(6) A. J. Staverman, *J. Polym Sci., Polym. Symp.*, **No. 51**, 45 (1975).
(7) J. E. Mark, *J. Am. Chem. Soc.*, **92**, 7252 (1970); R. S. Johnson and J. E. Mark, *Macromolecules*, **5**, 41 (1972); C. U. Yuh and J. E. Mark, *ibid.*, **6**, 751 (1973).
(8) D. Froehlich, D. Crawford, and W. Prins, *Macromolecules*, **5**, 100 (1972).
(9) L. Mullins, *J. Polym. Sci.*, **19**, 225 (1956); C. G. Moore and W. F. Watson, *ibid.*, **19**, 237 (1956); L. Mullins, *J. Appl. Polym. Sci.*, **2**, 1 (1959).
(10) A. M. Bueche, *J. Polym. Sci.*, **19**, 297 (1956).
(11) D. J. Walsh, G. Allen, and G. Ballard, *Polymer*, **15**, 366 (1974).
(12) G. Allen, P. L. Egerton, and D. J. Walsh, *Polymer*, **17**, 65 (1976).
(13) L. R. G. Treloar, "The Physics of Rubber Elasticity", Oxford University Press, London, 1958.
(14) J. E. Mark, *Rubber Chem. Technol.*, **48**, 495 (1975).
(15) P. J. Flory and Y-I. Tatara, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 683 (1975).
(16) C. Price, G. Allen, F. de Candia, M. C. Kirkham, and A. Subramaniam, *Polymer*, **11**, 486 (1970).
(17) F. de Candia, L. Amelino, and C. Price, *J. Polym. Sci., Part A-2*, **10**, 975 (1972).
(18) G. Kraus and G. A. Moczvgemba, *J. Polym. Sci., Part A*, **2**, 277 (1964).
(19) R. F. Landel, "Polymer Networks, Structure and Mechanical Properties", A. J. Chömpff and S. Newman, Ed., Plenum Press, New York, N.Y., 1971, p 219.
(20) J. Schwarz, *Kolloid-Z. Z. Polym.*, **251**, 215 (1973).
(21) A. Posthuma de Boer and A. J. Pennings, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 187 (1976).
(22) A. Posthuma de Boer and A. J. Pennings, to be published.
(23) J. F. M. Oth and P. J. Flory, *J. Am. Chem. Soc.*, **80**, 1297 (1958).
(24) A. Posthuma de Boer, Thesis, University of Groningen, The Netherlands, 1977.
(25) R. G. C. Arridge and M. J. Folkes, *Polymer*, **17**, 495 (1976).
(26) A. M. Hassan and L. N. Ray, Jr., *J. Appl. Polym. Sci.*, **15**, 1837 (1971).
(27) A. N. Gent and V. V. Vickroy, Jr., *J. Polym. Sci. Part A-2*, **5**, 47 (1967).
(28) A. Ciferri, C. A. Hoeve, and P. J. Flory, *J. Am. Chem. Soc.*, **83**, 1015 (1961); P. J. Flory, A. Ciferri, and R. Chiang, *ibid.*, **83**, 1023 (1961).
(29) M. Shen and M. Croucher, *Macromol. Sci., Rev. Macromol. Chem., C*, **12**, 287 (1975).
(30) J. J. Hermans, *Trans. Faraday Soc.*, **43**, 591 (1947); K. J. Smith, Jr., "Polymer Science", A. D. Jenkins, Ed., North-Holland Publishing Co., Amsterdam, 1972, Chapter 5.
(31) K. Dušek, *Collect. Czech. Chem. Commun.*, **33**, 1100 (1968).
(32) A. Ziabicki, *Colloid Polym. Sci.*, **254**, 1 (1976).
