Molecular Structure Effects on the Secondary Relaxation and Impact Strength of a Series of Polyester Copolymer Glasses

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Received November 13, 1997; Revised Manuscript Received April 27, 1998

ABSTRACT: The secondary relaxations of a series of glassy copolymers based on poly(ethylene terephthalate) (PET) and poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) involve cooperative motions of the cyclohexylene rings. The cooperativity gives rise to longer range motions which create significant volume fluctuations that can facilitate macroscopic shear yielding. Comparison of the secondary loss peaks and activation energies by dynamic mechanical spectroscopy between the copolyesters and poly(cyclohexyl methacrylate) and poly(1,4-cyclohexylenedimethylene 2,5-dimethylterephthalate) indicates that the secondary relaxation of the copolyesters involve motions of the cyclohexylene ring. Dipolar rotational spin−echo ^{13}C NMR confirmed large amplitude motions of the cyclohexylene ring faster than 10 kHz at 300 K. By examining feasible ring conformations, we conclude that transitions between chair and twist−boat conformations are possible for *trans*-cyclohexylene rings and cis-rings that prefer chair conformations. (Cis-rings that reside in boat conformations are more restricted.)

Introduction

In the past 3 decades, many studies have focused on the secondary relaxation of polymers.[1−4] Part of the impetus has been to establish a relationship between these secondary relaxations and mechanical properties. However, identifying the molecular origin of the secondary relaxation for many polymers has proven to be a difficult task. Much progess has nonetheless been made in elucidating the molecular origin of the secondary relaxation for several families of glassy polymers, e.g., Bisphenol A polycarbonate[2,5−7] and acrylate polymers.[1,8−11] These successes were largely due to dynamic mechanical spectroscopy (DMS) of a homologous series of specially synthesized polymers where systematic variations were made to the chemical structure. In the case of Bisphenol A polycarbonate (henceforth referred to simply as polycarbonate), a comprehensive review of the previous studies of the secondary relaxation was conducted by Yee and Smith.[2] It was apparent to previous investigators that several groups along the backbone were capable of motion: rotation of the methyl groups in the isopropylidene group, a rocking motion of the isopropylidene group and of the carbonate group, and flips of the phenylene groups. However, it was uncertain whether these motions were correlated to each other. They concluded that the motions of these small molecular moieties by themselves could not induce the mechanical loss of the secondary relaxation since each provides only small volume fluctuations if any. They further concluded that the motions of the groups must therefore be closely associated with the motion of the repeat unit as a whole. Jho and Yee[5] and later Xiao and Yee[6] were able to estimate the extent of the correlation by conducting DMS on alternating multiblock copolymers based on polycarbonate and tetramethyl-substituted polycarbonate. On the basis of DMS studies, they concluded that the motions of the small molecular moieties were indeed linked to each other over a length of approximately 7 repeat units. This notion of cooperativity was also correlated to the polymer's ability to shear yield.[7] Their study revealed not only that is the activation of the secondary relaxation necessary for the polycarbonate based copolymers to yield but also that the availability of large-scale main-chain cooperative motion is beneficial for shear yielding. They found that when the scale of the cooperative motion was small, a higher temperature was needed to achieve yielding at moderate strain rates despite all secondary relaxations being thermally activated at this temperature. (The phrase "thermally activated" is used here and throughout this paper to mean at or above the temperature at which the effective frequency of the motion is fast compared to the inverse of the effective time scale of the measuring method, such that the motion becomes observable.) When the scale of cooperative motion was increased, ductile behavior was observed at room temperature. Despite these advances, exactly how the cooperative motions associated with the secondary relaxation in BPA−PC enhance shear yielding still remains speculative. The greatest stumbling block has been in determining the exact nature of the secondary relaxation, i.e., the molecular motions themselves driving the relaxation.

In the case of poly(methyl methacrylate) (PMMA), Heijboer[1,8] believed that the secondary relaxation was associated with the rotation of the methoxy−carbonyl side group about the bond linking the group to the main chain. When the rotation of the side group was restricted by systematically attaching bulkier and stiffer groups, the secondary loss peak was depressed.[9] Heijboer had strong evidence that the side group contributes to the secondary relaxation of PMMA, but he acknowledged that he did not fully understand to what extent the main chain participates in the side chain motion. In a molecular mechanics study,[10] it was found that the rotation of the ester side group accounted for less than half of the secondary-relaxation activation energy. Also Yee and Takemori[11] from their bulk relaxation studies

S0024-9297(97)01671-9 CCC: \$15.00

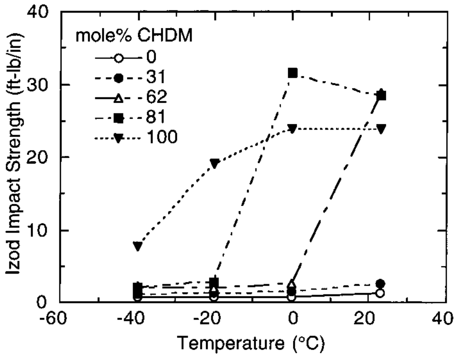


Figure 1. Change in ductile–brittle transition temperatures from Izod impact studies of copolymers with increasing CHDM content.[12]

concluded that the secondary relaxation of PMMA is not purely a side group motion but is coupled to the main chain, and hence to the bulk. Although the main-chain motion does appear to contribute to the secondary relaxation substantially, its contribution is not large enough to promote as much ductility in PMMA as in the case of polycarbonate. At room-temperature, PMMA is considered to be a brittle polymer relative to polycarbonate. However, at temperatures greater than 60 °C, PMMA exhibits significant ductility.

The above examples illustrate the fact that the mere occurrence of secondary relaxations is insufficient to ensure ductile behavior in glassy polymers. An understanding of how molecular motions associated with the secondary relaxation contribute to the shear yielding process is needed. Thus, it becomes even more apparent that the nature, extent, and effects of such motions be well defined in order to examine their relevance to shear yielding. It has been shown that, for a series of ductile copolyesters based on poly(ethylene terephthalate) (PET) and poly(1,4-cyclohexylenediemethylene terephthalate) (PCT), the ductile–brittle transition temperature from Izod impact tests (Figure 1)[12] shifts to lower temperatures as the copolymers become more PCT-like. This is an obvious case where a systematic change in the chemical structure has facilitated the polymer's shear yielding process. We chose then to study the origin of the secondary relaxation motion of this series to further our understanding of its relationship to shear yielding. In this paper, we are interested in determining the changes in molecular motion that result directly from the variation in chemical structure of these copolymers.

Relaxation Studies of PET and PCT

The secondary relaxation of PET has been studied for nearly half a century with a majority of investigations concentrating on the effects of crystallinity and orientation on the relaxation. The relaxation we are interested in is the one associated with the DMS peak of PET located at approximately −70 °C at 1 Hz. Following convention, we will refer to this relaxation as the γ relaxation or simply the secondary relaxation. In this section, we will briefly review the results of previous investigations of the secondary relaxations of amorphous PET and PCT. Because we are working with glassy polymers, we will not include those studies examining the influence of crystallinity or drawing.

Reddish[13] conducted dielectric studies on wet and dry PET and attributed the secondary relaxation to reorientation of the terminal −OH groups in the noncrystalline phase of the material. His conclusion was based on his calculations of the hydroxyl content from the magnitude of the secondary loss peak. The dielectric estimates for wet and dry PET agree fairly well with infrared measurements of the hydroxyl content. The activation energy of the low-temperature process was calculated at 12.4 kcal/mol. However, if the secondary relaxation were indeed the result of the terminal −OH groups, a molecular weight dependence of the data should be evident. Secondary relaxations are generally independent of the degree of polymerization. This directly refutes Reddish's arguments.

