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Studies of Chain-Extended Morphology in Polyethylene by Vibrational Spectroscopy

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ABSTRACT: Investigations of the 39-cm^{-1} band observed at low temperatures in the far-infrared region suggest that this band is characteristic of chain-extended polyethylene (CEPE). In the process of chain extension via the hexagonal phase, partial disclinations (long chain twists) and gauche bond defects are most certainly introduced. During the transition from the hexagonal to the orthorhombic phase upon cooling, these defects can be "frozen in" and activate the spectroscopically inactive modes of the PE chain and lattice by a lowering of the molecular symmetry in the vicinity of the defect. This mechanism is believed to be the origin of the IR band at 39 cm^{-1}. Spectroscopic studies do not support the assignment of this band to the monoclinic phase known to be present in mechanically processed PE.

Introduction

When chain-extended polyethylene was first reported by Wunderlich and Arakawa,[1] it attracted much attention because of its novel morphological structure and potential for enhanced mechanical stiffness. Recently, it has been suggested[2,3] that the intermediate hexagonal phase[4] which exists at high temperature and pressure plays an important role in the formation of this chain-extended morphology. Crystallization of PE via this hexagonal phase proceeds very rapidly with a large lamellar growth rate resulting in lamellar thicknesses in the 2000–7000 Å range.[3] Unfortunately, in this thickness range, many of the standard characterization methods (SAXS, IR, and Raman) are ineffective, and hence most of the useful information on CEPE has been provided by thermal analysis and electron microscopy.[3] Recently, a low-frequency Raman-active longitudinal acoustical mode (LAM) has been observed[5] in CEPE by Fabry–Perot interferometry, and thus this technique shows considerable promise as a future characterization method.

An interesting study of CEPE in the far-infrared region has been reported by Frank et al.[6] in which a distinctive feature at 39 cm^{-1} was observed below 170 K. Although intermolecular vibrations of the crystalline lattice are generally found in this region, the usual characteristic temperature-dependent frequency shift associated with lattice modes was not observed for this band, with its position remaining unchanged down to 12 K. The absence of this band in melt- or solution-crystallized PE has added to the apparent intrigue surrounding this mode and led to the suggestion that its origin may be due to the presence of a monoclinic crystalline modification known to be present[7,8] in mechanically deformed PE. An alternative explanation attributed this band to the A_u (IR and Raman inactive) *c*-axis translatory mode[9] made spectroscopically active by molecular disorder within the crystal, but no attempt to definitely assign this band was made.

It is the purpose of this work to explore the origin of the 39-cm^{-1} band through a series of spectroscopic measurements obtained at 10 K from samples with varying morphologies prepared with different thermal and mechanical processing histories. These results have been combined with those obtained from DSC measurements and those published previously[5] using Fabry–Perot interferometry to propose an assignment of this low-frequency band.

Experimental Section

The material used in the preparation of CEPE was that obtained from BASF (Lupolen 6011L) or ICI (Rigidex 50). Both were high-density PE with a weight-average molecular weight near 100 000. They were subjected to high-temperature annealing (498–503 K) while under a pressure of about 5 kbar and were similar to those used in the study of Frank et al.[6] DSC traces of these CEPE samples gave a peak melting temperature of 142 °C at the deepest minimum. Two considerably weaker minima were observed at 130 and 136 °C and most probably correspond to crystal populations resulting from segregation due to molecular weight and/or branching content.[2]

The PE used for the deformation studies was Dow LP 51.1-6 high-density polyethylene. Samples were used without further purification. Deformation was induced by simply pressing in a KBr pellet die while higher deformation was achieved by grinding at room temperature either with a mortar and pestle or with a "Wiggle-Bug" grinder followed by cold pressing at 20 000–30 000 psi.

