controlled by some higher order Markov process or even a non-Markov process.

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

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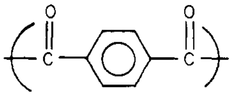
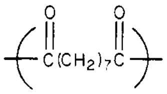
ABSTRACT: Detailed ^{13}C NMR spin–lattice relaxation measurements have been made for the methylene carbons of polyesters composed of terephthalic acid and azelaic acid, in various ratios, esterified with ethylene glycol and butanediol in the molar ratio 70:30. The solvent was methylene chloride. The 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.


T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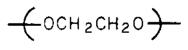
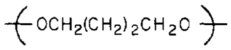
A


$$\left(OCH_2CH_2O \right)$$
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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Table I
^{13}C Spin-Lattice Relaxation Times (s) for Polymers of Terephthalic Acid, Azelaic Acid, and 70% Ethylene Glycol with 30% Butanediol

	mol % A							
sequence	20	30	40	50	60	70	80	100
$T—OCH_2(CH_2)_3O—$	0.35	0.36	0.43	0.44	0.46	0.51	0.56	
$—OCH_2(CH_2)_2CH_2O—$	0.42	0.47	0.56	0.59	0.63	1.00	1.02	1.09
$A—OCH_2(CH_2)_3O—$	0.57	0.63	0.65	0.75	0.88	0.89	0.91	0.97
$T—OCH_2CH_2O—T$	0.22	0.22	0.25	0.25	0.23	0.31	0.39	
$T—OCH_2CH_2O—A$	0.32	0.34	0.42	0.40	0.40	0.50	0.47	
$T—OCH_2CH_2O—A$	0.36	0.35	0.39	0.39	0.38	0.45	0.51	
$A—OCH_2CH_2O—A$	0.54	0.66	0.72	0.70	0.73	0.72	0.79	0.78
$—C(O)CH_2(CH_2)_6C(O)—$	0.96	0.92	0.98	1.02	1.08	1.20	1.19	1.17
$—C(O)CH_2CH_2(CH_2)_5C(O)—$	0.98	0.96	1.00	1.04	1.07	1.20	1.17	1.18
$—C(O)(CH_2)_2(CH_2)_3(CH_2)_2C(O)—$	0.94	0.97	1.00	1.02	1.03	1.11	1.15	1.20

Table II
NOE Values[a] for Polymers of Terephthalic Acid, Azelaic Acid, and 70% Ethylene Glycol with 30% Butanediol

	mol % A							
sequence	20	30	40	50	60	70	80	100
$T—OCH_2(CH_2)_3O—$	1.86	1.82	1.55	1.53	1.89	1.94	*b*	
$—OCH_2(CH_2)_2CH_2O—$	2.00	2.02	1.84	1.73	1.91	1.12	1.78	1.82
$A—OCH_2(CH_2)_3O—$	*b*	1.83	1.65	1.81	1.74	1.80	1.87	1.86
$T—OCH_2CH_2O—T$	1.75	1.77	1.71	1.54	2.05	2.12	*b*	
$T—OCH_2CH_2O—A$	1.97	1.83	1.71	1.74	1.78	1.73	*b*	
$T—OCH_2CH_2O—A$	1.93	1.94	1.92	1.63	1.90	2.02	*b*	
$A—OCH_2CH_2O—A$	*b*	2.05	1.84	1.72	1.84	1.82	1.92	1.89
$—C(O)CH_2(CH_2)_6C(O)—$	*b*	1.89	1.75	1.70	1.86	1.86	1.90	1.84
$—C(O)CH_2CH_2(CH_2)_5C(O)—$	*b*	1.98	1.89	1.74	1.82	1.83	1.85	1.81
$—C(O)(CH_2)_2(CH_2)_3(CH_2)_2C(O)—$	*b*	1.90	1.77	1.70	1.80	1.83	1.86	1.87

[a] Out of a maximum of 1.99. Some authors refer to this value as an NOE "factor". [b] Low signal intensities made values unreliable.

