Ministerio de Educación y Ciencia. We also wish to thank Miss M. D. Casado who performed the NMR experiments.

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# High-Frequency Ultrasonic Studies of Poly(ethylene), Poly(propylene), and Poly(vinyl chloride)

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ABSTRACT: Ultrasonic attenuation measurements on films of poly(ethylene), poly(propylene), and poly(vinyl chloride) are reported over a frequency range of 0.1 to 1.0 GHz and over a temperature range from 230 to 303 K. The data correlate well with published observations from lower frequency ultrasonic attenuation and higher frequency Brillouin scattering measurements. In the case of a crystalline sample of poly(propylene) a decrease in the high-frequency absorption is attributed to relaxation of an intergranular thermoelastic loss. An increase in the attenuation in poly(ethylene) is ascribed to scattering by domains of different modulus (crystallites). In the case of poly(vinyl chloride) it is possible to observe the effect of plasticization on the background thermally activated structural relaxation process.

The dissipation of mechanical energy in amorphous polymeric materials at low frequencies (ca. 1 Hz) can be described adequately in terms of viscoelastic relaxation ascribable to specific molecular relaxation processes.[1] The same is true through the normal acoustic and ultrasonic frequency ranges. However, at high frequencies (above 100 MHz) additional dissipation processes become important.[2-5] Two such are phonon–phonon scattering, in which the propagating wave interacts with thermal phonons, and the scattering of elastic waves at the discontinuity of modulus, which occurs at the boundary between different morphological domains when the domain size (or interdomain separation) becomes comparable with the hyper-sound of ultra-sound wavelength.

The three polymers chosen for this first study of acoustic attenuation in the GHz region, poly(ethylene), poly(propylene), and poly(vinyl chloride), exhibit a range of morphologies as well as different interchain interaction potentials.

The aim of this study was to determine whether high-frequency ultrasonic observations could be used to observe morphology-related phenomena not usually detected using conventional methods and to give information on phonon processes in such solids.

## Experimental Section

**(1) Acoustic Attenuation Measurements.** The longitudinal attenuation measurements were made with a pulsed apparatus designed to operate between 0.1 and 1.0 GHz. The electronic system has been described elsewhere.[6] The cell used is of a novel design and is illustrated in Figure 1. The use of coaxial symmetry, and careful selection of the materials used, allowed precise alignment of the two lithium niobate transducer crystals to be maintained over the entire temperature range. The acoustic beam was generated by surface excitation of the Z-cut lithium niobate crystals, using field strengths up to 5 kV mm$^{-1}$. The surfaces of the crystals were polished to optical standards. The resulting narrow beam of ultra-sound propagates through an immersion liquid in which the polymer film is suspended. The change in signal level produced by removal of the sample from the beam gave (after correction for the interfacial reflection losses) the excess attenuation of the sample over that of the liquid.

Samples were prepared as films with thicknesses ranging between 25 and 300 μm. For the temperature range studied the immersion liquids were either pure water or analytical reagent grade ethanol. The attenuation of these liquids measured over the above frequency range agreed with published values.[7,8] Systematic errors due to diffusion of the immersion liquid into the sample were tested for and found to be negligible.

The temperature of the immersion cell was measured to ±0.01 K using a 33 Ω platinum resistance thermometer. The ultrasonic frequency was measured to ±0.1% using the beat frequency technique.[9]

The immersion cell was mounted in a liquid nitrogen cryostat which gave temperature stability to better than ±0.2 K for periods of up to 30 min at all temperatures between 173 and 303 K. The thermal and mechanical stability of the cell showed a reproducibility of the attenuation data better than ±5% even at the lowest temperatures. A higher precision was achieved at temperatures close to ambient. No anisotropy was detected in the measured acoustic attenuation of the samples studied.

Acoustic attenuation data in the frequency range 5–35 MHz were obtained using a conventional liquid immersion apparatus.[12]

**(2) Characteristics of the Polymer Samples Studied.** The polymer films were prepared from commercial polymers, Table I. A number of different poly(ethylene) and poly(propylene) samples were examined and these included extruded and rolled samples. The poly(vinyl chloride) samples were of differing purity.

The thickness and uniformity of the films were investigated using a precision micrometer and infrared interference techniques.[10]

The morphologies were investigated using a Philips scanning electron microscope Model 500 which has a resolution better than 10 nm. Samples for microscopic examination were prepared by washing in detergent solution, cleaning in an ultrasonic bath, and coating with a 10-nm gold layer. The densities of all the samples were measured using a flotation technique[11] and have a precision of ±0.2%.