Broad-line ^{1}H NMR studies of PET[14,15] revealed only a gradual reduction in the second moment (derivative of the NMR absorption against magnetic field) with increasing temperature in the range of the secondary relaxation. The decrease indicated very small and restricted molecular motions and was interpreted as consistent with a hindered rotation of the methylene groups about the C−C bond. These rotations are considerably more restricted than those of the methylene groups in polyethylene. In a subsequent study, the dynamic mechanical spectra of a series of poly(methylene terephthalate) polymers[16] were investigated. This study revealed that increasing the number of methylene units resulted in a decrease in the secondary loss peak temperature. In addition, it was noted that the shape of the loss peak was asymmetric and reversed itself through the series, i.e., the peak became steeper on the low-temperature side with increasing numbers of methylene groups. In fact, in the case of poly(nonamethylene terephthalate) a definite shoulder appeared on the high-temperature side, implying the presence of another loss peak with a different activation energy. Similar results were reported for poly(*n*-propylene terephthalate)[17] which exhibited an additional peak on the low temperature side of the secondary loss peak. These results suggest that the secondary relaxation may actually be composed of two loss processes superimposed on each other. Farrow and co-workers correlated these results with the NMR study above and concluded that only very small molecular motions could occur in the temperature range of the secondary relaxation and that these motions are associated with the aliphatic portion of the chain. In addition, they believed that more extensive motions involving the phenylene rings occur at temperatures approaching the glass transition.

Illers and Breuer[4] found that as the water content in PET increased to 1.2 wt %, not only did the temperature of the shear loss peak decrease, but the shape of the peak changed as well. The low temperature shoulder was no longer visible. The high-temperature side of the peak, however, remained unchanged. They suggest that the presence of water influences the COO groups, a reasonable deduction considering the dipolar nature of carboxyl groups. Therefore, they postulate that the secondary relaxation involves motions of the carboxyl groups as well. In fact, Illers and Breuer also propose that the observed secondary relaxation is composed of a superposition of more than one relaxation peak. In an attempt to better resolve the asymmetric features of the loss peak, they calculated the slope of the shear modulus versus log(frequency) curves taken at 1 cycle/s and different temperatures, i.e., $(\partial G'/\partial(\log f))_T$, and plotted it against temperature. The plot resolved three peaks at −165, −105, and −70 °C. The small −165 °C peak was attributed to the hindered rotations of the methylene units and the more substantial −105 and

−70 °C peaks to the motions of the −COO− groups with a distinction made between their association with the trans or gauche $O{-}CH_2{-}CH_2{-}O$ conformations, respectively. In addition, they calculated an activation energy of 17 kcal/mol for the secondary relaxation of dry PET. A similar treatment of the data was given by Armeniades,[18] who calculated the slope of the shear loss modulus versus temperature, $\partial G''/\partial T$, and plotted it against temperature. The inflection points were used to locate the peaks of the component relaxations; three components were found with peak temperatures near −163, −117, and −67 °C. Following the assignments made by Illers and Breuer above, Armeniades also associated the peaks to glycol and carboxyl group motions. The activation energy calculated was near 16 kcal/mol.

In the above cases, the larger resolved peaks, which account for the majority of the complete relaxation loss peaks have been assigned to the −COO− groups. However, as the fraction of gauche conformations decreases by induced isomerization to trans conformations during uniaxial drawing, the shape of the secondary relaxation has been shown to remain broad and asymmetric.[19] This implies that the separate contributions from the localized motions of the trans or gauche glycol units are not significant in themselves. Moreover, by deconvoluting the data into several peaks, the above researchers make the underlying assumption that the secondary relaxation consists of several separate and independent motions of each of the molecular linkages. This assumption was made without any direct evidence, and it clearly does not admit to the possibility that any cooperativity exists. It is feasible that in the secondary relaxation of PET, being another heteroatom main-chain polymer like BPA−PC, the motions of the different molecular moieties or even segments may very well be correlated to each other and possess some degree of cooperativity.

Sacher[20] observed a loss peak with a low-temperature shoulder when he probed the secondary relaxation of biaxially oriented PET by dielectric tests. By using molecular models, Sacher noted that dipolar orientations were not possible without the cooperative movement of the adjoining segments. Sacher[21] later proposed that the movements are not those of restricted rotations, as previously suggested, but are actually "normal modes" of vibration-like motions. On the basis of an infrared normal-mode analysis of the glycol linkages of PET which focused on the wagging and rocking vibrations of the trans and gauche conformations, he concluded that the electric field induces similar wagging of the dipoles which can only be accommodated by cooperative motions of adjacent segments. Despite his findings, he recognized the difficulty in making comparisons between the secondary relaxation probed by dynamic mechanical tests and those probed by dielectric tests.[22] For example, although the dynamic mechanical spectrum for amorphous unoriented PET showed signs of being composed of several overlapping peaks, only a single, inseparable dielectric loss peak was observed for the same case. Moreover, Sacher calculated activation energies from the dielectric tests and found values approximately 10 kcal/mol higher than for those found from dynamic mechanical studies.

Although the sets of data are difficult to compare, the possibility of cooperative motion cannot be dismissed. Tatsumi et al.[23] attribute the dielectric relaxation to local relaxational modes, i.e., the torsional vibrations of the main chain in the neighborhood of its local equilibrium conformation. Furthermore, the torsional vibrations of the motional units along the main chain are limited to a given correlation distance. They attempted to determine the correlation distance by comparing dielectric measurements of PET, poly(ethylene isophthalate), and copolyesters of the two. They found that normalized plots of the measured loss gave identical peaks for all the samples regardless of the isophthalate content. The activation energies calculated were similar for all (13.6 kcal/mol). From these findings, they concluded that the relaxation is characterized by the molecular structure between the aromatic groups and is not affected by the motions of the phenylene groups. In other words, the motional unit extends only over part of a single monomer.

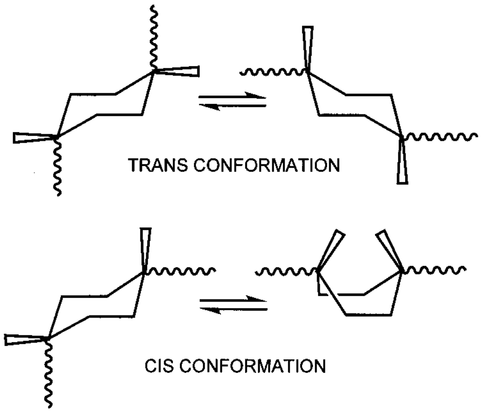
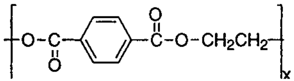
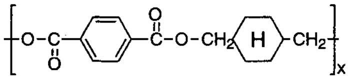
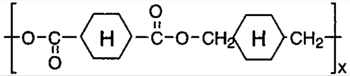
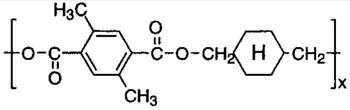


Figure 2. Schematic of possible conformations for *trans*- and *cis*-1,4-cyclohexylene linkages.

Compared to PET, relatively few studies have examined the secondary relaxation of PCT. Reddish[24] compared the dielectric losses between PET and PCT, although without making any motional assignments for the losses. He found the PCT loss peak to be slightly higher in temperature and slightly lower in magnitude compared to PET at 60 cycles/s. The activation energy for PCT was calculated at 13.2 kcal/mol.

