water, acetonitrile, and methanol.[28] The conformation of the oligomers with DP 6 and 8 is found to be form II, yet high molecular weight polyproline appears to be in form I in methanol.[29] The end effects in this solvent thus also favor form II. Some counterevidence to this attractive agreement between theory and experiment exists. For example, oligomers with DP 6 and 12 were shown by Yaron and Berger[30] to be capable of adopting form I in a certain solvent (unspecified); presumably the solvent was so poor that end effects were overpowered. However, studies in the solvent system trifluoroethanol–*n*-propyl alcohol for polyprolines with DP 17 and 550 (Backman and Holzwarth, unpublished) show an absence of end effects, *i.e.*, the I–II transition curves are symmetrical about the same solvent composition for both DP's. These experiments suggest that the magnitude of the end effect may depend upon the nature of the particular solvent system employed.

2. Junction Energy. The experimental evaluations of junction energy are commonly expressed in terms of a parameter σ, where σ is the weight factor used in statistical–thermodynamic theories of conformational transitions.[6,13,18] Since σ equals $\exp[-J/RT]$, where J is an average junction energy, the experimental junction energies, +4 and +7 kcal/mol, correspond to $\sigma = 10^{-3}$ and 10^{-5}. The two experimental evaluations of junction energy are based upon the pressure dependence of the proline I–II transition[5] and upon the kinetics of the I–II transformation.[4,6] The former measurement, carried out by Rifkind and Applequist,[5] actually yields the quantity $\Delta\bar{V}^2/\sigma$, where $\Delta\bar{V}$ is the change in partial residue–molal volume for the *trans–cis* conversion at infinite dilution. Unfortunately, $\Delta\bar{V}$ is not known, so that the value of σ obtained is uncertain. Similarly, the kinetic measurements of Engel[4] yield σ directly only under certain simplifying assumptions.[6] Thus neither value of σ is untainted.

Now, the experimental evaluations of σ correspond to an equilibrium constant for the process in which a molecule with q *cis* sequences is converted into a molecule with $q + 1$ *cis* sequences while the total number of *cis* residues remains invariant. Such a process must, on the average, be compared to $J_{\text{I–II}} + J_{\text{II–I}}$ since both a I–II and a II–I junction are created as q increases by 1. The quantity $J_{\text{I–II}} + J_{\text{II–I}}$ is conveniently designated as J. The calculated intramolecular value of J then falls between +1.5 and +6.0 kcal/mol, depending upon the particular value of τ_4 and ψ_4 chosen. The lower calculated value of J consists of a +2.1-kcal/mol unfavorable electrostatic term and a favorable −0.6 kcal/mol net van der Waals term as indicated in Table II.

These results suggest that the cooperativity of the poly-L-proline does not originate primarily in intramolecular steric effects. Rather intramolecular electrostatic and intermolecular polymer–solvent interactions appear to be the source of the observed positive cooperativity. Polymer–solvent interactions are implicated here because the smaller calculated value of J is less than half the lower of the two experimental values of J. Convincing experimental evidence for the importance of these interactions in polyproline must however await measurements of σ by the same method in a variety of solvents.

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(28) T. Isemura, H. Okabayashi, and S. Sakakibara, *Biopolymers*, **6**, 307 (1968).

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The Configurational Entropy of Polyethylene at the Melting Point

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ABSTRACT: The configurational entropy of polyethylene at the melting point is obtained from the measured entropy of fusion, the excess nonconfigurational entropy of the glass calculated from heat capacity data, and an estimated nonconfigurational entropy for expanding the liquid from the volume of the glass to the volume of the melt at atmospheric pressure. The value obtained is 0.536 ± 0.045 J/°K g (1.79 ± 0.15 eu/mol of CH_2). Other, more simply made estimates compare as follows. The entropy of fusion is 33% larger; Mandelkern's approximate entropy of fusion at constant volume is within our estimated error; and our estimate of the entropy of fusion at constant volume is 25% smaller.

The configurational entropy is the entropy of the variety of shapes assumed by the polymer molecules. It describes the variability in the internal rotation about each single bond and, to a minor extent, the variability in bond lengths and bond angles. Unfortunately, the configurational entropy cannot be measured directly but must be derived from other quantities.

