used to generate the correct selection from the ϕ array for integration segments of this type.

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Crystal Structure of Isotactic Poly(methyl methacrylate)

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ABSTRACT: The structure of isotactic poly(methyl methacrylate) (it-PMMA) has been determined by X-ray analysis and energy calculations. X-ray diffraction photographs were taken from an oriented sample of high crystallinity and the intensities and positions of the observed reflections were measured. The results indicate that the unit cell is triclinic although the unit-cell parameters are only slightly different from those of the orthorhombic cells reported in the literature. Favorable conformations are calculated by energy minimization, applying the virtual bond method. Our results support the suggestion of Tadokoro that it-PMMA crystallizes in a double-stranded 10/1 helix with a stabilization energy of 12.4 kJ/(base mol).

Introduction

The structure of isotactic poly(methyl methacrylate) (it-PMMA) is still an open problem, although a considerable number of papers have appeared on this subject. Stroupe and Hughes claimed that their X-ray diffraction patterns could best be interpreted in terms of an orthorhombic unit cell and a 5/2 helical conformation of the backbone.[1] Several studies have appeared since then, using X-ray diffraction[2] and X-ray diffraction combined with energy calculations and infrared spectroscopy.[3,4] All results pointed to a 5/1 helix of the backbone, although different workers suggested different conformations of the side groups. But no one has succeeded in making a complete structural analysis, because of difficulty in indexing the reflections.

A recent communication reported the possibility of a double-stranded 10/1 helix for crystalline it-PMMA.[5] Energy calculations showed this structure to be the more stable one and, furthermore, good packing in a lattice was possible. Other authors objected to this view and considered the single 5/1 helix to be the correct structure,[6] while an examination of the X-ray pattern of it-PMMA in its noncrystalline form showed no evidence that the molecules are paired.[7] So, when double helices were present in crystalline it-PMMA, the chains should pair and intertwine as a part of the crystallization process, which is compatible with the very low rate of crystallization of it-PMMA from the melt.[8] Furthermore, Sundararajan supported the double-stranded helical structure by applying the virtual bond method to it-PMMA, resulting in a more stable 10/1 helix with respect to a 5/1 helix.[9] In this paper we discuss the crystal structure of it-PMMA as determined by X-ray diffraction and energy calculations.

Experimental Section

it-PMMA was prepared from the monomer according to known procedures.[10] The $\bar{M}_v$ of this sample measured in chloroform at 25 °C was 570000. The tacticity as determined from a 5 wt % *o*-dichlorobenzene solution at 150 °C by 60-MHz NMR spectroscopy was I:H:S = 91:6:3. Uniaxial orientation of the polymer was achieved by stretching a platelet about 300% at 55 °C and subsequently crystallizing it for 3 weeks at 120 °C. The X-ray fiber diagram was recorded photographically with a Statton camera, using Ni-filtered Cu Kα radiation. The intensities of the reflections were measured with an Optronics optical densitometer and stored on magnetic tape. A graphical representation of the intensities along the layer lines was obtained with a digital computer.

Results

The entire fiber diagram and the equatorial reflections are presented in Figures 1 and 2, respectively. Obviously, the reflections are rather diffuse and spread along an arc, as a result of incomplete orientation of the fiber (tangential spread). The intensity along the equator, as determined with the optical densitometer, is given in Figure 3.

When the sample is tilted by 21° with respect to the incident X-rays, the apparent meridional reflection on the fourth layer line (Figure 1) is split into two reflections while a new, really meridional reflection appears on the fifth layer line, indicating a fivefold screw axis. As a matter of

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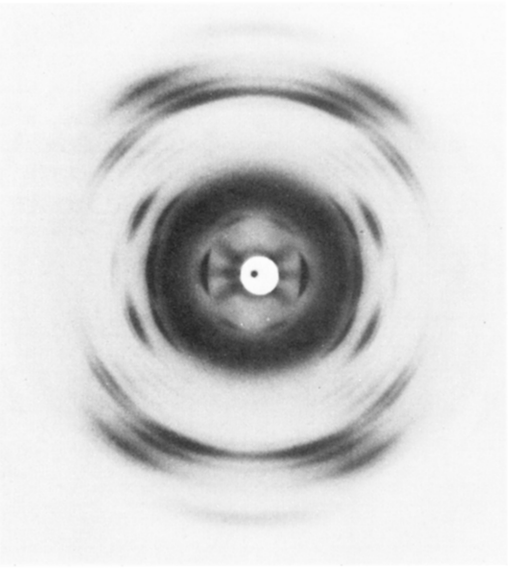

Figure 1. X-ray fiber diagram of it-PMMA.

