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Intrachain Rotations in the Poly(ester carbonates). 2. Quantum Mechanical Calculations on Large Model Molecules Fully Representing Each Type of Phenyl Ring Environment

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ABSTRACT: This paper continues the presentation of the results of a project to relate the properties of bisphenol A (BPA) polycarbonate and of its poly(ester carbonates) (PEC) with terephthalic and/or isophthalic acids to their structure at the molecular level, by use of the techniques of applied theoretical chemistry. Intrachain rotations and rocking motions of the phenyl rings were studied by means of detailed calculations utilizing the PRDDO and AM1 techniques on large molecules fully representing each type of phenyl ring environment. The major conclusions presented in the preceding paper, concerning the motions of the phenyl rings attached to isopropylidene groups and the motions of ester phenyl rings in terephthalic PEC, all remain valid, showing that the judicious use of calculations on smaller molecules is a valid procedure. There is no simple or cooperative low-barrier flipping motion for the ester phenyl ring in isophthalic PEC. In addition, the low-energy oscillation or rocking motion range for the isophthalic phenyl ring is only ±15°, while the range in terephthalic PEC is ±30°. The most complete description of the relaxations observed by dynamic mechanical spectroscopy, which can be obtained by only considering isolated chain segments, is also presented.

Introduction

This paper continues the presentation of the results of a project to relate the properties of poly(ester carbonates) (PEC) to their structure at the molecular level by use of the techniques of applied theoretical chemistry.

The work reported here consists of the continuation of the characterization of the molecular motions associated with relaxations observed by dynamic mechanical spectroscopy (DMS),[1-5] by use of quantum mechanical calculations utilizing the PRDDO[6] and AM1[7] techniques. Intrachain rotations and rocking motions of the phenyl rings were studied by means of detailed calculations on large molecules fully representing each type of phenyl ring environment. The reader is referred to the preceding paper[8] for a more detailed exposition of the problem, including a schematic illustration of the polymers being studied and most of the notation and acronyms being used.

Comparison of the present and the previous[8] results shows that the judicious use of calculations on smaller molecules is a valid procedure. The two sets of results are combined to provide the most complete description of the DMS γ and δ relaxations that can be obtained by considering isolated chain segments. This description is relevant both for the intrachain interactions in the solid

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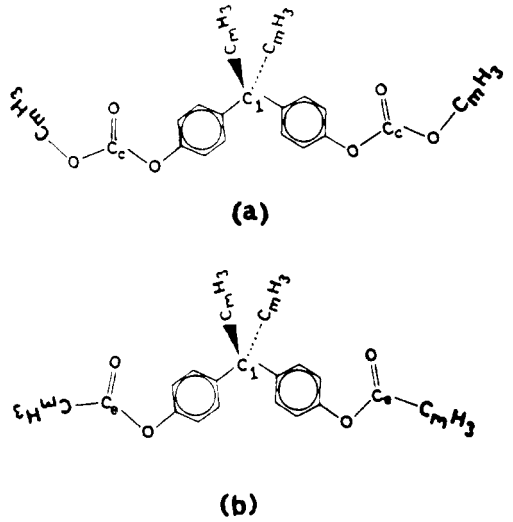

Figure 1. Schematic drawings of (a) the large carbonate (LC) molecule and (b) the large ester (LE) molecule.

polymers and for the dynamical interactions in dilute (up to 10%) solutions of the polymers. In such dilute solutions, intrachain interactions will necessarily dominate over interchain interactions in determining the dynamical processes. By contrast, the relative importance and types of interchain interactions in the solid polymers are complex problems, which will be addressed in the next phase of the project.

The Model Molecules

Generation of Large Model Molecules from Smaller Ones. The simplest model molecules which can be used to study the intrachain rotations in PEC are 2,2-diphenylpropane, diphenyl carbonate, and phenyl benzoate.[8] The results of calculations on several larger model molecules in which the phenyl rings are attached at both ends to the functional groups which provide for the chain continuation in the polymer, instead of being terminated by a hydrogen atom at one end, are summarized in the present paper.

The starting points of the present calculations were the base-point geometries determined for 2,2-diphenylpropane, diphenyl carbonate, and phenyl benzoate.[8] The MOGLI molecular modeling program[9] was used on an Evans & Sutherland PS300 color graphics station to generate the large model molecules of interest by joining portions of these three small model molecules.