transesterification to high molecular weight was completed under vacuum. The materials were isolated by cooling the reaction mixture to room temperature and breaking the reaction flask. Samples were used without further purification. Light scattering photometry was used to determine the weight-average molecular weight of selected samples. All had $\bar{M}_w > 100000$. All of the copolymers had a random sequence distribution.[3]

Samples for Nuclear Magnetic Resonance Spectroscopy. Except where indicated, solutions were 25 g/dL in methylene-d_2 chloride. The solutions were not degassed because the T_1 relaxation times were short and oxygen is not expected to contribute to relaxation significantly.[4] Likewise, sample size was not restricted because errors in T_1 values due to diffusion should not be important for polymers.

Spin-Lattice Relaxation Time Measurements. The fast inversion-recovery technique[5] was used for all determinations. Spectra were acquired with quadrature detection on a Bruker WH 270 spectrometer at 68 MHz. To minimize variations in pulse power across the spectrum, the pulse was set near the peaks of interest. Generally, T_1 values were calculated from a least-squares fit of 10–15 points in a plot of the logarithm of intensity differences vs. time. Each spectrum was an average of ~1000 transients.

Variations in the probe temperature of only a few degrees affected the results significantly. For the final measurements, the B-ST 100/700 temperature controller was modified to operate with maximum heating power of 11 W instead of 280 W so that temperature could be maintained at 34 ± 1 °C, the temperature for all of the measurements.

The T_1 values were uniformly reproducible to within 10% and usually to within 5%. The reported values represent averages of two or more determinations. Reference to the preceding paper shows that some of the T_1 values are for peaks which are partly overlapped. The overlap introduces some systematic error, but most of the overlapped peaks had very different T_1 values, as indicated by the fact that spectra could be obtained in which one of the peaks was inverted and the other was upright. We feel justified, therefore, in drawing conclusions based on the differences in the T_1 values for these peaks.

Nuclear Overhauser enhancements (NOE) were measured out of a maximum of 1.99 with the gated decoupling technique. Delays of at least 10 times the longest relaxation times were used between pulses to ensure complete restoration of equilibrium. In some cases values greater than the theoretical maximum were obtained, especially when a small signal partly overlapped a much larger one. We believe the values to be accurate to ±0.20, but NOE's are especially difficult to measure with accuracy.[6]

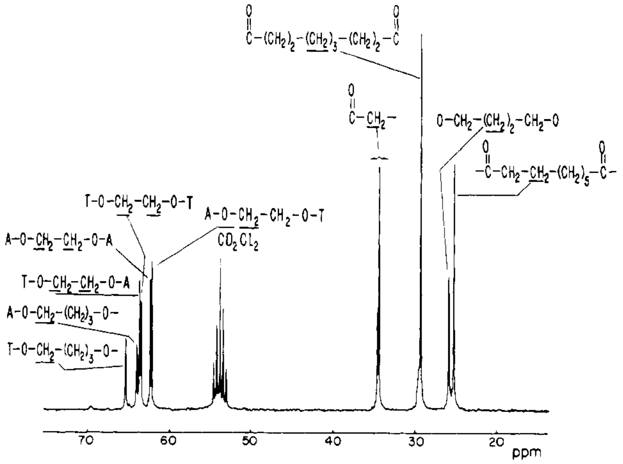


Figure 1. Upfield portion of the ^{13}C NMR spectrum of a polyester containing equal molar amounts of terephthalic acid and azelaic acid and a 70:30 ratio of ethylene glycol and butanediol. The chemical shift scale puts the deuterated methylene chloride pattern at 53.8 ppm.