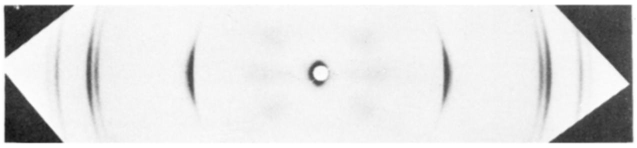

Figure 2. Equatorial reflections of the fiber-diagram of it-PMMA.

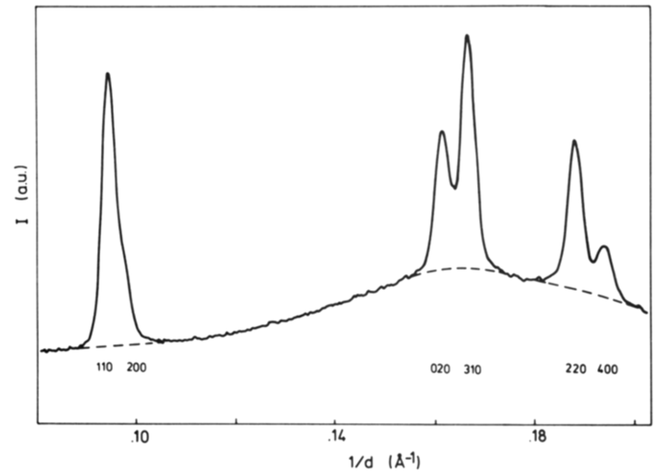

Figure 3. Intensity along the equator as determined with the optical densitometer.

course this reflection does not appear on the bottom side of the equator.

Analysis

Starting from the orthorhombic parameters from the literature, we indexed the observed reflections. After a least-squares procedure the unit cell was calculated to be triclinic. The parameters and their standard deviations are as follows: $a = 20.57$ (5) Å, $b = 12.49$ (3) Å, $c = 10.56$ (2) Å, $\alpha = 92.9$ (2)°, $\beta = 88.2$ (2)°, and $\gamma = 90.6$ (2)°. In all recent papers that have appeared on this subject, orthorhombic cells were reported.[1-4] From these orthorhombic parameters it is possible to recalculate the positions of all reflections, and it appears that the reflections, which partially overlap in Figure 3, would completely overlap for the above-mentioned cells. So it seems that we report for the first time a separation of these reflections. In addition to this it should be mentioned that Stroupe and Hughes reported already in 1958:[1] "Fine splitting of many reflections is observed, however, and the true unit cell is triclinic, pseudoorthorhombic".

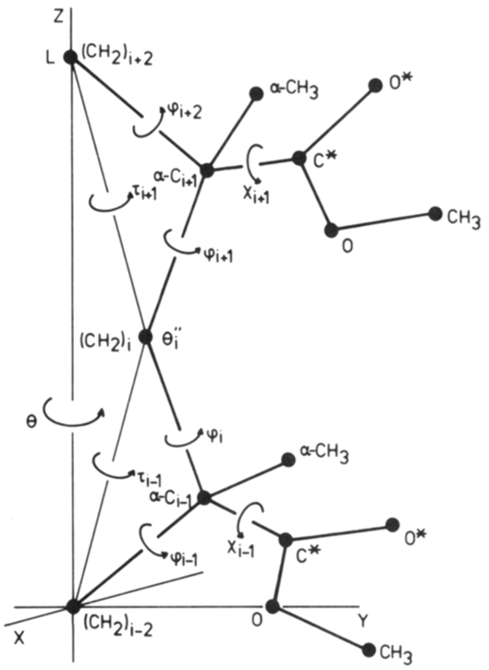

Figure 4. Schematic representation of one residue of it-PMMA.

On the basis of energy calculations and a patterson function,[11] Tadokoro et al. suggested a double-stranded 10/1 helix.[5] Sundararajan confirmed this suggestion by energy calculations applying the virtual bond method.[9] Furthermore, we found it impossible to fill the unit cell with four single 5/1 or 5/2 helices without overlapping of the chains, and for these reasons we also prefer the double-stranded helices. As the period of a single helix in a double-stranded helix of identical chains is twice the translational identity period, the pitch of the helix is set to be 21.12 Å. The screw symmetry of a double-stranded 10/1 helix is in accordance with the fivefold screw axis as deduced from our X-ray data.