Fourier transform IR spectra were recorded with an IBM IR 98 vacuum interferometer. A high-pressure mercury vapor lamp was used as a source, with detection of the transmitted radiation being provided by either a DTGS pyroelectric crystal fitted with

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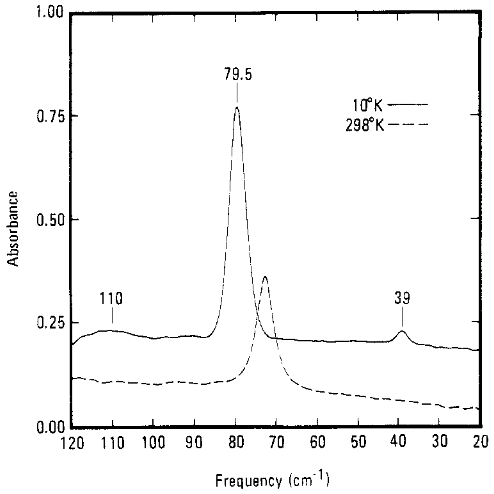

Figure 1. Far-infrared spectra of CEPE at 300 and 10 K.

a polyethylene window or a germanium-doped bolometer cooled to 1.5 K.

The Raman system consisted of a J-Y HG-2S double monochromator, Nicolet 1180 computer, and a Spectra-Physics 165-08 argon ion laser. Appropriate laser line filters, polarizers, scramblers, and focusing optics were used to deliver and collect the incident and scattered light.

The low-temperature cryostat was manufactured by Oxford Instruments and could be fitted with several window materials. It is a helium flow-type cryostat which could be pumped so that potentially a temperature of 2 K could be achieved. A resistive heating element equipped with a feedback circuit allowed temperatures in the range 10–300 K to be maintained to within ±2 K.

Since semicrystalline PE cryostat windows were used in the far-infrared region, it became important to use a "cold" reference in the FTIR measurements since slight changes in the temperature of the cryostat windows would introduce artifacts into the absorbance spectrum because of slight shifts in the low-frequency bands found in the PE windows.[10] Spectral artifacts in this region (15–120 cm^{-1}) were avoided by ratioing a low-temperature sample to that of an empty cryostat also recorded at low temperatures.

Results and Discussion

A. Low-Frequency IR and Raman Spectra. The far-infrared spectra of CEPE at 10 and 298 K are shown in Figure 1. As can be seen in the room-temperature spectrum, only a single band was observed at 72.5 cm^{-1}, corresponding to the B_{1u} translatory lattice mode assigned previously.[10,11] When the temperature was lowered to 10 K, additional bands were found[6,12] at 110 and 39 cm^{-1}. The former has been assigned[12] to a B_{2u} translatory lattice mode which had been located at 94 cm^{-1} at room temperature by far-infrared interferometry with high radiometric precision.[13] The sharper feature at 39 cm^{-1} is identical with that reported by Frank et al.[6] and did not appear to shift in frequency from the value reported at 170 K.

In order to determine the spectral activity of the 39-cm^{-1} band, Raman spectra at 300 and 10 K were recorded and are shown in Figure 2. At 300 K, a single broad band is observed at 100 cm^{-1} which splits at low temperatures (10 K) into components at 129 and 106 cm^{-1}, assigned to the A_g and the B_{3g} rotatory lattice modes, respectively.[14] No other Raman bands are apparent in the low-frequency region near 39 cm^{-1} at 10 K. An extremely weak band, whose intensity is further diminished by the temperature and frequency dependence of the Boltzmann population distribution of states present in the Raman effect, cannot be entirely ruled out but seems unlikely.

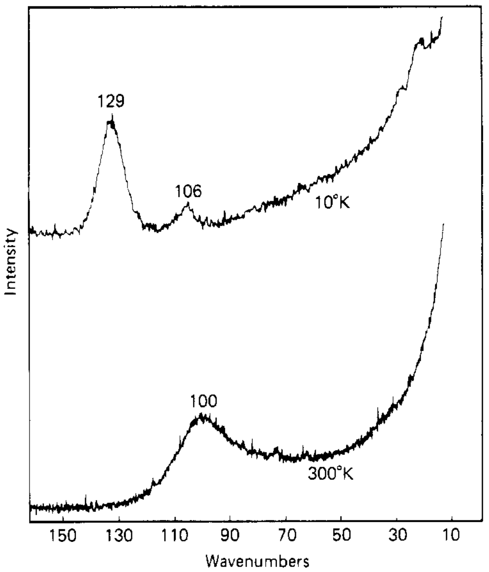

Figure 2. Low-frequency Raman spectra of CEPE at 300 and 10 K.

