slower in the case of 34 bonds (PEO 1000), and only 1.7 times slower in the case of 51 bonds (PEO 1500).

Conclusion

The carbon-13 spin–lattice relaxation time determinations performed on bulk poly(propylene oxide) and linear and cross-linked poly(ethylene oxides) have confirmed the results obtained on poly(vinyl methyl ether) and reported in the preceding paper in this issue. Indeed, the segmental dynamics of these polymers are satisfactorily described by considering a fast libration of limited extent of the internuclear CH vectors about their rest position and a damped bond orientation diffusion process. In addition, the data on poly(propylene oxide) show that the amplitude of the rapid CH libration mode depends on the steric hindrance at the site of the considered carbon. On the other hand, the results obtained on cross-linked poly(ethylene oxides) clearly demonstrate that the cross-links interrupt the orientation diffusion process along the chain and that the segmental motions of the central flexible units are quite significantly slowed down by the constraints arising from the cross-links. It is worthwhile to note that when the central PEO units are located at a distance of about 50 bonds from the urethane junction, their dynamics are about twice as slow as in linear PEO.

Acknowledgment. We express our gratitude to Dr. H. Cheradame for supplying the cross-linked poly(ethylene oxides) samples.

Registry No. PEO, 25322-68-3; (PEO)(triphenylmethane-p,p',p''-triisocyanate) (copolymer), 114379-12-3; poly(propylene oxide), 25322-69-4.

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^{2}H NMR Analysis of the Molecular Origin of the Thermal Relaxations in Polycarbonates

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ABSTRACT: ^{2}H NMR spectroscopy has been utilized to characterize the molecular dynamics associated with the thermal relaxations in amorphous polycarbonate materials. The methyl and phenyl groups of bisphenol A polycarbonate (BPA PC) and poly(ester carbonates) derived from BPA and tere- or isophthalic acid were independently deuterium labeled so as to characterize the molecular dynamics of each group as a function of temperature. The phenyl motions of both the BPA and terephthalate units were characteristic of 180° ring flips and large angle rocking motions. These motions ceased (relative to 100 KHz) between 40 and −30 °C. The terephthalate phenyls were more motionally restricted at temperatures between −30 and 120 °C than the BPA phenyls. The backbone motions of these systems were also shown to be quite restricted until very near T_g. Physical aging was observed to have much more of an effect on the dynamics of the terephthalate phenyl than those of the BPA phenyl. PEC systems, however, have been shown to be much more aging resistant and to possess ductility at lower temperatures than the BPA homopolymer, thus indicating that simple free volume arguments are not sufficient to explain these observations.

Introduction

The relationship between the molecular dynamics of a glassy polymer and its deformation properties remains a controversial subject. The spectroscopic investigation of the molecular motions of solid polymers in general has attracted much attention for the purpose of defining such a relationship. Polycarbonate polymers have been the focus of much of this attention for many reasons, not the least of which is the unusual toughness that this engineering plastic exhibits at room temperature.[8]

The molecular dynamics of bisphenol A polycarbonate (BPA PC) have been extensively characterized in the solid state by NMR techniques. The phenyl motions (at ambient temperature) were defined as 180° ring flips about the C_2 symmetry axis, superimposed upon approximately 30° ring oscillations.[1-3,11] Schaefer et al.[3] also observed

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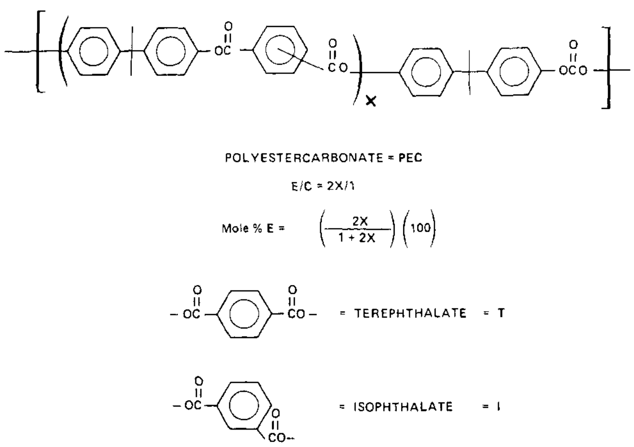

Figure 1. Molecular architecture and definitions.

significant backbone motions with amplitudes of about 20°. Methyl group motion was defined by ^{2}H NMR as rapid rotation at ambient temperature.[1,4] At temperatures lower than −100 °C, three site jump motions were observed, superimposed upon a static pattern at still lower temperatures.[4] The carbonate carbonyl motions were investigated by analysis of the ^{13}C chemical shift anisotropy powder patterns of enriched samples.[10] The motions were described as about 40° chain oscillation motions.

