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Long-Range Conformational Structure and Low-Frequency Isotropic Raman Spectra of Some Highly Disordered Chain Molecules

We report here measurements on a unique Raman band whose position and shape are directly related to statistical averages associated with the conformation of highly disordered chain molecules. The band of interest, the "D-LAM" band, has previously been identified only in the low-frequency isotropic Raman spectra of polyethylene[1,2] and poly(tetrafluoroethylene).[1] The aim of the present work is to demonstrate that D-LAM bands exist in the Raman spectra of other kinds of polymers. Measurements on some simple chain molecules in the amorphous and liquid states are presented and, in all cases, D-LAM bands are found.

It is possible, at least in principle, to relate parameters associated with the D-LAM band, in particular its frequency and half-width, directly to certain conformational statistics. The band itself is highly inhomogeneous, being comprised of a complex of bands representing delocalized skeletal-bending modes. Its intensity is attributable to the LAM-like "in-phase", or "breathing" character of the contributing modes, and for this reason the resulting complex is referred to as the "D-LAM band", where LAM is an acronym for longitudinal acoustic mode and D stands for disorder. Because the band has a low depolarization ratio, it can be distinguished from nearly all other kinds of bands in the low-frequency Raman spectrum. Although D-LAM is intrinsically inhomogeneous, it behaves in some ways like a homogeneous band. For example, its frequency depends in a simple way on the number, n, of skeletal atoms in the chain; i.e., its frequency is proportional to $1/n^2$, and depends on the average conformation of the chain.[1] The bandwidth is determined by the dispersion about the average conformation. Both the peak frequency and bandwidth have been shown to increase with the number of gauche bonds in the case of poly(methylene)-type chains.[1] These relations have been used to advantage to characterize the highly disordered, amorphous component in semicrystalline polyethylene.[2]

The chain molecules for which new Raman data are presented here are listed in Table I along with polyethylene and poly(tetrafluoroethylene). The Raman spectra, which are shown in Figures 1–3, were measured with an ISA Ramanor U-100 spectrometer system. The measurements were made with a right-angle scattering geometry, with 300–350 mW of the argon ion 5145-Å line, and with a resolution of 2–3 cm^{-1}. The isotropic spectra were obtained in the usual manner by subtracting the perpendicular spectrum from the parallel spectrum, i.e., $I_{iso} = I_{\parallel} - sI_{\perp}$, where the parameter s was adjusted to eliminate depolarized bands. Depending on experimental conditions, s had a value between 1.18 and 1.75.

For the polymers we studied, the D-LAM band appears below 300 cm^{-1} and is the prominent feature in all the isotropic Raman spectra shown in Figures 1–3. Its shape tends to be symmetric, but there are a number of complicating spectral features. A more complete and quantitative interpretation of these spectra will be reported later. Here we will briefly discuss some of the more ap-

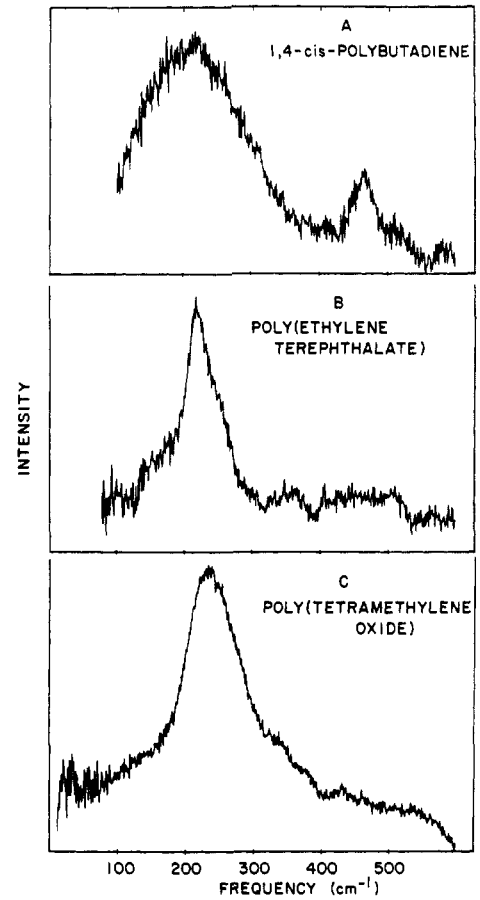

Figure 1. Low-frequency isotropic Raman spectra of liquid (A) 1,4-*cis*-polybutadiene, (B) poly(ethylene terephthalate), and (C) poly(tetramethylene oxide).