It is possible for the cyclohexylene ring in the PCT repeat unit to exist in a chair or boat conformation depending on whether it is substituted axially or equatorially. If the substitutions are both axial or both equatorial, the cyclohexylene ring is in the trans configuration (Figure 2). In this case the chair conformation is preferred, specifically the diequatorial chair conformation. If one substitution is axial while the other is equatorial, the cyclohexylene ring takes on the cis configuration, which can exist either in the boat or chair conformation. The differences between cis and trans configurations of the cyclohexylene ring on the dynamic mechanical response of PCT were investigated by Hiltner and Baer.[25] They also compared the results to PET. The logarithmic decrement measured from their torsion pendulum experiments exhibits significant differences. PCT with all-cis configurations shows a narrow peak at −73 °C while the all-trans counterpart exhibits a broader peak at −100 °C (1 Hz for both). The logarithmic decrement of PCT with a molar ratio of trans to cis configurations of 68:32 shows an asymmetric peak at −73 °C with a trace of a low-temperature shoulder. Hilter and Baer treat the latter peak as a composite peak and resolved it into cis and trans components. They further conclude that the additivity of the trans and cis processes imply that they occur

Table 1. Molecular Weights and Molding Temperatures

Polymer	Repeat Unit	M_n (g/mole)	M_w (g/mole)	Molding Temp (°C)
PCT/PET				
0/100 (PET)		22,000	42,500	280
3.5/96.5	copolymer based on PCT and PET	25,300	49,900	280
31/69	"	22,700	44,900	250
62/38	"	23,700	46,200	265
81/19	"	22,500	41,800	280
100/0 (PCT)		15,500	30,500	315
PCC		18,000	25,000	250
DM-PCT		24,600	51,700	270

independently and may be associated with motions of a single residue. The similarity in shape and temperature between PCT (with a trans-to-cis molar ratio of 68:32) and PET loss peaks indicate to them that a common mechanism for the secondary relaxations exists. They suggest an analogy between the cis and trans components of the relaxation of PCT to trans and gauche conformations of the methylene bonds comprising the loss peak for PET.

Although many investigations of the secondary relaxation of PET have been conducted, it can be seen from the above studies that the conclusions are inconsistent and that the nature of the relaxation is elusive and complicated. Specifically, there is much controversy regarding the size of and the moieties involved in the moving segments comprising the secondary relaxation. A study of a homologous series of polyesters with known systematic structural variations is needed to resolve some of these inconsistencies. This study of PET, PCT, and their copolyesters is of special interest from the viewpoint of molecular motion. The change in ductility apparently is due to the inclusion of the cyclohexane ring into the main chain. We are aware of no study of the secondary relaxation of PCT that specifically delves into the motions contributed by the ring. For this reason, we intend to examine the secondary relaxation from a motional viewpoint and to attempt to determine how the motion of the ring influences chain mobility. We focus on amorphous polymers only in the present study, so as to remove complicating effects of crystallinity on molecular motion. We will explore the dynamic mechanical response of PET and PCT and their copolymers to determine the effects of the cyclohexylene ring on the γ relaxation. To verify the existence of conformational transitions of the cyclohexylene rings, we will also examine motions of specific carbons of the ring by solid state ^{13}C NMR. On the basis of these results, we will begin to address the issue concerning molecular motion and cooperativity in the copolyesters.

Experimental Section

Dynamic Mechanical Experiments. (1) Materials. A series of random, amorphous copolyesters derived from dimethyl terephthalate and ethylene glycol and/or 1,4-cyclohexylene dimethanol (CHDM) were used in this study. The copolymers were based on PET with the following increasing mole percentages of the diol CHDM: 3.5, 31, 62, and 81 mol %. In the case of the PCT, the homopolymer had 100 mol % CHDM. The cyclohexylene rings in the copolyesters and in PCT had a trans to cis molar ratio of 68:32. The materials were supplied by Eastman Chemical Co. in the form of pellets and were confirmed by them as random copolymers by their NMR results. Another amorphous polymer, poly(1,4-cyclohexylenedimethylene 1,4-cyclohexylenedicarboxylate) (PCC), had a trans-to-cis molar ratio of 95:5. PCC was also supplied by Eastman Chemical Co. in the form of injection molded bars. Last, poly(1,4-cyclohexylenedimethylene 2,5-dimethylterephthalate), a PCT derivative which we refer to as DM−PCT, was synthesized in our laboratory, as described in the synthesis section. The molecular weights of the materials used for DMS were determined by GPC as PET equivalents at Eastman Chemical Co. These and the repeat-unit structures of the polymers are given in Table 1.

(2) Sample Preparation and DMS Testing Conditions. Amorphous films of the polyesters were made for DMS. Pellets were first dried in a vacuum at 120 °C for 24 h. The samples were prepared by compression molding the dried pellets into films of thickness of 0.1 mm and then quickly quenching them to obtain amorphous films. The compression molding temperature used in each case is given in Table 1. All the films were optically clear and were confirmed to be amorphous by wide-angle X-ray scattering (data not presented here). The films were cut giving rectangular strips of 5 mm width and 10 mm gage length. The DMS tests were performed using a Polymer Laboratories DMTA MkIII instrument in tensile mode. A peak-to-peak strain of 0.226% was applied at frequencies of 0.3, 1, 10, and 30 Hz. The specimens were run in an iso-step mode from −140 to +50 °C in 5 °C intervals with cooling achieved by a liquid nitrogen cooling accessory. The specimens were held for 3 min at each temperature interval to allow for thermal equilibration.

Solid State ^{13}C NMR Experiments. (1) Materials. Sodium 1,4-cyclohexylene dicarboxylate (trans:cis of 40:60) and poly(cyclohexyl methacrylate) (PCMA) were used as standards. The latter represented the case where the cyclohexyl groups were mobile and was synthesized in our laboratory, as described in the synthesis section. The sodium 1,4-cyclohexylene dicarboxylate was made by reacting 1,4-cyclohexylene dicarboxylic acid supplied by the Aldrich Chemical Co. with a stoichiometric amount of NaOH. This crystalline standard represented the immobile case for the cyclohexane ring. The PET, PCT, and copolymers used were the same as those for DMS above.

(2) Sample Preparation and ^{13}C NMR Spectrometer. Amorphous disks of the polyesters for ^{13}C NMR were made by first drying pellets in a vacuum at 120 °C for 24 h. The disks were prepared by compression molding the dried pellets in a stainless steel mold at the same temperatures used above for film preparation for DMS (Table 1) and then quickly quenching the mold in ice-cold water. The flat faces of the disks were then sanded to remove any mold-release agent and to ensure that flat, smooth surfaces were obtained. The disks were 8.636 mm in diameter, approximately 2 mm in thickness, and were optically clear. The NMR samples of the standards were cold-pressed powders. The salt standard was lyophilized for several days prior to pressing.

Cross-polarization magic-angle spinning ^{13}C NMR spectra of the copolymers were obtained on a home-built spectrometer based on a 12-in. iron magnet with a proton operating frequency of 60 MHz. Half gram samples were spun in a double-bearing rotor at 1859 Hz. The long-term stability of the spinning speed was ±1 Hz. Carbon dipolar line shapes were characterized by dipolar rotational spin−echo (DRSE) ^{13}C NMR.[26] This is a two-dimensional experiment in which, during the additional time dimension, carbon magnetization is allowed to evolve under the influence of H−C coupling while H−H homonuclear couplings are suppressed by using the MREV-8 pulse sequence. The cycle time for the homonuclear decoupling pulse sequence was 33.6 μs. Sixteen MREV-8 cycles fit exactly in one rotor period. Isotropic ^{13}C chemical shifts were refocused by a ^{13}C π pulse after the first rotor cycle (pulse sequence for dipolar rotational spin−echo ^{13}C NMR experiment shown in ref 27). A 16-point Fourier transform of the time dependence of the intensity of any peak resolved by magic-angle spinning in the chemical-shift dimension yielded a 16-point dipolar spectrum, scaled by the MREV-8 decoupling and broken up into sidebands by the spinning. All NMR experiments were conducted at room temperature.