(33) M. L. Huggins, *Ann. N.Y. Acad. Sci.*, **41**, 1 (1942); *J. Phys. Chem.*, **75**, 1255 (1971); *Pure Appl. Chem.*, **31**, 245 (1972).
(34) G. Gee and W. J. Orr, *Trans. Faraday Soc.*, **42**, 507 (1946).
(35) An excellent review is given by Dušek and Prins (ref 2a); a more recent theory based on this idea is developed by Schwarz (ref 15).
(36) R. S. Stein and S. D. Hong, *J. Macromol. Sci., Phys.*, **12**, 125 (1976).
(37) E. W. Fisher, J. H. Wendorf, M. Dettenmaier, G. Leiser, and I. Voigt-Martin, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **15**, 8 (1964); G. Leiser, E. W. Fisher, and K. Ibel, *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 39 (1975); J. Schelten, G. D. Wignall, and D. G. H. Ballard, *Polymer*, **15**, 682 (1974); D. Y. Yoon and P. J. Flory, *Macromolecules*, **9**, 294, 299 (1976). See also: *J. Macromol. Sci., Phys.*, **12**, parts 1 and 2 (1976).
(38) J. Schelten, D. G. H. Ballard, G. D. Wignall, G. Longman, and W. Schmatz, *Polymer*, **17**, 751 (1976).
(39) L. F. Gölz and H. G. Zachmann, *Makromol. Chem.*, **176**, 2721 (1975); P. Schmedeling and H. G. Zachmann, *Colloid Polym. Sci.*, **253**, 527 (1975).
(40) G. W. Longman, G. D. Wignal, and R. P. Sheldon, *Polymer*, **17**, 485 (1976). See also: I. Voigt-Martin and F. C. Mijlhoff, *J. Appl. Phys.*, **46**, 1165 (1975); Yu. K. Ovchinnikov, G. S. Markova, and V. A. Kargin, *Vysokomol. Soedin. Ser. A*, **11**, 329 (1969).
(41) R. F. Boyer and R. L. Miller, *Polymer*, **17**, 925 (1976).
(42) P. J. Flory, *J. Macromol. Sci., Phys.*, **12**, 1 (1976).
(43) J. L. Sullivan and K. J. Smith, Jr., *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 857 (1975).
(44) T. R. Manley and M. M. Qayyum, *Polymer*, **13**, 587 (1972).
(45) G. Ronca and G. Allegra, *J. Chem. Phys.*, **63**, 4990 (1975).
(46) P. J. Flory, *Proc. R. Soc. London, Ser. A*, **351**, 351 (1976).
(47) J. E. Mark and J. L. Sullivan, *J. Chem. Phys.*, **66**, 1006 (1977).
(48) J. E. Mark and P. J. Flory, *J. Appl. Phys.*, **37**, 4635 (1966).
(49) Since the intramolecular links will be formed by the same mechanism as the intermolecular links, one can write: $L = E_b\varphi_{coil}$, where φ_{coil} denotes the effective volume occupancy or volume fraction of the segments in the coil. In a first approximation, φ_{coil} may be taken independent of dilution in the system polyethylene–trichlorobenzene. The order of magnitude of φ_{coil} may amount to a few percent depending on molecular weight. For polyethylene in a theta solvent φ_{coil} can be estimated using the following expression:

$$\varphi_{coil} = \frac{\text{actual vol of a chain}}{{}^4\!/_3\pi R_g{}^3} = \frac{6.2}{M^{1/2}}$$

where R_g is the radius of gyration and M is the molecular weight. Equation 17 may then be rewritten as:

$$\frac{\nu_{intra}}{\nu_{inter}} = \frac{\varphi_{coil}}{\varphi_{2c}} = \frac{6.2}{\varphi_{2c}M^{1/2}}$$

which reduces to $\nu_{intra}/\nu_{inter} = 0.01/\varphi_{2c}$ for a polyethylene with molecular weight of 400 × 10^3. This shows that the number of intramolecular cross-links in the present case is small as a result of starting form a high molecuar weight polymer.[11,12,31]

Study of Conformational Changes of *N*-(*n*-Alkyl) Maleimides with Chain Length†

J. I. González de la Campa, J. M. Barrales-Rienda,* and J. González Ramos

Instituto de Plásticos y Caucho, C.S.I.C., Juan de la Cierva, 3, Madrid 6, Spain.

Received May 3, 1977

ABSTRACT: The intramolecular structure of a series of *N*-(*n*-alkyl) maleimides in solution was studied by a high-resolution nuclear magnetic resonance technique. A sharp transition in the NMR spectra of *N*-(*n*-alkyl) maleimides in benzene at 60 °C was observed at *N*-(*n*-decyl) maleimide, above which there exist two distinguishable NMR peaks for internal methylene protons, and below which only a single peak was observed. The NMR signals of the internal methylene protons taken in carbon tetrachloride are not resolved as in those NMR spectra taken in benzene solutions. The experimental results are discussed in terms of a mechanism developed by Ando and Nishioka. These authors have assumed that the double peaks of some *n*-alkanes in α-chloronaphthalene could arise from a contribution of the methylene groups adjacent to gauche bonds which are incompletely averaged along the chain. The incomplete averaging may be due to a strong interaction between the *n*-alkyl chain and the α-chloronaphthalene molecules. In our case a specific interaction between the *N*-(*n*-alkyl) maleimides and benzene has been considered. This interaction arises from 1:1 exo-stereospecific association of the *N*-(*n*-alkyl) maleimide and benzene molecules.

In a recent paper,[1] the conformation and packing in the solid state of a series of poly[*N*-(*n*-alkyl) maleimides] has been studied by means of x-ray diffraction. From this work a sudden transition has been found at $n \geq 10$ in the relationship between the diffraction maximum corresponding to the side chains and n (number of carbon atoms in the lateral side chain), showing that the conformation of the side chains deviates from the planar zig-zag if it has more than ten carbon atoms.

Conformational transitions of such a type have been ob-

---

† Dedicated to Professor Dr. M. L. Huggins on his 80th birthday.

served in substances containing *n*-alkane chains by means of several experimental techniques not only in the pure state but also in solution. Thus Liu[2] has studied the structural variations of *n*-alkanes in solution as a function of the chain length by means of NMR. He found a sharp conformational transition when $n = 17$–18 in certain bulky aromatic solvents depending on the size of the solvent molecules.

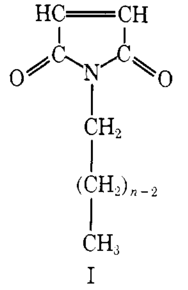
In nonaromatic solvents such as CCl_4 the transition could not be detected, but it was not possible absolutely to exclude its existence. Later on, in a more elaborate study, Liu[3] has observed by using *n*-alkanes both in the pure liquid state and in C_6H_6 solution that the change of the relative solvent effect on the methylene chain with respect to *n* drastically deviates from the expected behavior when $n = 9$.

Schaufele[4] has studied a series of *n*-alkanes ($n = 5$ to 35) in the pure state by using laser vibrational scattering and found that the accordion mode bands resulting from the fully extended chain structure are strong when $n < 9$. However, when $n \geq 9$ the abundance of the trans conformation in these compounds is extremely small in favor of chain-shortened forms.

Liu and Ullman,[5] taking as a base statistical thermodynamic arguments, have presented a theoretical model in which the possibility of intramolecular chain folding in *n*-alkane solutions can be explained when $n \geq 15$, supporting the NMR spectra in bulky aromatic solvents. Moreover, this mechanism can also be used to explain the chain folding when $n \geq 10$.

Ando and Nishioka[6,7] have also studied the NMR spectra from Liu[2] and proposed a mechanism in which the interaction between solvent and solute molecules may be ascribed to two states: in one the chemical shifts of $-CH_2-$ groups in *n*-alkanes are not averaged over the possible conformations due to the strong restraints by the bulky aromatic solvent; and in the other they are averaged over those due to the weak restraints of molecular motions of the *n*-alkane molecules.

We have studied the solute–solvent interactions of the *N*-(*n*-alkyl) maleimides in aromatic solvents by means of NMR in order to confirm the conclusions obtained from these products in a polymerized form and to see the differences in the solute–solvent interactions due to the introduction of the *N*-maleimide ring, in relation to the case of *n*-alkanes. *N*-(*n*-Alkyl) maleimides can be represented by the structural formula I. The methylene groups in parentheses are defined here as internal methylenes.