Molecular motions in polymer glasses are not described by a single correlation time. A distribution of correlation times must be utilized due to the distribution of packing arrangements in the glass. A thorough discussion of this topic is given elsewhere.[4]

Even though it is possible to define the dynamics of a polymeric material on the molecular level, the relationship between these molecular processes and the sample's deformation properties is not a simple problem to address. Several variables must be considered when attempting such a correlation. These include the relative frequencies of the measuring devices, the coupling of the molecular motions to the mechanical device, the effects of morphology, impurities, molecular weight, thermal history, etc. One example of the role of the sample's thermal history, which will be discussed in this investigation, is the extent to which it has been physically aged. Physical aging is a purely physical (as opposed to chemical) process in which a sample densifies and often embrittles. The effects of physical aging can be erased by heating the specimen above its T_g and quenching. The rate of physical aging can be greatly accelerated by heating the sample near but below its T_g (i.e., annealing). The deformation characteristics of glassy polymers such as PC are known to be strongly affected by physical aging.[5,6,8]

This investigation was an attempt to carefully control as many of these variables as possible, in order to relate the temperature dependence of the molecular motions to the dynamic mechanical spectra (DMS) of PC and the terephthalate (T) and isophthalate (I) polyester carbonates (PEC) of BPA. The effect of physical aging upon the molecular dynamics of the polymers was also investigated. ^{2}H NMR spectroscopy of labeled samples was utilized for this analysis. Reviews of this NMR technique are given elsewhere.[1,7]

Experimental Section

The polymers included in this study were deuterium-labeled BPA PC and PEC, whose structures are given in Figure 1. The PEC samples all had 50 mol % ester, E ($X = 0.5$, $E/C = 1/1$). The preparation of the samples and their mechanical properties are given elsewhere.[8] The samples were all completely amorphous. The molecular weight values of the samples are given in Table I. The ^{2}H NMR studies were performed on deuterium-labeled samples by using a Bruker CXP-200 spectrometer. The quadrupole echo pulse sequence was utilized for data acquisition.[1] The $\pi/2$ pulse width was 4 μs; a 40-μs delay between pulses and a 5-s repetition rate were utilized. The sweep width was 1.0 MHz with 1K data points and 1K zero fill. Data acquisition was initiated on the top of the echo.

Table I
Average Molecular Weight Values As Determined by Size-Exclusion Chromatography

sample	M_z	M_w	M_n	M_w/M_n
TPEC-D8	33 300	21 500	9300	2.3
TPEC-D4	12 600	8 000	3300	2.4
BPA PC-D8	36 000	22 600	8700	2.6

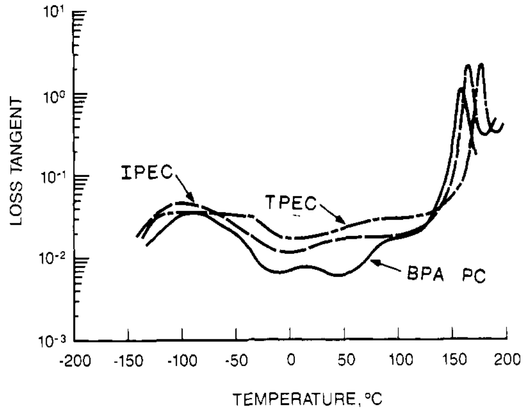

Figure 2. Dynamic mechanical spectra of 1/1 TPEC, 1/1 IPEC, and BPA PC.

Results

A. Dynamic Mechanical Analysis. The DMS loss tangent spectra of the three polymers of this report are given in Figure 2. It has been shown that the terephthalate PEC (TPEC) system possesses better resistance to embrittlement associated with physical aging than BPA PC. Aging is observed in the DMS spectrum as a decrease in the intensity of the tan δ in the β relaxation (located from about 80 °C to T_g), corresponding to a dramatic decrease in the toughness and an embrittlement of the sample. TPEC also has a combination of less notch sensitivity and better low-temperature performance as measured by notched Izod impact.[12] The resistance to embrittlement of isophthalate PEC (IPEC), however, is very similar to that of BPA PC. A knowledge of the molecular dynamics associated with the γ and β regimes is required to interpret these properties.