Results

As in the previous paper,[3] the basic series of polymers were derived from a constant 70:30 ratio of ethylene glycol to butanediol and various proportions of terephthalic acid and azelaic acid. Typical spectra for these materials in methylene-d_2 chloride are shown in ref 3. The upfield portion of the spectrum of one of the samples is shown in

Table III
Solvent Effects on T_1 Values (s)

sequence	solvent	
	CD_2Cl_2	25% hexafluoroisopropyl alcohol + 75% CD_2Cl_2
T—OCH$_2$(CH$_2$)$_3$O—	0.43	0.25
—OCH$_2$(CH$_2$)$_2$CH$_2$O—	0.56	0.33 + 0.56[a]
A—OCH$_2$(CH$_2$)$_3$O—	0.65	0.43
T—OCH$_2$CH$_2$O—T	0.25	0.16
T—OCH$_2$CH$_2$O—A	0.42	
T—OCH$_2$CH$_2$O—A	0.39	0.24
A—OCH$_2$CH$_2$O—A	0.72	0.39
—C(O)CH$_2$(CH$_2$)$_6$C(O)—	0.98	0.68
—C(O)CH$_2$CH$_2$(CH$_2$)$_5$C(O)—	1.00	0.82
—C(O)(CH$_2$)$_2$(CH$_2$)$_3$(CH$_2$)$_2$C(O)—	1.00	0.63

[a] Separate resonances were resolved.

Table IV
Concentration Effects on ^{13}C T_1 Values (s)[a]

sequence	50 mol % A		100 mol % A	
	concentration, g/dL			
	10	25	10	25
T—OCH$_2$(CH$_2$)$_3$O—	0.47	0.44		
—OCH$_2$(CH$_2$)$_2$CH$_2$O—	0.74	0.59	1.03	1.09
A—OCH$_2$(CH$_2$)$_3$O—	0.83	0.75	1.30	0.97
T—OCH$_2$CH$_2$O—T	0.31	0.25		
T—OCH$_2$CH$_2$O—A	0.46	0.40		
T—OCH$_2$CH$_2$O—A	0.52	0.39		
A—OCH$_2$CH$_2$O—A	0.87	0.70	0.86	0.78
—C(O)CH$_2$(CH$_2$)$_6$C(O)—	1.12	0.98	1.44	1.17
—C(O)CH$_2$CH$_2$(CH$_2$)$_5$C(O)—	1.12	1.04	1.32	1.18
—C(O)(CH$_2$)$_2$(CH$_2$)$_3$(CH$_2$)$_2$C(O)—	1.17	1.02	1.29	1.20

[a] Ratio of ethylene glycol to butanediol is 70:30.

Figure 1 with assignment of the relevant peaks. The measured T_1 values are in Table I; the nuclear Overhauser enhancements (out of a maximum value of 1.99) are shown in Table II. We were unable to get data for either table for samples containing no azelaic acid because these polymers are insoluble in methylene chloride.

Differences in the T_1 values of different carbons in the same sample are useful because we do not have to worry about possible effects of viscosity or temperature variations from sample to sample, even though we consider such effects minimal. In each column of Table I, the ethylene glycol T_1 values decrease with increasing numbers of terephthalic acid attached to the diol. Although some of the relevant resonances are partly overlapped, the differences in T_1 values are so large that we think they are significant. The carbon attached to oxygen in butanediol also has a shorter relaxation time when it is attached to terephthalic acid than when it is attached to azelaic acid.

When we compare the T_1 values of carbons in polymers of different composition, we note that there is a general trend for all sites in the polymers to reduced T_1's with increased terephthalic acid content. This decrease occurs for each of the ethylene glycol carbons, for example, regardless of the nature of the acids attached to the diol. Because we can resolve all four resonances for the three different types of triads centered about ethylene glycol, the changes in T_1 values are apparently caused by chemical modifications at remote sites on the polymer chains. We also note a similar trend in the azelaic acid carbons, although the relative sizes of the changes in T_1's are somewhat smaller. The solution viscosities in these samples decreased with increasing terephthalic acid content, a trend opposite to what would be expected if viscosity were causing the observed effects. The decrease was probably a result of (1) decreasing M_w with increasing terephthalic acid content and (2) possible changes in coil expansion with changes in composition.

Table III indicates the effect of addition of a hydrogen-bonding solvent, hexafluoroisopropyl alcohol, to the methylene chloride solutions. The spectrum of the methylene region is shown in Figure 1. We estimated that with 25% hexafluoroisopropyl alcohol, there were roughly equal numbers of ester groups and hydrogen-bonding solvent molecules. Each T_1 value is reduced by about 40% by the hexafluoroisopropyl alcohol. The central carbon of the butanediol group gave rise to partly resolved resonances in the mixed solvent for which substantially different relaxation times were apparent.

