type of diacid (or diol).

We find it convenient to generalize a special parameter which has been defined for polyesters to avoid this problem. This parameter, the B value, has been defined for a polyester having one diacid and two diols A and B as follows:

$$B = [\text{A–B}]/2[\text{A}] + [\text{A–B}]/2[\text{B}] \qquad (8)$$

Because $[\text{A}] + [\text{B}] = 1$, however, it is easy to show that

$$B = [\text{A–B}]/2[\text{A}][\text{B}] \qquad (9)$$

Therefore, the B value is simply the inverse of the persistence ratio defined earlier with the diacid and one of the diols defined as a single component. The B value has a range from 0 to 2, however, rather than the range of 0.5 to infinity for the persistence ratio. Another parameter, K_m, defined in the same way as B, has been widely used by Korshak and co-workers to describe sequences in equilibrium and nonequilibrium polycondensation polymers. We show below that the B value concept can easily be generalized to multicomponent polyesters and provides a useful means by which sequencing in samples containing various proportions of the same monomer units can be compared.

Four-Component Polyesters. Using eq 3, we determine that there are ten possible dyad sequences in a four-component copolymer. Six of these are forbidden because the diacids cannot be directly linked and the diols likewise cannot be linked. We also know that

$$\begin{aligned}
[\text{T}] &= \tfrac{1}{2}[\text{T–E}] + \tfrac{1}{2}[\text{T–B}] \\
[\text{A}] &= \tfrac{1}{2}[\text{A–E}] + \tfrac{1}{2}[\text{A–B}] \\
[\text{E}] &= \tfrac{1}{2}[\text{T–E}] + \tfrac{1}{2}[\text{A–E}] \\
[\text{B}] &= \tfrac{1}{2}[\text{T–B}] + \tfrac{1}{2}[\text{A–B}] \qquad (10)
\end{aligned}$$

These equations cannot be solved without one additional piece of information. Thus, we need one parameter to characterize dyad sequencing in the four-component system. We choose the following, designated B_2(T–E):

$$B_2(\text{T–E}) = [\text{T–E}]/[\text{T}][\text{E}] \qquad (11)$$

The diacid and diol concentrations should be normalized separately to take into account the fact that they cannot be interchanged at specific locations in the polymer chain. It can be verified easily that B_2(T–E) is the ratio of the concentration of T–E sequences observed to the concentration expected for random statistics. In a qualitative sense B_2(T–E) represents the degree to which the diols may be restricted to linkage to one or the other of the diacids.

We now consider the triad sequences. Equation 4 tells us that there are 40 different types of triads possible for a four-component system. We can eliminate 26 of these because of chemical restrictions. Furthermore, there are 10 equations which link the triad concentrations to the monomer and dyad concentrations. This means that we need four parameters to describe completely the triad sequencing in this system. We will consider each component separately and will define B values around each component unit. In effect, this means that we will treat each triad segment centered around a particular monomer unit as if it were part of a simple copolyester containing only one diacid and two diols or one diol and two different diacids. We will call these values B_3(T), B_3(A), B_3(E), and B_3(B) to differentiate them from the B_2(T–E) value defined earlier for the dyad sequences.

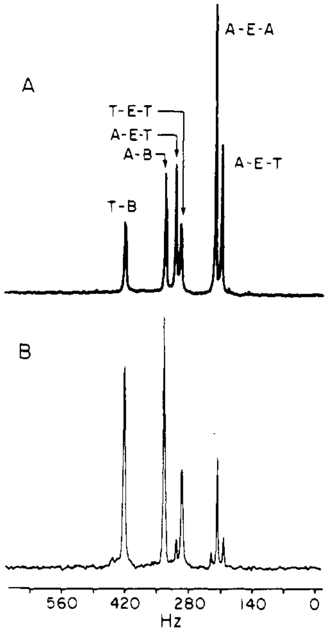

Figure 7. High-field (67.9 MHz) ^{13}C NMR spectrum of a melt polycondensation polymer (A) and nonrandom sample I (B). Compositions are described in Table I. Spectra were obtained from an average of about 500 transients obtained with a separation of 51 s between 90° pulses. There were 32K total data points, and no exponential broadening was used.

Remember that our ability to determine experimentally the B values depends on the amount of spectral information available. The B_3 values require that some spectral feature be found that reflects the nature of both diols attached to a given diacid or both diacids attached to a given diol. For the four-component system, the 270-MHz ^{1}H spectrum gives such information for the butanediol, the ^{13}C spectrum is adequate for the ethylene glycol units, and the aromatic carbon resonances suffice for the terephthalic acid residues. For the azelaic acid, sufficient spectral features are not resolved in either type of spectrum. It is not possible to calculate a B_3 value for the azelaic acid portion of the polymer based on the other B_3 values, so we are limited in the amount of information available.