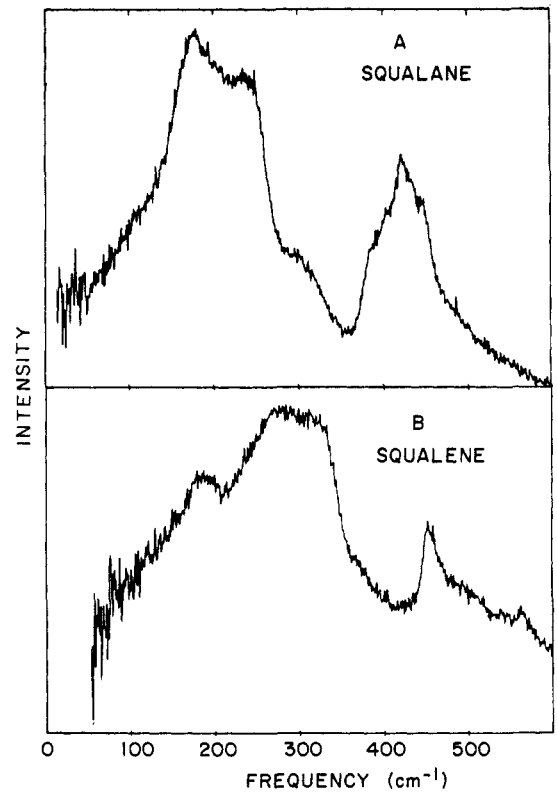

Figure 2. Low-frequency isotropic Raman spectra of liquid (A) squalane and (B) squalene.

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Table I
Frequencies and Normalized Bandwidths of the D-LAM Bands of Disordered Chain Molecules

chain molecule	frequency, cm^{-1}	rel bandwidth[a]
1,4-polybutadiene, cis[b]	223	1.18
squalene[c]	298[j]	1.0
poly(ethylene oxide)[d]	264	0.94
poly(ethylene)[e]	200[k]	0.81
poly(tetramethylene oxide)[f]	240	0.79
poly(ethylene oxide) in aq soln[g]	286	0.60
poly(ethylene terephthalate)[h]	220	0.50
poly(tetrafluoroethylene)	65[k]	0.34[l]
squalane[i]	174	(m)

[a] The relative bandwidth is measured by the quantity $\Delta\lambda_{1/2}/\lambda_0$. In this expression, $\lambda \propto \nu^2$ so that $\Delta\lambda_{1/2}$ is the full half-width at half-height expressed in terms of ν^2; λ_0 refers to the square of the D-LAM frequency. The half-width is expressed in terms of λ because changes in the variance tend to be linearly related to changes in λ, but not to ν.[1] The distinction between λ and ν is important at low frequencies when $\Delta\nu_{1/2}$ and ν_0 are of the same order of magnitude. Division by λ_0 is necessary to normalize the half-width so that the gross effects of mass and force constant differences are eliminated. [b] Amorphous pellet. [c] Squalene: $[(CH_3)_2C{=}CH(CH_2)_2C(CH_3){=}CH(CH_2)_2C(CH_3){=}CHCH_2]_2$. [d] Liquid, MW = 600. [e] Melt. [f] Liquid, MW = 2723. [g] 25% by volume. [h] Poly(ethylene terephthalate): $[(CH_2)_2O(CO)C_6H_4(CO)O]_x$; amorphous pellet; MW = 40,000. [i] Squalane: $[(CH_3)_2CH(CH_2)_3CH(CH_3)(CH_2)_3CH(CH_3)(CH_2)_2]_2$. [j] Average of 279- and 317-cm^{-1} bands. [k] From ref 1. [l] Bandwidth estimated from the spectrum of n-$C_{20}F_{42}$ (ref 6). [m] Not measured.

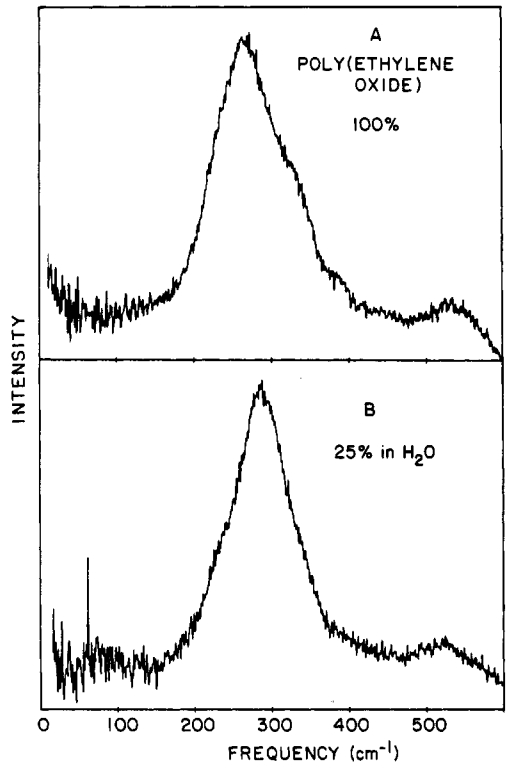

Figure 3. Low-frequency isotropic Raman spectra of liquid (A) poly(ethylene oxide) and (B) poly(ethylene oxide) dissolved in water (1:3 by volume).

parent and interesting relations between spectra and structure in the limit of an infinitely long chain.