Concentration effects on the T_1 values of the polymers in methylene chloride are shown in Table IV. Reduction of the concentration from 25 to 10 g/dL increased the T_1 values 10–20%.

Discussion

It is generally recognized that a single correlation time is insufficient to relate nuclear relaxation to internal motion in polymers.[1] Even for small molecules more than one correlation time is required to describe motion in the general case. Only in the very restricted circumstance that the relaxation results from dipolar interactions with other nuclei at fixed distances from the ^{13}C of interest, and the molecular motion is isotropic, is a single correlation time sufficient.[7]

For most molecules the motion is not isotropic, and in principle, several correlation times must be used in the calculation of relaxation times.[8] When multiple correlation times are required, the relevant spectral distribution function is non-Lorentzian in shape, being the sum of several Lorentzian functions.[9]

For small molecules, tumbling rapidly in solution, the important portions of the curves of these component functions and of the sum of these functions will also be flat. It then makes no practical difference whether we describe the spectral distribution functions as sums of flat Lorentzians or as single flat Lorentzians. The inability to describe the exact shape of the distribution functions is, however, an experimental problem and should not be taken to imply that only a single correlation time (corresponding to the spectral distribution functions being Lorentzian) is sufficient theoretically.

In polymers the internal motions are slow relative to the tumbling of small molecules and are necessarily highly anisotropic as a result of restrictions on the motions by the chain ends. Furthermore, in many cases the various modes of motion within the chain do not occur independently but are correlated. Both the anisotropy of the slow motion and the interdependence of motions can lead to the need for multiple correlation times in the mathematical description of the motion. The autocorrelation functions which describe these motions will, therefore, be composed of the sums of exponentials, and the spectral distribution functions will be the sums of Lorentzians.

An area of active research is the calculation of such functions for various types of motions[10–15] and comparison of the calculation with experimental data.[16–23] For many polymers the slow motions responsible for NMR relaxation permit detection of the nonexponential character of the correlation function through comparison of various types of information, such as T_1, T_2, and NOE values. The exact shape of the correlation function contains information about the motions involved. The polyesters under consideration here are rather mobile polymers, however, and interpretation of the data in terms of a distribution of correlation times would be difficult.

For small molecules the presence of anisotropic motion can be detected by comparison of data for several different carbon nuclei[4] even in the case of extreme narrowing where the spectral distribution function is flat. Therefore, we expect that the use of relaxation measurements from a number of chemically different nuclei, such as we have for the polyesters, should be useful. The polyesters of this paper are good subjects for study because their complexity gives rise to a number of different resonances corresponding to different chemical sequences within the polymer chain.[3] Individual relaxation measurements can be made on each of these signals.

To facilitate the analysis, we have made several simplifying assumptions. To begin with, we assume that the only relaxation mechanism which is important is the dipolar one. This seems reasonable for methylene carbons,[1] although even for polymers other mechanisms sometimes may play a role for nonprotonated carbons.[6] This assumption means that we are interested only in motions which lead to reorientations of the CH bond vectors and thus can modulate the dipolar interaction between the carbon and hydrogen nuclei.

Because the relaxation times of the carbons of interest are long when compared to typical relaxation times for methylene carbons in other polymers, we assume that we are sufficiently close to the extreme narrowing situation that we may treat the data with an effective, single correlation time which is directly proportional to the observed spin-lattice relaxation time. The assumption of fast motion is justified by the fact that the nuclear Overhauser enhancements are all close to the theoretical maximum.

We will further assume that we may use barriers to internal rotation measured for small molecules as a basis for our analysis of the motion in the polyesters. Although most of the small-molecule data were measured in the gas phase by microwave techniques, the relative differences in barrier heights should still be a useful starting point for analysis of motions in the polymers.

