Morphological Characterization of High-Pressure Crystallized Polyethylene by Raman and Brillouin Scattering

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ABSTRACT: The low-frequency Raman-active longitudinal acoustical mode (LAM) has been observed in high-pressure crystallized polyethylene (HPCPE), which exhibits an extended-chain morphology. Through the use of a multipass Fabry-Perot interferometer a band at 0.5 cm^{-1} has been observed in the low-frequency spectral region and tentatively assigned to LAM. After melting and recrystallization this band shifted to 12.8 cm^{-1} and was then observed with standard Raman instrumentation, with its position reflecting a significant reduction in lamellar thickness.

Introduction

Evidence exists that suggests a strong correlation between extended-chain morphology and high mechanical stiffness in polymeric materials. Unfortunately, extended-chain polymers with lamellar thicknesses greater than 200.0 nm cannot be studied by the standard techniques such as small-angle X-ray (and neutron) scattering or the longitudinal acoustical mode (LAM) using conventional Raman instrumentation since neither has the extremely high resolution required to observe the spectrum arising from chains of such an extended length. Hence, characterization of extended-chain polymers has relied primarily on thermal and mechanical methods and electron microscopy.

The Raman-active LAM has been used extensively to study the morphological structure[1-3] of polymers and copolymers[4,5] that have been subjected to various thermal and mechanical processing histories. Raman studies of the LAM in polyethylene[6-8] have been correlated with small-angle X-ray (SAXS) measurements, and it has been determined that, whereas the SAXS long period includes both the crystalline stem and a portion of the fold surface, the LAM is characteristic solely of the lamellar stem length. Recently, Snyder and Scherer[9] observed, in an annealed melt-crystallized polyethylene (PE) sample, a LAM band at 3.6 cm^{-1} corresponding to a lamellar stem length of approximately 70.0 nm. This represents the lower limit of accessibility of currently available Raman instrumentation and thus relegates the LAM in extended-chain PE to a frequency region that is generally inaccessible.

Although the region below 3 cm^{-1} cannot be studied by conventional Raman spectroscopic techniques because of stray light considerations, a portion of this region is accessible through the use of multipass Fabry-Perot interferometry routinely used in Brillouin scattering experiments.[10] Operating with a large free spectral range (5–10 cm^{-1}) in a high-contrast multipass Fabry-Perot interferometer, one expects to observe both the usual Brillouin spectra associated with the long-wavelength acoustic phonons and the low-frequency (<3 cm^{-1}) Raman-active LAM band characteristic of extended-chain polymers. It is worth noting that since the LAM is a localized accordion-like vibration of a polymer chain stem in a crystalline lamella, its frequency is independent of scattering angle while, in contrast, the long-wavelength acoustic phonons are nonlocalized and involve both crystalline and amorphous regions and hence their frequencies depend critically on the scattering angle. Thus, the LAM can be conveniently differentiated from the acoustic phonon peaks in a Brillouin scattering spectrum by varying the scattering angle.

This article presents the first observation of a low-frequency LAM in high-pressure crystallized polyethylene (HPCPE) having an extended-chain morphology using a Fabry-Perot interferometer. As evidence for this assignment it has been demonstrated that upon melting and subsequent recrystallization (chain-folded morphology), the LAM shifts to the frequency region readily accessible by Raman techniques.

Experimental Section

Polyethylene ($M_w \approx 100\,000$) was anabarically crystallized[11,12] under high pressure as described by Frank et al.[13] The result yielded a very highly crystalline brittle material (DSC melting point, 142 °C), which was studied without subsequent exposure to elevated temperature.

In order to produce a sample of chain-folded PE, a small amount of the original HPCPE was sealed in a glass tube under vacuum and placed in an oil bath held at 160 °C for a period of 1.5 h. It was then removed from the oil bath and allowed to cool to room temperature.

Raman measurements were obtained with a Jobin Yvon HG-2S double monochromator equipped with standard photon-counting electronics and a Nicolet 1180 data system. Raman scattering was excited by using the 514.5-nm line of a Spectra Physics 165-08 argon ion laser, and the collected radiation was passed through an iodine filter to remove the elastically scattered component.

Interferometric measurements were carried out with a piezoelectrically scanned Fabry-Perot interferometer operated in five passes. Several free spectral ranges varying from 0.70 to 10.0 cm^{-1} were used to record the spectra. The overall finesse of the optical system was about 50.