## Results and Discussion

**(1) Diffusion of Immersion Liquid into Samples.** The rates of diffusion of water and ethanol into the samples were measured at 293 K. In all cases the equilibrium liquid uptake and derived diffusion coefficients were low. The effects of ethanol and water absorption on ultrasonic relaxation be-

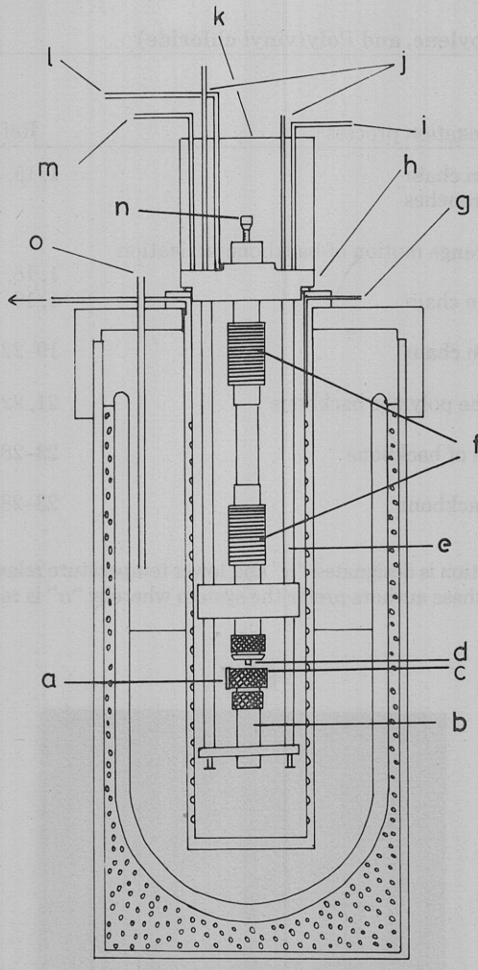

**Figure 1.** High-frequency immersion cell. (a) Platinium resistance thermometer; (b) lower transducer housing and alignment plate; (c) sample holder and cup; (d) lithium niobate transducer; (e) alignment bars; (f) bellows support assembly; (g) heater leads; (h) Teflon gasket; (i) P.R.T. leads; (j) signal leads; (k) head cover; (l) immersion liquid in; (m) nitrogen gas in; (n) transducer head movement; (o) liquid nitrogen in.

**Table I**
**Characteristics of Polymer Films Studied**

| Polymer | Fabrication technique | Density, kg $m^{-3}$ | Morphology | Note on sample |
|---|---|---|---|---|
| PE-1 | Rolled | 914 | Domains 4 $\mu$m | |
| PP-1 | | 902 | Apparently homogeneous | |
| PP-2 | Rolled | 925 | Domains 0.2 $\mu$m | |
| PP-3 | Extruded | 901 | Domains 10 nm | |
| PVC-1 | Solvent cast | 412 | Domains 50 nm | Reprecipitated |
| PVC-2 | Blown | 1408 | Apparently homogeneous | |
| PVC-3 | Rolled | 1379 | Apparently homogeneous | |
| PVC-4 | Blown | 1258 | Apparently homogeneous | 21% DIOP plasticizer |