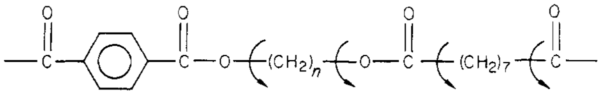
Barriers to Rotation in Small Molecules. It is well-known that the barrier for internal rotation about typical alkyl CH_2–CH_2 bonds is slightly over 3 kcal/mol.[24] As we will see, 3 kcal/mol is a relatively high barrier. We will assume, therefore, that rotations about CH_2–CH_2 bonds do not lead directly to significant spin–lattice relaxation compared to rotations about other types of bonds.

Studies of propionic acid,[25] propional,[26] propionyl chloride,[27] and propionyl fluoride[28] suggest that the barrier to rotation about the CH_2–CO bond is typically about 2 kcal/mol, much reduced from the barrier to rotation about the alkyl CH_2–CH_2 bonds. The most stable conformation is one in which the carbonyl group is eclipsed with the adjacent carbon–carbon bond. This is the trans conformation with respect to the other atom. The gauche form is slightly more than 1 kcal/mol less stable. For the polyesters we then expect the all-trans, zigzag conformation of the azelaic acid backbone through the ester groups to predominate.

By contrast, a number of studies have shown that the barrier to rotation about the C–CO bond of a carbonyl attached to an aromatic ring is very large, in some cases over 5 kcal/mol.[29] Thus we do not expect the C–CO bond in terephthalic acid to be involved significantly in internal motion.

The other type of bond which should be particularly susceptible to internal motion in the polyesters is the CH_2–O bond. The barrier to rotation about that bond in ethyl formate and related compounds is about 1 kcal/mol.[30] We expect that barrier about the O–CO bond to be very large, owing to conjugation effects such as lead to high barriers in amides.

Overall we can illustrate the pivot points in the four-component polyester about which we expect motion to occur by the following structure.



n = 2, 4

Possible Mode of Motion. We now need to use the small-molecule data to help us pinpoint conformations and internal motions important in ^{13}C relaxation. It will be convenient to use the nomenclature of Helfand.[14] Conformations will be indicated as sequences of trans orientations (t) and either positive or negative gauche orientations (g^+ and g^-). For polyesters both gauche conformations are equivalent energetically by symmetry. In fact, it is not generally possible to differentiate them by the direction of rotation about the bond, since it is arbitrary from which way we look down the polymer chain. We will use the g^+ and g^- nomenclature simply to indicate that the direction of rotation about two bonds is different when one looks down the polymer chain the same direction for both bonds.

Helfand has classified polymer motions in terms of the effect of the motion on the chain ends attached to the portion of the polymer actually involved in the motion.[14] Type 1 motions leave the chain ends completely unrotated and untranslated. Because the chain ends are not involved, these motions are particularly favorable. In type 2 motions, on the other hand, the chain ends are translated relative to each other by the motion, but the angular orientation of the two is unaffected. Although the displacement of the chain ends makes type 2 motions less favorable than type 1 motions, Helfand found that the difference in energy requirements is not extreme, and type 2 motions could be involved in some NMR relaxation processes. In type 3 processes, the angular orientation of the chain ends is changed, and the necessity for large-scale rearrangement of solvent by the chain ends is expected to result in high barriers.

In evaluating individual motions in polymers, Helfand found it convenient to calculate specific angles between different bonds in the chain by considering changes of coordinate systems fixed to the backbone bonds. He used Euler angles to define the relationships of the various coordinate systems. We have used a modified form of his procedure to evaluate various types of motions in the polyesters, as described below.

The simplest type of motion which can occur in the polyesters is a one-bond rotation, possibly around the CH_2–O bonds. The result is a type 3 motion which results in a displacement of the chain ends. If we have two rotations in opposite directions about bonds separated by an even number of carbon atoms, however, the two bends in the chain cancel each other. The overall result is a type 2 motion. For the polyesters such a motion could occur at the CH_2–O bonds on either side of either the ethylene glycol or butanediol groups, for example.