Large Carbonate and Large Ester Structures. The larger model molecules chosen to represent the environments of the phenyl rings attached to isopropylidene groups in the carbonate and ester fragments are shown in schematic drawings in Figure 1 and in space-filling drawings in Figure 2. These molecules have been labeled as large carbonate (LC) and large ester (LE), respectively. In these two molecules, the geometries of the isopropylidene group and of the two phenyl rings attached to it were taken to be the same as in 2,2-diphenylpropane. The geometries of the carbonate and ester linkages were taken to be the same as in diphenyl carbonate and phenyl benzoate, respectively. The terminating methyl groups were taken from the structure determined for dimethyl carbonate.[8]

The transition-state geometries of the LC and LE molecules, for rotation of the phenyl rings attached to the isopropylidene group, were obtained by carrying out a synchronous rotation of one phenyl ring by +90° and the other phenyl ring by −90°, about the axis connecting the two C_p atoms in each phenyl ring, and then allowing the geometrical parameters that were reoptimized in previous

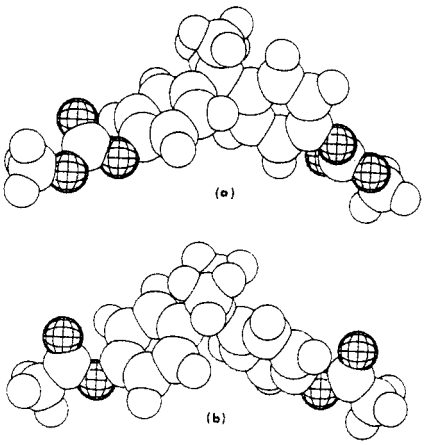

Figure 2. Space-filling drawings of (a) LC and (b) LE.

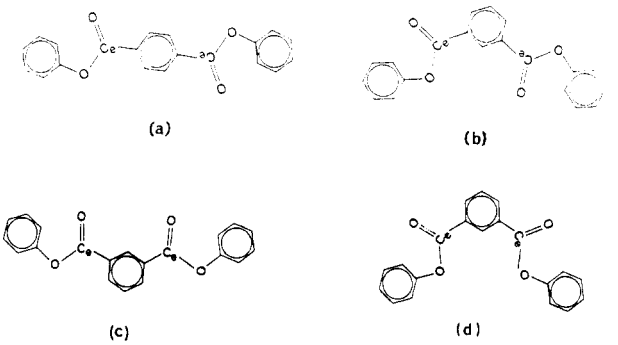

Figure 3. Schematic drawings of the (a) terephthalic (T); (b) isophthalic (I); (c) isophthalic, linear (IL); and (d) isophthalic, kinky (IK) structures.

work[8] during the rotation barrier calculation on 2,2-diphenylpropane to acquire the same values as they did for the transition-state geometry in 2,2-diphenylpropane. This simple procedure makes use of the fact that the largest part of the barrier to phenyl ring rotation is caused by rotation past the isopropylidene group. It only requires a total of four single-point energy evaluations for the LC and LE structures to determine the two rotation barriers, but it can overestimate these rotation barriers. More detailed optimizations of the rotational transition-state geometries are in progress.

Terephthalic and Isophthalic Ester Structures. Many molecular conformations can be used to represent the terephthalic and isophthalic ester structures. These conformations only differ in having (a) the end-point phenyl rings tilted in the same direction or in opposite directions relative to the plane of the central phenyl ring and the two ester linkages; (b) the carbonyl groups of the two ester linkages pointed toward the same side or toward opposite sides of the central phenyl ring; and/or (c) the two end-point phenyl rings oriented relative to the two carbonyl groups in any one of several possible ways. Preliminary calculations showed that these conformational variations make negligible differences in the calculated results. The structures on which detailed calculations were performed, T (terephthalic), I (isophthalic), IL (isophthalic, linear), and IK (isophthalic, kinky), are shown in schematic drawings in Figure 3 and in space-filling drawings in Figure 4. The transition-state geometry obtained by a 90° rotation of the central phenyl ring in the T structure is also shown in Figure 4. Phenyl benzoate, which has no symmetry elements, belongs to the C_1 symmetry point group. On the other hand, the T, IL, and IK structures each have a twofold axis of symmetry and belong to the C_2 symmetry point group. Therefore, the initial T, IL, and IK structures

Table I
Results for the LC and LE Structures[a]

rel energy, kcal/mol		molecular	heat of formatn,	dipole moment,	ionization potential,
PRDDO	AM1	vol, Å^3	kcal/mol	D	eV
		LC, Base-Point Structure			
0.0	0.0	288.23	−173.5	0.313	9.304
		LC, Rotational Transition State Structure			
9.9	4.4	286.93	−169.1	0.293	9.303
		LE, Base-Point Structure			
0.0	0.0	274.12	−96.8	2.464	9.183
		LE, Rotational Transition-State Structure			
10.4	4.6	272.67	−92.2	2.498	9.156

[a] See Figure 1 for schematic drawings and Figure 2 for space-filling drawings. Notation: LC = large carbonate; LE = large ester. Relative energies have been calculated both with PRDDO and with AM1. Molecular volumes have been calculated with CHEMLAB-II. Heats of formation, dipole moments, and ionization potentials have been calculated with AM1.

obtained by joining together portions of phenyl benzoate molecules were symmetrized to C_2. The two C_e–C_p bond lengths were reoptimized in each calculation on the T, I, IL, and IK structures, resulting in very small changes in bond lengths and relative energies.