Using the above concepts, let us now examine our data for several copolyesters and see how their sequence distributions differ. The ^{13}C NMR spectrum for the CH_2O carbons of a polycondensation copolymer of B, E, A, and T is shown in Figure 7A, and that of a solution (nonrandom sample I) copolyester is shown in Figure 7B. Comparison of the ethylene glycol methylene resonances in the two spectra illustrates the effect of sequential addition of the diacid chlorides; the T–E–A (A–E–T) resonance is reduced in intensity in sample I relative to the T–E–T and A–E–A resonances. This is to be expected, since only one diacid chloride is present in the reacting mixture at a given time. Thus, T–E–A sequences should occur only at the junction of two blocks.

Gel permeation chromatography of I in tetrahydrofuran showed that the molecular size distribution is unimodal, and $\bar{M}_w/\bar{M}_n \sim 1.7$. It is unlikely, therefore, that the sample is composed of a mixture of homopolymers. This is further confirmed by the solubility of the copolymer in CH_2Cl_2 and in tetrahydrofuran, both of which are nonsolvents for terephthalate-containing homopolymers.

Table I
Sequence Distribution Parameters for Random and Nonrandom Polyesters

polymer	[T] [a]	[A] [a]	[E] [a]	[B] [a]	B_2(T-E)	B_3(T)	B_3(E)	B_3(B)
melt polycondensations	0.56	0.44	0.69	0.31	1.01	1.04	0.99	1.03
nonrandom sample I	0.54	0.46	0.34	0.66	1.16	1.01	0.56	0.38
nonrandom sample II	0.34	0.66	0.32	0.68	1.50	0.97	0.96	1.01

[a] Determined by NMR.

In Table I we compare the B values from the melt polycondensation with those from the sequential-addition sample I and with those for the alternate-addition nonrandom sample II. The table confirms the qualitative differences noted above. For the melt polycondensation polymer, all of the B values are very close to 1.00, indicating a random sequence distribution. For the sequential-addition sample I, on the other hand, both B_3(E) and B_3(B) are significantly less than 1.00, indicating blocking about those units. On the other hand, the diols are distributed randomly about the terephthalic acid residue. The B_2(T–E) value slightly in excess of 1.00 indicated some partitioning of the diols between the two types of acid.

The most noticable feature about the alternate-addition sample II is the large B_2(T–E) value. This indicates that terephthaloyl chloride reacted preferentially with ethylene glycol (or that azelaic acid reacted preferentially with butanediol). On the other hand, the triad sequence distribution was close to random, as shown by the B_3 values. This sample thus comes much closer to being random than does sample I.

The differences between B_3 values for diacid-centered and diol-centered triads illustrate the importance of a complete sequence distribution analysis. Calculation of B_3(T) alone would mislead one as to the large differences in sequence distribution among the samples. Similarly, determination of B_3(E) or B_3(T) alone would lead one to conclude that the nonrandom sample I was a block copolymer but would not distinguish between one of the type $-(\mathrm{E{-}T})_x-(\mathrm{B{-}A})_y-$ and one of the type $-(\mathrm{E{-}T{-}B})_x-(\mathrm{E{-}A{-}B})_y-$, which is actually observed. Thus we can see that four B values are required in addition to one dyad parameter to describe fully the triad sequence distribution in PBEAT. Were it not for the inability of two diols or two diacids to react with one another, even more parameters would be required.

Conclusions

We have characterized a four-component system using ^{13}C NMR at 67.9 MHz and ^{1}H NMR at 270 MHz. We have extended the use of the statistics of stationary random processes to multicomponent systems and have quantitatively compared the sequence distributions arising from two different types of polycondensation copolymerization. We can conclude the following:

1. Sequence distributions for ethylene glycol centered and terephthalic acid centered triads can be determined from the ^{13}C NMR spectrum of PEBTA at 67.9 MHz. In favorable cases, chemical shift differences due to longer sequences (tetrads and pentads) are observed in the terephthalic acid aromatic carbons. In addition, all compositional dyads can be determined from the ^{13}C NMR spectrum.
2. Butanediol-centered triads can be determined from the ^{1}H NMR spectrum of PEBTA at 270 MHz. Ethylene glycol centered triads can also be determined, but not as readily as from the ^{13}C NMR spectrum.
3. Comparison of the B_3 values (triad sequence distribution parameters) for a melt polycondensation copolymer, a sequential-addition solution copolymer, and an alternate-addition copolymer showed that the ethylene glycol and butanediol-centered triad distributions were dependent upon the mechanism of polycondensation. For the melt polycondensation copolymer the sequence distribution was random. For the sequential-addition solution there is a preponderance of homogeneous triads (e.g., T–E–T or A–E–A), and the diacids therefore occur in blocks rather than being randomly distributed along the chain. For the alternate-addition polymer the monomer units were distributed nonrandomly, but blocking was not severe.

Appendix

We have stressed that a mathematical description of sequence distribution in a polymer sample is simple only when the sample is compositionally homogeneous. For example, simply mixing a copolymer containing a Bernoullian distribution of 75% of a component A with 25% of a component B with a second sample containing a Bernoullian distribution of 25% A and 75% B results in a mixture having an apparent sequence distribution which is non-Bernoullian. Actually, the apparent sequence distribution of the mixture cannot be described in terms of Markovian statistics of any order. The apparent B value for this mixture, B(A–B), would be 0.75, indicating "blockiness". The problem of mixtures arises in a real situation when addition polymers are made to high conversion.