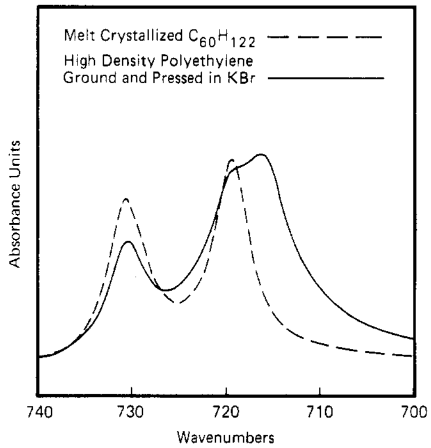

Figure 3. IR spectra in the $-CH_2-$ rocking region of melt-crystallized $C_{60}H_{122}$ (dashed line) and high-density PE ground and pressed in KBr (solid line).

B. Transformation from Orthorhombic to Monoclinic Crystal Structure. In an effort to understand the origin of the 39-cm^{-1} IR band, several additional experiments were undertaken. Initially, the presence of an alternate crystal structure was considered.[7,8] Seto et al.[8] reported the existence of a monoclinic crystal modification in PE when it was subjected to plastic deformation. The unit cell was found to contain two molecules and belong to the monoclinic crystal system with space group $C2/m$ (C_{2h}^3). The spectroscopic or primitive unit cell contains only one molecule and is similar to that of the triclinic *n*-alkanes.[15] With one molecule per unit cell, only one librational lattice mode is expected, and under C_{2h} symmetry, it should be Raman active only. As mentioned previously, the 39-cm^{-1} band was observed in the IR spectrum.

A more detailed study of the monoclinic phase in the far-infrared region was undertaken after WAXS studies on our CEPE sample indicated the presence of 5–10% of the monoclinic modification. As Seto et al.[8] suggested, deformation of PE produces a transformation from the orthorhombic to the monoclinic phase. Thus, a PE specimen containing a small amount of monoclinic phase could be deliberately produced by shearing the powdered sample with a mortar and pestle. Kikuchi and Krimm[16] and Painter et al.[17] have shown that the presence of monoclinic phase can be detected by the presence of an IR band at 717 cm^{-1} in the $-CH_2-$ rocking region. Shown

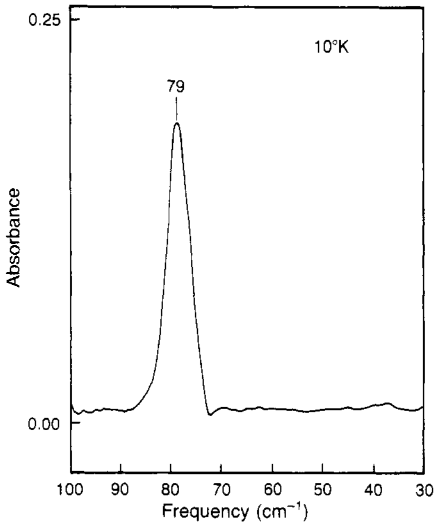

Figure 4. Far-infrared spectrum of ground and pressed high-density PE recorded with a liquid helium cooled (1.5–2.0 K) bolometer.

in Figure 3 is the 700–740-cm^{-1} region of a sheared PE powder sample. For comparison, a similar spectrum of orthorhombic $C_{60}H_{122}$ is included. The components at 730 and 719 cm^{-1} result from crystal field splitting of the $-CH_2-$ rocking fundamental due to the presence of two molecules per unit cell. Clearly, in the sheared PE spectrum, an intense band is present at 716 cm^{-1}. Pressing PE powder into a KBr pellet was also found to induce a transformation from the orthorhombic to the monoclinic phase as indicated by the presence of the 716-cm^{-1} band. It is interesting to note that the presence of only a single $-CH_2-$ rocking mode attributable to the monoclinic modification is further evidence of only one molecule per primitive unit cell.

The sheared PE powder, known to contain the monoclinic phase, was then pressed into a self-supporting pellet and investigated in the far-infrared region at 10 K, using a high-sensitivity bolometer detector operating in the range 1.5–2.0 K. The results are shown in Figure 4, where the intensity of the B_{1u} lattice mode has been scaled for comparison with that of Figure 1. The cutoff at 100 cm^{-1} is due to the presence of a diamond scatter plate in the bolometer used to reject IR radiation of higher wavenumbers. Upon inspection of the low-frequency region of Figure 4, it is apparent that there is no band present at 39 cm^{-1}, thus supporting the earlier group theoretical argument that this band is not attributable to a vibration of the monoclinic lattice.