B. ^{2}H NMR Investigation of the Motions Occurring in the γ Relaxation. 1. Methyl Group Motions. The motion of the methyl groups of TPEC-D6 (methyls deuterium tagged) was characterized as fast above 0 °C, as discussed earlier. The temperature-dependent ^{2}H NMR spectra of TPEC-D6 are given in Figure 3. As the temperature was decreased from 0 °C, the patterns began to change as the three-site jump and static patterns became more prominent.[4] The "static" pattern, which resulted from methyl deuterons experiencing motions slower than about 100 KHz, was observed at about −110 °C. The quadrupole splitting of the static pattern was determined to be 129 ± 2 KHz.

Differences in the temperature dependence of the spectra from the deuterium-tagged methyl groups of the TPEC-D6 and BPA PC-D6 samples were insignificant (Figure 4). A comparison of the temperature dependence of the spectra of the methyl-tagged samples, both aged and quenched, also showed no significant differences. Thus,

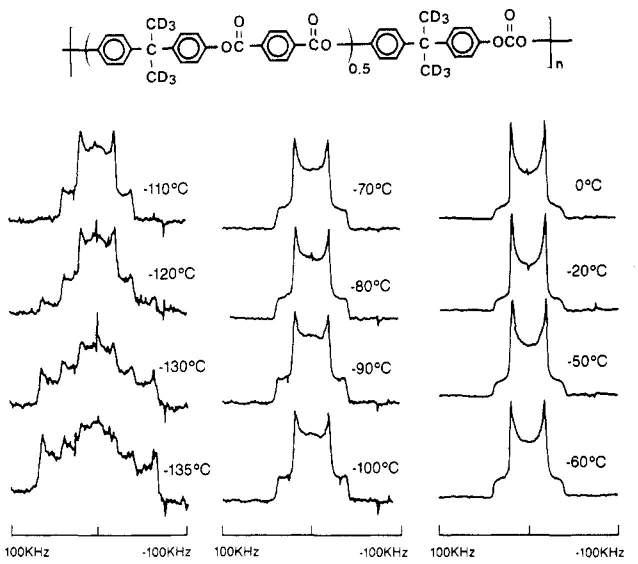

Figure 3. ^{2}H NMR powder patterns for PEC-D6 as a function of temperature.

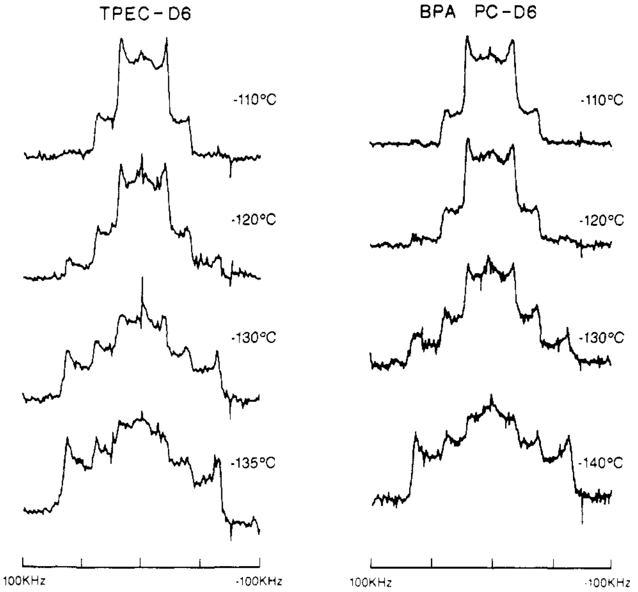

Figure 4. Comparison of the temperature dependence of the ^{2}H NMR spectra at low temperatures of BPA PC-D6 and TPEC-D6.

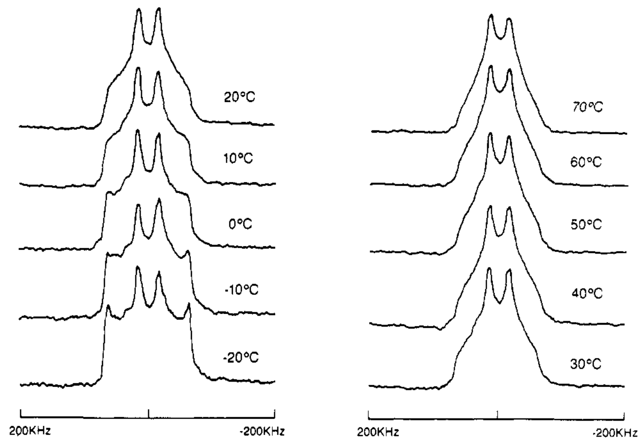

Figure 5. ^{2}H NMR spectra of BPA PC-D8 as a function of temperature from −20 to 70 °C.