Details of Calculations

Quantum mechanical calculations were carried out by the partial retention of diatomic differential overlap (PRDDO) technique.[6] Molecular volumes were calculated by using the SPACE program in the CHEMLAB-II software package.[10] In addition, the AM1 program in the MOPAC software package[7] was calibrated by performing AM1 calculations on the same molecular geometries and comparing their results with the PRDDO results. All the calculations were carried out on VAX 8600 and VAX 11/785 computers.

Results

The most important results of the PRDDO, AM1, and CHEMLAB-II calculations are summarized in Table I for LC and LE and in Table II for T, I, IL, and IK. The rotational angles, relative energies, molecular volumes, heats of formation, dipole moments, and ionization potentials have the same meaning here as in the preceding paper.[8] The only new quantities are the Armstrong–Perkins–Stewart bond orders[11] given for the C_e–C_p bonds in Table II. These bond orders are obtained by an arbitrary but sensible partitioning of the quantum mechanical density matrix of a molecule. They are excellent semiquantitative indicators of bond strength, a very useful concept from classical chemistry, which has no unique and simple definition within the framework of quantum mechanics.

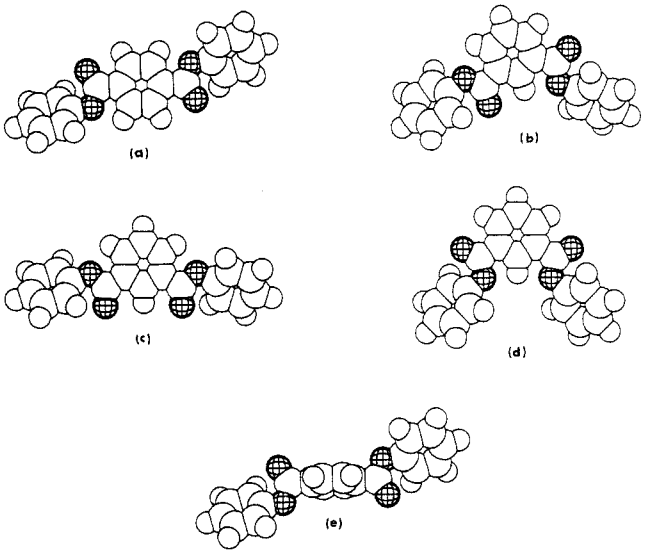

Figure 4. Space-filling drawings of (a) T, (b) I, (c) IL, (d) IK, and (e) the rotational transition state of T.

Discussion

Rotations of Phenyl Rings Attached to Isopropylidene Groups. These phenyl rings are attached to an isopropylidene group at one end and to a carbonate linkage in the carbonate fragments or an ester linkage in the ester fragments, para to the isopropylidene group, at

Table II
Results for Terephthalic and Isophthalic Structures[a]

Str[b]	REP[c]	REA[c]	vol[d]	APS-BO[e]	HOF[f]	DM[g]	IP[h]
			Base-Point Structures				
T,0	2.0	0.5	250.10	0.989	−55.7	0.125	9.588
I,0	0.9	−0.3	250.13	0.991, 0.990	−56.5	1.732	9.517
IL,0	2.0	0.0	250.15	0.989	−56.2	3.331	9.557
IK,0	0.0	0.0	250.06	0.989	−56.2	1.298	9.559
			Structures with Rotations or Rocking Motions				
T,15	0.5	−0.3	250.06	0.991	−56.0	0.123	9.586
T,30	2.6	0.1	250.25	0.987	−55.6	0.114	9.584
T,45	5.8	1.0	250.38	0.980	−54.7	0.098	9.583
T,60	9.4	2.4	250.48	0.970	−53.3	0.080	9.583
T,75	12.0	3.3	250.47	0.964	−52.4	0.067	9.583
T,90	13.1	4.0	250.58	0.959	−51.7	0.062	9.584
I,15	2.6	1.4	250.22	0.993, 0.986	−55.1	1.675	9.519
I,30	10.5	5.6	250.22	0.989, 0.988	−50.9	1.706	9.515
IL,15	2.5	1.3	250.12	0.990	−54.9	3.283	9.555
IL,30	10.4	5.8	250.05	0.989	−50.4	3.140	9.553
IK,15	2.4	1.1	250.16	0.989	−55.1	1.425	9.558
IK,30	10.3	5.0	250.24	0.990	−51.2	1.733	9.558

[a] See Figure 3 for schematic drawings and Figure 4 for space-filling drawings. Notation: T = terephthalic; I = isophthalic; L = linear; K = kinky. [b] Str = structure. After the symbol of each structure, the angle of rotation or rocking motion of the central phenyl ring about the C_p–C_p' axis is listed in degrees. [c] REP and REA = relative energy in kcal/mol, calculated with PRDDO and with AM1, respectively. Listed relative to the IK structure in part A and relative to the appropriate base-point structure in part B. [d] Volume = molecular volume in Å^3, calculated with CHEMLAB-II. [e] APS-BO = Armstrong–Perkins–Stewart bond orders for C_e–C_p bonds, calculated from the PRDDO density matrix. The bond orders for the two C_e–C_p bonds are equal by symmetry for the T, IL, and IK structures. [f] HOF = heat of formation in kcal/mol, from AM1. [g] DM = dipole moment in debyes, from AM1. [h] IP = ionization potential in electron volts, from AM1.