I

$n = 2, 4, 6, 8, 10, 12, 14, 16,$ and 18

Experimental Section

N-(*n*-alkyl) maleimides used in the present work were synthesized previously[8] by using a method developed by Searle.[9] Benzene and carbon tetrachloride (Uvasol, Merck, A.G.) were used as solvents without further purification. NMR spectra were recorded at 60 °C by means of a 100-MHz spectrometer, Varian Model XL-100 (Varian Associates, Calif.). Hexamethylene disilane (0.5%) was used as internal standard. The chemical shifts are expressed in cycles per second (Hz) downfield. Diluted solutions (5% w/v) were used so as to eliminate any chemical shift contribution due to solute–solute interactions. Concentrations were calculated to have always the same relative amount of $-CH_2-$ groups throughout the series.

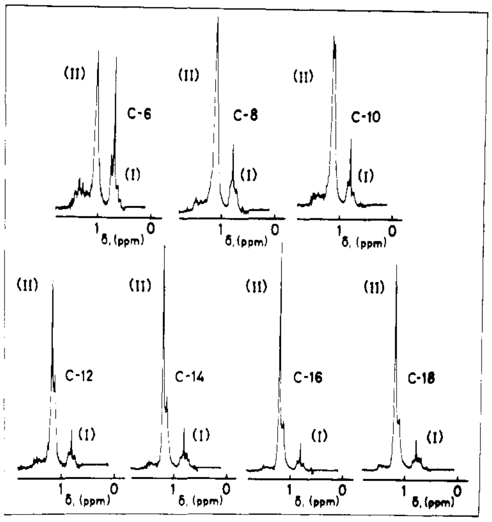


Figure 1. The NMR spectra of *N*-(*n*-alkyl) maleimides in 5% C_6H_6 solution at 60 °C.

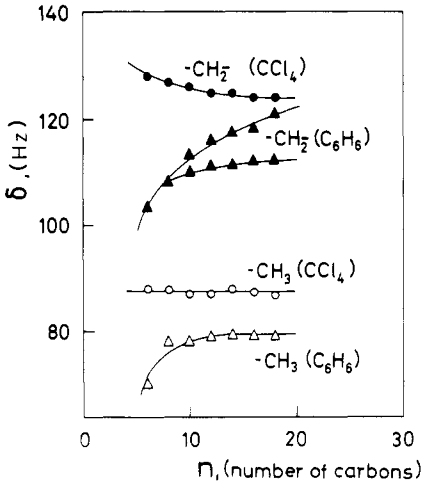


Figure 2. Plots of chemical shifts of internal $-CH_2-$ and $-CH_3$ protons of *n*-alkyl chains of a series of *N*-(*n*-alkyl) maleimides in C_6H_6 and CCl_4 at 60 °C vs. number of carbon atoms, h.

Results and Discussion

Figure 1 shows the spectra of the *n*-alkyl side chain in *N*-(*n*-alkyl) maleimides using C_6H_6 as solvent. Peaks I and II are due to the methyl and methylene protons respectively except for the methylene groups adjacent to the imido groups which appear at a lower field. The splitting due to the methylene protons adjacent to the end methyl groups is masked in the spectra because of the greater number of internal $-CH_2-$ contributing to peak II. In the case of C_6H_6 we can see that the $-CH_2-$ protons show a single NMR peak for compounds with *n* ranging from 6 to 8. When $n \geq 10$ two partially resolved peaks appear in the spectrum. Spectra made in CCl_4 do not show any resolved peak when the number of carbons grows.

On the other hand, in Figure 2 the chemical shifts of the $-CH_3$ and $-CH_2-$ groups are shown in both C_6H_6 and CCl_4 solutions. In the CCl_4 solutions δ_{-CH_2-} diminishes to a virtually constant value whereas δ_{-CH_3} remains constant throughout the series. In C_6H_6 solution both δ_{-CH_2-} and δ_{-CH_3} increase with chain length but in the case of the δ_{-CH_3} the slope has an abrupt change when $n = 8$–10. In order to compare the solvent effect due to the C_6H_6 on the chemical shifts of $-CH_3$ and $-CH_2-$ groups, the differences between the chemical shifts of $-CH_3$ and $-CH_2-$ in C_6H_6 and CCl_4 are shown as a function

