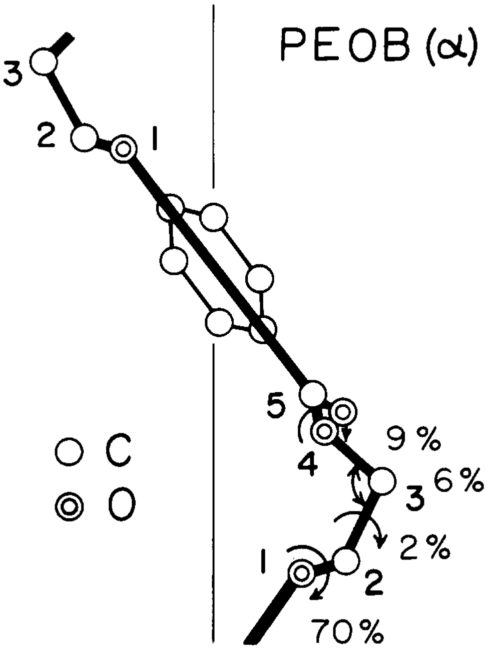

Figure 5. Potential energy distributions for poly(ethylene oxybenzoate) α form. The bold line represents the model used in calculation.

as expected from the approximated eq 37, where the condition of $\Delta\theta = 0$ is neglected. In fact, PED to τ(G) and τ(T) have almost the same values without the condition of $\Delta\theta = 0$, as shown in Table III. But under the condition of $\Delta\theta = 0$, PED to τ(T) is nearly zero. From eq 31 the condition of $\Delta\theta = 0$ is expressed by

$$\Delta\phi_1 - \Delta\phi_2 + 2.1\Delta\tau(\mathrm{T}) = 0 \qquad (39)$$

where $\phi_1 = \angle \mathrm{CH_2{-}CF_2{-}CH_2}$ and $\phi_2 = \angle \mathrm{CF_2{-}CH_2{-}CF_2}$. $\Delta\phi_1$ and $\Delta\phi_2$ are calculated to have values of the same order, so that $\Delta\tau$(T) becomes very small using eq 39, resulting in the nearly zero PED. $\Delta\tau$(G) has high PED as expected from the large value of $(\partial d/\partial\tau(\mathrm{G}))^2$ in Table III, since $\Delta\tau$(G) is an independent variable. Thus the very small PED to τ(T) in Figure 4 may be due to the existence of the condition of $\Delta\theta = 0$, unexpected from eq 37. As described above, eq 37 and 38 are very useful for the discussion of the elastic deformations of the chains. We must, however, remember that these equations have some limitations because of neglecting the condition of $\Delta\theta = 0$, when we discuss the potential energy distributions of chains in the "crystal lattice", as found in the case of PVDF form II.

In the above discussion, $(\partial d/\partial R_i)^2$ is dimensionless and the unit of $F_{ii}{}^{-1}$ is mdyn/Å. Such dimensions were adjusted for the bond angles (indicated by the atoms i, j, and k) and internal rotation angles (indicated by the atoms i, j, k, and l) according to the following equations.

$$\partial d/\partial\phi(\text{dimensionless}) = \partial d/\partial\phi(\text{Å/rad})/(r_{ij}r_{jk})^{1/2}$$

$$\partial d/\partial\tau(\text{dimensionless}) = \partial d/\partial\tau(\text{Å/rad})/(r_{ij}r_{kl}\sin\phi_{ijk}\sin\phi_{jkl})^{1/2}$$

$$F_\phi{}^{-1}(\text{Å/mdyn}) = F_\phi{}^{-1}(\text{rad}^2/\text{mdyn Å})r_{ij}r_{jk}$$

$$F_\tau{}^{-1}(\text{Å/mdyn}) = F_\tau{}^{-1}(\text{rad}^2/\text{mdyn Å})r_{ij}r_{kl}\sin\phi_{ijk}\sin\phi_{jkl}$$