the other end. The lowest barrier rotation pathways occur for the synchronous motion of the two phenyl rings attached to the same isopropylidene fragment, and two barriers of almost identical energy are encountered, at rotations of 90° and 270° relative to the base-point structure.[8]

The rotation barriers calculated at a rotation of 90°, by single-point energy evaluations at approximate transition-state geometries in which the most important geometrical parameters have been readjusted, are 9.9 and 10.4 kcal/mol for LC and LE, respectively. These results are in good agreement with the estimate, based on consideration of the results of calculations, at the same level of approximation, on the smaller molecules,[8] that the heights of these barriers are 9–10 kcal/mol, and probably a little higher when there is an ester linkage rather than a carbonate linkage attached to one end of the phenyl ring. This agreement indicates that the judicious use of the calculations on smaller molecules, in order to estimate the rotation barriers at a given level of approximation, is a valid procedure.

The decrease in molecular volume, in going from the base-point to the transition-state geometries of LC and LE, is comparable to the decrease in 2,2-diphenylpropane. This result is not surprising, since the rotation barrier is primarily determined by the much greater difficulty of rotation past the isopropylidene group than rotation past the carbonate or ester linkage, which are the sources of ductility in these systems.

The transition-state relative energies obtained by AM1 are smaller than the relative energies obtained by PRDDO by a factor of ~2.3. These single-point energy evaluations were, however, carried out at approximate transition-state geometries in which the most important geometrical parameters were readjusted by using the results of PRDDO (and not AM1) calculations on 2,2-diphenylpropane. It is quite likely, therefore, that the exact AM1 barriers are slightly more overestimated in percentage than the exact PRDDO barriers. The PRDDO/AM1 ratio is therefore probably slightly larger, between 2.5 and 3.

Rotations of Phenyl Rings Flanked by Two Ester Linkages. One-third of the phenyl rings in the ester fragments of PEC are flanked by two ester linkages instead of being attached to an isopropylidene group at one end. Detailed conclusions can be reached about the phenyl ring motions in these terephthalate and isophthalate units by considering the results presented in Table II and by using molecular graphics to examine the structures of interest. These conclusions are summarized in the remainder of this subsection.

The least linear base-point geometry (IK) is the most stable, and the most linear base-point geometries (T and IL) are the least stable, although it is not clear how much significance such small energy differences have. The relative energies of all four base-point geometries are within 2 kcal/mol. AM1 predicts the four base-point geometries to be even closer to each other in energy, all four being within a range of 0.8 kcal/mol. AM1 agrees with PRDDO that T is the least-stable structure but predicts I to be the most stable structure.

There is clearly very little reason to choose between the four structures on grounds of stability at the molecular level. The incorporation of different types of ester linkages results in polymers with different properties because each type of ester linkage has different effects on the winding and packing of chains and on the types of rotations and rocking motions which can occur. For example, the terephthalate units will always be highly linear, while several conformations having very different amounts of nonlinearity (kinkiness) may occur in comparable abundance in the isophthalate units, unless one of the isophthalic conformations turns out to be strongly favored over the others by chain-packing considerations.

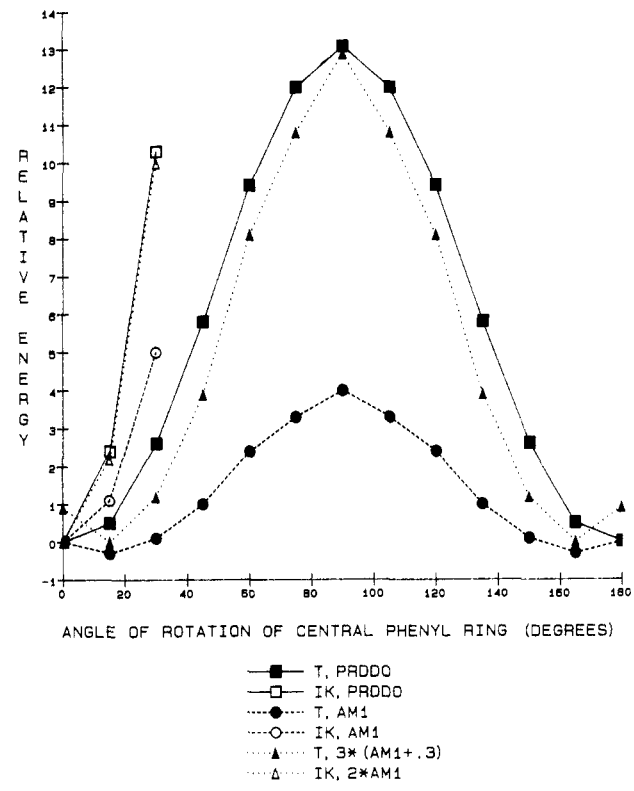

Figure 5. Relative energy, in kcal/mol, as a function of the angle of rotation of the central phenyl ring for T and IK.