Results and Discussion

It has been shown by Bassett et al.[14] that at elevated temperatures (T = 230 °C) and pressures (5–6 kbar) PE exists in an intermediate phase in which extended chains are packed into a hexagonal lattice. Subsequent recrystallization under pressure via this hexagonal phase has been suggested as the major cause of the extended-chain morphology. Examination of the low-frequency Raman spectrum of such a suitably prepared sample (Figure 1a) shows the absence of any band that might be assigned to the Raman-active LAM. This is understandable since HPCPE has an extended-chain structure containing crystalline stems whose length exceeds 200.0 nm. Using the simple elastic rod model first proposed by Mizushima

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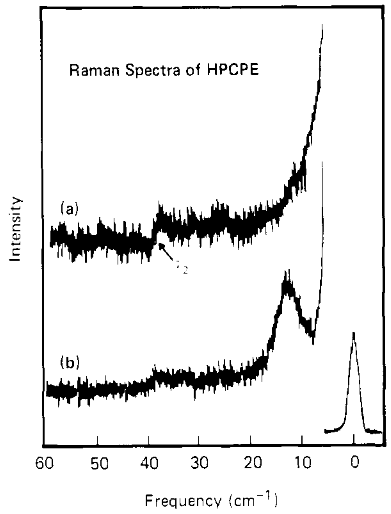

Figure 1. Room-temperature Raman spectra of PE: (a) high-pressure crystallized PE; (b) melted and recrystallized HPCPE.

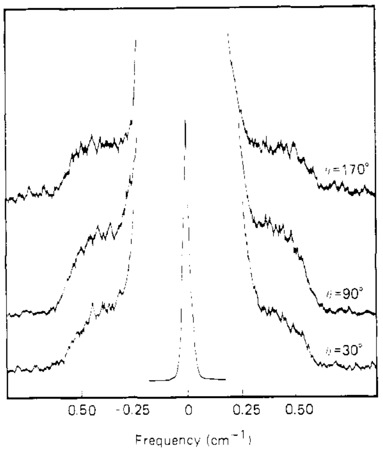

Figure 2. Low-frequency light scattering spectra of HPCPE obtained with a multipass Fabry-Perot interferometer. θ is the scattering angle.

and Shimanouti,[15] one would expect a LAM frequency less than 2 cm^{-1}. This is inaccessible with current Raman instrumentation.

As discussed previously, spectral information in this region is attainable by Fabry-Perot interferometry. As seen in Figure 2 in the region below 1 cm^{-1} a band is observed whose position is independent of scattering angle. This scattering angle independence is characteristic of localized modes, and hence the band at 0.5 cm^{-1} is assigned to the Raman-active LAM of extended-chain PE. The very narrow bandwidth, <0.3 cm^{-1}, is at first surprising since LAM bands in *n*-paraffins generally have natural bandwidths in the 3.0–6.0-cm^{-1} range. However, as the chain extension increases, the static structural factor decreases rapidly, and as the chain approaches infinite lengths, the scattering intensity will appear mostly in the Rayleigh peak; thus, the bandwidths expected for HPCPE will be very narrow. In fact, Snyder and Scherer[9] have reported a bandwidth of 1.5 cm^{-1} for a LAM located at 3.6 cm^{-1} in annealed PE containing crystalline stem lengths exceeding 50.0 nm.

After correcting the scattering intensity for background, frequency, and temperature,[16] the data are replotted in terms of the change in polarizability (to the square), upon which the band is observed to undergo a slight shift to 0.522 cm^{-1}. Such a small shift is expected since the LAM bandwidth is very narrow. A further recasting of the data in terms of a distribution of chain lengths, $f(n)$, vs. chain length, L, can be accomplished according to Snyder et al.,[17] provided that the calibration curve established[17] for *n*-paraffins and chain-folded PE can be extrapolated to chain lengths >100.0 nm. This is not an unreasonable assumption since, in essence, it asserts the validity of the uniform elastic rod model first suggested by Mizushima and Shimanouti.[15] Although the perturbative effects of interlamellar forces and end-group masses on the frequency and intensity of the LAM have been the subject of discussion,[18,19] it is expected that the end-group effects on the LAM frequency of an extended chain are negligible. This point is being specifically addressed in an investigation of LAM-3 (longitudinal acoustical vibration containing three nodes in atomic displacement) in HPCPE currently in progress.