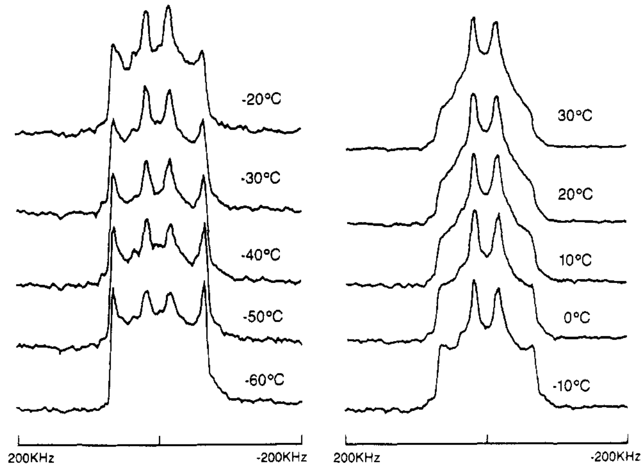

Figure 6. ^{2}H NMR spectra of BPA PC-D8 as a function of temperature from −60 to 30 °C.

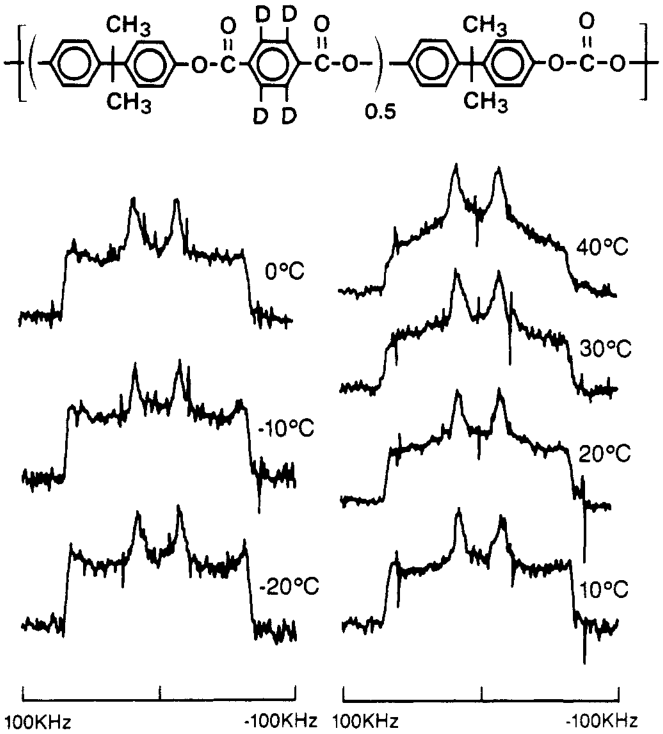

Figure 7. ^{2}H NMR spectra of PEC-D4 (aged) as a function of temperature from −20 to 40 °C.

the differing environments which resulted from these chemical and physical changes did not measurably affect the dynamics of the methyl group.

2. Phenyl Group Motions. A series of phenyl labeled BPA PC and PEC samples, BPA PC-D8 and PEC-D8, were synthesized in order to define the temperature dependence of BPA phenyl motions. Figures 5 and 6 show the temperature dependence of the ^{2}H NMR spectra of the BPA PC-D8 system. The motions which contributed to line narrowing have been previously described as 180° ring flips superimposed upon large angle oscillation motions. The spectra proceeded from motionally narrowed to static in the temperature range of 30 to −30 °C.