References and Notes

(1) K. H. Meyer and W. Lotmar, *Helv. Chim. Acta*, **19**, 68 (1935).
(2) H. Mark, *Trans. Faraday Soc.*, **32**, 144 (1936).
(3) W. J. Lyons, *J. Appl. Phys.*, **29**, 1429 (1958); **30**, 796 (1959).
(4) L. R. G. Treloar, *Polymer*, **1**, 95, 279, 290 (1960).
(5) T. Shimanouchi, M. Asahina, and S. Enomoto, *J. Polym. Sci.*, **57**, 93 (1962).
(6) M. Asahina and S. Enomoto, *J. Polym. Sci.*, **59**, 101 (1962).
(7) S. Enomoto and M. Asahina, *J. Polym. Sci.*, **59**, 113 (1962).
(8) H. Sugeta and T. Miyazawa, *Polym. J.*, **1**, 226 (1970).
(9) T. R. Manley and C. G. Martin, *Polymer*, **14**, 632 (1973).
(10) T. Miyazawa, *J. Polym. Sci.*, **55**, 215 (1961).
(11) I. Sakurada and K. Kaji, *J. Polym. Sci., Part C*, **31**, 57 (1970).
(12) T. Uchida and H. Tadokoro, *J. Polym. Sci., Part A-2*, **5**, 63 (1967).
(13) R. G. Snyder and G. Zerbi, *Spectrochim. Acta*, **23a**, 391 (1971).
(14) R. Hasegawa, Y. Takahashi, Y. Chatani, and H. Tadokoro, *Polym. J.*, **3**, 600 (1972).
(15) M. Kobayashi, K. Tashiro, and H. Tadokoro, *Macromolecules*, **8**, 158 (1975).
(16) R. Hasegawa, M. Kobayashi, and H. Tadokoro, *Polym. J.*, **3**, 591 (1972).
(17) K. Tashiro, M. Kobayashi, and H. Tadokoro, *Macromolecules*, **10**, 413 (1977).
(18) H. Kusanagi, H. Tadokoro, and Y. Chatani, *Macromolecules*, **10**, 405 (1977).

Brillouin Scattering from Molten Linear Polyethylene

G. D. Patterson* and J. P. Latham

Bell Laboratories, Murray Hill, New Jersey 07974. *Received February 7, 1977*

ABSTRACT: Brillouin scattering from several molten linear polyethylenes is examined. The master relation between phonon velocity and relative free volume given by Champion and Jackson is extended and confirmed. A more general relation is used to examine in detail the phonon velocity and conclusions are drawn about the local structure in polyethylene melts.

Brillouin scattering from liquid n-alkanes has been extensively studied by Champion and Jackson.[1] A master relation between longitudinal phonon velocity V_l and relative free volume, V_0/V_f, where V_0 is the specific volume extrapolated to 0 K without chnge of phase and V_f is the free volume

$$V_l \propto (V_0/V_f)^{1/3} \qquad (1)$$

was found to hold for the n-alkanes in the temperature range 20–140 °C. Also, the phonon velocity at each temperature appeared to be approaching an asymptote with chain length. The present work extends the measurements of V_l to include higher molecular weight polyethylenes in the molten state. The results are then discussed in terms of the general theory of sound velocity in liquids. Conclusions are also drawn about the nature of molten linear polyethylene.

Theory

Longitudinal thermal acoustic phonons interact with light to give frequency shifted scattered light with splitting

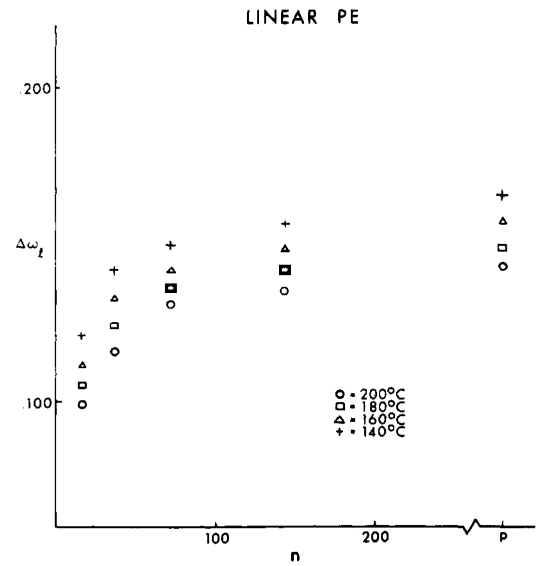

Figure 1. Brillouin splitting $\Delta\omega_l$ vs. chain length at 140, 160, 180, and 200 °C.