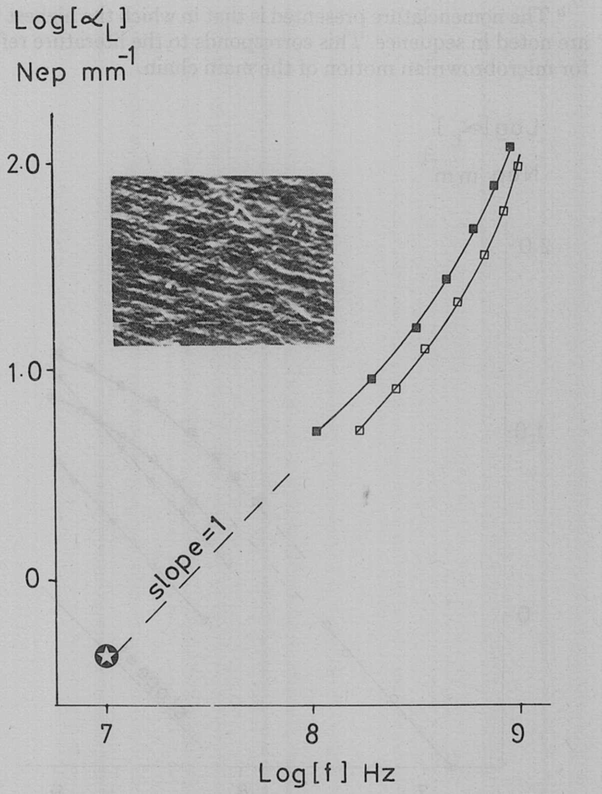

**Figure 2.** Ultrasonic attenuation in polyethylene. Inset: electron micrograph of sample, marker, 1 $\mu$m. Np $\mathrm{mm}^{-1}$ = 8.685 $\partial\beta$ $\mathrm{mm}^{-1}$. ✪ low density polyethylene; (■) PE-1 at 296 K; (□) PE-1 at 233 K.

havior of poly(ethylene) and poly(propylene) have not been reported hitherto. Attenuation measurements made at 293 K on a range of film thicknesses of samples PE-1 and PP-1 to PP-3 in both liquids, and covering different periods of immersion, showed no discrepancies within the experimental error. For poly(vinyl chloride) the equilibrium diffusant content is sufficient to give rise to a small shift in the static glass transition temperature, but again no differences in the acoustic attenuation behavior were observed after different immersion times.

**(2) Ultrasonic Attenuation Data. (a) Poly(ethylene).** The ultrasonic attenuation data, Figure 2, show an initial linear dependence on frequency, with a marked increase in the attenuation above approximately 0.4 GHz. The electron micrographs of the sample show a ridge textured structure with a ridge width of about 0.2 $\mu$m and a ridge length of 10 $\mu$m. Such structures are not atypical of crystalline domains in an oriented structure produced in rolled film.

The relaxation behavior of poly(ethylene) has been studied extensively[1,12–14] and is summarized in Table II.

It is clear that the present acoustic observations occur in a time–temperature region where no appreciable relaxation effects are to be expected. The fact that the lower frequency absorption increases as the first power of the frequency appears to suggest that there exists a dissipation mechanism with a broad distribution of relaxation times which we believe to be described in terms of a thermally activated phonon relaxation process. Such a loss could arise from relatively local motion of the polymer chains although its precise description is uncertain. By analogy with the behavior observed in amorphous glasses we can picture librational or torsional molecular chain oscillations coupled to lattice modes and describe the overall phenomenon as a form of structural relaxation.

However, an alternative explanation is required for the increased attenuation above 0.4 GHz. Calculation of the expected phonon–phonon loss for this polymer, Appendix I, indicates that such interactions should not account for more than 0.1 Np $\mathrm{mm}^{-1}$ of attenuation at room temperature.[2] Dislocation damping and thermal elasticity together should not add more than another 0.2 Np $\mathrm{mm}^{-1}$.[3,4] In addition, in-

Table II
Relaxation Characteristics of Polyethylene, Polypropylene, and Poly(vinyl chloride)

| Polymer | Freq of observation, Hz | Peak temp, K | Note on relaxation process[a] | Ref |
|---|---|---|---|---|
| Polyethylene | 1 | 350 | $\alpha$ relaxation, motion of the main chain | 1, 15, 18 |
| | 1 | 263 | $\beta$ relaxation, motion of chain branches | |
| | $10^4$ | 293 | | |
| | 1 | 158 | $\gamma$ relaxation, librational short-range motion of backbone-activation energy, 50 kJ/mol | 1, 15, 18 |
| Polypropylene | 1 | 335 | $\alpha$ relaxation, motion of the main chain | 1, 16 |
| | 500 | 418 | | |
| | 1 | 276 | $\beta$ relaxation, motion of the main chain | 19–22 |
| | $5 \times 10^6$ | 343 | | |
| | 1 | 183 | $\gamma$ relaxation, local motions of the polymer backbone | 21, 22 |
| | 10 | 33 | | |
| Poly(vinyl chloride) | 0.01 | 355 | $\alpha$ relaxation, large-scale motion of backbone | 23–28 |
| | $10^5$ | 423 | | |
| | 2 | 223 | $\beta$ relaxation, local motions of backbone | 23–28 |
| | $10^5$ | 343 | | |

[a] The nomenclature presented is that in which the highest temperature relaxation is designated "$\alpha$" and lower temperature relaxations are noted in sequence. This corresponds to the literature references, although these authors prefer the system whereby "$\alpha$" is retained for microbrownian motion of the main chain.