The simplest estimate for the configurational entropy of a liquid at the melting point is the entropy of fusion. Since the configurational entropy is all developed as the molecules are released from their sameness of shape in the crystal, all of the configurational entropy is contained in the entropy of fusion. But the entropy of fusion also includes a certain amount of nonconfigurational entropy from changes in the entropy of the lattice vibrations induced by fusion. Thus, to obtain a better value for the configurational entropy than the entropy of fusion, we must eliminate the nonconfigurational entropy.

Estimates of the nonconfigurational entropy made up to now have been based on the assumption that the configurational entropy equals the entropy of fusion when fusion is carried out at constant volume.[1] Since the entropy of the lattice vibrations at a given temperature does depend on the average separation between molecules, the constant volume entropy of fusion contains little nonconfigurational entropy. The only nonconfigurational entropy comes from the probably minor difference between the lattice entropy of the regular array in the crystal and the lattice entropy of the disordered array in the liquid, both at the same density. Nonetheless, the configurational entropy so obtained refers to the liquid under the high pressure required to compress it to the volume of the crystal. The configurational entropy of the liquid at atmospheric pressure will be shown later to differ appreciably from this.

In the estimate of the nonconfigurational part of the entropy of fusion to be described, we have used the excess nonconfigurational entropy of the glass calculated from the heat capacities of several polyethylene specimens measured down to 4°K plus an interpolated value for the rate of increase in nonconfigurational entropy with volume for the expansion of the glass to the volume of the liquid at the melting point.

Results

Excess Volume of the Liquid at the Glass Transition Temperature and at the Melting Point. Since the nonconfigurational part of the entropy of fusion is introduced mainly by the volume expansion, we need the excess volumes of both the glass and the liquid at the melting point relative to the crystal. These can be obtained from Miller's Figure 3.[2] The excess volume of the glass is 0.068 cc/g, which is the difference between the volume of the glass (1.078 cc/g) and the crystal (1.010 cc/g) at the glass transition temperature (−73°). The excess volume of the volume of the liquid at the melting point (140°) is 0.212 cc/g, which is the difference between 1.262 and 1.050 cc/g.

Miller's graph of the liquid volume was obtained by extrapolating from the volumes of the linear paraffins.[3] His graph of the crystalline volume was obtained from separate literature values at 0°K, 25°C, and an average of the values computed from the unit cell dimensions at the melting point. Finally, Miller obtained the glass transition temperature (−73°) by extrapolating to polyethylene the temperatures at which the linear paraffins reached the viscosity of 10^{13} P.[3]

These fairly rough estimates for the volume differences are probably moderately reliable. The estimated excess volume of the liquid at the melting point is within 10% of the value obtained by Karasz and Jones,[4] whose value of 0.194 cc/g was obtained by measuring the effect of pressure on the melting point.

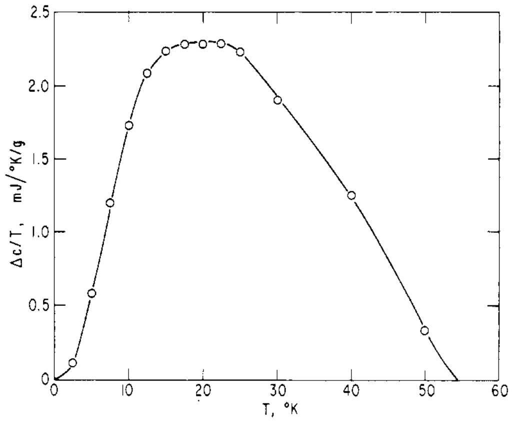

Figure 1. Excess heat capacity of polyethylene glass, over that of the crystal, divided by the temperature *vs.* temperature.

Excess Nonconfigurational Entropy of the Glass. The excess nonconfigurational entropy of the liquid at the volume of the glass can be calculated directly from heat capacity data. Because the polymer configurations are frozen in the glass, the configurational entropy and enthalpy are independent of temperature. Thus, any excess heat capacity of the glass, over that of the crystal, will be nonconfigurational, making the entropy computed from the excess heat capacity a nonconfigurational entropy.