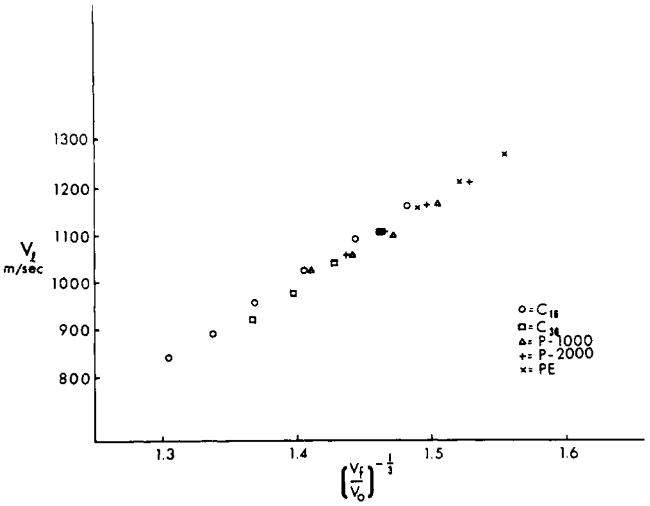

Figure 2. Phonon velocity V_l vs. $(V_f/V_0)^{-1/3}$ for polyethylene.

$$\pm\Delta\omega_l/\omega_0 = 2\bar{n}\,\frac{V_l}{C}\sin\theta/2 \qquad (2)$$

where ω_0 is the incident frequency, $\bar{n}$ is the refractive index, V_l is the longitudinal phonon velocity, C is the speed of light in a vacuum, and θ is the scattering angle in the scattering plane. If there is little or no dispersion in the phonon velocity, the value of V_l obtained by Brillouin scattering should equal the low-frequency speed of sound

$$V_l(0) = \left(\frac{\gamma}{\rho\kappa_T}\right)^{1/2} \qquad (3)$$

where $\gamma = C_P/C_V$ is the ratio of specific heats, ρ is the density, and κ_T is the isothermal compressibility.

Experimental Section

Brillouin spectra were obtained as described previously.[2,3] The incident light had a wavelength of 5145 Å and the scattered light was observed at 90°. The phonon velocities were then calculated from the measured values of $\Delta\omega_l$ and calculated values of the refractive index.

n-Hexadecane and *n*-hexatriacontane were obtained from the Chemical Samples Co. Linear polyethylenes of number average molecular weight 1000 and 2000 were from the Petrolite Corp. These waxes have a narrow molecular weight distribution. Polyethylene of melt index 21.5 was obtained from the Phillips Petroleum Co. The number average molecular weight was approximately 10 000.

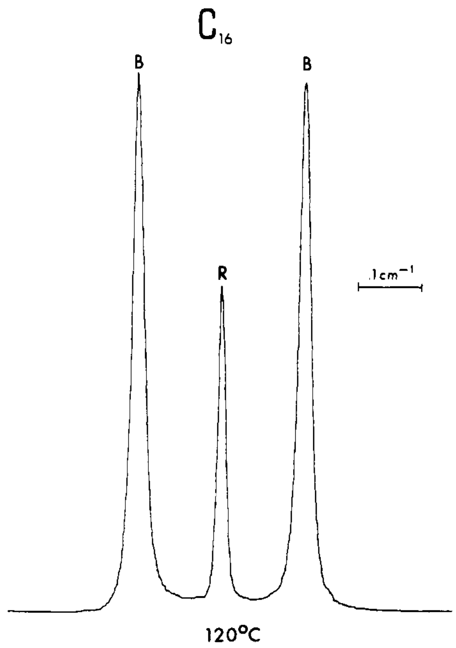

Figure 3. Rayleigh–Brillouin spectrum of *n*-hexadecane at 120 °C.