The molecular parameters for a single 10/1 helix are determined by energy minimization using the virtual bond method.[9] As the side groups of two contiguous monomeric units can differ in steric conformation, the residue of the helix, represented schematically in Figure 4, is built up of two monomeric units.

So one residue is defined by a set of parameters $S = \{L, \tau_{i-1}, \tau_{i+1}, \chi_{i-1}, \chi_{i+1}\}$. For each S the virtual bond method is applied and the coordinates of all atoms and groups are computed as well as the rotational parameters φ and the bond angles θ''. From these values the conformational energy and additionally the stabilization energy due to nonbonded and Coulombic interactions in the case of good fitting of two intertwined chains are calculated. The parameters for the calculation of the conformational energy are the same as used by Sundararajan,[9] with the exception of the partial charges (Ooi et al.[12]).

In the calculation of the conformational energy four contributions are considered: (i) deformation energy due to the distortion of a bond angle with respect to the tetrahedral angle, (ii) torsional energy due to rotations around the skeletal C–C bonds and the αC–C* bonds, (iii) nonbonded interactions for each pair of interacting atoms or groups, and (iv) electrostatic interactions for each pair of atoms or groups to which partial charges are assigned.

The energy of deformation of the angle θ'' was estimated according to

$$E = A(\Delta\theta'')^2 \qquad (1)$$

Table I
Parameters Used for Evaluation of the Nonbonded and Coulombic Interaction Energy

atom or group	van der Waals radius, Å	eff no. of electrons N_i	polarizability α_i, Å^3	charges δ_i, esu
CH_2	1.9	7	1.77	
C	1.7	5	0.93	
αCH_3	1.9	7	1.77	
C*(carbonyl)	1.7	5	1.23	0.517+
CH_3(ester)	1.9	7	1.77	0.102+
O*(carbonyl)	1.5	7	0.84	0.417−
O(ester)	1.5	7	0.70	0.202−

Table II
Geometrical Parameters Used for PMMA[13]

bond	length, Å	bond angle	angle, deg
$\alpha C-CH_2$	1.53	$C-\alpha C-C$	110.0
$\alpha C-\alpha CH_3$	1.53	$C-\alpha C-C^*$	109.5
$\alpha C-C^*$	1.52	$\alpha C-C^*-O$	114.0
$C^*=O^*$	1.22	$\alpha C-C^*=O^*$	121.0
C^*-O	1.36	C^*-O-CH_3	113.0
$O-CH_3$	1.45	$\alpha C-C-\alpha C$	θ''

where $\Delta\theta''$, expressed in radians, is the distortion of the angle θ'' with respect to the tetrahedral angle, and A = 334.4 kJ·mol^{-1}·rad^{-2}.[13,14]

The energy coupled with the internal rotation potential was described by the sinusoidal function[11]

$$E = (E_0/2)(1 - \cos 3\omega) \tag{2}$$

with barriers E_0 of 11.7 and 4.18 kJ·mol^{-1} assigned to rotations $\omega = \varphi$ about the skeletal C–C bonds and $\omega = \chi$ about the αC–C* bonds, respectively.[13]

Nonbonded interactions were computed with Lennard-Jones functions[13]

$$E_{ij} = \frac{a_{ij}}{r_{ij}^{12}} - \frac{b_{ij}}{r_{ij}^{6}} \tag{3}$$

for each pair of interacting atoms or groups at distance r_{ij} from each other. The constants b_{ij} were evaluated according to the Slater–Kirkwood formula from atom or group polarizabilities α_i and the effective numbers of electrons N_i

$$b_{ij} = \frac{\frac{3}{2}e(\hbar/m^{1/2})\alpha_i\alpha_j}{(\alpha_i/N_i)^{1/2} + (\alpha_j/N_j)^{1/2}} \tag{4}$$

The values of the parameters α_i and N_i used in our calculations are given in Table I, together with the van der Waals radii[9] ($\hbar$ equals Planck's constant divided by 2π and e and m are the charge and mass of an electron, respectively). The values a_{ij} were calculated by assuming that the energy E_{ij} has a minimum if r_{ij} equals the sum of the van der Waals radii for the given pair.

