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Multiple Field Spin–Lattice Relaxation Study of Dissolved Poly[4,4'-bicyclo[2.2.1]heptan-2-ylidenebis(phenyl carbonate)]

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ABSTRACT: A dilute-solution spin–lattice relaxation time study was performed on a bisphenol polycarbonate similar to the polycarbonate of bisphenol A except the methyl groups of the bisphenol unit are replaced by a norbornyl ring. Carbon-13 relaxation times are measured at three Larmor frequencies: 22.6, 62.9, and 126 MHz. Motion of the norbornyl group is seen to be isotropic, which implies segmental motion is isotropic since the group is rigidly incorporated into the backbone. Relaxation caused by this segmental motion is interpreted in terms of the Hall–Helfand correlation function. The apparent activation energies for cooperative and individual bond transitions are 24 and 30 kJ/mol, respectively, while the corresponding Arrhenius prefactors are 6×10^{-14} and 17×10^{-14} s, respectively. The phenyl groups undergo this same segmental motion plus restricted rotation about the C_1C_4 axis but not full anisotropic rotation. Since full anisotropic rotation is observed in bisphenol A polycarbonate, the larger norbornyl group would appear to sterically hinder phenylene group rotation. In the bulk polymer a low-temperature dynamic mechanical loss peak comparable to that of bisphenol A polycarbonate has been observed for the norbornyl-substituted polymer. This implies phenylene group rotation is not the primary element contributing to dynamic mechanical loss. An alternative motion based on correlated conformational interchange between carbonate groups is an explanation for the low-temperature loss peak, which is in better agreement with the findings of this study.

Introduction

A series of dilute-solution spin–lattice relaxation studies have been made on the polycarbonate of bisphenol A (BPA) and related structural analogues.[1-4] These studies have shown the presence of several rapid local motions in BPA including cooperative segmental transitions, phenylene group rotations, and methyl group rotations. The addition of substituents to the phenylene ring of BPA significantly slows phenylene group rotation and, to a lesser extent, slows segmental motion. The BPA analogue of interest in this report is abbreviated NBPC and is shown in Figure 1 relative to BPA.

This repeat unit is selected because the large norbornyl ring should alter the local motions and yet the low-temperature dynamic mechanical loss peak remains similar to that of BPA.[5] An association between phenylene group motion in solution and the γ or low-temperature loss peak has been noted before.[2] Solution spin-lattice relaxation measurements are capable of determining the motion of the phenylene group and the associated apparent activation energies in a situation where these parameters are dominated by intramolecular interactions.

The NBPC has an added bonus as a subject of a dilute-solution study. The norbornyl ring is most likely rigid and rigidly attached to the backbone. If this is true, all carbons in the ring should only be undergoing segmental motion. However, nearly every carbon has a different direction for the carbon–proton dipolar vectors. This situation can provide a test for the isotropic character of segmental motion, in the sense that all carbon-13 T_1's should be equal despite the differences in orientation if the number of directly bonded protons and differences in bond length are considered.

Also a correlation function recently developed by Hall and Helfand[6] has been used to characterize segmental motion in dissolved polymers.[3,4,7] The NBPC data reported here provide an additional test of this function since three different carbon-13 Larmor frequencies were employed.

Experimental Section

High molecular weight NBPC was dissolved to 10 wt % in perdeuterio-1,1,2,2-tetrachloroethane, subjected to five freeze-pump-thaw cycles, and flame sealed. Three spectrometers were used: a Bruker WM250 and a Bruker SXP (20-90), both at Clark University, and a Bruker WM500 at Yale University. The pulse sequence was the standard (π–τ–$\pi/2$). A temperature calibration was carried out for each probe. For the SXP, a thermocouple was inserted in the probe, while for the WM500 and WM250 the chemical shift vs. temperature method was employed. The standard calibration samples were, for high-temperature, ethylene