All samples were heated in quartz cuvettes until fully melted. The cuvettes were then flushed with dry nitrogen and stoppered. Measurements of $\Delta\omega_l$ were carried out between the melting points and 200 °C for all samples.

Results and Discussion

Values of $\Delta\omega_l$ at temperatures of 140, 160, 180, and 200 °C are plotted vs. *n*, the number of carbon atoms, in Figure 1. Data at lower temperatures for *n*-hexadecane (C_{16}) and *n*-hexatriacontane (C_{36}) agree well with the results of Champion and Jackson.[1] The Brillouin splitting $\Delta\omega_l$ reaches an asymptote with chain length in molten polyethylene.

In the work of Champion and Jackson[1] the free volume was calculated as described by Doolittle[4]

$$V_f = V - V_0 \qquad (4)$$

where V is the specific volume. The phonon velocities V_l are plotted vs. $(V_f/V_0)^{-1/3}$ in Figure 2. As found previously,[1] all the data fall on a master line. The phonon velocity is sensitive only to the linear density within the homologous series of polymethylenes.

As noted above, if there is no dispersion the phonon velocity should depend only on γ, ρ, and κ_T. The density of *n*-hexadecane at 120 °C is 0.7036 g/cm^3.[5] The compressibility is 161 $\times 10^{-12}$ cm^2/dyn.[6] The ratio of specific heats can be obtained from the Rayleigh–Brillouin spectrum shown in Figure 3. The ratio of the Rayleigh peak intensity I_R to the Brillouin peak intensities $2I_B$ is equal to $\gamma - 1$.[7] The value obtained from the spectrum is $\gamma = 1.227$. Thus the calculated phonon velocity for *n*-hexadecane at 120 °C is $V_l(0) = 1.04$ km/s. The observed value of V_l was 1.03 ± 0.1 km/s in good agreement with the thermodynamic value. The present results on molten polyethylene are also in agreement with ultrasonic measurements of V_l by Boyd and Biliyar[8] and Eby.[9] Thus, it is reasonable to conclude that $V_l(0)$ is obtained from the Brillouin scattering measurements.

The relation between $V_l(0)$ and free volume can be understood by examining the equation of state for fluids. A commonly used equation of state is that derived by Tonks[10]

$$\frac{pV}{RT} = \frac{1}{1-(V_0/V)^{1/3}} \qquad (5)$$

where now V is the molar volume for a collection of hard spheres. For a polymer liquid, a question arises as to what the appropriate molecular weight should be for these hypothetical units, but we will assume that such a unit can be defined with molecular weight M. The phonon velocity is then given by

$$V_l = \left(\frac{\gamma RT}{M}\right)^{1/2} \left[\frac{1 - \frac{2}{3}(V_0/V)^{1/3}}{(1 - (V_0/V)^{1/3})^2}\right]^{1/2} \tag{6}$$

The value of M calculated from the measured phonon velocity of n-hexadecane at 120 °C is 159 g/mol. This is approximately the molecular weight of n-undecane.

If the free volume is small relative to V_0, eq 6 can be approximated as

$$V_l = K\left(\frac{\gamma RT}{M}\right)^{1/2} \left(\frac{V_0}{V_f}\right)^{1/3} \tag{7}$$

where K is a constant. Thus, the relation found by Champion and Jackson[1] appears reasonable for a homologous series of molecules.

The fact that the Brillouin results yielded $V_l(0)$ demands that the local structural relaxation times in molten polyethylene be fast relative to 10^{-10} s. The relaxation time for trans-gauche conformational changes in butane would be near 10^{-10} s at 120 °C,[11] but for longer chains the internal bonds should relax much slower. Thus, rapid local structural relaxation must be taking place essentially without change of conformation from trans to gauche states. The above results also suggest that conformation changes contribute a negligible fraction to the total compressibility of the fluid in molten polyethylene.