Tucker and Reese[5] measured the heat capacities of three samples of polyethylene, each with a different degree of crystallinity, and extrapolated to the heat capacities of the completely crystalline and the completely amorphous or noncrystalline materials. Since the heat capacities of both the crystalline and noncrystalline materials were zero at 0°K, the excess nonconfigurational entropy of the polyethylene glass is equal to the integral with respect to the temperature from 0°K of the excess heat capacity divided by the temperature. In Figure 1 is plotted the excess heat capacity divided by the temperature *vs.* the temperature. Above 55°K the excess heat capacity of the glass becomes zero, at which it remains until the vicinity of the glass transition temperature is reached.[6] From the area under the curve, the excess nonconfigurational entropy at temperatures above 55°K is 75.2 mJ/°K g.

Just how well the heat capacity of the extrapolated noncrystalline polyethylene represents the heat capacity of an amorphous linear polyethylene is a little uncertain, however. The heat capacity of the extrapolated noncrystalline polyethylene contains an Einstein term in addition to the expected Debye term. Tucker and Reese[5] suggested that this term might arise from low-frequency, nonpropagating vibrational modes associated with "loosely bound chain segments." This

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(1) See, for example, L. Mandelkern, "Crystallization of Polymers," McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p 130.

(2) A. A. Miller, *J. Chem. Phys.*, **49**, 1393 (1968).

(3) A. A. Miller, *J. Polym. Sci., Part A-2*, **6**, 249 (1968).

(4) F. E. Karasz and L. D. Jones, *J. Phys. Chem.*, **71**, 2234 (1967).

(5) J. E. Tucker and W. Reese, *J. Chem. Phys.*, **46**, 1388 (1967).

(6) B. Wunderlich, *ibid.*, **37**, 1203 (1962).

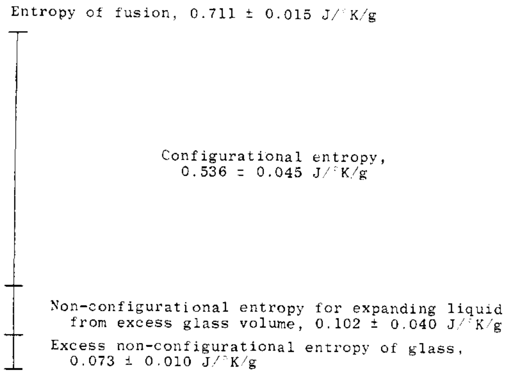

Figure 2. The apportionment of the entropy of fusion.

suggestion was further supported by data on radiation cross-linked polyethylene in which the Einstein term was considerably less.[7] Since the noncrystalline fraction of polyethylene tends to contain the branched materials, the "loosely bound chain segments" may be short branches, which would be absent from a linear amorphous material. From Tucker and Reese's data we find that the Einstein term contributes 6.0 mJ/°K g to the nonconfigurational entropy. The excess nonconfigurational entropy of a linear polyethylene glass may then be as small as 69.2 mJ/°K g, though whether a linear glass would have a larger, compensating Debye term is unknown.

Thus, the excess nonconfigurational entropy of liquid, linear polyethylene with the excess volume of the glass is probably between 69.2 and 75.2 mJ/°K g.

The Excess Nonconfigurational Entropy for Expanding the Liquid from the Volume of the Glass to Its Volume at the Melting Point and Atmospheric Pressure. Unfortunately, we have little data in this range. Hence, the following approximation is made. In isothermally disordering and expanding the crystal to the volume of the glass the nonconfigurational entropy increases, with the volume increase of 0.068 cc/g, at the average rate of between 69.2/0.068 and 75.2/0.068 or between 1.02 and 1.10 J/°K cc. Let us assume that the nonconfigurational entropy continues to increase at this same rate as the liquid expands from the glass. However, as the liquid continues to expand, the rate decreases. For the liquid at the melting point and atmospheric pressure the total entropy increases with volume at the rate of only 0.69 J/°K cc. Let us assume that only one-half of the total entropy change at atmospheric pressure is nonconfigurational and that the nonconfigurational entropy decreases linearly with volume from between 1.02 and 1.109 J/°K cc for the volume of the glass to 0.35 J/°K cc for the volume at 1 atm. Integrating from the excess volume of the glass (0.068 cc/g) to the excess volume of the liquid at 140° and 1 atm (0.212 cc/g) gives between 0.099 and 0.104 J/°K g. This is the nonconfigurational entropy change on expanding at 140° the liquid to its volume at atmospheric pressure from an excess volume equal to that of the glass.