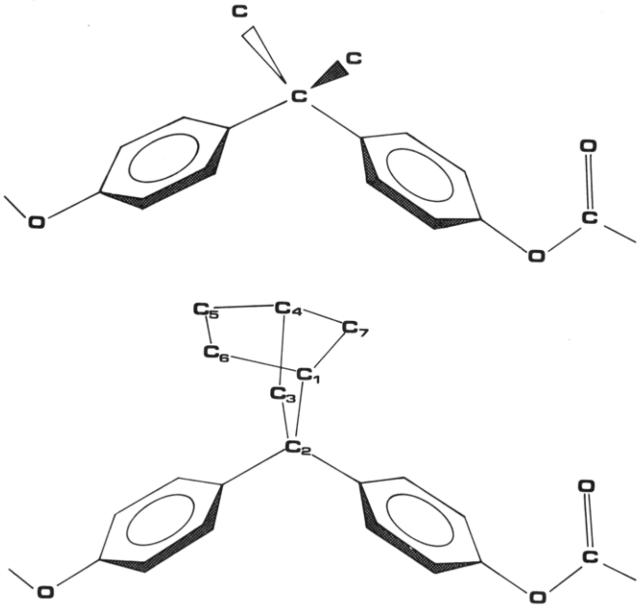

Figure 1. Carbon skeleton of the repeat unit for the polycarbonate of bisphenol A and for the norbornyl-substituted polycarbonate.

glycol and, for low temperature, methanol. The experimental error in reported T_1 values is 10%, which includes errors in temperature control, sample preparation, pulse widths, fitting return of the magnetization to equilibrium, random error, and all other sources.

Results

Phenyl and norbornyl ring carbon magnetizations, excluding C_4–C_7 peak, followed a simple exponential dependence on delay time, τ. The data were fitted with standard linear regression and with more general two- and three-parameter fits, all of which yielded similar results.

The NMR signals of atoms C_4 and C_7 in the norbornyl ring overlapped. These data were fitted as a sum of two exponentials based on the assumption that equivalent motion occurred at both positions and the differences in relaxation time depended only on the number of directly bonded protons and internuclear distances. On the basis of this approach T_1 for the C_4 carbon was set at 1.8 times the T_1 for the C_7 carbon by using known internuclear distances.[8-10] A summary of T_1 values is contained in Table I.

Interpretation

The interpretation begins with an analysis of segmental motion. In order to make an internal comparison of the norbornyl ring T_1 data to test the isotropic character of segmental motion, it is first necessary to account for distance effects. To do this, the quantity N^* is defined as

$$N^* = \sum_j \langle r_j^{-3} \rangle_0^{\,2} \qquad (1)$$

For directly bonded protons, the appropriate internuclear distance corrected for vibrational effects in nonoriented systems is[11-13]

$$\langle r^{-3} \rangle_0^{-1/3} = r_\alpha + (\langle \delta x^2 \rangle + \langle \delta y^2 \rangle - 4\langle \delta z^2 \rangle)/2r_e \qquad (2)$$

where r_α is the distance between average nuclear positions (thermal equilibrium), $\langle \delta x^2 \rangle$ and $\langle \delta y^2 \rangle$ are mean square displacements perpendicular to the bond, $\langle \delta z^2 \rangle$ is the mean square displacement parallel to the bond, and r_e is the distance between equilibrium nuclear positions. Doms et al.[10] report Cartesian coordinates from which r_α values were obtained. Since minima at three frequencies are availabile, the depth of these minima can be used to estimate vibrationally corrected values of $\langle r^{-3} \rangle_0^{-1/3}$. This approach

Table I
Spin–Lattice Relaxation Times (T_1)

temp, °C	T_1, ms																				
	norbornyl carbons																		protonated phenylene carbons[a]		
	C_3			C_5			C_6			C_7			C_1			C_4					
	126 Hz	62.9 Hz	22.6 Hz	126 Hz	62.9 Hz	22.6 Hz	126 Hz	62.9 Hz	22.6 Hz	126 Hz	62.9 Hz	22.6 Hz	126 Hz	62.9 Hz	22.6 Hz	126 Hz	62.9 Hz	22.6 Hz	126 Hz	62.9 Hz	22.6 Hz
−20	290	95		269	89	28	287	94	28	300	109	29	453	159	48	538	196	50	373	179	65
0	218	82		208	82	27	214	77	28	222	91	30	339	149	47	398	164	54	298	157	62
20	179	81		162	78	37	170	81	35	191	90	39	303	149	60	343	162	71	266	164	77
40	155	95	40	164	86	45	150	85	42	181	96	43	294	163	79	325	172	77	263	185	103
60	160	110	51	179	95	63	161	99	52	187	111	59	319	193	105	335	199	106	296	221	137
80	183	125	79	195	134	80	199	127	77	203	130	79	361	255	156	364	243	152	351	287	201
100	209	139	106	214	151	105	218	142	98	222	146	107	405	297	197	399	275	192	397	356	277
120	228	170	124	258	197	126	232	170	115	266	189	126	502	365	233	478	349	225	485	470	344

[a] All protonated phenyl carbon magnetizations are the same within experimental error, so the average value is reported.