It is easy to show from molecular models and from calculations of the type mentioned above that no combinations of rotations about bonds separated by an odd number of carbons will lead to either type 1 or 2 motions, however. In fact, the resulting angles between the chain

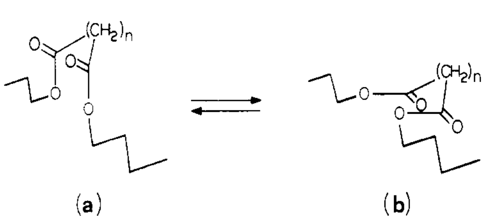


Figure 2. Typical "wagging" motion for the acid portion of a polyester.

ends are about 90° when two rotations are combined. Motions within the azelaic acid groups, which have an odd number of carbons between the mobile CH_2–O and CH_2–CO bonds, must therefore be of some other nature. Experimentally we found that the relaxation times for the azelaic acid methylene carbons were the longest observed for any methylene carbon in the polyesters. Therefore, we need to find other, very efficient motions which will result in reorientations of the azelaic acid bond vectors.

For acids with an odd number of carbons, the $g^+tg^-(t)_ng^+tg^-$ conformation shown in Figure 2a should be accessible to the polymer. This conformation can be converted into the $g^-tg^+(t)_ng^-tg^+$ conformation shown in Figure 2b by concerted rotations about both CH_2–O bonds and both CH_2–CO bonds. These are precisely the bonds in polyesters for which internal rotation is facile. We will refer to this motion as a "wagging" motion. It should be very effective in leading to NMR relaxation because of the reorientation of the CH bond vectors in the portion of the chain which is "wagged".

The wagging motion is one example of motion on a diamond lattice. Monnerie and co-workers have considered explicitly the case in which n is 1.[15] For $n = 1$, the wagged portion of the chain corresponds to the end of a six-membered-ring chair conformation. The generalized motion with n equal to an arbitrary number may occur as long as n is odd. The allowance of longer chains of arbitrary length between the pivot points provides a mechanism for rather long-range motions, although presumably the central portion eventually becomes too long to be "wagged" efficiently through the solvent.

We have illustrated this motion with gauche bonds on either side of the active portion of the chain. Actually, the nature of the conformations at the outer bonds is not critical. The example we have chosen has the chain ends coaxial. Other conformations will have a bend in the chain. The presence of such a bend in the chain is not at all a problem, however.

If we had been working with polyesters containing diols with an odd number of carbons, similar wagging motions could be proposed for them. Of course, the role of he CH_2–CO and CH_2–O bonds would be reversed in the active conformation, and there might be some differences in the rates of the motions leading to ^{13}C relaxation.

The formation of the conformation necessary for the wagging motion requires that there be an odd number of carbons between the pivot points (the ester groups for the polyesters). When there is an even number of carbons, a comparable conformation can be formed, however, which makes possible the so-called crankshaft motion.[14,31] We will illustrate the crankshaft motion for the diol groups, since those are the even-carbon moieties in the polyesters of interest (Figure 3). The conformation shown is $g^+(t)_ng^+$. Its important feature is that the CH_2–CO bonds are coaxial. Thus rotation about them can occur in a concerted manner without the need for rotations about any other bonds in the chain. Polyesters are ideally suited for this motion because it involves bonds in which the barriers to rotation are low. Once again, we point out that there are actually several conformations which can undergo the crankshaft motion, because the orientation of the chain ends is arbitrary. The important point is that the positions of the chain ends are not changed by the crankshaft motion; it is thus a type 1 motion.

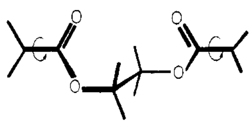


Figure 3. Conformation which allows for the crankshaft motion of the glycol portion of the polyesters.

We now have two reasonable types of motions which can occur in polyesters, one for those portions of the chain in which there are an odd number of carbons between the ester groups and one for those in which there are an even number of carbons. When butanediol has azelaic acid on both sides, it has T_1 values almost equal to those of the azelaic acid itself, as is indicated by the right-hand column of Table I. Both the wagging and crankshaft motions appear to be very efficient, therefore. When a terephthalic acid group is attached to the diol, the motions of the diols are much more restricted, apparently because there is one less bond in the ester group about which facile motion can occur. The ester group in azelaic acid is almost like a "universal joint", but that in terephthalic acid is not.