C. Defect Structures. A possible origin of the 39-cm^{-1} band due to defect structures induced during the high-pressure crystallization process was also considered. From the information obtained from WAXS studies, Bassett et al.[4] initially suggested the presence of gauche structures in the high-temperature, high-pressure, hexagonal phase due to an observed reduction of the *c*-axis (chain axis) repeat distance from that of the orthorhombic phase. Raman measurements in the hexagonal phase[18,19] have since confirmed the presence of gauche bonds due to the observation of a band of medium intensity in the 1060–1100-cm^{-1} region attributable to a CC stretching vibration of a gauche bond.

The crystallization of PE into the orthorhombic phase via the hexagonal intermediate phase has been considered[2] to play an important role in the formation of CEPE. However, the extent of defect structures (gauche bonds) which remain after crystallization and hence have been "frozen in" has not yet been determined. This becomes spectroscopically important because the presence of disorder in the crystalline lattice can give rise to a breakdown in the optical selection rules. Thus, the IR and Raman spectra may contain new bands attributable to both the characteristic defect structures (e.g., gauche bonds) and the normal modes of the polymer chain which previously were not IR and Raman active.

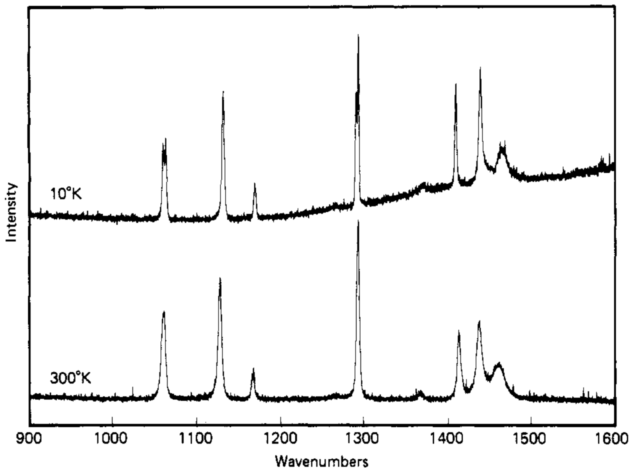

Figure 5. Raman spectra of CEPE at 300 and 10 K.

In Figure 5 are shown the Raman spectra of CEPE in the 900–1600-cm^{-1} region at 300 and 10 K. In the 1060–1100-cm^{-1} region, the presence of gauche bonds would be evident[18,19] since a broad band at 1080 cm^{-1} would be expected to appear. As clearly seen in Figure 5, there is no such band present at either room temperature or 10 K, thus indicating that very few (<1%) gauche bonds are present.

Several other features shown in these spectra are consistent with this observation. In the 1295-cm^{-1} region, no broad feature[20] (at ~1303 cm^{-1}) was present, which would have indicated the existence of an amorphous component. Also, in the low-temperature spectrum of Figure 5, the bands at 1060 and 1295 cm^{-1} are split[21,22] into two components by crystal field interactions. Although this splitting has been observed[21] in "single-crystal-texture" PE, this is the first reported observation in CEPE. This splitting is emphasized at low temperatures due to contraction of the unit cell parameters,[11] which already are at a minimum due to the chain-extended morphology. Thus, all factors appear to support the high crystallinity of CEPE with the possible presence of a small amount of gauche defects. This does not, however, rule out the presence of other defect structures that do not contain gauche bonds. Recently, Reneker and Fanconi[23] and Reneker and Mazur[24] have investigated several conformational defects involving a slow twist of the polymer backbone. These partial disclinations not only can be accommodated in the lattice but also have been shown[23,24] to undergo the accordion-like motion associated with the Raman-active longitudinal acoustic mode (LAM). Thus, a recent report of the observation of LAM in CEPE using Fabry–Perot interferometry[5] could be attributed to vibrations of trans-planar chains and/or chains that contain partial disclinations. This is an important observation and will be discussed in further detail in a later section.