Table II
Proton–Carbon Internuclear Distances

atom	r_α, Å	$\langle r^{-3}\rangle_0^{-1/3}$, Å	N	F	N^*, Å^{-6}
C_1	1.093	1.128	1	1.068	0.518
C_3	1.096	1.131	2	1.015	0.971
C_4	1.093	1.129	1	1.102	0.533
C_5	1.096	1.131	2	1.029	0.985
C_6	1.096	1.131	2	1.027	0.983
C_7	1.096	1.131	2	1.022	0.975
phenyl	1.073	1.079	1	1.007	0.638

Table III
$\langle N^*T_1\rangle$ for Norbornyl Ring Carbons

	$\langle N^*T_1\rangle$, Å^{-6} ms		
temp, °C	126 MHz	62.9 MHz	22.6 MHz
−20	274	94	27
0	205	82	27
20	171	81	36
40	160	88	41
60	169	102	55
80	191	128	78
100	211	144	102
120	246	181	120

indicates an increase of 3% over r_α values, which is a reasonable magnitude[12] so all norbornyl carbon–proton distances were corrected by this amount. Internuclear interactions between carbons and nonbonded protons were also estimated from published coordinates[8,10] though vibrational corrections were not estimated here since the nonbonded interactions only change N^* by 2–8%. Including all effects, N^* can be rewritten as

$$N^* = N\langle r^{-3}\rangle_0^{\,2}F$$

where the term F corrects for nonbonded interactions. A similar procedure was carried out for the protonated phenyl carbons using known internuclear distances and vibrational corrections for benzene.[14,15] Table II summarizes the various contributions to N^*.

For the relaxation data, the quantity N^*T_1 is calculated for all carbons at each temperature and frequency. The value of N^*T_1 averaged over all positions in the norbornyl ring is listed in Table III as a function of temperature.

If the motion of all norbornyl carbons is equivalent, N^*T_1 would be the same for the various norbornyl carbons at a given temperature. To test this proposition, the deviations between the individual N^*T_1 values and the average value at each temperature are calculated. The root mean square average deviation for all positions and temperatures is 5.2%, and the maximum deviation is 14%. From these results, it is fair to conclude that all norbornyl ring carbons are undergoing equivalent motion and therefore segmental motion is isotropic. The limitation of this conclusion is the 10% uncertainty in the experimental N^*T_1 values.

The next step is to interpret the average value of N^*T_1 as a function of temperature. This can be done by using the standard equations relating T_1 to the spectral densities, J, the only difference being that an average value of N^* is used in place of $\sum_j r_{ij}^{-6}$ in the expressions for transition probability, W.

$$1/T_1 = W_0 + 2W_{1C} + W_2$$

$$W_0 = \sum_j \gamma_C^2\gamma_H^2 h^2 J_1(\omega_0)/20r_j^6$$

$$W_{1c} = \sum_j 3\gamma_C^2\gamma_H^2 h^2 J_1(\omega_c)/40r_j^6$$

$$W_2 = \sum_j 3\gamma_C^2\gamma_H^2 h^2 J_2(\omega_2)/10r_j^6$$

$$\omega_0 = \omega_H - \omega_C \qquad \omega_2 = \omega_H + \omega_C \tag{3}$$

Table IV
Comparison of BPA and NBPC Phenylene T_1's

	T_1, ms			
	NBPC		BPA	
temp, °C	62.9 MHz	22.6 MHz	62.9 MHz	22.6 MHz
−20	179	65	143	73
0	157	62	198	126
20	164	77	278	217
40	185	103	436	380
60	221	137	657	586
80	287	201	933	931
100	356	277	1320	1172
120	470	344	1943	1673

The Hall–Helfand[4,6] expression for the spectral density from segmental motion is employed.

$$J(\omega) = 2\{[(\tau_0^{-1})(\tau_0^{-1} + 2\tau_1^{-1}) - \omega^2]^2 + [2(\tau_0^{-1} + \tau_1^{-1})\omega]^2\}^{-1/4} \cos[\tfrac{1}{2}\arctan 2(\tau_0^{-1} + \tau_1^{-1})\omega/(\tau_0^{-1}(\tau_0^{-1} + 2\tau_1^{-1}) - \omega^2)] \tag{4}$$

The correlation time for single-bond conformational transitions is τ_0 and the correlation time for cooperative or correlated conformational transitions is τ_1. At each temperature τ_0 and τ_1 were chosen to simulate the observed average norbornyl T_1's at three frequencies. The values of τ_0 and τ_1 including the temperature dependence can be summarized by an apparent activation energy and Arrhenius prefactor. The activation energies for cooperative and single-bond transitions are 24 and 30 kJ/mol, respectively; and the prefactors are 6×10^{-14} and 17×10^{-14} s, respectively.