The spectra of the alkyl ethers poly(tetramethylene oxide) and poly(ethylene oxide), which we will abbreviate as POM_4 and POM_2, when considered along with the spectrum of polyethylene (PM), provide an opportunity to check qualitatively the predicted dependence of the D-LAM frequency on the trans/gauche ratio for poly(methylene)-type chains.[1] The observed D-LAM frequencies of liquid PM,[1] POM_4 (Figure 1), and POM_2 (Figure 3) are 200, 240, and 264 cm^{-1}, respectively. Relative to PM, the D-LAM bands of POM_4 and POM_2 are displaced upward in frequency by 40 and 64 cm^{-1}, respectively. However, part of this observed displacement is accountable to differences in the angle-bend force constants and atom masses. The effect of these factors must be evaluated to ensure a meaningful comparison. The relevant force constants are those associated with CCC, OCC, and COC angle bending. Their values, which increase in the order just given, are available from a vibrational analysis of aliphatic ethers.[3] The frequency shift in D-LAM due solely to differences in force constants and atom masses is estimated to be less than +10 cm^{-1} for POM_4 and less than +20 cm^{-1} for POM_2. Thus a shift of at least +30 and +44 cm^{-1} is attributable to differences in conformation. According to our earlier treatment,[1] if this shift is positive, it must reflect an increase in the overall average concentration of gauche bonds. The concentration of gauche bonds is thus found to increase in the order PM, POM_4, and POM_2 for these polymers in the liquid state. This ordering is consistent with the relative values of the characteristic ratios C_∞, 6.7 (140 °C), 4.8 (25 °C), and 4.0 (25 °C), measured for PM, POM_4, and POM_2.[4] The conformational energy considerations that argue for the ordering observed are summarized in ref 4.

The sensitivity of the D-LAM band to conformational changes is evident when we compare the spectrum of neat POM_2 with that of POM_2 diluted with water (Figure 3). The frequency of D-LAM is about 20 cm^{-1} higher when the polymer is in solution. This indicates a higher concentration of gauche bonds for the aqueous solution, an interpretation that is in agreement with the results of an independent, infrared study on this system by Matsuura and Fukuhara.[5] In interpreting their results, these authors suggested that the gauche conformation of the C–C bond of POM_2 in aqueous solution is stabilized by hydrogen bonding between water molecules and the oxygens of the POM_2 chains, specifically between a given water and the two nearest-neighbor POM_2 oxygens adjoining a C–C bond.

The bandwidth of the D-LAM band can be related to the conformational statistics of a disordered chain since it is in large part determined by deviations from the average conformation. If there is complete conformational order, the D-LAM band, which in this case now becomes the LAM-1 band, is narrow since it is not inhomogeneously broadened. However, with increasing conformational disorder, the variance associated with the average conformation increases and so therefore does the inhomogeneous contribution to the broadening. If the conformations of different bonds are not highly correlated, the variance will have a maximum value when the concentrations of the various possible bond conformations are approximately equal. It is therefore possible to use the width of the D-LAM band as a measure of the variance associated with the average conformation. In Table I the chain molecules have been ordered in terms of their normalized D-LAM bandwidth. (The measure of bandwidth we have used is defined in footnote *a* in Table I.) The ranking given in Table I correlates in a crude way with chain flexibility; e.g., *cis*-1,4-polybutadiene is the most flexible chain and poly(tetrafluoroethylene) the least. This correlation is reassuring in that, according to our model, narrower D-LAM bands are predicted for chains with the fewest conformational possibilities; i.e., narrow bands go with "stiff" chains.

Intermolecular factors that tend to increase conformational order will promote band narrowing. POM_2 serves as an example: the width of the D-LAM band of POM_2

undergoes a significant decrease in going from the neat liquid to an aqueous solution. This happens in spite of the fact that the band moves to a higher frequency, which indicates an increase in the gauche bond concentration. Therefore we might have expected an increase in bandwidth. Detailed infrared studies of Matsuura and Fukuhara indicate that POM_2 is more ordered in dilute solution than as a neat liquid,[5] and this accounts for the observed D-LAM band narrowing.

In summary, our measurements suggest that vibrational spectroscopic measurements in the low-frequency region can provide information on *long-range* conformational disorder in highly disordered chain systems.

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Registry No. polybutadiene, 9003-17-2; squalene, 111-02-4; poly(ethylene oxide), 25322-68-3; poly(tetramethylene oxide), 25190-06-1; poly(ethylene terephthalate), 25038-59-9; squalane, 111-01-3.