Coulombic interactions were computed by assuming partial charges on the atoms or groups.

$$E_{ij} = 322\delta_i\delta_j/Dr_{ij} \tag{5}$$

A value D = 3.5 was used for the effective dielectric constant.[15] The values δ according to the experimental dipole moments[12] are also summarized in Table I. Finally, the geometrical parameters of PMMA are listed in Table II.

From a great number of calculations we obtained several 10/1 helices with low conformational energy and the corresponding stabilization energy for a double-stranded 10/1 helix up to 12.4 kJ/(base mol). In Table III the molecular parameters of the most favorable conformation are listed. The structure factors were calculated from the well-known formula

Table III
Molecular Parameters of the Most Favorable Conformation of a Double-Stranded 10/1 Helix

θ_i'', θ_{i+2}''	126°, 126°
χ_{i-1}, χ_{i+1}	150°, 340°
φ_{i-1}, φ_i, φ_{i+1}, φ_{i+2}	5°, 40°, 0°, 20°

$$F(hkl) = \int_{j=1}^{N} f_j \exp\{2\pi i(hx_j + ky_j + lz_j)\} \tag{6}$$

in which

$$f_j = f_{0,j} \exp\left\{-B\frac{\sin^2\theta}{\lambda^2}\right\} \tag{7}$$

The summation is over all atoms in the unit cell, but the hydrogen atoms are not taken into account. Values of the $f_{0,j}$'s, denoting the atomic scattering factors, are taken from ref 16. For the isotropic temperature factor B a value of 8 Å^2 is assumed to be reasonable.[11]

These calculated structure factors, $|F_c|$, have to be compared with the observed ones, $|F_o|$, for which the following equality holds:

$$|F_o|^2 = I\Gamma/KmpLA \tag{8}$$

I is the observed intensity, K is a scale factor, m is the multiplicity, and p is the polarization factor:

$$p = (1 + \cos^2 2\theta)/2 \tag{9}$$

with 2θ being the diffraction angle. Because absorption is assumed to be negligible, A = 1.[11] For both fiber and rotation photographs, the Lorentz factor, L, is given by

$$L = \frac{1}{\sin 2\theta}\,\frac{\cos\theta}{(\cos^2\psi - \sin^2\theta)^{1/2}} \tag{10}$$

in which ψ is the angle between the fiber axis and the reflecting planes. As a result of the tangential spread the reflections are rather broad and the intensities should be multiplied by an arc correction factor. These arc correction factors, Γ, are calculated on the assumption that there is a symmetrical distribution of crystal axes about the fiber axis.[17] If the intensities are measured along a layer line, Γ is given by

$$\Gamma = \frac{\sin\theta\cos\psi}{1 - 2\sin^2\theta} \tag{11}$$

In Table IV the observed and calculated structure factors and the interplanar distances are listed.

Discussion

From the values of α, β, and γ we know that the unit cell can be considered nearly pseudoorthorhombic as mentioned by Stroupe and Hughes in 1958[1] and can be compared with the orthorhombic cells from the literature. If the double-stranded helices are considered as rigid cylinders with a radius of about 12.5 Å, a nearly hexagonal, close packing can be obtained by placing four cylinders at the corners of the unit cell and one in the center. From the unit cell parameters the theoretical density can be calculated. The calculated density ρ_c = 1.23 g/cm^3 is in very good agreement with the observed density ρ_0 of 1.21 g/cm^3.[5]

We attribute the stabilization energy of the intertwined helices mainly to the backbone atoms and the ester methyl

Table IV
Observed ($|F_o|$) and Calculated ($|F_c|$) Structure Factors and Interplanar Distances (d) of the Reflections on Different Layer Lines (l)

layer line	$\|F_c\|$	$\|F_o\|$	d
$l = 0$	84.4	47.9	10.54
	50.2	28.1	10.29
	45.0	52.3	6.20
	66.0	71.2	6.00
	61.8	68.0	5.32
	41.4	42.7	5.13
	37.1	33.3	3.94
$l = 1$	19.8	10.5	9.30
	41.5	20.7	7.93
	79.7	116.0	6.37
	50.8	57.7	5.88
	57.3	53.1	5.08
	21.1	44.5	4.36
	21.1	49.1	4.25
$l = 2$	17.9	14.4	3.92
	26.4	15.2	3.71
	26.4	31.1	3.46
	34.4	52.4	3.21
	38.0	58.0	3.11
$l = 3$	63.3	43.9	3.16
	55.7	33.6	3.00
	79.2	48.3	2.78