Next we turn our attention to the motion of the phenylene group. The phenylene group is assumed to undergo the same segmental motion as the norbornyl group since they are both in the polymer backbone. In addition, the phenylene groups could be imagined to rotate about the C_1C_4 axis as has been observed in BPA. However, if one compares the T_1 data for BPA at the same frequencies and temperatures as shown in Table IV, the phenylene group can be seen to be reflecting much less motional freedom in NBPC relative to BPA. In NBPC, a T_1 minimum is observed which occurs at the same temperatures as the T_1 minimum of the norbornyl ring carbons. This indicates virtually no additional rotational freedom of the phenylene group relative to the norbornyl group.

To quantitatively model the phenylene group data, the segmental motion can be combined with a possible phenylene group rotation about the C_1C_4 axis as was done for BPA.[4] The resultant composite spectral density is written as

$$J(\omega) = AJ_a(\tau_0,\tau_1,\omega) + BJ_b(\tau_{b0},\tau_1,\omega) + CJ_c(\tau_{c0},\tau_1,\omega) \tag{5}$$

$$A = (3\cos^2\Delta - 1)^2/4$$

$$B = 3(\sin^2 2\Delta)/4$$

$$C = 3(\sin^4\Delta)/4$$

For a twofold jump

$$\tau_{b0}^{-1} = \tau_0^{-1} + \tau_{ir}^{-1}$$

$$\tau_{c0}^{-1} = \tau_0^{-1}$$

For stochastic diffusion

$$\tau_{b0}^{-1} = \tau_0^{-1} + \tau_{ir}^{-1}$$

$$\tau_{c0}^{-1} = \tau_0^{-1} + (\tau_{ir}/4)^{-1}$$

The form of J_a, J_b, and J_c is the same as in eq 4 with τ_0 replaced by τ_0, τ_{b0}, and τ_{c0}, respectively. The correlation time for internal rotation of the phenylene group is τ_{ir}.

From −20 to +40 °C the combination of internal rotation about the C_1C_4 axis and segmental motion with parameters set from the norbornyl ring cannot simulate the phenylene data. From +60 to +120 °C the phenylene group relaxation can be modeled in this fashion, but a physically unreasonable activation energy for phenylene group rotation of 8 kJ/mol results. This value is not physically sensible because an apparent activation of 22 kJ/mol is found in the mobile BPA.

A consistent interpretation can be found for the data at all temperatures using a model for restricted rotation about the C_1C_4 axis in addition to segmental motion determined at the norbornyl ring. A restricted rotation model developed by Gronski[16] has been combined[3,4] with the Hall–Helfand segmental motion correlation function. The composite spectral density can be written as

$$J_i(\omega_i) = AJ_i^{01}(\omega_i) + \frac{B}{l^2}\{[(1-\cos l)^2 + \sin^2 l]J_i^{01}(\omega_i) + \frac{1}{2}\sum_{n=1}^{\infty}\left[\left\{\frac{[1-\cos(l-n\pi)]}{(1-n\pi/l)} + \frac{[1-\cos(l+n\pi)]}{(1+n\pi/l)}\right\}^2 + \left\{\frac{\sin(l-n\pi)}{(1-n\pi/l)} + \frac{\sin(l+n\pi)}{(1+n\pi/l)}\right\}^2\right]J_i^{\lambda_n}(\omega_i)\} + \frac{C}{2l^2}\{\frac{1}{2}[(1-\cos 2l)^2 + \sin^2 2l]J_i^{01}(\omega_i) + \sum_{n=1}^{\infty}\left[\left\{\frac{[1-\cos(2l-n\pi)]}{(2-n\pi/l)} + \frac{[1-\cos(2l+n\pi)]}{(2+n\pi/l)}\right\}^2 + \left\{\frac{\sin(2l-n\pi)}{(2-n\pi/l)} + \frac{\sin(2l+n\pi)}{(2+n\pi/l)}\right\}^2\right]J_i^{\lambda_n}(\omega_i)\} \quad (6)$$