The ^{2}H NMR line shapes of the T phenyl of TPEC-D4 were very similar to those of the BPA phenyl (Figures 7 and 8). This indicated that they underwent the same types of motions as the BPA phenyls. The transition from motionally narrowed to static for the spectra of the TPEC-D4 occurred between 50 and −10 °C. This transition was at least 20 °C above that for the phenyls of the BPA unit. This point is better demonstrated by plotting the line width of the patterns as a function of temperature (Figure 9). The plot shows that the motions of the BPA phenyls of BPA PC-D8 and TPEC-D8 had an indistinguishable temperature dependence. However, the tem-

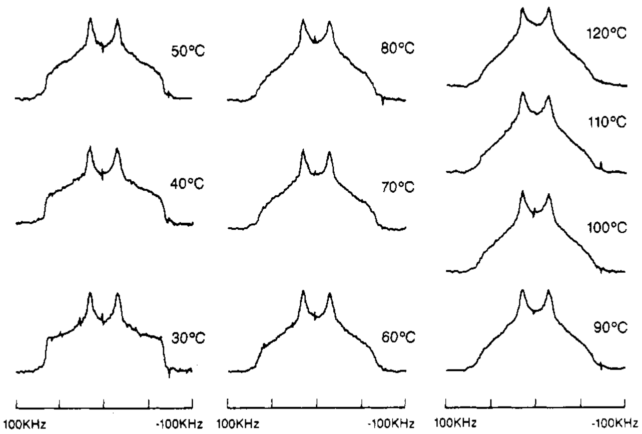

Figure 8. ^{2}H NMR spectra of PEC-D4 (aged) as a function of temperature from 30 to 120 °C.

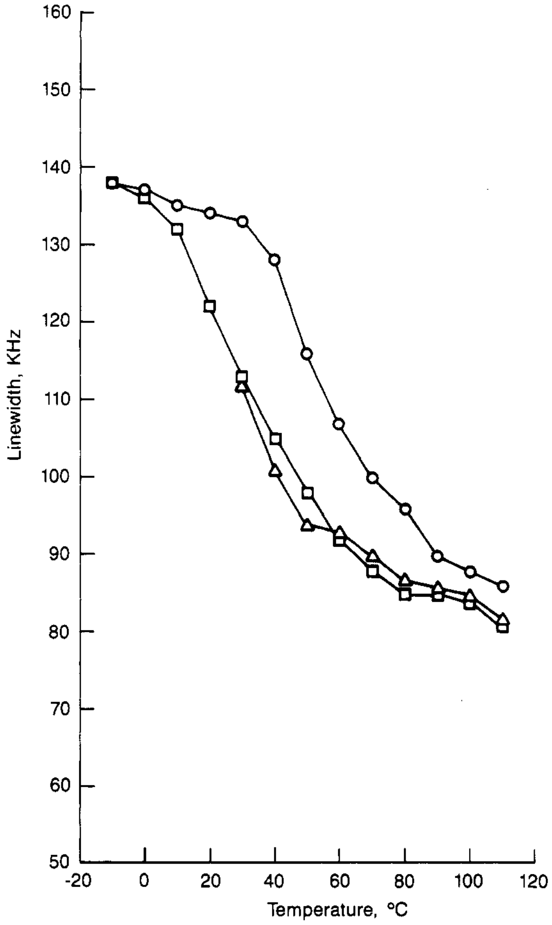

Figure 9. Temperature dependence of the ^{2}H NMR line widths of quenched PEC-D8 (squares), BPA PC-D8 (triangles), and PEC-D4 (circles) samples.

Table II
List of the Molecular Processes Associated with Corresponding DMS Relaxations

molecular process[a]	temp range, °C	DMS relaxtn
BPA methyl rotation	−100 to −150	γ
BPA phenyl ring flips	10 to −30	γ
terephthalate phenyl ring flips	40 to −10	γ
BPA phenyl large angle rocking motions	10 to −30	β, γ
terephthalate large angle rocking motions	40 to −10	β, γ
cooperative backbone motions (small angle)	above 50°C	
extended backbone motion	above 140°C	

[a] The defined motions go from rapid to "static" (at about 100 kHz) in this temperature regime. The assignment to DMS relaxations is complicated by the fact that NMR measurements are done at much higher frequencies than DMS. Therefore, the relaxations would be expected to be observed by ^{2}H NMR at higher temperatures.