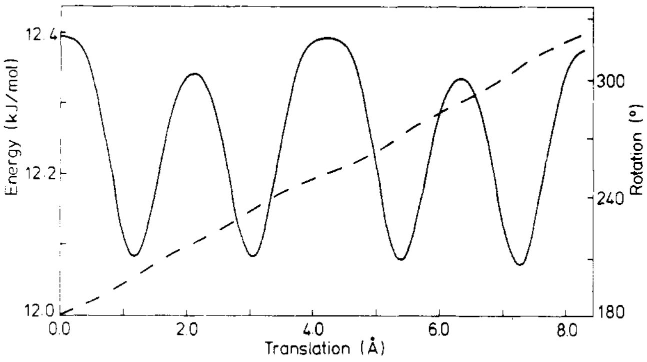

Figure 5. (—) Stabilization energy and (---) rotation angle as a function of the translation when two chains are screwed through each other.

groups with χ = 150°. If the contributions of the methylene hydrogen atoms are also taken into account, as been done by Tadokoro, the calculated stabilization energy will increase somewhat. As a double-stranded helix consists of two single helices, it should be possible to screw them into each other. One chain is considered to be fixed and the other one travels through it by a translation in the direction of the fiber axis combined with a rotation about the fiber axis. At any value of the translation, the rotation angle is calculated starting from the assumption that the stabilization energy has a maximum. In Figure 5 this value of the rotation angle and the corresponding stabilization energy are plotted against the translation. Clearly, the energy has a periodicity of 4.224 Å as a function of the translation. A very remarkable result of this calculation is that the energy difference by screwing the helices through each other is only 0.3 kJ/(base mol) and the difference of two maxima in Figure 5 is about 0.05 kJ/(base mol).

In the latter situation the translation is 2.112 Å and ester groups with χ = 150° are placed opposite to the ester groups with χ = 340°, and an exact translation period of 10.56 Å of the unit cell is obtained. This is in good agreement with the X-ray fiber pattern, as no layer lines with spacings corresponding with 21.12 Å were observed.

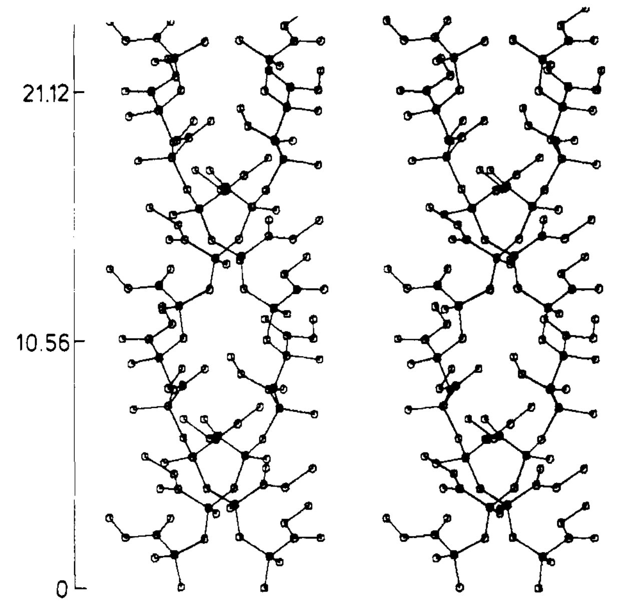

Figure 6. Stereoview of a right-handed upward double-stranded 10/1 helix of it-PMMA (distances are given in Å).

As a measure of the agreement between the observed and calculated structure factors from Table IV the discrepancy factor R is used.[11]

$$R = \sum||F_o| - |F_c||/\sum|F_o| \tag{12}$$

Unfortunately, the discrepancy obtained is still 0.3. This may be due to a disordered structure.

According to Hosemann[18] there are lattice distortions of the first and the second kind. Distortions of the first kind include the disorder in up- and downward helices and right- and left-handed helices, while the long-range order is preserved. In lattices possessing distortions of the second kind, each lattice point has only a relation to its nearest neighbors and the long-range order is lost. A measure of the distortion of the second kind is the g factor, which can be calculated from diffraction data using[11]

$$(\delta\beta)^2 = \frac{1}{\langle d\rangle^2}\left(\frac{1}{N^2} + \pi^4h^4g^4\right) \tag{13}$$

In this expression $\delta\beta$ is the half-width for a series of reflections with different diffraction order and N is the number of lattice planes with interplanar distance d. When $g < 0.01$, distortions of the second kind are negligible. However, as g increases, broadening of the reflections occurs and if $g > 0.35$, only the first-order reflection can be observed. When $\delta\beta$ of the 110 and 220 reflections are measured and the squares of it are plotted against h^4, a value of $g = 0.02$ is calculated from the slope of the line; although only two reflections are involved in this treatment, we conclude that distortions of the second kind are nearly negligible. From the ordinate intercept, a value of N of about 30 is obtained. As the interplanar distance of the 110 planes is 10.62 Å, the crystal size in this direction is about 300 Å.