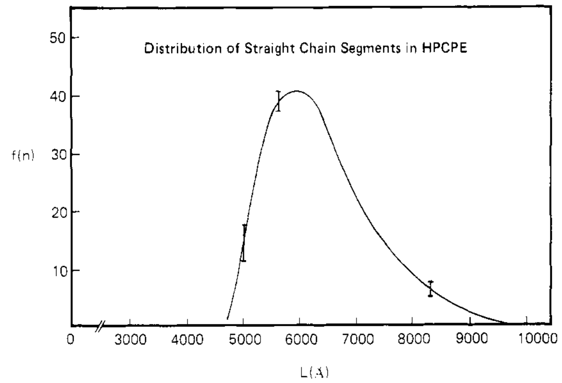

Figure 3. Distribution of straight-chain segments in HPCPE derived from Raman bandshape. Error bars represent uncertainty due to conversion from observed Raman intensity to $f(n)$.

The distribution of straight-chain segments in HPCPE is shown in Figure 3. Since conversion from the observed Raman intensity to $f(n)$ involves multiplication by ν^2, the uncertainty in the high-frequency data (short chain lengths) is greater than that for the low-frequency region (long chain lengths). In Figure 3 it is shown that the most probable chain length is 590.0 nm, in agreement with that expected[20] for PE in an extended-chain morphology. It is interesting to note that the straight-chain distribution is considerably asymmetric and extends more to the long chain length region, indicating the presence of extended chain lengths in excess of 750.0 nm. Qualitatively similar observations of asymmetry in the straight-chain distribution have been made in solution-crystallized,[21] extruded,[17] and drawn PE.[22] Although the breadth of the distribution is quite large (~190.0 nm) in comparison to that observed for melt- or solution-crystallized PE (2.0–10.0 nm), this contrast can be put in better perspective by considering the empirical order parameter, μ_L, first suggested by Snyder and Scherer.[9] The order parameter, μ_L, was defined as the quotient of the distribution bandwidth at half peak height, $\Delta L_{1/2}$, divided by the most probable chain length, $L_{\max}$. For HPCPE this order parameter has a value of 0.32 compared to a value of 0.33 determined[9] for the LAM band found at 3.6 cm^{-1} in highly annealed melt-crystallized PE. These similar values obtained for two specimens having completely different thermal and mechanical processing histories lend credence to the use of such an empirical quantity to compare different morphological structures, both containing a high degree of order.

The results of melting HPCPE with subsequent recrystallization at room temperature are shown in Figures 4 and 1b. Interferometric measurements on HPCPE using the special geometry employed in the previous experiment[10] (Figure 4) indicate the presence of a band in the vicinity of 0.23 cm^{-1}. The position of this band is de-

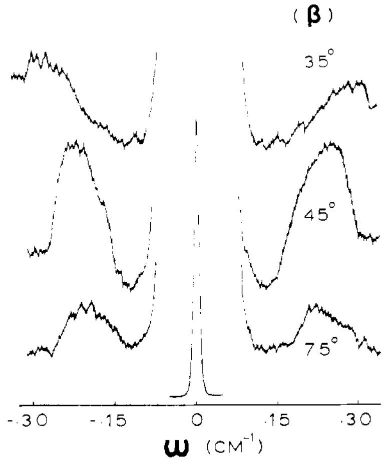

Figure 4. Brillouin scattering peaks observed in HPCPE using a multipass Fabry-Perot interferometer. Angle β is related to the scattering vector, **q**.

pendent on the scattering vector, **q**, and thus corresponds to a Brillouin peak. The value of the sound velocity calculated from the frequency shift is in agreement with that of an unoriented high-density polyethylene film.[23] The disappearance of LAM from this region is expected due to recrystallization which results in a decrease in lamellar thickness. Consequently, the LAM of these shorter stem lengths will appear at higher frequencies and, as seen in Figure 1b, a band at 12.8 cm^{-1} is observed in the low-frequency Raman spectrum. Correction of the band intensity for frequency and temperature shifts its position to 13.5 cm^{-1}, corresponding to a lamellar stem length of 22.7 nm. This is in accordance with what would be expected for melt-crystallized PE.

Conclusion

Because of the inaccessibility of currently available Raman instrumentation to the region below 1 cm^{-1}, a multipass Fabry-Perot interferometer was used to locate a LAM band at 0.5 cm^{-1} in HPCPE, which exhibits an extended-chain morphology. Analysis of the chain length distribution obtained from the spectrum indicates that the most probable chain length is 590.0 nm, giving an empirical order parameter[9] of 0.32, in the region of extended-chain materials.

Melting of HPCPE with a subsequent recrystallization at room temperature shifts the LAM to 13.5 cm^{-1}, which can once again be observed by conventional Raman scattering techniques. In the recrystallized HPCPE, bands attributable to long-wavelength acoustic phonons were then observed in the Brillouin spectrum.

The application of Fabry-Perot interferometry to extended-chain materials should lead to studies of morphological structure in polymers such as PTFE, which have long evaded characterization by standard spectroscopic techniques.

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