D. Assignment of 39-cm^{-1} IR Band. During the investigation of the origin of the 39-cm^{-1} band, it became apparent that a vibrational mode with such a low-frequency most likely could be attributed to an intermolecular or lattice mode since the lowest frequency skeletal vibration predicted by normal coordinate analysis[25] was con-

Table I
Polyethylene Lattice Modes: Calculations

symmetry species	TS65[9]	KM65[26]	TK67[27]		HH73[28]	BF78[29]	Ko79[30]	activity
	300 K	300 K	300 K	77 K	300 K	300 K	300 K	
A_u $\nu_9^b(0)$	59–61	50	51	58	44	55	38	I
B_{1u} $\nu_5^a(\pi)$	76–77	65	71	81	81	86	66	IR
B_{2u} $\nu_5^b(\pi)$	105–117	95	109	113	104	109	85	IR
B_{3g} $\nu_5^b(0)$	134–138	115	121	139	95	102	93	R
A_g $\nu_5^a(0)$	171–188	152	172	182	136	141	115	R

Table II
Polyethylene Lattice Modes: Experimental Data[a]

symmetry species	INS[31]	IR[27]	IR[12]		INS[32]			activity
	300 K	300 K	300 K	2 K	300 K	77 K	300 K	
A_u $\nu_9^b(0)$	39				34	47	63	I
B_{1u} $\nu_5^a(\pi)$	67	73	73	80	75	77	71	IR
B_{2u} $\nu_5^b(\pi)$	114			109	97	97	118	IR
B_{3g} $\nu_5^b(0)$	147				113	122	130	R
A_g $\nu_5^a(0)$	167				178	186	163	R

symmetry species	IR[13]		R[28]	IR[6]	R[b]		IR[b]	activity
	300 K	77 K	300 K	12 K	300 K	10 K	10 K	
A_u $\nu_9^b(0)$				39			39	I
B_{1u} $\nu_5^a(\pi)$							79.5	IR
B_{2u} $\nu_5^b(\pi)$	94	107					110	IR
B_{3g} $\nu_5^b(0)$			108		~100	106		R
A_g $\nu_5^a(0)$			133		~100	129		R

[a] INS = (incoherent) inelastic neutron scattering, IR = infrared, R = Raman. [b] This work.

siderably higher. A survey of theoretical[9,26–30] and experimental (IR, Raman, and inelastic neutron scattering (INS)[6,12,13,27,28,31–33]) results published over the past 20 years provided the interesting information shown in Tables I and II. In addition to the two IR-active and two Raman-active modes described earlier, a fifth A_u mode corresponding to the *c*-axis translatory lattice mode has been predicted[9,26–30] but should be spectroscopically (IR and Raman) inactive. Fortunately, incoherent INS measurements[31–33] are not subject to the same selection rules and hence all vibrational modes are potentially observable. As seen in Table II, there have been a number of INS studies that report the presence of a band in the vicinity of 39 cm^{-1}. In some instances, an assignment to the A_u translatory mode has actually been made. As seen in Table I, the calculated values of the A_u mode have decreased as a function of time but, of course, clearly depend on the choice of intermolecular potential functions. It does, however, appear reasonable to conclude that both theoretical and experimental results indicate that a low-frequency mode occurs in the 30–60-cm^{-1} region and is associated with a translatory out-of-phase motion of the two molecules in the unit cell moving parallel to their chain axis. On the basis of the above discussion, it is possible that the 39-cm^{-1} IR band is, in fact, the A_u mode optically activated by defects within the lattice. The translatory character of this mode parallel to the chain axis would also explain the insensitivity of its position to temperature since a lattice contraction and the subsequent increase in intermolecular forces would not be expected to perturb such a vibrational mode. In order to be consistent with the data previously described concerning gauche bonds and the presence of LAM,[5] the defect structures would be of the slow twisting variety.[23,24] This is not an unreasonable suggestion since during crystallization at high temperature and pressure, extended-chain lengths[2] in the 0.5–1-μm range are not unusual and the coordination of chain ends to maintain a planar molecule over these extensions is highly unlikely.

Recent calculations by Reneker and Mazur[24] on disclinations in crystalline regions of PE indicate that 180° twist boundaries and/or 360° gently twisted disclinations may be possible in an extended-chain crystal without the interruption of LAM. Furthermore, they found that the packing forces exerted by the lattice tend to keep the distorted region confined. It is these types of defects that could give rise to the activation of the 39-cm^{-1} band in the IR spectrum of CEPE.