It has previously been shown that the local orientational order in molten polyethylene is essentially constant for chains larger than about 20 carbons compared at constant density.[12] The present results also confirm the similarity of the local structure in polyethylene melts. It seems reasonable to conclude that the lower homologues of polyethylene are good representatives of the local melt properties of the whole series.

References and Notes

(1) J. V. Champion and D. A. Jackson, *Mol. Phys.*, **31**, 1169 (1976).
(2) G. D. Patterson, *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 415 (1975).
(3) G. D. Patterson, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 741 (1976).
(4) A. K. Doolittle, *J. Appl. Phys.*, **22**, 1471 (1951).
(5) F. D. Rossini, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds", API Research Project No. 44, Carnegie Press, Pittsburgh, 1953.
(6) R. A. Orwoll and P. J. Flory, *J. Am. Chem. Soc.*, **89**, 6814 (1967).
(7) L. Landau and G. Placzek, *Phys. Z. Sovjetunion*, **5**, 172 (1934).
(8) R. H. Boyd and K. Biliyar, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **14**, 329 (1973).
(9) R. K. Eby, *J. Acoust. Soc. Am.*, **36**, 1485 (1964).
(10) L. Tonks, *Phys. Rev.*, **50**, 955 (1936).
(11) J. E. Piercy and M. G. S. Rao, *J. Chem. Phys.*, **46**, 3951 (1967).
(12) G. D. Patterson, *J. Macromol. Sci., Phys.*, **12**, 61 (1976).

Local Polymer-Segment Density as Studied from NMR Observed on Highly Concentrated Polyisobutylene Chain Solutions. Determination of Thermodynamic Interaction Parameters Characterizing High Polymer–Solvent Mixtures

J. P. Cohen-Addad* and C. Roby

Laboratoire de Spectrométrie Physique associé au C.N.R.S., Université Scientifique et Médicale de Grenoble, 38041 Grenoble-Cedex, France.

Received September 7, 1976

ABSTRACT: It is attempted to relate high-resolution nuclear magnetic spectroscopy measurements to thermodynamic interaction parameters of high polymer chain concentrated solutions. It is proposed to use the characteristic polymer concentration and temperature dependences of the line width observed on polyisobutylene chain solutions in $CDCL_3$, CS_2, and C_7D_8 to calculate: (i) the variation of enthalpy as a temperature function for the formation of a single unlike contact pair; (ii) the variation from a reference temperature of the change in free energy for the formation of an unlike contact pair. These parameters are shown to have an order of magnitude in satisfactory agreement with that of parameters derived from other types of experiments.

I. Introduction

When time-dependent chain fluctuations can be left aside, properties of concentrated polymer–solvent mixtures at equilibrium may be considered as characterized in two ways. The first one is the determination of the structure of high polymer chain solutions, concentrated enough to give rise to entanglement formation. An accurate description of such a structure has been recently given from elegant neutron scattering experiments performed on polystyrene.[1,2] The other way corresponds to the determination of thermodynamic properties on a macroscopic scale. Solvent vapor pressure measurements or osmometry lead to the determination of the solvent activity.

Numerous polymer–solvent systems have been experimentally studied to attempt to establish the relationship existing between macroscopic thermodynamic data and molecular interaction parameters.[3,4] Several interpretations based on combinatorial analysis have been proposed besides the simple and illustrative model leading to the Flory–Huggins equation.[5-7] More recently, a magnetic analogue of polymer chain–solvent systems has been found. The state equation of polymer solutions has been derived from the properties of second order phase transitions observed on magnetic systems.[8]

The present paper aims at defining a complementary experimental way to characterize polymer–solvent mixture properties. It will be shown that thermodynamic parameters derived from NMR data and characterizing polymer–solvent