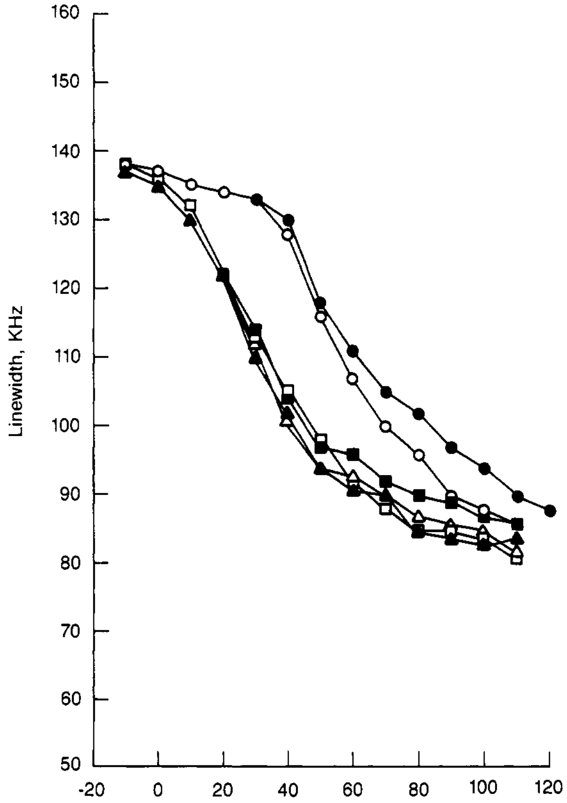

Figure 10. Temperature dependence of the ^{2}H NMR line widths of aged (dark characters) and quenched (open characters) samples of PEC-D4 (circles), PEC-D8 (squares), and BPA PC-D8 (triangles).

perature dependence of the TPEC-D4 (T phenyl labeled) line widths indicated that the T phenyls did not experience motional narrowing until at least a 20 °C higher temperature than the BPA phenyls. These data were consistent with the extension to higher temperatures (about 25 deg) of the γ relaxation in TPEC as compared to BPA PC. The BPA phenyl motions were very similar in both TPEC and BPA PC systems, but the motions of the T moiety (which was obviously not present in BPA PC) were initiated at the higher temperature.

A comparison of the temperature dependence of the NMR line widths to the DMS spectra of these materials indicates that the relaxation is observed by NMR about 50 °C higher in temperature than by DMS (compare Figures 2 and 9). This is presumably observed because of the difference in sampling frequency between DMS (1–10 Hz) and ^{2}H NMR (10–100 kHz).

The molecular motions which contribute to the γ relaxation are summarized in Table II. The molecular motions which are present in the γ-temperature regime are on a very local scale, involving sub-monomer units as described by Boyer.[9]

C. Physical Aging Investigations. Careful attention was given to sample preparation for the study of physical aging effects on the molecular dynamics of the samples. Duplicate samples were heated to 250 °C for 1 h in a vacuum oven followed by quick quenching in ice water. One sample of the set was then physically aged in an oven at 120 °C for 10 days. The spectra of BPA PC-D6 and PEC-D6 samples analyzed in the quenched state and after

Table III
^{2}H NMR Line Widths of BPA PC and PEC Samples as a Function of Temperature. Terephthalate Ring Labeled (D4) and BPA Rings Labeled (D8)

	PEC-D4		PEC-D8		BPA PC-D8	
temp, °C	quenched	aged	quenched	aged	quenched	aged
-10	138		138			137
0	137		136			135
10	135		132			130
20	134		122			122
30	133	133	113	114	112	110
40	128	130	105	104	101	102
50	116	118	98	97	94	94
60	107	111	92	96	93	91
70	100	105	88	92	90	90
80	96	102	85	90	87	85
90	90	97	85	89	86	84
100	88	94	84	87	85	83
110	86	90	81	86	82	84
120		88				

annealing showed no measurable differences between the BPA PC and (I or T) PEC samples or with regard to aging. However, the TPEC-D4 phenyl line shapes were observed to be sensitive to aging effects. The line width of its powder pattern plotted against temperature (Figure 10) showed the quenched sample to be more motionally narrowed at a given temperature in the β regime than the aged sample. The differences observed between the ^{2}H NMR line shapes of quenched and aged samples of TPEC-D4 were admittedly small. However, they were repeated several times with equivalent results.

The molecular process responsible for the restricted dynamics upon physical aging for the T unit has not been defined but could result from either inter- or intrachain effects. Interchain packing is enhanced with physical aging (the bulk density increases slightly) which in turn could cause a restriction in molecular motion. The T phenyl may be more sensitive to aging effects than the BPA phenyl because the T moiety is a planar structure and more amenable to packing arrangements. Ring flips and phenyl rocking motions could be inhibited by the packing of polymer chains above and below, since ring flips would require cooperative motions of the molecular network. Thus, as the chains pack more efficiently due to the effects of physical aging, the ring flip motions would be expected to become more hindered.