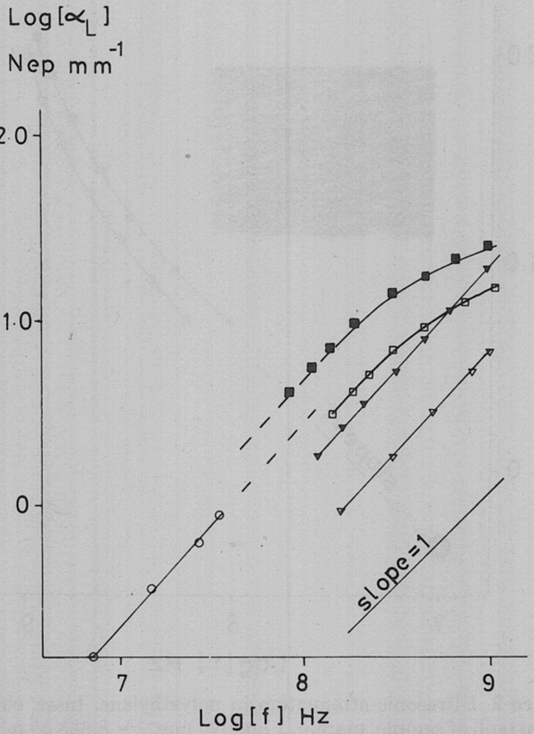

**Figure 3.** Ultrasonic attenuation in polypropylene: Np mm$^{-1}$ = 8.685 $\partial\beta$ mm$^{-1}$ (○) PP-1 at 296 K; (■) PP-2 at 296 K; (□) PP-2 at 250 K; (▼) PP-3 at 296 K; (▽) PP-3 at 250 K.

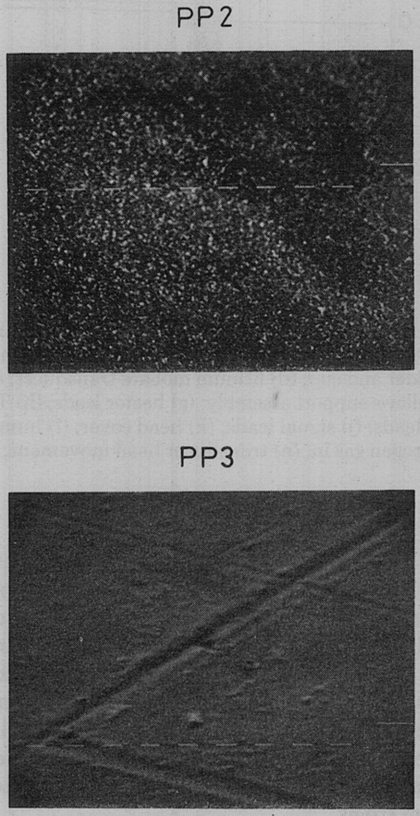

**Figure 4.** Electron micrographs of polypropylene samples; marker, 1 $\mu$m.

tergranular thermal elasticity should relax out at frequencies well below 0.4 GHz for the size of domains observed in these electron micrographs. Since at 0 °C the acoustic wavelength is about 4 $\mu$m, which is comparable with the size of the crystallite domains, we ascribe this marked increase in the attenuation to stochastic scattering. For independent spherical scattering centers, we would expect a contribution of the order of 10 Np mm$^{-1}$ at 1 GHz, which attenuation should increase as the square of the frequency.[29] The rapidly increasing attenuation observed in polyethylene does appear consistent with this predicted stochastic scattering.

**(b) Poly(propylene).** The ultrasonic data in Figure 3 show at low frequencies a similar linear dependence on frequency to that observed in poly(ethylene). The same behavior is apparent in the sample poly(propylene) (3), which exhibits domain structure in the $\mu$m size range, Figure 4.[30,31] However, poly(propylene) which has a clearly defined domain structure, Figure 4, exhibits a higher attenuation, the increment in which decreases at the highest frequencies. Differences in the amplitudes of the measured attenuation of PP-1 and PP-3 (low- and high-frequency data) can be attributed to differences in the thermal history of the sample. For domains of size about 0.2 $\mu$m the stochastic scattering attenuation would not be expected to be observed until the frequency is higher than 10 GHz. On the other hand, intergranular thermoelastic loss processes might be expected to contribute an attenuation of about 1 Np mm$^{-1}$ relaxing at frequencies above 0.1 GHz. Consequently we ascribe the attenuation in the highly crys-