Synthesis. (1) Poly(1,4-cyclohexylenedimethylene 2,5-dimethylterephthalate). A 10 g (51.5 mmol) sample of 2,5-dimethylterephthalic acid purchased from Chem Service, Inc. and 270 mL of hexamethylphosphoramide were placed in a three-neck flask, equipped with a mechanical stirrer. The mixture was stirred at room temperature until all the 2,5-dimethylterephthalic acid was dissolved. The 25% NaOH (51.5 × 4 mmol) aqueous solution was added into the above mixture gradually under vigorous stirring in order to keep NaOH well dispersed. The reaction was allowed to stay for an hour at room temperature. Then 27.5 mL of CH_3I was added into the reaction mixture. The reaction was continued at room temperature for another 30 min. The above solution was poured into 750 mL of 5% HCl aqueous solution. The solution was extracted with 400 mL of ethyl acetate. The organic layer was then combined and dried with anhydrous sodium sulfate. The product was recrystallized in hexanes for further purification. The overall yield of the reaction is about 87%. The polymerization reaction was carried out in a three neck tube shape vessel equipped with a mechanical stirrer. A 8.7 g (39.1 mmol) sample of dimethyl 2,5-dimethylterephthalate and 22 g (152 mmol) of cyclohexyldimethanol were placed into the vessel. The cyclohexyldimethanol had a trans-to-cis molar ratio of 70:30 and was purchased from Aldrich Chemical Co. It was used without further purification. The mixture was then purged with Argon, and heated gradually by an oil bath. Then 0.25 mL of 1% titanium(IV) isopropoxide (in *n*-butanol) was added while the temperature reached 129 °C. The titanium(IV) isopropoxide was purchased from Aldrich Chemical Co. and was used without further purification. The temperature was then controlled in the range 245−260 °C for about an hour to complete the first stage of the reaction. A vacuum was applied to the reaction mixture gradually by slowly reducing the flow rate of Ar gas. In the meantime, the temperature was raised. The excess amount of cyclohexyldimethanol was driven out of the vessel in about 15 min. The polymer melt was allowed to stay at 285−300 °C for another 30 min.

(2) Poly(cyclohexyl methacrylate). A 20 g (119 mmol) sample of cyclohexyl methacrylate purchased from Aldrich Chemical Co. was placed in a dropping funnel along with 0.25 g of AIBN dissolved in 50 mL of toluene. The dropping funnel was attached to a three necked flask equipped with a mechanical stirrer, and the entire system was flushed with N_2 for the duration of the polymerization. Approximately one-third of the solution was allowed to drip into the flask and was heated with stirring and maintained at 80 °C for about 1.5 h. The remainder of the solution was added over a 3 h period and maintained at 90 °C for an additional 3 h. The reaction mixture was poured into 500 mL of methanol, and a white precipitate was obtained. The precipitate was filtrated, washed with copious amounts of methanol, and dried in a vacuum at 80 °C overnight. The final yield was 63%. The T_g of PCMA measured by DSC was 106 °C.

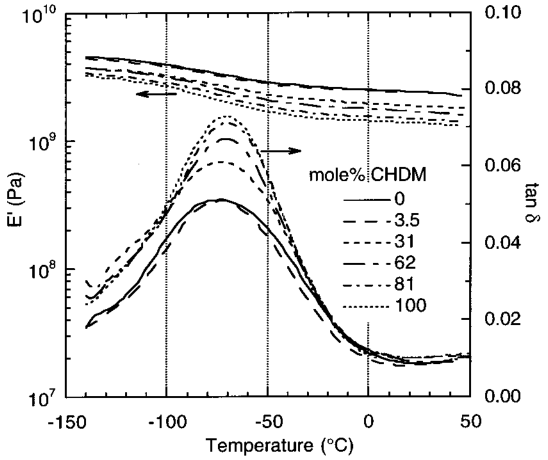


Figure 3. γ relaxation from DMS of PET/PCT copolymers at 1.0 Hz.

Results and Discussion

The Effect of the Cyclohexylene Ring on Dynamic Mechanical Behavior. In this section, the dynamic mechanical responses of PET and PCT and their copolyesters are examined to determine the effects of the cyclohexylene ring on the γ relaxation. In Figure 3, the DMS of the polyesters at 1 Hz are compared. For the temperature range tested, a single relaxation peak is seen for each polymer. The testing temperature did not exceed 50 °C due to the significant amount of creep experienced by the tensile specimens above this temperature. The tan δ peaks are very similar on the high-temperature side but differ in magnitude at the peak and on the low-temperature side. Also, the tan δ peak temperature increases only slightly from approximately −75 °C for PET to −70 °C for PCT. The asymmetry of the peaks are similar to those observed by the previous investigators mentioned above. Specifically, the peaks are all broader on the low-temperature side and steeper on the high-temperature side. Moreover, the asymmetry is accentuated as increasing numbers of cyclohexane groups are incorporated into the chain backbone. This is in accordance with the explanation given by Illers and Breuer[4] that the low-temperature side of the peak is associated with the glycol segments. The fact that the loss peak is asymmetric implies that more than one process is occurring. In fact the noticeable increase in breadth and height of the loss peaks with increasing CHDM content indicates that multiple processes and greater numbers of moving units are giving rise to the relaxation. Alternatively, the CHDM units may have stronger intermolecular coupling which could also give rise to a broader relaxation peak. In either case, Illers and Breuer also suggest that the motion of the chain is composed of independently moving units. We will address this notion later in this paper.

The testing frequency and peak temperature of the γ peaks follow an Arrhenius relationship from which the activation energies are determined (Table 2). The γ relaxation activation energy for PET is 11.2 kcal/mol,

Table 2. DMS Activation Energies of the γ Relaxation of PET/PCT Copolymers

PCT/PET	E_{act} (kcal/mol)	PCT/PET	E_{act} (kcal/mol)
0/100	11.2	62/38	13.4
3.5/96.5	13.3	81/19	13.9
31/69	14.0	100/0	15.5

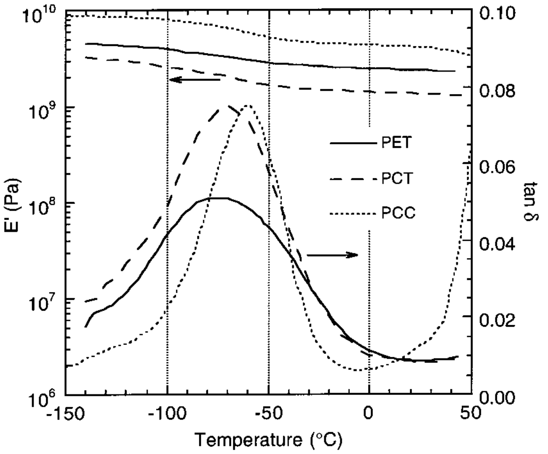


Figure 4. γ relaxations from DMS of PET, PCT, and PCC at 1.0 Hz.

which is comparable to those calculated in previous studies. We attribute any differences to specimen preparation and different testing conditions. The γ relaxation activation energy for PCT is 15.5 kcal/mol, and those for the copolymers are intermediate of the homopolymers. The similarities in activation energies, tan δ peak positions, and the shape of the peaks seem to support Hiltner and Baer's assertion that the motions of PET and PCT have a common mechanism for the secondary relaxation.[25] However, if that were the case and we assume the γ relaxation to be correlated with large strain mechanical behavior, then there should not be such large differences in mechanical properties, such as the ductile−brittle transition temperature. Therefore, we believe that the cyclohexylene ring should impart some motion to the polymer chain, but how this occurs without greatly increasing the activation energy of the γ relaxation needs to be understood.