where

$$J_i^{01}(\omega_i) = \{[\tau_0^{-1}(\tau_{01}^{-1} + \tau_1^{-1}) - \omega_i^2]^2 + (2\tau_{01}^{-1}\omega_i)^2\}^{-1/4} \times \cos\left[\frac{1}{2}\arctan\frac{2\tau_{01}^{-1}\omega_i}{\tau_0^{-1}(\tau_{01}^{-1} + \tau_1^{-1}) - \omega_i^2}\right]$$

and

$$J_i^{\lambda_n}(\omega_i) = \{[\tau_0^{-1}(\tau_{01}^{-1} + \lambda_n)(\tau_{01}^{-1} + \tau_1^{-1} + \lambda_n) - \omega_i^2]^2\}^{-1/4}\cos\left[\frac{1}{2}\arctan\frac{2(\tau_{01}^{-1} + \lambda_n)\omega_i}{(\tau_0^{-1} + \lambda_n)(\tau_{01}^{-1} + \lambda_n) - \omega_i^2}\right]$$

$$\tau_{01}^{-1} = \tau_0^{-1} + \tau_1^{-1}$$

$$\lambda_n = (n\pi/l)^2 D_{\mathrm{ir}}$$

where D is the diffusion constant for restricted diffusion and l is the angular amplitude of the restricted diffusion. If the restricted rotation is a harmonic well, l should be proprotional to $T^{1/2}$ and D should be proportional to T. A fit of the phenylene T_1's yields

$$D = (8.3 \times 10^6)T - 1.25 \times 10^9$$

$$l = 16.74 \times T^{1/2} - 187$$

where T is in kelvin. In terms of angular width l increases from 81° at −20 °C to 147° at +120 °C.

Discussion

NBPC undergoes isotropic segmental motion well described by the Hall–Helfand correlation function.[6] The activation energy for correlated motions at 24 kJ is slightly higher than the corresponding value of 19 kJ observed for BPA. On the other hand, the activation energy for single-bond conformational transitions is 30 kJ in NBPC and 16 kJ in BPA. Since the glass transition of NBPC is dramatically higher, 232 °C, relative to BPA, 150 °C, the glass transition would appear to be correlated with single-bond conformational transitions.

The phenylene group does not rotate about the C_1C_4 axis near room temperature as is the case for BPA. It appears that the inclusion of the large norbornyl group in the backbone blocks phenylene group rotation. A restriction of motion is also seen in solid NBPC by NMR.[17] However, bulk NBPC shows a low-temperature or "γ" mechanical loss peak at a temperature of −108 °C which is rather similar to BPA. If phenylene group rotation is the primary source of the loss peak, the similarity between BPA and NBPC is anomalous since phenylene group rotation is much slower or nonexistent in dissolved NBPC. It also has been argued that π flips of a phenylene group are insufficient to produce a large loss peak of the type observed in BPA.[18,19] It is true that substituents on the phenylene ring block phenylene group rotation[2] and shift the γ dynamic mechanical peak to higher temperatures. However, the lack of phenylene group rotation is not the key issue.

An alternative motional model has been proposed[19] which suggests the major factor leading to the low-temperature loss peak is a correlated conformational interchange produced by rotations about two backbone carbonate CO bonds. It is a correlated interchange in the sense of the Hall–Helfand model;[6] that is, the two backbone bond rotations are close in time but not simultaneous. The motion consists of an interchange of a trans–trans carbonate conformation with a cis–trans carbonate conformation separated by one bisphenol unit. In BPA itself, flips are coupled to this motion by intermolecular and intramolecular interactions. In NBPC, the phenylene ring motion is impeded by the large norbornyl ring, which is however well separated from the critical CO bonds, so the conformational interchange is still possible. As mentioned, phenylene group substitution in both positions ortho to the carbonate group is observed both to block phenylene group rotation[2] and raise the temperature of the loss peak. In the correlated interchange model, this is plausible since the steric interaction is between the groups on the phenylene ring and the carbonate. This effect is the source of the earlier correlation between phenylene group rotation and the γ loss peak but the NBPC results show this correlation to be only part of a larger picture.