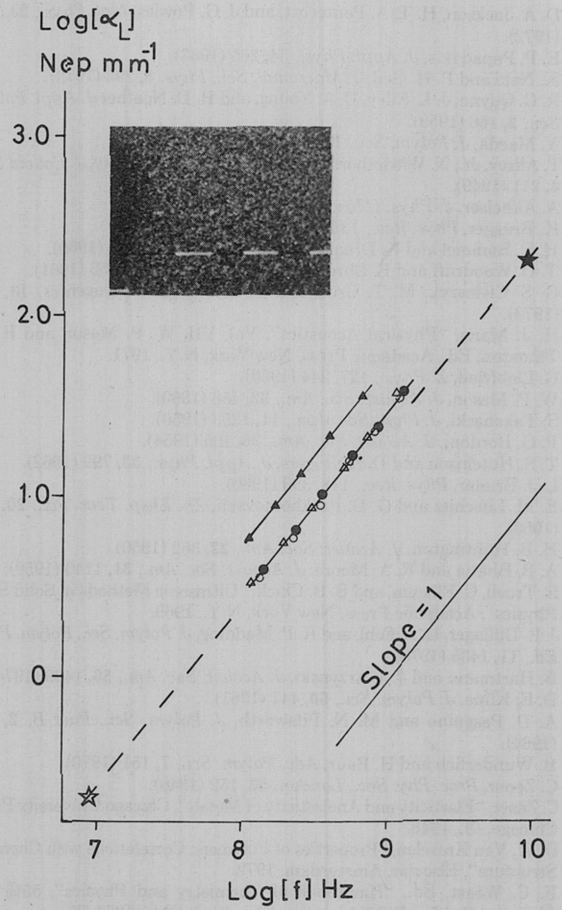

**Figure 5.** Ultrasonic attenuation in poly(vinyl chloride). Inset: electron micrograph of solvent cast sample; marker, 1 μm. Np mm$^{-1}$ = 8.685 ∂β mm$^{-1}$. (△) PVC1 at 296 K; (○) PVC2 at 296 K; (●) PVC3 at 296 K; (▲) PVC4 at 296 K; (☆) PVC 8 MHz data; (★) PVC, 10 GHz data.

talline poly(propylene) (2) to the combination of structural relaxation and intergranular thermoelastic losses.

**(c) Poly(vinyl chloride).** The ultrasonic attenuation in these polymers, Figure 5, exhibits a linear dependence on frequency over the entire range 5 MHz to 10 GHz.[28,32] The electron micrographs of the polymers are consistent with a morphology of microgranular particles of size approximately 50 nm.[33] Since the domain dimensions are very small compared with the wavelengths used in this study scattering processes such as those which dominate in poly(ethylene) can be discounted, as can intergranular thermoelastic losses.

The frequency dependence of the absorption must then be connected in some way with the molecular motion occurring in the polymer. In addition the combined loss processes associated with the glass transition (αβ processes) should peak at about 425 and 0.4 GHz.[23–28] The dependence of the loss on the amount of plasticizer present, and the linear dependence on frequency, suggest that the absorption arises from very local motions of the polymer chains described by a very wide distribution of relaxation times. Again we ascribe this to a "structural relaxation" in which localized chain modes are coupled to modes of the amorphous lattice.

## Conclusions

Study of the high-frequency ultrasonic attenuation can, in favorable cases, show the existence of attenuation phenomena related to the polymer morphology. In this way phonon scattering and intergranular elastic effects which are not usually detected using conventional methods can be observed. Consequently such studies have considerable potential in furthering a detailed understanding of the fundamental phonon interaction processes in solids.

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## Appendix I

A detailed discussion of the calculation of the contributions to the acoustic loss (α) from various mechanisms has been presented elsewhere.[3,4] The relevant equations are presented here for completeness.

**(i) Phonon–Phonon Interactions**[34,39]

$$\alpha = \frac{\gamma_G{}^2 k T \omega^2}{\rho c_1{}^5} \qquad (\omega\tau \leqslant 1) \qquad \text{(A1)}$$

$$\alpha = \frac{3\pi\gamma_G{}^2 k T \omega}{4\rho c_1{}^5} \qquad (\omega\tau \geqslant 1) \qquad \text{(A2)}$$

where $\gamma_G$ is the Grunsisen tensor, $k$ is Boltzmann's constant, $T$ is the temperature, $\omega$ is the radial frequency, $\rho$ is the density, and $c_1$ is the longitudinal wave velocity. In a polymer $\omega\tau \approx 1$ at 1 GHz at a temperature of approximately 10 K.