The dynamic mechanical spectrum of PCC is given in Figure 4. Compared to those of PET and PCT, the loss peak of PCC is narrower and occurs at −60 °C when tested at 1 Hz. Both the PCT and PCC peaks are prominent, similar to the secondary relaxation of poly(cyclohexyl methacrylate) (PCMA) studied by Heijboer.[28,29] In his investigations of PCMA, Heijboer found a very sharp secondary loss peak at −75 °C at 1 Hz which he specifically attributed to motions of the cyclohexyl ring. He tested his hypothesis by making a methyl substitution onto the ring at the 4-position and then finding the loss peak suppressed. In fact replacement of the cyclohexyl ring with the immobile, planar phenyl ring eliminated the peak altogether. The similarities in the loss peaks between PCMA and PCC led us to believe that the motions responsible for the PCC loss peak involve the main-chain cyclohexylene rings. Because there are two cyclohexylene rings per repeating unit in PCC, it is conceivable that concerted movements of the rings are possible. The observations that the peak is considerably narrower than the PCT peak (Figure 4) suggest that the motion may be more specific and more independent of ongoings of other units along the chain. The fact that the peak temperature of PCC is higher than that of PCMA at 1 Hz (−60 and −75 °C, respectively) can be explained by noting the position of the cyclohexane ring in each case. The cyclohexane ring is bonded to the main chain in the 1- and 4-positions in the former case while in the latter case it is only a pendant group attached at one end. It is reasonable that the restriction of the rings in the main chain should result in a greater thermal energy for excitation. The activation energy for the γ relaxation of PCC is 15.8 kcal/mol, which supports this contention.

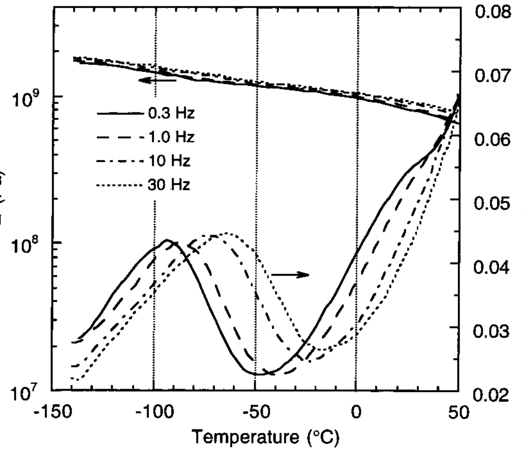


Figure 5. Secondary relaxation peaks from DMS of DM−PCT at 1.0 Hz (upper temperature relaxation peak is further resolved in Figure 6).

Because the dynamic mechanical loss peak of PCC at 1 Hz occurs in the same temperature range as PCT (Figure 4), it is possible that cyclohexylene motions are occurring in PCT. If we assume that the loss peak of PCT consists of two components, i.e., motions from the dimethyl cyclohexylene portion and motions of the terephthalate portion (the −COO motions suggested by Illers and Breuer), then the cyclohexylene loss peak may be obscured by the presence of the terephthalate peak. In other words, the motions of the chain, excluding contributions from the cyclohexylene ring, occur at the same temperature as the motions of the cyclohexylene ring. On the basis of the assumption that the two motions are independent, it would be to our advantage to separate the loss peaks associated with these two motions. We accomplish this by following the example set by Bussink and Heijboer.[30] By introducing methyl substituents to the phenylene rings of the terephthalate groups of aromatic polyesters, they were able to shift the secondary relaxation peak from −80 to +60 °C at 1 Hz. Likewise, by attaching bulky substituents to the phenylene rings of PCT, we hope to shift the terephthalate loss peak contributions to higher temperatures thereby exposing the remaining cyclohexylene loss peak. To this end, we examined the dynamic mechanical response of DM−PCT in which the phenylene rings are modified by methyl substitutions in the 2 and 5-positions. From the dynamic mechanical spectra of DM−PCT given in Figure 5, evidence of a second, higher temperature peak emerges. So as to remove any possibility that the peak may be due to structural relaxation, we tested DM−PCT in this upper temperature range again but only after annealing the film for 12 h at 65 °C. Because the β relaxation in some glassy polymers is believed to be the result of the relaxation

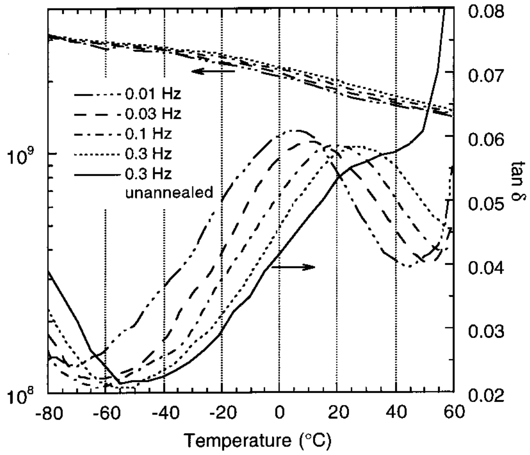


Figure 6. Upper temperature 2,5-dimethylterephthaloyl relaxation peak from DMS of annealed DM−PCT.

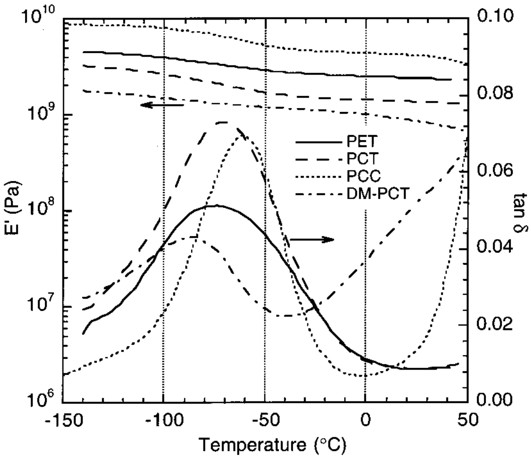


Figure 7. γ relaxations from DMS of PET, PCT, PCC, and DM−PCT at 1.0 Hz.

of residual stress or orientation from molding or drawing of the specimen,[4,31] annealing at temperatures just above T_β will relax the residual stress and remove any orientation. If the β relaxation is due to residual stress, its magnitude can be decreased, or the peak can be erased altogether by annealing. Last, at the frequencies given in Figure 5, the higher temperature peak of DM−PCT occurs at temperatures near its T_g. We wish to resolve better this peak from its T_g which can be accomplished by testing at much lower frequencies. The dynamic mechanical spectrum for annealed DM−PCT is given in Figure 6. By using frequencies ranging from 0.01 to 0.3 Hz and by annealing the specimen, we were able to successfully separate this higher temperature secondary relaxation from its T_g and ensure that the peak is not due to processing effects. The 0.3 Hz spectrum from Figure 5 is included in Figure 6 to demonstrate that annealing above the peak temperature and below T_g can successfully resolve the peak.

The fact that DM−PCT exhibits two separate secondary relaxation peaks indicates that the motions responsible for these peaks are separable. The shift to higher temperatures due to the methyl substitution indicates that this peak involves motions of the phenylene ring. Moreover, the motions are likely to involve the ester groups as well. Further elaboration on the terephthalate motion is given later in this paper. At this point, it is sufficient to note that the higher temperature relaxation peak involves motions of the terephthalate linkage. Likewise, in PCT, PET, and the copolyesters, a portion of their secondary loss peaks is attributed to the motions of the terephthalate groups. In PET the motion of the terephthalate group is probably dominant. In the other polyesters the remaining portion is then likely to result from the motions of the aliphatic linkages. A composite figure of all the spectra is given in Figure 7. The low-temperature relaxation peak of DM−PCT occurs at a lower temperature and has a smaller magnitude than the PCC peak. Nevertheless, the low temperature relaxation peak of DM−PCT closely resembles that of Heijboer's PCMA in both the peak temperature and the activation energy, indicating that it most likely also involves cyclohexylene motion. The PCC peak occurs at a higher temperature than the DM−PCT peak which can be explained as follows. Because there are two cyclohexylene groups per repeat unit in PCC, the motions of these rings are likely to be highly coupled. This might give rise to larger amplitude and more extensive motions which would require greater thermal energy for excitation. Evidence for the larger amplitude motions can be found in the greater relaxation strength of the secondary relaxation peak. This explanation is not to say that motions of the cyclohexylene groups in DM−PCT cannot be coupled. The amplitude of these motions is much less than those in PCC because of the greater distance between cyclohexylene rings.