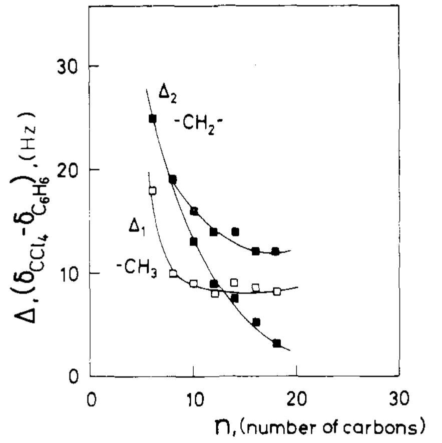


Figure 3. Plots of the relative solvent effect on the chemical shift $\Delta(\delta_{CCl_4} - \delta_{C_6H_6})$ vs. number of carbon atoms, *n*.

of the number of carbon atoms in Figure 3. From this figure it can be seen that the Δ_{-CH_2-} of the -CH$_2$- is larger than Δ_{-CH_3} of the -CH$_3$ protons when $n < 13$ and becomes less than Δ_{-CH_3} of the methyl group when $n > 13$.

These results indicate that the relative solvent effect on chemical shifts is larger for the internal methylenes than for the final methyl when $n < 14$. Whereas for $n > 14$, the solvent effect on the internal -CH$_2$- protons becomes so small that it is even less than that of the final methyl protons. A representation of these differences $D = (\Delta_{-CH_2-} - \Delta_{-CH_3})$ as a function of chain length is shown in Figure 4. This plot is equivalent to the plot of Δ_{-CH_2-} shown in Figure 3 if the chemical shift of the methyl protons is used as reference and it is a good representation of the chain length effect.

When the chain length is greater than 8 the relative solvent effect decreases with the increasing chain whereas it drastically deviates from the expected behavior when $n < 8$. When *n* increases from 6 to 8 the relative solvent effect increases and there is a maximum when $n = 8$.

From all these data a sudden conformational change in the lateral side chain of *N*-(*n*-alkyl) maleimides may be concluded. This type of change has been explained by Ando and Nishioka[7] in the case of *n*-alkane solutions in bulky aromatic solvents such as α-chloronaphthalene when $n \geq 18$ in two different ways. These authors have calculated the chemical shifts of a series of *n*-alkanes in the cases of weak and strong interactions with the solvent by using Pople's approximation and the Monte Carlo method.

The calculations in the case of strong interactions were made without averaging over the generated Monte Carlo chains and are in good agreement with their own experimental data and with those reported by Liu.[2] They suggested that the strong interactions are due to the planar molecules of α-chloronaphthalene which partially produce a sandwich structure and restrict the internal motions of *n*-alkane molecules. These interactions diminish the exchange among the various gauche conformations.

They have also calculated that the methylene protons next to the gauche methylene groups and the methylene protons next to the end methyl groups appear at higher field than the other methylene protons.

Then, the existence of a splitting when *n* reaches a certain value may be interpreted by suggesting that the *n*-alkyl chains are predominantly in a fully extended planar zig-zag conformation for the lower members of the series, when they are dissolved in liquids with a planar structure. When a sufficient number of carbon atoms in the *n*-alkyl chains is attained a fold occurs giving place to protons with different chemical shifts which results in a deshielding of the methylene peak.

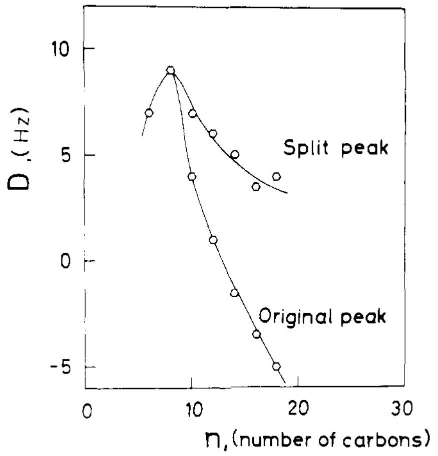


Figure 4. Plot of the differences between the relative solvent effects on chemical shifts of the internal -CH$_2$- and of the end -CH$_3$ groups ($D = \Delta_2 - \Delta_1$) vs. number of carbon atoms, *n*.