The barrier to the rotation of the terephthalic phenyl ring is smooth and sinusoidal, as illustrated by the curve labeled "T,PRDDO" in Figure 5, where the relative energies listed in Table II are plotted as a function of the rotation angle. The barrier height is 13.1 kcal/mol, almost equal to the barrier height of 13.4 kcal/mol estimated previously[8] by assuming that the barrier to the rotation of the ester phenyl rings in terephthalic PEC will be approximately equal to twice the barrier of 6.7 kcal/mol calculated for phenyl benzoate.

Nuclear magnetic resonance (NMR) studies[1,12] have shown that the phenyl rings in the terephthalate units are somewhat more motionally restricted than the phenyl rings in BPA, causing the terephthalic phenyl ring motions to occur at the high-temperature end of the DMS γ relaxation. In the preceding paper,[8] calculations on the smaller molecules and considerations of intrachain effects were used to reach conclusions as to why this occurs. These conclusions remain valid.

The terephthalic phenyl rings have a large-amplitude (±30°), low-energy (~2.6 kcal/mol) oscillation range about their equilibrium positions, just like the phenyl rings attached to isopropylidene groups, for which the existence of a similar oscillation range was discussed in the preceding paper.[8]

The AM1 relative energy curve, labeled "T,AM1" in Figure 5, is very flat. The AM1 base-point structure occurs at a rotation angle of 15°, with a slightly lower energy than at 0°. The relative energy at a rotation angle of −15° (not shown) is equal, by symmetry, to the relative energy at a rotation angle of 15°. AM1 therefore predicts the 0° (coplanar) structure to be a very low barrier between two shallow noncoplanar minima. This result may, however, be an artifact, since the final AM1 calculations involved no

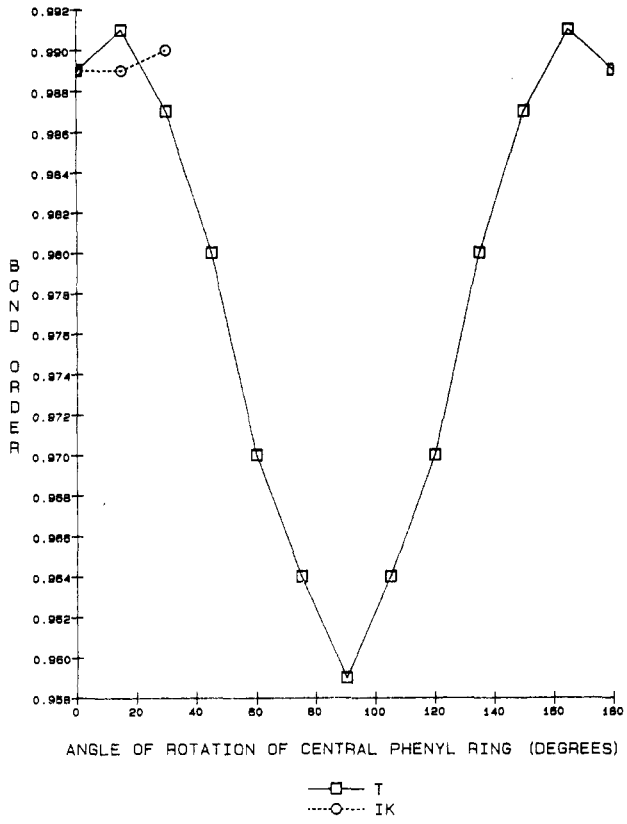

Figure 6. Armstrong–Perkins–Stewart bond order of the two equivalent C_e–C_p bonds, as a function of the angle of rotation of the central phenyl ring, for T and IK.