If the cyclohexylene ring is capable of undergoing conformational transitions in DM−PCT (and therefore in PCT), as we suggest, then the low-temperature peak observed in the secondary relaxation is likely the manifestation of this motion. The fact that the dimethyl substitution of the phenylene rings does not completely hinder the motion of the cyclohexylene rings suggests that either the ring motion occurs independent of adjacent linkages or the amplitude of the ring motion is sufficiently large to overcome the increased bulk of the phenylene units. Since independent cyclohexylene ring motion is unlikely, as we explain later, the latter explanation is more reasonable. If the cyclohexylene motion is activated at low temperatures, such a motion could explain the decrease in the ductile−brittle transition temperature as the cyclohexylene concentration increases. It becomes necessary for us to verify that the cyclohexylene ring is indeed in motion at temperatures above the secondary relaxation. Confirmation can be made by examining the motions of specific carbons of the ring.

Motions of Cyclohexylene Carbons by Dipolar Rotational Spin−Echo NMR. If the dipolar coupling between carbons and directly attached protons is measured using dipolar rotational spin−echo ^{13}C NMR,[32] comparisons can be made of the amplitudes of molecular motions faster than 10 kHz at 300 K. We compared DRSE results of PET, PCT, and two of the copolymers with standards in which the cyclohexylene rings are either mobile or immobile to evaluate whether the cyclohexylene rings in the homopolymers and copolymers are undergoing any motion. The standard representing the case of little or no mobility of the ring is sodium 1,4-cyclohexylene dicarboxylate. Because of its crystallinity, little motion of the cyclohexylene ring is expected. The standard representing facile cyclohexyl chair−boat−chair motion is PCMA, where the cyclohexyl ring is tethered to the end of an ester side group. As mentioned previously, the sharp secondary loss peak

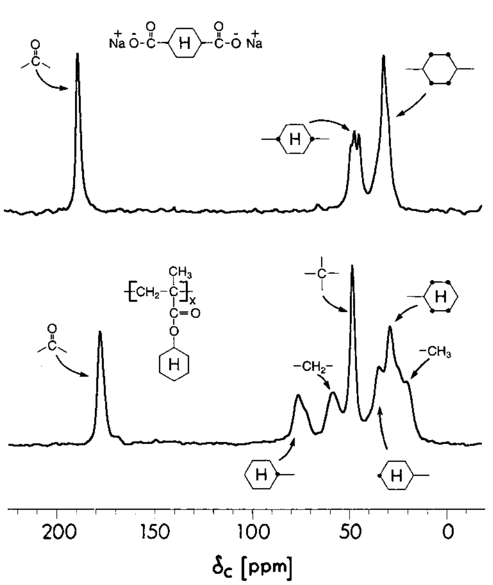


Figure 8. ^{13}C NMR spectra of the salt standard (top) and PCMA (bottom).

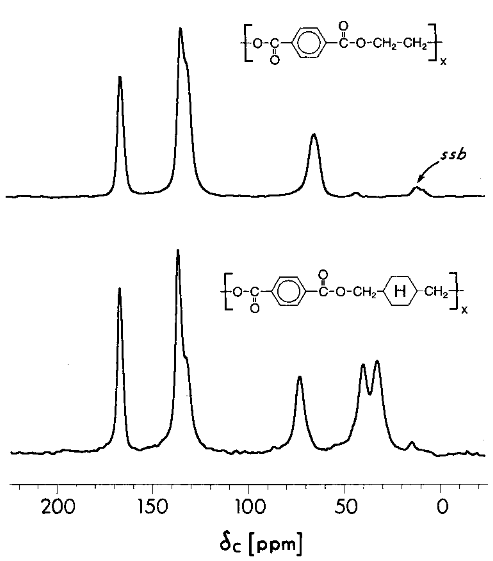


Figure 9. ^{13}C NMR spectra of PET (top) and PCT (bottom).

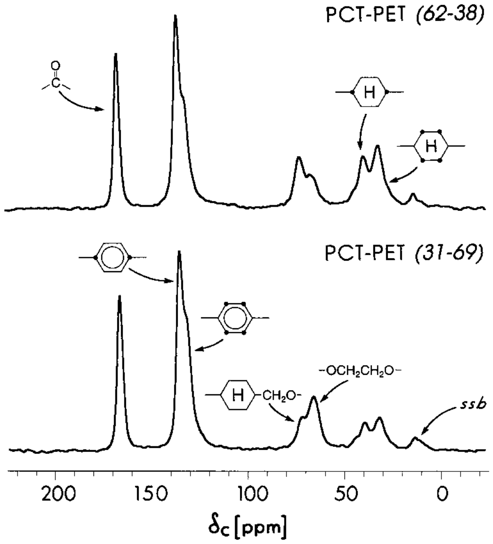


Figure 10. ^{13}C NMR spectra of copolyesters with 62 mol % CHDM (top) and 31 mol % CHDM (bottom).

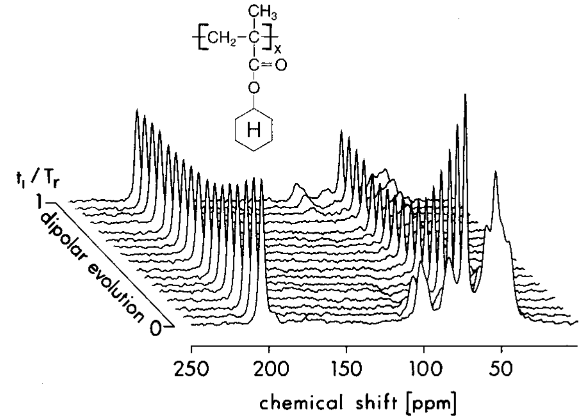
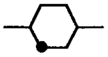
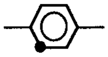
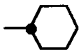
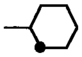
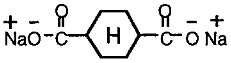
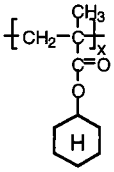


Figure 11. Dipolar modulation of PCMA.

of PCMA was attributed to motions of the cyclohexyl ring by Heijboer.[28,29] The nature of the cyclohexyl motion was also investigated by Heijboer. By comparing the dielectric loss between PCMA chloro-substituted in the 4-position of the cyclohexyl ring and that chloro-substituted in the 2-position, he demonstrated that the loss peak was the result of chair–chair transitions and not simply chair–boat transitions. In the chair–chair transition, the C–Cl dipole in the 2-position changes its spatial orientation to a much greater extent than that in the 4-position; the opposite holds true for a chair–boat transition. Heijboer found that the dielectric loss of the polymer substituted in the 2-position had a cyclohexyl loss peak amplitude about 3 times higher than that substituted in the 4-position. This increase in peak height is expected for a chair–chair transition where the C–Cl dipole in the 2-position changes from an axial to equatorial position and vice versa. In addition, the activation energy of the secondary relaxation of PCMA was calculated by Heijboer to be 11.3 kcal/mol which agrees well with that found from NMR measurements for the chair–chair transition (11.4 kcal/mol). Thus, he concluded that the motion of the cyclohexyl group involves a chair–chair transition in PCMA.