An alternate explanation for the restriction of molecular motion upon aging could be proposed from intrachain effects. As the polymeric glass approaches the equilibrium condition, the average flexibility of the polymer backbone could decrease due to a changing distribution of molecular conformations. These conformational changes could also alter the conjugation between the carbonyl and the phenyl groups of the T moiety, giving rise to restricted molecular motion in this group.

The temperature dependence of the ^{2}H NMR line widths for quenched and aged TPEC-D4, TPEC-D8, and BPA PC-D8 samples is given in Figure 10 (see also Table III). This plot illustrates two points. First, motional narrowing due to the onset of T motions in the kHZ frequency occurs at higher temperatures than does that of the BPA phenyls. Second, the T phenyl line widths show a greater difference between quenched and aged samples than do the BPA phenyls. The terephthalate phenyl line widths show a 5–10 kHz difference between quenched and aged samples. (The aged samples possess broader lines at a given temperature due to more restricted motions.) The line widths of the BPA phenyls of the TPEC show a similar trend with the aged sample giving broader lines than the quenched sample at a given temperature. However, the difference between the set of line shapes is much smaller, 2–5 kHz, and may or may not be real. There is no measurable difference between the line widths of the aged and quenched samples of the BPA homopolymer.

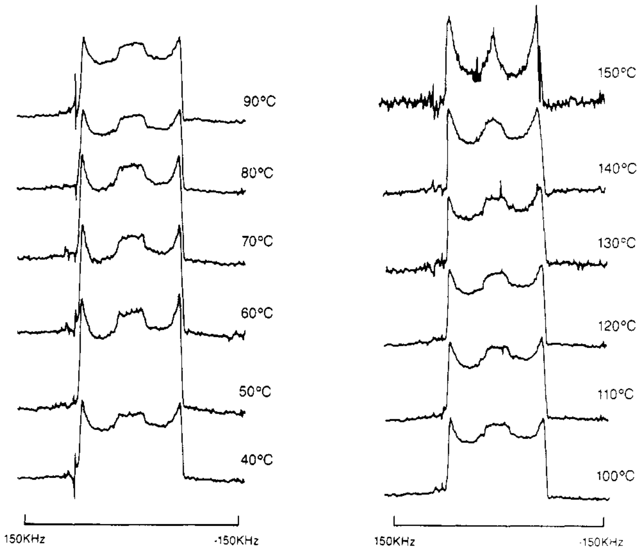

Figure 11. ^{2}H NMR spectra of PEC-D4 isophthalate as a function of temperature.

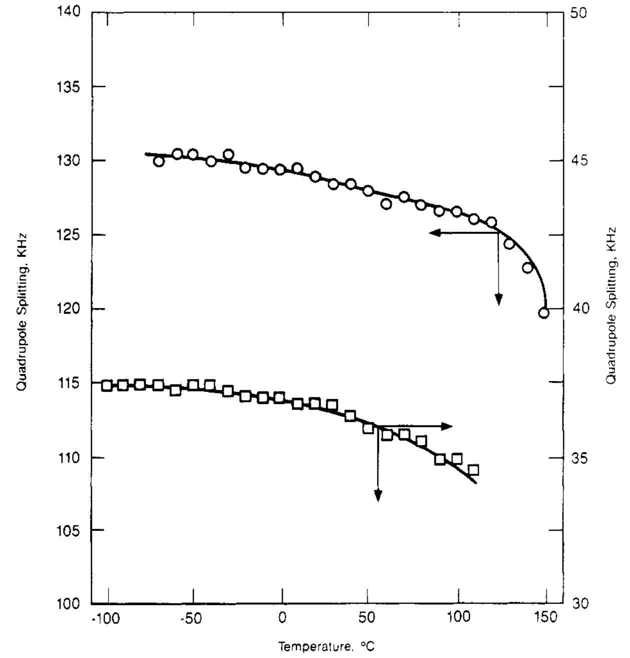

Figure 12. Quadrupole splitting of the PEC isophthalate phenyls (circles) and methyls (squares) as a function of temperature.

D. Backbone Motions. The motions of the backbone were probed by using phenyl-labeled isophthalate PEC samples (IPEC-D4). Since the I unit is linked to the polymer through the meta position, the entire backbone must undergo a concerted process in order for this unit to experience torsional motions. Therefore, the I unit would be expected to probe long-range backbone motions.