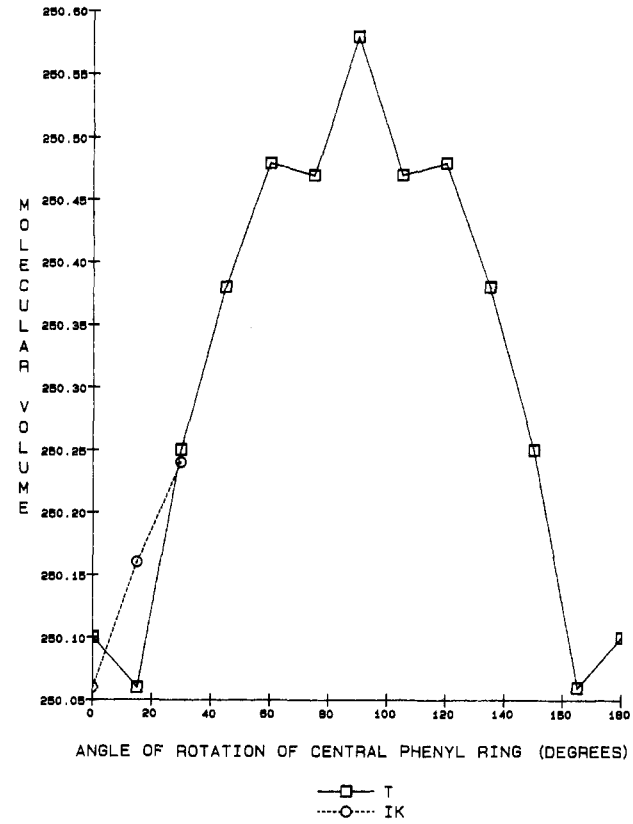

Figure 7. Molecular volume, in Å^3, as a function of the angle of rotation of the central phenyl ring for T and IK.

further reoptimization of the acyclic bond lengths and angles reoptimized by PRDDO.[8] Reoptimization by AM1 may well lead to a minimum at 0°, since AM1 predicts a rotation angle of 0° for the ground state of phenyl benzoate.[8]

AM1 underestimates the height of the barrier at 90°, and hence the resonance stabilization, by a factor of ~3. As can be seen from the curve labeled "T,3*(AM1+.3)" in Figure 5, by appropriate calibration, the results of AM1 calculations can be used to predict the shape of the relative energy curve and the height of the rotation barrier. In this curve, (a) 0.3 kcal/mol has been added to each of the relative energies obtained by AM1, in order to bring the conformation at a rotation angle of 15°, which has the lowest energy, to the base-point, and (b) the AM1 relative energies have then been scaled up by a factor of 3. The result is a modified AM1 rotation barrier which has a somewhat less smooth Gaussian shape than the PRDDO barrier and a height of 12.9 kcal/mol.

The variation of the Armstrong–Perkins–Stewart bond orders for the C_e–C_p bonds is shown in Figure 6 as a function of the angle of rotation. A gradual reduction of resonance stabilization is seen for the T structure as the rotation angle is gradually increased to 90°, making the plane of the central phenyl ring less and less coplanar with the planes of the two ester linkages. The bond order slightly increases for a 15° rotation, because a reduction of the very small amount of steric repulsion between nonbonded atoms compensates for the small loss of resonance stabilization. At larger angles of rotation, there are no remaining steric repulsions to be reduced, so that the bond order smoothly decreases.

The molecular volume increases in going from the base-point T structure to the rotational transition state with the central phenyl ring perpendicular to the two ester linkages, as shown in Figure 7. This increase is slightly larger in amount (0.48 versus 0.34 Å^3) but slightly smaller in percentage (0.19% versus 0.21%) than that calculated for the same motion in phenyl benzoate.[8]

The low-energy oscillation or rocking motion range of the isophthalic phenyl rings is much more restricted (±15°). Furthermore, the relative energies for a rocking motion of 30° are >10 kcal/mol, showing that the walls of the potential wells are very steep, as illustrated for the IK structure by the curve labeled "IK,PRDDO" in Figure 5. A simple flipping motion of the isophthalic phenyl rings is therefore impossible.

No low-barrier cooperative phenyl ring flipping motions exist either for the ester phenyl ring in isophthalic PEC. The absence of low-energy cis conformations about the C–O bonds in ester fragments,[8] and the resulting impossibility of crankshaft-type motions such as the one proposed by Jones,[13] is the major reason for the lack of easy cooperative motions. NMR experiments[1,12] show that the phenyl rings in the isophthalate units are much more motionally restricted than the phenyl rings in the terephthalate units. There is very little motional narrowing of the deuterium NMR pattern in isophthalic PEC, and thus very little backbone motion, until the temperature is increased to near the glass transition temperature of the system.[1,12] Consideration of the results of the present calculations together with the results of the NMR experiments[1,12] suggests that cooperative motions involving the ester phenyl rings in isophthalic PEC are disfavored both statistically because of their great complexity and kinetically because of their very high rotation barriers.

As shown in the curve labeled "IK,2*AM1" in Figure 5, by appropriate calibration, the results of AM1 calculations can be used to predict the relative energy curve for the rocking motion. In the "IK,2*AM1" curve, the AM1 relative energies plotted in the "IK,AM1" curve have been scaled up by a factor of 2. The scaling factor was 3 for the rotation of the phenyl ring in T. Therefore, AM1 comes closer to correctly predicting the energetic effects of structural