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Blends of Homo- and Copolymers of Ethylene and Vinyl Chloride: A Compatibility Study

We have recently[1] obtained a complete series of ethylene–vinyl chloride (E–V) copolymers through the reductive dechlorination of poly(vinyl chloride) (PVC) with tri-*n*-butyltin hydride. ^{13}C NMR spectroscopy was utilized to determine the microstructures of these E–V copolymers, including their comonomer compositions, their sequence distributions, and the stereosequences of neighboring V units. Solid-state and solution measurements[2,3] performed on these E–V copolymers have demonstrated a remarkable sensitivity of their physical properties to their microstructures.

We have begun to study the blend properties of these E–V copolymers. In this communication we report on our initial studies of the compatibility of E–V copolymer blends, using differential scanning calorimetry (DSC) as a probe of blend compatibility.

Blends were made by casting films from dilute solutions (1–2 wt %) composed of equal volumes of E–V copolymers or their constituent homopolymers PVC and polyethylene (PE). For blends with amorphous E–V copolymers and PVC, tetrahydrofuran was used as the casting solvent, while toluene was employed for the crystalline E–V co-

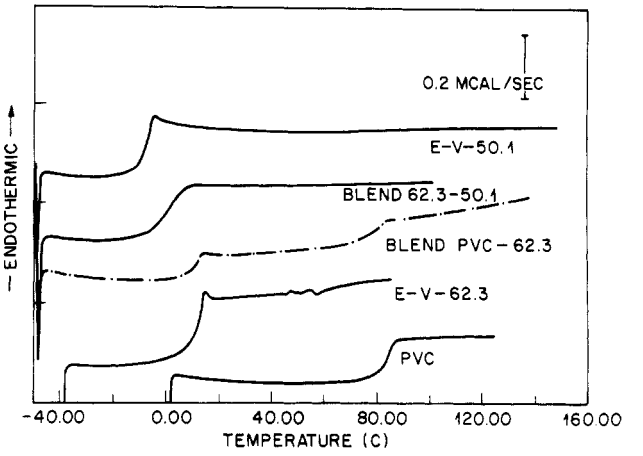

Figure 1. DSC scans for PVC, E-V-62.3, E-V-50.1, 100–62.3 blend, and 62.3–50.1 blend.

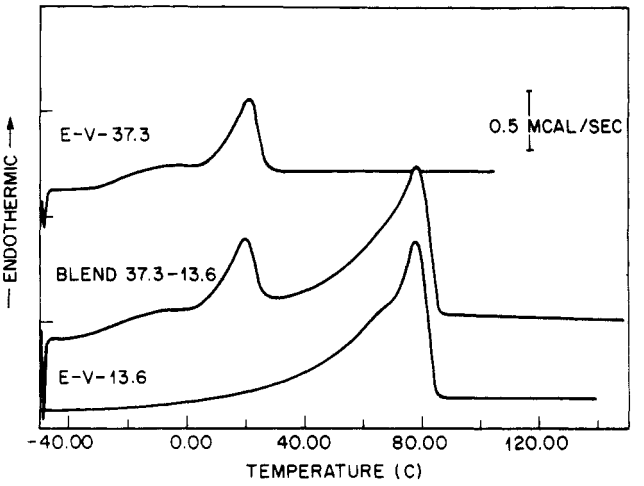

Figure 2. DSC scans for E-V-13.6, E-V-37.3, and 37.3–13.6 blend.

polymers and PE. The blend films were cast in a poly(tetrafluoroethylene) trough and, after ambient drying, were removed and dried further in a vacuum oven for 1 h at 90 °C to remove residual solvent.

DSC scans were recorded for all the individual E–V copolymers, PVC, PE, and their blends on a Perkin-Elmer Model DSC-4. Sample sizes ranged from 6 to 16 mg and a fixed heating rate of 10 °C/min was employed throughout. Illustrative DSC traces are shown in Figures 1 and 2 for several of the E–V copolymers and their blends.

Glass transition temperatures (T_g) are defined as the midpoints of the transitions in the DSC scan, while melting temperatures (T_m) are identified with the maxima of the fusion endotherms. T_g's and T_m's observed for the blends and their constituents are reported in Table I. The final column in Table I indicates the compatibility (C)/incompatibility (I) of each blend based on a comparison of the T_g's and T_m's observed for the blends and their individual components. For blends composed of two amorphous components, observation of a single T_g(blend) intermediate between the T_g's (T_{g1}, T_{g2}) of the components is taken as proof of compatibility. Blends with at least one crystalline component are designated incompatible if the T_m's and T_g's of the blend and the pure crystalline and amorphous components are the same.

These initial compatibility measurements performed on 50/50 (v/v) blends of E–V copolymers are summarized in Figure 3. All blends with at least one crystalline component (<37.3 mol % V) are found to be incompatible, while those composed of two amorphous components are compatible only when their compositions differ by less

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