However, there are two main differences among the *n*-alkanes and the *N*-(*n*-alkyl) maleimides studied in the present paper. First of all, *n*-alkane spectra registered by Liu[2] in CCl$_4$ and in C$_6$H$_6$ are not resolved as those made in α-chloronaphthalene solutions. On the contrary, in our case spectra made in C$_6$H$_6$ are very easily resolved. Second, NMR spectra of *n*-alkanes show the splitting in the internal methylene peak when $n = 17$ contrary to the *N*-(*n*-alkyl) maleimides which show that splitting when $n = 10$.

These differences may be interpreted by the existence of some kind of characteristic interaction of our compounds with the aromatic solvents which diminishes the local segmental motions of the chain.

In order to elucidate the types of interaction, the effect of the *N*-maleimide ring on the transition must be taken into account. Thus Bryce-Smith and Hems[10] have found that large upfield chemical shifts of ethylenic protons in *N*-maleimides are induced by the benzene solvent and these have been attributed to an 1:1 exo-stereospecific association of the *N*-maleimide ring with solvent molecules.

Such a type of charge-transfer complex has been used by the present authors to explain the alternating copolymerization of *N*-phenylmaleimide and styrene.[11] Thus we have found that benzene and styrene induce a chemical shift of the ethylenic protons of *N*-phenylmaleimide due to complex formation between the aromatic ring and the double bond.

These interactions, which are sufficiently strong to make the complex NPMI–ST polymerize as a monomer, in the case of *N*-(*n*-alkyl) maleimides, hinder the internal motions of the *n*-alkyl side chains and decrease the rate of exchange among the various conformations giving rise to double peaks when $n \geq 10$ even in benzene.

In conclusion it may be said that the *n*-alkanes present a type of conformational transition when $n \simeq 9$–10 as has been shown by Schaufele[4] and Liu.[3] However, NMR resolution is not sufficient to split the methylene signal when $n \simeq 10$ and it is necessary to reach a value of *n* double this to detect the splitting. When a group which diminishes the mobility is linked to the *n*-alkyl chain, the resolution is sufficient enough to detect the splitting in solution at $n = 10$. Finally, it can be concluded, from the experimental results obtained in the present study, the great importance played by the solute–solvent interaction in the detection of this type of structural transition.

Acknowledgment. J. I. G. de la C. gratefully acknowledges support of this work by a grant from the Spanish Plán para la Formación del Personal Investigador, sponsored by the

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

References and Notes

(1) J. M. Barrales-Rienda, J. G. Ramos, and M. S. Chaves, *J. Polym. Sci., Polym. Phys. Ed.*, submitted for publication.

(2) K. J. Liu, *J. Polym. Sci., Part A-2*, **5**, 1209 (1967).

(3) K. J. Liu, *Polymer*, **10**, 951 (1969).

(4) R. F. Schaufele, *J. Chem. Phys.*, **49**, 4168 (1968).

(5) K. J. Liu and R. Ullman, *J. Polym. Sci., Part A-2*, **6**, 451 (1968).

(6) I. Ando and A. Nishioka, *Makromol. Chem.*, **152**, 7 (1972); **160**, 145 (1972).

(7) I. Ando and A. Nishioka, *Makromol. Chem.*, **171**, 195 (1973).

(8) J. G. Ramos, J. M. Barrales-Rienda, and M. S. Chaves, *Anales Quim. (Madrid)*, **73**, 139 (1977).

(9) N. E. Searle, U.S. Patent 2 444 536 (1948); *Chem. Abstr.*, **42**, 7340 (1948). Corrected September 21, 1948.

(10) D. Bryce-Smith and M. A. Hems, *J. Chem. Soc., Perkin Trans. 2*, 812 (1968).

(11) J. M. Barrales-Rienda, J. I. G. de la Campa, and J. G. Ramos, *J. Macromol. Sci. Chem.*, **11**, 167 (1977).

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

Alastair M. North,* Richard A. Pethrick, and David W. Phillips

Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL, Scotland. *Received May 3, 1977*

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-