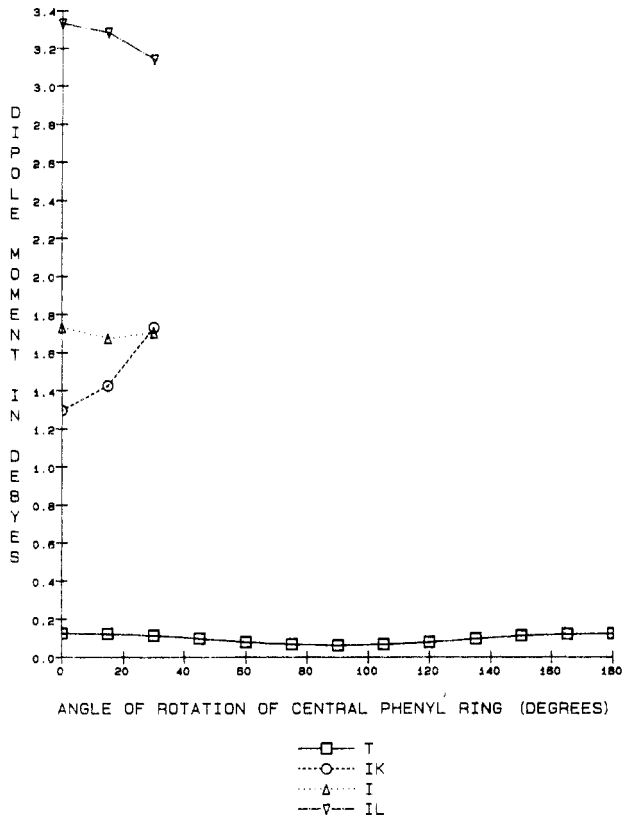

Figure 8. Dipole moment, in debyes, as a function of the angle of rotation of the central phenyl ring for T, IK, I, and IL.

distortions such as the rocking motion than to predicting the energetic effects of resonance stabilization.

The variation of the dipole moment is shown in Figure 8 as a function of the angle of rotation. The dipole moments follow the order IL $\gg$ I > IK $\gg$ T.

The ionization potentials calculated for all of the structures are almost equal, being very slightly higher for T than for IL, IK, and I. This is to be expected, since the ionization potential, which is determined by the energy of the highest occupied phenyl ring π orbital, is a very weak function of molecular conformation.

Intrachain Motions and the DMS Spectra. The most complete description of the DMS γ and δ relaxations in the PEC that can be obtained by only considering isolated chain segments is summarized below. Each one of the basic motions mentioned, is also important in interpreting NMR spectra. It is essential to develop a model which will be able to reliably estimate the effect of various superpositions and/or couplings of these basic motions on the DMS and NMR spectra, as a function of relevant parameters such as polymeric composition, temperature, frequency of observation, and physical aging.

Three "*large*" *motions* of subunits of a monomer, each one of which involves going over a rotation barrier, are the major constituents of the γ relaxation. These motions are as follows:

1. 180° flip of phenyl rings attached to an isopropylidene group on one side. These phenyl rings preferentially flip in synchronized pairs attached to the same isopropylidene group. The rotation barrier is very slightly higher if there is an ester linkage rather than a carbonate linkage para to the isopropylidene group.

2. 180° flip of phenyl rings attached to two ester linkages in a terephthalic configuration. This motion has a considerably higher barrier than the first motion. It should, therefore, occur on the higher temperature side of the γ relaxation. It has a higher statistical weight, however, since it is a simple motion which does not require any synchronization. It is therefore not much more disfavored than the first motion and occurs as a part of the same relaxation, as observed by NMR experiments.[1,12]

3. Methyl group rotation. This simple motion, which does not require any special synchronization, has a much lower barrier than both of the first two motions, so that it can be expected to contribute especially to the low-temperature end of the γ relaxation.

Five "*small*" *motions* of subunits of a monomer, each one of which involves oscillations about an energy minimum in a potential well, are also important. These motions can facilitate the γ relaxation. In addition, their superpositions and/or couplings can add up to the extremely low-temperature δ relaxation. As discussed in the preceding paper,[8] the δ relaxation cannot be adequately explained by any single motion. When extremely low temperatures are reached, all of the "large" motions cease and the five "small" motions are the only ones left to make up the δ relaxation:

1. Oscillation of phenyl rings attached to an isopropylidene group on one side, over a ±30° range. At higher temperatures, these oscillations can facilitate the 180° flips of the phenyl rings, and their being correctly accounted for is therefore crucial.[8,14]

2. Oscillation of phenyl rings attached to two ester linkages in a terephthalic configuration, over a ±30° range. At higher temperatures, these oscillations can also facilitate the 180° flips of the phenyl rings.

3. Rocking motion of phenyl rings attached to two ester linkages in an isophthalic configuration, over a ±15° range, with no possibility of flipping.

4. Oscillation of methyl groups.

5. Rocking motion of carbonyl groups over a total angular range of ~70°.

Finally, two major types of *isomerizations* are possible in the generic PEC, each of which can have significant implications in terms of the DMS and NMR spectra, as well as affecting the viscoelastic properties:

1. The ~24% presence of trans,cis or cis,trans conformations about the C–O bonds in carbonate linkages, in addition to the predominant trans,trans conformations,[8] can provide low-barrier mechanisms for crankshaft-type cooperative motions, such as the mechanism proposed by Jones[13] for the flipping of phenyl rings in glassy polycarbonate.