The ^{2}H NMR spectra of this IPEC-D4 sample as a function of temperature are given in Figure 11. This pattern is a static pattern below 80 °C. Above this temperature, however, the pattern narrows slightly, but even at 150 °C, the perpendicular edges of the static pattern remain. A plot of the quadrupole splitting of this pattern as a function of temperature (Figure 12 and Table IV) indicates that there is very little motional narrowing of the

Table IV
^{2}H NMR Quadrupole Splitting of I PEC Samples

temp, °C	D4-isophthalate ring labeled	D6-methyls labeled	temp, °C	D4-isophthalate ring labeled	D6-methyls labeled
−100		37.4	30	128.4	36.8
−90		37.4	40	128.4	36.4
−80		37.4	50	128.0	36.0
−70	129.9	37.4	60	127.1	35.8
−60	130.4	37.2	70	127.6	35.8
−50	130.4	37.4	80	127.0	35.6
−40	129.9	37.4	90	126.6	35.0
−30	130.4	37.2	100	126.6	35.0
−20	129.4	37.0	110	126.1	34.6
−10	129.4	37.0	120	125.9	
0	129.4	37.0	130	124.4	
10	129.4	36.8	140	122.8	
20	128.9	36.8	150	119.8	

pattern, and thus very little backbone motion, until the temperature is increased to near the T_g of the system (160 °C).

The backbone motions were also probed by using the quadrupole splitting of the BPA methyl groups of an IPEC-D6 system (also given in Figure 12). The pattern of these groups was motionally narrowed above −60 °C due to continuous C_3 rotational motions. This splitting remained nearly constant from −60 to about 20 °C, where the β relaxation began. Above this temperature, splitting narrowed increasingly as the T_g of the system was approached. These data were also consistent with enhanced backbone motions giving rise to additional narrowing of the quadrupole splitting of the methyl deuterons.

The quadrupole splitting of the methyl units of IPEC-D6 and that of the phenyls of IPEC-D4 showed very similar trends, as expected, since they both probed the backbone motions of the system. These data emphasized the fact that there was very little backbone motion below T_g in the 10–100 kHz frequency regime.

Discussion

The applied strains in the DMS experiment are relatively low, less than 0.3%. In mechanical tests at larger displacements, such as an impact test or a tensile test, the correlation with the molecular dynamics of the system is more tenuous. Molecular flexibility is necessary but not sufficient for ductile yield. Ductile yield also requires some ability of the polymer chains to move cooperatively over comparably large displacements. Despite these problems, this investigation has (1) further demonstrated a correlation between the molecular dynamics of the three polymers studied and their DMS spectra and (2) made possible a partial explanation of mechanical properties on a molecular level. The relationship between the DMS spectra and the backbone motions near T_g, as probed by the methyl and I phenyl patterns, is difficult to dispute. The cessation of methyl rotation on the NMR time scale was observed to occur in the low temperature portion of the γ relaxation. The broadening of the γ relaxation by about 25 °C on the high-temperature side in the TPEC system relative to BPA PC was shown to correlate with the onset of T phenyl motion which was observed at about 20 °C higher in temperature for TPEC.

The T ring motions were shown to be more inhibited relative to those of the BPA phenyls upon aging. The T unit is a planar structure whereas the BPA unit is bulky and kinked. Again, from the viewpoint of intramolecular contributions, the planar structure of the T unit may facilitate local packing relative to the BPA structure and, thereby, show more dependence upon the local packing of the system. Local molecular nesting may account for the enhanced restriction of motion of the T phenyl upon aging. The T phenyl, however, is more susceptible to aging than the BPA phenyls, which raises the question of why the TPEC is more resistant to embrittlement due to aging than BPA PC? TPEC also densifies much less upon aging than BPA PC,[8] thereby illustrating the fallacy of applying free volume arguments to explain physical aging phenomena. From the intramolecular viewpoint, the NMR results (and variable-temperature FT-IR results reported elsewhere[6]), suggest that the T ester linkage in PEC may reconform during the physical aging process in such a way as to preserve the mobility of the carbonate linkage, resulting in the superior resistance to embrittlement with physical aging of TPEC over BPA PC.

It has been shown that the physical aging characteristics of IPEC are very similar to those of the BPA PC.[6,8] The severe restriction of motion of the I phenyl below T_g is consistent with the observed physical aging result. If the mobility of the I ester phenyl is very limited, then the negation of its contribution leaves only BPA PC as the molecular remainder, hence their very similar physical aging/ductile–brittle behavior.

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Registry No. TPEC, 31133-78-5; IPEC, 31133-79-6; BPA PC (copolymer), 25037-45-0; BPA PC (SRU), 24936-68-3.

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