The ^{13}C NMR spectra of the standards, the homopolymers, and the copolymers are shown with line assignments in Figures 8–10, respectively. If Fourier transforms are taken of the centers of lines of interest with respect to the dipolar modulation time (Figure 11), dipolar line shapes are obtained, broken up into sidebands separated by the spinning frequency of 1.859 kHz. The ratio of intensities of the second to the first spinning sideband (n_2/n_1) has been shown to be a sensitive measure of the averaging of H–C dipolar coupling by molecular motion.[33,34] The sideband intensities of the standards and the polyesters are given in Table 3. For the singly protonated cyclohexylene carbon (referred to hereafter as C_1) and the doubly protonated cyclohexylene ring carbon (C_2) of the salt standard, n_2/n_1 are 1.31 and 0.93, respectively. This ratio has been shown to change from 1.3 for systems with little motion to 0.5 for systems with substantial motion for singly protonated phenylene carbons.[34] For the singly protonated cyclohexylene carbon, an n_2/n_1 of 1.31 indicates it is static in the salt. For PCMA, n_2/n_1 values are 0.78 and 0.64 for C_1 and C_2 respectively. Comparisons with sideband ratios of the salt indicate that both C_1 and C_2 in PCMA undergo larger amplitude motions than in the salt. These are consistent with Heijboer's contention

Table 3. Ratio of Intensities of Second to First Dipolar Rotational Sidebands

		n_2/n_1				
polymer	structure					
Salt		1.31	0.93	----		
PCT/PET						
0/100	see Table 1	----	----	1.36		
31/69		0.96	0.79	0.93		
62/38		0.89	0.72	0.85		
100/0		0.89	0.74	0.78		
PCMA		----	----	----	0.78	0.64

that the cyclohexyl ring in PCMA is capable of chair–boat–chair conformational transitions. The sideband ratios for C_1 and C_2 of the polyesters fall between the values of the standards (Table 3), which indicates more motion of the cyclohexylene ring in the polyesters than the salt, but less than PCMA. This finding is intuitive, considering that the cyclohexylene ring of PCMA is a pendant group. The overlap of the peak for the main-chain methyl substituent with the C_2 peak in PCMA makes it difficult to compare sideband ratios for the C_2 peaks in the polyesters and PCMA. The sideband patterns of C_2 in the polyesters are narrower than those in the salt, however. Typically narrower patterns are observed for carbons with more averaging by molecular motion at a given temperature. This demonstrates the fact that the cyclohexylene rings in the polyesters are indeed undergoing large-amplitude molecular motion at room temperature. As the CHDM content increases from 31 to 62 mol %, n_2/n_1 for C_1 and C_2 decrease. In other words, an increase in the number of cyclohexylene rings along the main chain provides a more extensive motion for the rings themselves. However, increasing the CHDM content from 62 to 100 mol % does not result in any further decrease in n_2/n_1 for C_1 and C_2. Apparently, the amplitude of the motions of the cyclohexylene ring are similar for the copolymer containing 62 mol % CHDM and PCT. The larger amplitude molecular motions of PCT compared to PET were also verified by our initial ^{13}C $T_{1\rho}$ measurements which are sensitive to molecular motions in the 50 kHz regime (data not included in this paper). These relaxation curves were monoexponential and are consistent with the previous data that PCT exhibits larger amplitude motions than PET at 300 K.

With this evidence, we see that the cyclohexylene rings are capable of motion in the main chain of the polyesters. We raise several questions in regard to this motion. For instance, is it feasible for the rings to undergo chair–boat–chair transitions despite being tethered at both ends to the main chain? Moreover, how does this motion affect the main chain, much less the adjacent linkages. We address these questions in the following sections by speculating on possible motions.

Possible Motions of the Cyclohexylene Ring in PET/PCT Copolymers. At this point, it is useful to take a closer look at possible conformations of a cyclohexane ring. The most stable conformation of a cyclohexane ring is the chair conformation. The ring can also take on the boat conformation when it converts from one chair form to another, although the boat form is energetically less favorable. The transition state for the interconversion of two chair conformations is roughly 10 kcal/mol higher and is therefore less stable than that for the chair conformation. The instability of the boat conformation arises from both van der Waals and torsional strain. From Figure 2, it can be seen that the hydrogens in the 1 and 4 positions of the ring sterically hinder each other in the boat form and that the 2,3 and 5,6 C–C bonds have the eclipsed orientation. Both of these strain effects can be partially relieved if the cyclohexane ring takes on a twist–boat conformation. Still, the chair form is the preferred conformation. In fact, at any instant, only 9 out of 100 000 cyclohexanes are in the boat form at 25 °C.[35] In the case of the polyesters, the question that arises is the likelihood that the CHDM linkage undergoes a sequence that converts the ring from one chair form to the other chair form. With the cyclohexane ring incorporated into the polymer backbone, it is uncertain to what extent such conformational transitions occur. It is apparent that the energy barrier between the chair and boat states will be altered significantly for a cyclohexylene ring. In its crystalline form, the cyclohexylene ring in trans-PCT assumes the chair conformation with 1,4 disubstitutions in equatorial positions.[36] Moreover, the rings in crystalline *cis*-PCT are also thought to take on the chair conformation despite the break in collinearity of the chain due to the equatorial and axial substitutions (Figure 2). The chair conformation is the lower energy conformation and is likely to be the dominant form of the cyclohexylene ring in amorphous PCT. As suggested by Hiltner and Baer,[25] the boat form, however, of the *cis*-cyclohexylene ring is not unreasonable. At room temperature (well above the secondary relaxation temperature of PCT), the cyclohexylene ring is capable of other conformations of local energy minima. Heijboer[28] in his early studies suggested that chair conformations in PCMA interchange by way of the higher energy boat conformation with C1 and C4 in the bow and stern positions. Such an interchange is not possible when the cyclohexylene ring is a main-chain unit because of the large amplitude motions required of the C1 and C4 substituents in order to proceed to the boat conformation. However, motions are still possible for main-chain cyclohexylene rings. The possibility of a twist–boat with C3 and C6 (likewise with C2 and C5) in the bow

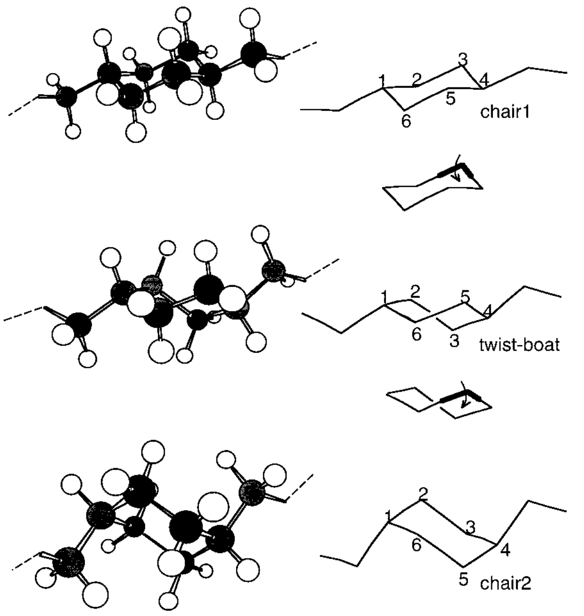


Figure 12. Schematic of possible conformational transitions of the cyclohexylene group in PCT. The transformation of chair1 to chair2 can proceed by way of a twist−boat (2 and 5 positions in the bow and stern) as shown.

and stern positions can be entertained. Figure 12 illustrates possible conformations. A *trans*-cyclohexylene ring is shown in its equatorially substituted chair conformation in the upper portion of the schematic. A downward movement of C3 results in a twist−boat conformation with C2 and C5 in the bow and stern positions (center). The twist relieves steric hindrance between the C2 and C5 axial protons. This twist boat conformation is of higher energy than the chair conformation but nevertheless is a local minimum. The twist−boat may return to its chair conformation whence it came or proceed to the other low-energy chair conformation by means of an downward motion by C5 shown in the lower schematic of Figure 12. The energy difference between the states is not large (less than 5 or 6 kcal/mol) making these motions viable at room temperature. In this scenario even the chair−chair transition is possible in main-chain cyclohexylene rings. Realistically, the motions of the cyclohexylene ring are not likely to follow exactly the regiment depicted in Figure 12. We simply use Figure 12 to demonstrate that such maneuvers are possible. These transitions are also possible in the *cis*-cyclohexylene linkages that reside in the chair conformation. However, it is likely that some of the cis-linkages prefer the boat (or twist−boat) conformation with C1 and C4 in the bow and stern positions; this allows a more extended chain configuration (Figure 2). Motions of the boat are more restricted, probably only consisting of wriggling of the boat to reduce steric hindrance between bow and stern protons. In this manner, *cis*-cyclohexylene linkages in the boat conformation do not contribute significantly to molecular motions of the polymer chain. We do not know, however, what percentage of *cis*-cyclohexylene linkages prefer the boat conformation. The rearrangement of C3 and C5 in Figure 12 gives rise to large changes in the direction of the H−C dipolar trajectories of the doubly protonated cyclohexylene carbons; this is in agreement with our DRSE observations. In addition, the conformational change of the chair to the twist−boat changes the direction of the H−C dipolar trajectories of C1 and C4 as well as of the main-chain methylene units. These changes agree with our DRSE findings for the cyclohexylene carbons and the main-chain methylene carbons (n_2/n_1 is 0.72).