The main disorder in the crystals is caused by distortions of the first kind. The two double-stranded helices have to be placed in the unit cell in such a way that the systematic absences $h + k$ = odd for $hk0$ is fulfilled (Figure 3). This is the case when one double-stranded helix is placed at the corner of the unit cell and the other one in the center. When the two double-stranded helices are exactly the same and one of them is shifted by $c/2$ along the fiber axis, systematic absences for $h + k + l$ = odd should occur. However, not all the helices can be the same since there is a statistical disorder caused by right- and left-handed, up- and downward helices. Therefore we assume that the crystallites are built up of double-stranded helices of the same kind and are randomly disordered by other double-stranded helices.

Conclusion

From the energy calculations and X-ray diffraction data we conclude that it-PMMA crystallizes as a double-stranded 10/1 helix. A stereoview of the double-stranded right-handed upward 10/1 helix of it-PMMA is shown in Figure 6. In the triclinic, pseudoorthorhombic cell, two equal double-stranded helices are placed, shifted about $c/2$ along the fiber axis with respect to each other, and lattice disorder is mainly attributed to distortions of the first kind, i.e., to statistical incorporation by other helix types.

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Dielectric Relaxation Studies on Bisphenol A Bis(cumylphenyl) Carbonate/Lexan Polycarbonate Solid Solutions

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ABSTRACT: The dielectric relaxation spectra of solid solutions of bisphenol A polycarbonate/bisphenol A bis(cumylphenyl) carbonate have been obtained as a function of composition. T_g varies continuously with composition and can be described by either a T_g–$\bar{M}_n^{-1}$ or polymer–diluent correlation. The former indicates that the low molecular weight material is a better model system for polycarbonate than bisphenol A diphenyl carbonate studied previously. Up to 87.5 wt % small molecule, the T_g relaxations are Arrhenius activated. The T_g activation energy is composition independent above 25 wt % small molecule. This observation correlates with the disappearance of the β relaxation of the polymer and indicates that localized motion of the polymer backbone is intimately related to the energetics of longer chain motion at T_g.

Introduction

The effect of additives on polymer properties is the basis for many industrial applications. These additives can provide polymer films that are homogeneous or phase separated on a microscale. Dielectric relaxation studies provide a method to study such systems and obtain information on the modes of relaxation as well as any specific interactions that may occur in polymer blends. We have been particularly interested in the effects of small molecular dopants on the relaxation behavior of polycarbonate (PC), in particular the sub-T_g relaxations and their interrelationship with the glass transition activation energy. Three systems have been studied thus far: bisphenol A diphenyl carbonate/PC,[1] bis[(diethylamino)phenyl]phenylmethane/PC,[2] and *n*-butyl 4,5,7-trinitrofluorenone-2-carboxylate/PC.[3] The latter two systems represent mixtures of dissimilar molecules whereas the first was studied to assess the effect of a molecule similar to the PC backbone. The first two systems show that elimination of the first sub-T_g relaxation of PC by the addition of the small molecule results in a composition-independent T_g activation energy. The fluorenone derivative–PC mixtures could not be used in those comparisons as they showed specific polymer–monomer interactions, which did not allow a clear interpretation of the sub T_g relaxations. The first two systems indicate that localized backbone motions in the polymer system play an important role in the T_g activation energy.

The bisphenol A diphenyl carbonate (MLEX) (see Figure 1) was originally chosen as a model monomer system to study the effects of a bimodal polymeric distribution on the relaxation processes of the system. It was shown,[1] however, that the MLEX/PC mixture T_g's could be represented better by polymer–diluent formulas such as the Fox equation[4] rather than the T_g–reciprocal molecular weight equation of a homopolymeric system. Part of the reason for this observation may have been the selection of such a "short" molecule that end groups played an important role in determining T_g. We have, thus, synthesized a longer polycarbonate model system, bis-

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