If this is the origin of this low-frequency band, it should also be observed in the Raman spectrum. Two explanations for its absence are possible. As mentioned previously, whereas low-frequency IR bands become sharper and more intense at low temperature, the same factors combine with Boltzmann statistics to diminish the intensity of Raman scattering. Another more obvious explanation for negligible intensity of the 39-cm^{-1} band in the Raman spectrum arises from consideration of the change in polarizability required for Raman intensity. If the change in molecular polarizability during *c*-axis translatory motion in regions of broken symmetry is small, then the corresponding Raman intensity would be weak.

The last consideration of concern deals with the observation that none of the other A_u modes predicted[29] at 1041 and 1181 cm^{-1} were present in the high-frequency Raman spectra of Figure 5. It is unclear why this is the case but perhaps again can be attributed to lack of intensity.

Conclusion

Structural and thermal studies of CEPE have been carried out. A weak band observed at 39 cm^{-1} in the IR at 10 K was not found in the low-frequency Raman spectrum at the same temperature. An investigation of the higher frequency Raman spectra did not reveal the presence of any bands attributable to gauche bonds indicative of molecular disorder. No evidence was found to assign the 39-cm^{-1} IR band to a monoclinic crystal modification known[7,8] to be introduced in PE by mechanical processing. Furthermore, group theoretical analysis of the primitive unit cell indicated that a single rotatory lattice mode should be spectroscopically active and appear only in the Raman spectrum.

Normal coordinate calculations[9,26-30] and INS measurements[31-33] support the presence of a low-frequency *c*-axis lattice mode that is both IR and Raman inactive. It was concluded that the only known type of defect model that could account for the presence of LAM in these CEPE crystals while also being responsible for a breakdown in the optical selection rules was a 180° twist boundary or a 360° gently twisted disclination as suggested by Reneker and Mazur.[24]

Registry No. PE, 9002-88-4.

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Dynamic Mechanical Properties of Perfluorocarboxylate Ionomers

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ABSTRACT: Two perfluorocarboxylate ionomers of different ion-exchange capacities (IEC) of 1.25 and 1.80 mequiv/g were studied to determine their dynamic mechanical behavior, water uptake, and rates of neutralization. These polymers consist of a fluorocarbon backbone containing short side chains on the end of which the carboxylate functionality resides. They are quite similar in many ways to the more familiar perfluorosulfonate ionomers that have been studied extensively. Methyl esters, free acids, and sodium, potassium, cesium, silver, barium, magnesium, and tetrabutylammonium salts were examined. In the case of the 1.25 mequiv/g IEC resin, a two-phase morphology consisting of a fluorocarbon matrix and a dispersed "ionic" phase could well explain the observed relaxation behavior for all the salts with the exception of the tetrabutylammonium salt. It, as well as the free acid in the dry state and the ester precursor, appeared to be single-phase materials. The derivatives of the 1.80 mequiv/g IEC resin showed no unambiguous evidence for phase separation. This was attributed to their high polar group content (ca. 36 mol %). The effect of polar diluents such as water and ethylene glycol could be accounted for in the above framework. In general, these perfluorocarboxylate polymers absorb much less water and show much slower neutralization rates than similar perfluorosulfonate polymers.

Introduction

Perfluorinated sulfonate and carboxylate ionomers have been the subject of numerous investigations in recent years, largely because of their technological interest as membranes in the water-swollen form.[1] The sulfonated ionomers have received more attention than the carboxylated ionomers, but the latter show very interesting properties somewhat distinct from the former. A recent study[2] of a commercial perfluorocarboxylate ionomer membrane indicates that the polymer contains only about 50% of its polar groups in the form of carboxylates, with the rest being sulfonates. Naturally, this tends to complicate the interpretation and obscure the differences between the two forms. In the present paper we present the results of a dynamic mechanical relaxation study of two perfluorinated derivatives, including esters, acids, and salts. The results clarify and supplement the assignments of relaxation peaks to particular mechanisms made previously. They also include the effect of polar diluents such as water and ethylene glycol on the relaxation behavior.

Especially striking is the similarity of the relaxation behavior of the perfluorinated carboxylate derivatives to

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