2. The possible presence, in comparable abundance, of several conformations having very different amounts of nonlinearity (kinkiness) in the isophthalate units can affect the winding and packing of chains and therefore also affect the types of motions which can take place.

Conclusions

The presentation of the results was continued for a project to relate the properties of BPA polycarbonate and the PEC of BPA and terephthalic and/or isophthalic acids to their structure at the molecular level, by use of the techniques of applied theoretical chemistry.

Quantum mechanical calculations utilizing the PRDDO and AM1 techniques were used to characterize the molecular motions associated with relaxations observed by DMS. Intrachain rotations were studied by means of detailed calculations on several large molecules which are representative of short chain segments and fully represent each type of phenyl ring environment.

The barriers estimated for the 180° flip of the phenyl rings attached to an isopropylidene group are 9.9 and 10.4 kcal/mol, when the phenyl rings are attached to a carbonate or to an ester linkage, respectively, at the para pos-

ition. These barriers are expected to decrease in a more complete optimization of the transition-state geometries.

The ester phenyl ring in terephthalic PEC has a rotation barrier of 13.1 kcal/mol, as well as a large-amplitude, low-energy oscillation range of ±30° about its equilibrium position. There is no simple or cooperative low-barrier flipping motion for the ester phenyl ring in isophthalic PEC, where the low-energy oscillation or rocking motion range is also much more restricted (±15°).

Comparison of the present results with the results presented in the preceding paper[8] showed that the judicious use of calculations on smaller molecules is a valid procedure. The two sets of results were combined to provide the most complete description of the DMS γ and δ relaxations that could be obtained by considering isolated chain segments. This description is relevant both for the intrachain interactions in the solid polymers and for the dynamical interactions in dilute (up to 10%) solutions of the polymers. In such dilute solutions, intrachain interactions will necessarily dominate over interchain interactions in determining the dynamical processes. By contrast, the relative importance of interchain interactions in the solid polymers is a controversial problem which needs further study.

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Registry No. a, 4824-74-2; b, 10192-62-8; (BPA)(carbonic acid) (copolymer), 25037-45-0; BPA polycarbonate, 24936-68-3; (BPA)(carbonic acid)(isophthalic acid) (copolymer), 31133-79-6; (BPA)(carbonic acid)(terephthalic acid) (copolymer), 31133-78-5; (BPA)(carbonic acid)(terephthalic acid)(isophthalic acid) (copolymer), 31133-80-9.

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Influence of the Dehydrochlorination Rate on the Degradation Mechanism of Poly(vinyl chloride)

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ABSTRACT: The degradation behavior of poly(vinyl chloride) (PVC) samples with considerably increased heat stability has been compared with that of an ordinary suspension PVC. The degradation rate was followed by measuring evolved HCl conductometrically. Structural changes in the polymer were monitored by several techniques: UV–visible spectroscopy was used to follow polyene sequences and GPC to detect changes in the molecular weight distribution and to determine the number of cleavages caused by ozonolysis, i.e., the number of polyene sequences. Besides decreased rate of dehydrochlorination the improved PVC samples become less discolored, i.e., the polyenes are shorter. The results obtained by ozonolysis and UV–visible spectroscopy show that this is not due to an increased frequency of secondary reactions but that a lower number of HCl molecules is evolved from each initiation point. The more severe discoloration, i.e., the longer polyenes, in the normal sample is most likely an effect of higher concentration of free HCl due to the lower initial stability. It is suggested that the polyene propagation, or the "zipper" reaction, is catalyzed by HCl.

Introduction

In thermal degradation of poly(vinyl chloride) (PVC), dehydrochlorination is the dominating reaction and it has been observed already at temperatures just above the glass transition.[1] The stability is thus much lower than could be expected and the reason to the low stability has been the subject of many investigations (see, e.g., ref 2–4). An important question has been the influence of labile chlorine. By using polymers prepared at reduced monomer pressure we have recently been able to correlate the rate of dehydrochlorination to the amount of tertiary chlorine (mainly associated with butyl branches but also with ethyl and long-chain branches) and internal allylic chloride.[5–7] According to our results, the higher content of tertiary chlorine (1–1.5 per 1000 monomer units) compared to internal allylic chlorine (0.1–0.2 per 1000 monomer units) implies that tertiary chlorine is the most important defect even in ordinary PVC. In agreement with other published reports,[2,8–10] we have also found evidence that the normal PVC units are unstable at the temperatures in question, i.e., random initiation will occur.

The dehydrochlorination will lead to conjugated double bonds in the polymer backbone resulting in unacceptable discoloration even at very low degrees of degradation. The maximum length of these polyenes is 20–30[11–13] while the average length is around 10 at low levels of dehydrochlorination.[10,14,15] At higher levels the length decreases according to observations by UV–visible spectroscopy.[14,15] This is the result of secondary reactions, e.g., intra- and intermolecular cyclizations. One observable result of intramolecular cyclizations is the formation of benzene.[16] The intermolecular cyclization will lead to cross-linking

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