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Polymorphic Transformations in Ferroelectric Copolymers of Vinylidene Fluoride Induced by Electron Irradiation

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ABSTRACT: Electron irradiation of vinylidene fluoride copolymers with tri- or tetrafluoroethylene was found to induce a room-temperature polymorphic transformation of the ferroelectric phase to one that is structurally equivalent to the paraelectric phase normally accessible only above the Curie temperature. This solid-state transformation is irreversible and precedes by far the eventual amorphization that takes place at higher electron doses. Both transformations are extremely sensitive to electron dose, amorphization occurring at ca. 14–20% of the corresponding dose for polyethylene, and polymorphic transformation at ca. 4–9% of the same dose. This polymorphic transformation is highly unusual in that it does not yield an intermolecularly defective lattice as do electron-induced transformations in other polymers; on the contrary, evidence from electron diffraction and dark-field electron microscopy shows that the resulting paraelectric-like phase exhibits significantly higher lattice perfection than the original ferroelectric phase. PVF_2 homopolymer (β-phase) does not undergo such an electron-induced transformation prior to amorphization. An explanation for the susceptibility of the copolymers, but not of the homopolymer, to polymorphic transformation is offered on the basis of structural differences between the two.

Introduction

Ferroelectric-to-paraelectric phase transformations in random copolymers of vinylidene fluoride (VF_2) and trifluoroethylene (F_3E) have been demonstrated in the last few years.[1-4] The molecular conformation of these copolymers in their ferroelectric phase is the same as in β-PVF_2, i.e., essentially all *trans* (TT); above the Curie temperature, this conformation changes to a disordered sequence of TG, T$\bar{G}$, and TT units as a result of the introduction of *gauche* bonds.[3,4] In both ferroelectric and paraelectric phases, the copolymer chains are packed on a lattice that is very close to hexagonal.[3,4] Similar transitions have recently been found also in a copolymer of vinylidene fluoride with tetrafluoroethylene (F_4E),[5,6] proving that this Curie behavior is not a result of any particular comonomer, but is an inherent property of the homopolymer, poly(vinylidene fluoride) (PVF_2); the latter copolymer (VF_2/F_4E) is, in fact, equivalent to PVF_2 having an increased content of head-to-head (i.e., CF_2–CF_2) defects.[7] On the other hand, PVF_2 homopolymer does not show a clear ferroelectric-to-paraelectric solid-state transformation upon heating. On the basis of the variation of the Curie temperature with VF_2 content in VF_2/F_3E copolymers, it was concluded[3] that for β-PVF_2 such a transition should be centered slightly above the melting point; the role of melting in aborting an ongoing ferroelectric-to-paraelectric transformation was clearly demonstrated in that study[3] for a 78/22 mol % VF_2/F_3E copolymer. In addition, indications of the earliest stages of such a transition have been recently reported for β-PVF_2 at temperatures just below the melting point.[4]

While such ferroelectric-to-paraelectric phase transformations are only a very rare and recently discovered phenomenon among polymers,[8] other crystallographic transformations are, of course, common and well-known. Within that category lie electron-induced transformations which generally lead to loss of crystallinity as a result of cross-linking or chain scission, but which may also include intermediate crystallographic phase changes.[9] The most widely studied polymer in this regard is polyethylene, which undergoes an orthorhombic-to-hexagonal phase transformation en route to amorphization when irradiated by electrons.[10-13] This transformation is evidenced by the following sequential changes that occur in the electron-diffraction pattern of single crystals of orthorhombic polyethylene during observations in the electron microscope: disappearance of the outer *hk*0 reflections, broadening of the inner *hk*0 reflections, increase in the (200) spacing to a value characteristic of the (110) spacing (thus leading to hexagonal symmetry), and, finally, fading of the remaining six reflections and their replacement by an amorphous halo. These manifestations are a direct consequence of the chemical and structural changes that result in cross-linking due to formation of free radicals by the high-energy electrons. Specifically, cross-linking causes at first crystalline distortions (with consequent loss of the outer *hk*0 reflections and broadening of the inner ones), followed by continuous expansion of the *a* axis of the unit cell (to the point of attainment of hexagonal symmetry), and eventually full amorphization. Similar phenomena have also been observed in other polymers, e.g., in even–even polyamides, where the separation between the (100) and (010/110) reflections was found to decrease with electron bombardment as these reflections were simultaneously becoming broader and more diffuse.[14]

These two areas—electron-induced phase changes and ferroelectric-to-paraelectric transitions—have been brought together in this study. An irreversible transformation of

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