When ethylene glycol has terephthalic acid on one or both sides, an appropriate conformation for the crankshaft motion cannot be formed because of the high barrier for rotation abbout the C–CO bond in terephthalic acid. A suitable conformation can be formed for butanediol with gauche conformations about CH_2–CH_2 bonds. The coaxial bonds in the crankshaft conformation are then the CH_2–O bonds. Conformations of this type have been observed for polyesters in the solid state,[32] but the shorter T_1 relaxation times observed for butanediol when terephthalic acid is present suggest that it is not an effective means by which the butanediol can undergo fast internal rotation in solution.

On the surface it would seem that the ethylene glycol group should take part in the crankshaft motion just as readily as the butanediol group, but its T_1 values are noticeably lower than those of the butanediol, even in those polymers which are very rich in azelaic acid. However, construction of models of the appropriate conformation for the crankshaft motion around the ethylene glycol group shows a close approach of the two carbonyl groups. Because of electrostatic repulsion this interaction should destabilize that conformation of the ethylene glycol group. The interference of carbonyl groups does not occur for the butanediol because of the longer chain separating the carbonyls. Thus the overall effective motion for the ethylene glycol group is less than for the butanediol because there are fewer ethylene glycols in a conformation which allows fast motion, and shorter T_1 values result.

An important aspect of all of the motions described above is that rotations about one or more of the bonds in the ester groups are essential. Any restrictions of the mobility off the ester groups should lead to reductions in the relaxation times. Komoroski did, in fact, find T_1 values much shorter than those we have observed for a number of polyesters dissolved in hexafluoroisopropyl alcohol.[33] This is a solvent which should hydrogen bond strongly to the ester groups. The fact that he worked at lower magnetic field strengths, however, makes uncertain whether the shorter relaxation times were a solvent or a field effect.[34] The reduced T_1 values we observed when 25%

hexafluoroisopropyl alcohol was added to the methylene chloride solutions suggest that there is indeed a solvent effect and support our contention that the ester linkages are the key to the motions in polyesters.

We noted above that the number of carbon atoms between the ester pivot points was not crucial as long as there was an odd number for the wagging motion and an even number for the crankshaft. Thus we have a mechanism for motions involving more than three units of the polymer chains. This might explain the fact that increases in the proportion of azelaic acid in the polymers led to increased relaxation times for the ethylene glycol groups, even for those ethylene glycols which were already attached to azelaic acids on both sides. In these cases the site of chemical modification had to be some distance down the chain. Increases in the relaxation times, even of the azelaic acid units themselves, were observed with increased azelaic acid content.

The possibility that chemical changes in the polymer chain can affect the T_1 values of rather distant carbons raises some interesting questions. It is obvious from the results of the preceding paper[3] that comparable long-range chemical shift effects do not occur for the methylene carbons. Thus we may very well have several signals having the same chemical shifts but different T_1 values. In principle, this would lead to nonexponential relaxation of the composite line. Such an effect might even allow the "resolution" of the resonances in terms of relaxation instead of chemical shift. In practice, it is essentially impossible to resolve sums of exponentials unless the respective time constants differ by a factor of 5 or more.[35] For polyesters the observed apparent relaxation time is the weighted average of the relaxation times of the constituent signals, and we see smooth changes in the T_1 values with composition in Table I.

Conclusions

Our results suggest that polyesters are useful models in which to study motions in polymers. Simple analysis shows that various crankshaft motions are possible. The role of crankshaft motions in polymers has been questioned recently,[36] however, and further experiments are needed for full clarification of their importance.

We are currently investigating the use of other methods, such as dynamic mechanical and dielectric relaxation, to gain further insight into the motions of polyesters. A combination of solid-state relaxation measurements with NMR data may be very informative[37] in relating the types of motions which control NMR relaxation to such parameters as the glass transition temperature.

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