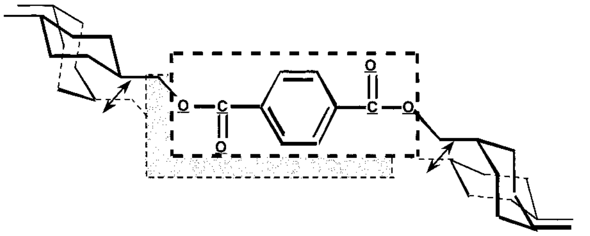


Figure 13. Schematic of cooperative conformational transitions of the cyclohexylene rings and consequential translational motions of the terephthalate linkage.

Cooperative Motions in PET/PCT Copolymers. The effect of cyclohexylene motions on the remainder of the chain is discussed in this section. The chair-to-chair motions of the rings outlined above give rise to small translational motions of adjoining units, namely the terephthalate units. Motions of the terephthalic units are evidenced by flips of the phenylene rings. These flips can be hindered, however, by neighboring molecules. In the case of PET, phenylene ring flips were not observed. DRSE ^{13}C NMR results of quenched PET give no evidence of ring flips at room temperature.[37] This is consistent with n_2/n_1 for the protonated phenylene carbon of PET measured in this study (Table 3). The terephthalate units of PET, although capable of some small amplitude rocking, can be considered as stiff linkages along the chain backbone. In the copolymers the combined effect of the motion of the cyclohexylene units on either side of the terephthalic unit is a translational movement of the latter. The cooperativity of the rings is illustrated in Figure 13 where motions of *trans*-cyclohexylene linkages result in longer-ranged excursions along the chain. When the cyclohexylene rings of adjacent repeat units undergo chair−chair transitions cooperatively (as in the case of PCT), the terephthalate linkage is forced to move also, in a transverse direction to the main chain. As a result, the activation of the cyclohexylene ring motion creates a larger scale motion. In this sense, the molecular motions of PCT are more cooperative and therefore more extensive than those in PET-like copolymers. The cooperativity is evidenced by the general increase in activation energy with increasing CHDM content (Table 2). In PCT, with more segments moving collectively, a higher activation energy is required.

The effect of the cyclohexylene ring on the terephthalic linkage can be observed by phenylene ring flips. The translational motion of the terephthalic unit imposed by the motions of the cyclohexylene ring further reduces steric interactions between phenylene rings and neighboring chains. The result is an increase in phenylene ring flips as evidenced by the decrease in n_2/n_1 from 1.36 to 0.78 for the protonated phenylene carbons as the polyesters become more like PCT. It is evident that the phenylene ring of PCT is capable of a larger range of motion than the corresponding ring in PET. In this sense, the cyclohexylene intramolecular motion affects both intra- and intermolecular interactions.

The cooperative motion of the cyclohexylene ring and the resulting motion of the terephthalate linkages produce local strain and are therefore mechanically detectable by DMS. For example, DM−PCT has two observable secondary relaxation peaks (Figures 5 and 6). The lower temperature peak correlates with the cyclohexylene motion, which gives rise to translational motion of the adjacent segments. However, the dimethyl substitution of the terephthalate group restricts this motion due to its bulkiness. The local volume fluctuations created by the cyclohexylene ring are probably small for DM−PCT. At higher temperatures (higher energy), the increased segmental motions reduce the barriers to terephthalate movement and result in additional local strain. In PCT, the barriers preventing terephthalate excursions can be overcome by the cooperative cyclohexylene motion. Therefore, the terephthalate relaxation peak occurs at much lower temperatures.

It becomes obvious that as the CHDM concentration decreases, the molecular motion of the main chain becomes limited. At this time, the extent of the cooperativity between cyclohexylene rings is unknown. That is, if the number of PET-like units between successive cyclohexylene rings is increased, the ability of the cyclohexylene rings to move the intermediary units collectively becomes increasingly questionable. It seems possible that the relatively soft ethylene linkage in the PET-like units may serve as a motional decoupler. However, if the amplitude of the cyclohexylene motion is significantly large, then these motions can dictate the movement of the next few repeat units. Such a concerted motion will give rise to longer ranged translational excursions along the chain backbone and create larger volume fluctuations. We believe that the molecular-scale motions are key to reducing the resistance to larger scale interchain slippage, which is the molecular description of yielding.

Conclusions

The secondary relaxations by dynamic mechanical spectroscopy of a series of copolymers based on poly(ethylene terephthalate) (PET) and poly(1,4-cyclohexylene terephthalate) (PCT) were found to involve motions of the cyclohexylene rings. The ring is believed to undergo chair-to-chair conformational transitions that can, when moving cooperatively with rings in the adjacent repeat units, induce translational motions of the terephthalate groups. The concerted motion gives rise to longer-ranged translational excursions along the chain which increase molecular volume fluctuations and facilitate macroscopic shear yielding. In our studies of the secondary relaxation, we make comparisons between the secondary loss peaks of the copolymers and poly(cyclohexyl methacrylate). By comparing the peak temperatures and activation energies between these materials, we conclude that the secondary relaxation of the copolyesters is likely to involve conformational transitions of the cyclohexylene ring. In addition, poly(1,4-cyclohexylenedimethylene 2,5-dimethylterephthalate) exhibits two secondary loss peaks, a lower temperature peak very similar in position to the poly(cyclohexyl methacrylate) peak and a higher temperature peak due to the substituted terephthalate linkage. We conclude that these polyesters have aliphatic and terephthalate motions which are separable. These results suggest that the main-chain cyclohexylene unit of these polyesters is capable of motion. Dipolar rotational spin−echo ^{13}C NMR detected large amplitude molecular motions faster than 10 kHz at 300 K of the cyclohexylene rings of the copolyesters and PCT. Both the singly and doubly protonated carbons of the cyclohexylene ring exhibit motion, as well as the main chain methylene groups. These results, along with an investigation of feasible ring conformations, lead us to believe that chair and twist−boat conformational transitions are possible for *trans*-cyclohexylene rings and cis-rings that prefer chair conformations. (Motions of the cis-rings that reside in boat conformations are probably more restricted.) When these transitions occur cooperatively, translational movements of the terephthalate linkages can result and can reduce interactions between phenylene rings of neighboring chains. This is evidenced by the increased motion of the phenylene rings as the copolyesters become more like PCT. The phenylene rings of PET are static at room temperature. The cooperative behavior of the cyclohexylene motions gives rise to a longer range motion along the polymer chain. The increase in activation energy of the secondary relaxation as the cyclohexylene concentration increases in these polyesters supports the notion of large-scale cooperative motion. We believe that the longer ranged molecular motion is important to reducing the resistance to larger scale interchain slippage, which is the molecular description of yielding.

Acknowledgment. This work is funded by Eastman Chemical Co. and by the National Science Foundation (Grants DMR-9422049, DMR-9015864, and DMR-9729734). We thank Dr. Eric Moskala of Eastman Chemical Co. for supplying materials and for valuable discussions.

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MA971671T