When we have independent evidence that the sequence distribution within individual polymer strands of a copolymer are random (for example, when the product of reactivity ratios for an addition copolymerization is 1), we can use the apparent sequence distribution data for the whole sample as a measure of the compositional heterogeneity. We will define the compositional heterogeneity as the standard deviation σ(A) of the distribution of composition of one of the monomer units within the sample. The standard deviation is defined as

$$\sigma(\mathrm{A}) = \langle [\mathrm{A}]^2 \rangle - \langle [\mathrm{A}] \rangle^2$$

But we assume that the sequence distribution within the individual chains is random so that

$$\langle [\mathrm{A}]^2 \rangle = \langle [\mathrm{A{-}A}] \rangle$$

Thus the difference in the average probability for the occurrence of the dyad A–A and the square of the monomer composition gives a measure of the distribution of composition. Higher moments of the distribution can easily be calculated from the average distribution of triads.

It is easily shown that

$$\sigma(\mathrm{A}) = \sigma(\mathrm{B})$$

We can also show that

$$\sigma(\mathrm{A}) = \langle [\mathrm{A{-}B}] \rangle - \langle 2[\mathrm{A}][\mathrm{B}] \rangle$$

Overall we have two independent ways to calculate the composition distribution. If the original assumption that the individual polymer strands can be described by Bernoullian statistics holds, these two values will agree. Disagreement may indicate that the polymerization was controlled by some higher order Markov process or even a non-Markov process.

References and Notes

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Long-Range Segmental Motion in Polymers: A ^{13}C NMR Spin–Lattice Relaxation Study of Polyesters

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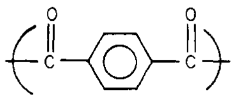
ABSTRACT: Detailed ^{13}C NMR spin–lattice relaxation measurements have been made for the methylene carbons of polyesters composed of terephthalic acid and azelaic acid, in various ratios, esterified with ethylene glycol and butanediol in the molar ratio 70:30. The solvent was methylene chloride. The long relaxation times of 0.22–1.20 s and the nearly full nuclear Overhauser enhancements suggest that internal motions are very fast for these polymers in methylene chloride. Consideration of the barriers to internal rotations in small molecules suggests that the motion is controlled by rotation about the CH_2–O and CH_2–CO bonds. Several models for internal motions involving these bonds are proposed, including crankshaft motions. Because of the presence of a few specific bonds with low barriers to internal rotation, polyesters are ideally configured to undergo many of the commonly proposed polymer motions. Motions involving more than three monomer units, such as crankshaft motions, are suggested by changes in the T_1's resulting from variations of the ratio of azelaic to terephthalic acid.

Determinations of ^{13}C NMR relaxation times have potential for elucidating the nature of internal motions in dissolved polymers.[1] Dipolar spin–lattice relaxation times of small molecules are usually controlled by the overall tumbling motion of the molecule, but nuclear relaxation of high-molecular-weight polymers stems from the internal, segmental motions.

Defining the exact relationship between observed relaxation times and internal motions of polymers can be quite complex, however. In a typical polymer, several different modes of motion must usually be considered.[1,2] The restraints of the polymer chain ends make each one of these modes highly anisotropic. Furthermore, in real systems we do not expect that the different modes will be independent; rather, the motions will be correlated. The combination of multiple, correlated, anisotropic motions requires that a multitude of time constants be used in the description of the overall motion.[1] As a rule, there is not enough experimental information even to define the number of correlation times required, let alone to determine their exact values.

One way to increase the overall amount of relaxation information is to work with very complex systems which give several resonance lines for each type of carbon nucleus. Relaxation measurements on these individual, resolved lines allow one to explore the effect of chemical differences within the polymer chain on internal motions. We showed in the preceding paper that a number of resonances for glycol units in different chemical sequences could be resolved in a four-component polyester made from terephthalic acid (T), azelaic acid (A), ethylene glycol (E), and butanediol (B).[3] We now show that spin–lattice relaxation measurements on the various methylene signals from these polymers give specific information about internal motions. By induction we can get information about motion in simpler, related polyesters.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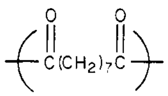
$-\!\!\left(\overset{O}{\overset{\|}{C}}(CH_2)_7\overset{O}{\overset{\|}{C}}\right)\!\!-$
A

$-\!\!\left(OCH_2CH_2O\right)\!\!-$
E

$-\!\!\left(OCH_2(CH_2)_2CH_2O\right)\!\!-$
B

Experimental Section

Preparation of Polymers. The polymers were prepared by a conventional two-stage melt polycondensation of the appropriate diols with the dimethyl esters of the appropriate diacids.[3] Esterification was carried out in the melt under nitrogen, and

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