**(ii) Dislocation Damping**[40–45]

$$\alpha = \frac{16LL_i{}^4\omega^2}{\pi^5 B' c_1{}^3}\left(1 - \frac{\omega^2}{\omega_d{}^2} + \left(\frac{\omega}{\omega_B}\right)^2\right)^{-2} \qquad \text{(A3)}$$

where $B'$ is the dislocation damping factor given by the relationship:

$$\omega_B = \omega_d{}^2 B' \qquad \text{(A4)}$$

where $\omega_B$ is the characteristic relaxation frequency and $\omega_d$ is the resonant frequency for the dislocation motion:

$$\omega_d = (\pi/2)^{1/2}\frac{c_1}{L_i} \qquad \text{(A5)}$$

where $L_i$ is the maximum defect spacing and $L$ is the dislocation density per unit area. The effects of strain amplitude on the observed relaxation process have been discussed elsewhere.[43]

**(iii) Scattering.**[46–48] The loss can be described conveniently in terms of the scattering cross section, for independent scattering centers

$$\alpha = {}^1\!/\!_2 n_{sc}\sigma_{sc} \qquad \text{(A6)}$$

where $n_{sc}$ denotes the density of volume filling scattering centers. Stochastic scattering from spheres gives, for longitudinal waves,

$$\sigma_{sc} = \frac{8P^2{}_d\omega^2}{525 n_{sc}\rho^2 c_1{}^6} \qquad \text{(A7)}$$

where $d$ is the diameter of the scattering sphere and $P$ is a measure of the scattering center anisotropy

$$P^2 = (S_{11} - S_{12} - 2S_{44})^2 \qquad \text{(A8)}$$

where $S_{ii}$'s are the elastic modulii in the designated direction.

**(iv) Thermoelasticity.**[49–54] This loss mechanism is associated with local temperature differences associated with the propagation of the sound wave within the sample and has the form:

$$\alpha = \frac{k\gamma^2 T\omega^2}{2\rho c_1 c_p{}^2}\left(1 - \frac{4c_t{}^2}{3c_1{}^2}\right)^2 \qquad \text{(A9)}$$

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# Crystal Structures of Optically Active and Inactive Poly(*tert*-butylethylene sulfide)

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ABSTRACT: The molecular and crystal structures of optically active and inactive poly(*tert*-butylethylene sulfide) were determined by x-ray analysis. Crystals of the optically active species are trigonal, $P3_1\text{-}C_3{}^2$, with cell dimensions $a = 16.91$ Å and $c$(fiber axis) = 6.50 Å. Three isotactic right-handed (3/1) helical chains possessing essentially $(SG\bar{S})_3$ conformation for the sinister configuration pass through the unit cell. The reflection intensities are, however, explained in terms of a statistical molecular packing with respect to upward and downward chains. Crystals of the optically inactive species are monoclinic, $P2_1/a\text{-}C_{2h}{}^5$, and the cell dimensions are $a = 16.67$ Å, $b = 19.27$ Å, $c$(fiber axis) = 6.52 Å, and $\beta = 90°$. The main chain conformation is essentially the same as that of the active species. Two pairs of rectus and sinsiter molecular chains pass through the unit cell; the optical compensation of the racemic polymer is attained by the formation of the racemic lattice. Remarkable difference in melting point and solubility for both the species might be explained in terms of these crystal structures.

In previous papers, we reported the crystal structures of several isotactic polymers which have true asymmetric carbon atoms in the main chain: poly(*tert*-butylethylene oxide),[2] poly(propylene sulfide),[3] poly($\beta$-hydroxy butyrate),[4] poly($\beta$-ethyl-$\beta$-propiolactone),[5] and poly(isopropylethylene oxide).[6] In these polymers, there are two kinds of optical isomers. According to the nomenclature proposed by Cahn, Ingold, and Prelog,[7] the absolute configurations of these two optical isomers can be indicated by rectus and sinister. Three modes of optical compensation in these racemic species were proposed.[2,3] In the case of the optically inactive poly(*tert*-butylethylene oxide), three crystalline forms are observed depending on the crystallization conditions. One of them forms a racemic lattice, the unit cell of which contains two pairs of rectus and sinister molecular chains. On the contrary, the crystallite of the second form contains only rectus (or sinister) chains; the optical compensation in this case is attained by the presence of equal amounts of crystallites of