Had we assumed that the entropy change with volume at the atmosphere were completely nonconfigurational, the estimate would have been between 0.123 and 0.129 J/°K g. Had the entropy change been completely configurational, the estimate would have been between 0.073 and 0.079 J/°K g.

The Configurational Entropy of the Liquid. Combining the excess nonconfigurational entropy from disordering and expanding the crystal to the volume of the glass with that from expanding the glass to the liquid at 140° and atmospheric pressure, we obtained 0.175 J/°K g for the nonconfigurational entropy to be subtracted from the entropy of fusion. For the heat of fusion for polyethylene, Karasz and Jones[4] have pointed out that the existing measurements range from 277 to 299 J/g, around their own measurement of 293.6 J/g. Their entropy of fusion, assuming the melting point of 140°, is 0.711 J/°K g. We then obtain 0.53$_6$ J/°K g (1.79 eu/mol of CH_2) for the configurational entropy of liquid polyethylene at the melting point. Our apportionment of the entropy of fusion among the various terms is thus that indicated in Figure 2.

Discussion

We wish to compare other estimates of the configurational entropy with that just calculated; but first we should estimate the over-all error in the calculation. The three parts contributing to the error are the entropy of fusion, the excess nonconfigurational entropy of the glass, and the change in the nonconfigurational entropy on isothermally expanding the liquid from the volume of the glass to the volume of the melt at atmospheric pressure. A first estimate of the error in the entropy of fusion would be the breadth of the range of entropies calculated from the heats of fusion, which is 0.52 J/°K g. Considering just the more recently measured heats of fusion, the uncertainty in the entropy of fusion is probably still ±0.015 J/°K g. The uncertainty in the nonconfigurational entropy of the glass arises principally from the uncertainty in what weight to give to the Einstein term in the heat capacity of the noncrystalline phase. This entails an uncertainty of approximately ±0.010 J/°K g. The last term, the nonconfigurational entropy change on isothermally expanding the liquid from the glass to the melt, contributes the largest uncertainty. The rates of increase of the nonconfigurational entropy with volume at both the glassy and the atmospheric pressure ends of the range each contribute an uncertainty of about ±0.0025 J/°K g. The volume change involved in the expansion contributes another uncertainty of about ±0.020 J/°K g. The combination gives an uncertainty of ±0.040 J/°K g. Combining the three parts, we then expect the true value of the configurational entropy to be within the range of 0.536 ± 0.045 J/K° g (1.79 ± 0.015 eu/mol of CH_2).

Let us now compare this with the numerical estimates obtained from two simpler procedures. The first estimate for the configurational entropy is the entropy of fusion alone. Comparing 0.711 with 0.536 J/°K g, we see for polyethylene that the entropy of fusion exceeds the configurational entropy by 33%. The second estimate is that used by Mandelkern as an approximation for the entropy of fusion at constant volume.[1] Multiplying the total entropy increase with volume evaluated at atmospheric pressure (0.69 J/°K cc) times the excess volume of the liquid over that of the crystal

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(7) W. Reese, P. J. Higgins, and G. W. Rostine, *J. Appl. Phys.*, **39**, 1800 (1968).

(0.212 cc/g) gives 0.146 J/°K g for the nonconfigurational part of the entropy of fusion. Subtracting from the entropy of fusion (0.711 J/°K g) gives 0.565 J/°K g for the configurational entropy, which is within the range estimated above.

Finally, let us compare our value for the configurational entropy with our best estimate for the entropy of fusion at constant volume. To compute the entropy of fusion at constant volume, we can subtract from the entropy of fusion at constant pressure the entropy change in compressing the liquid volume back to that of the crystal. To obtain an estimate of this latter quantity we started with pressure–temperature–volume data on *n*-nonane and *n*-hexadecane from measurements made up to pressures of 1200 kg/cm^2 and over the temperature range of 30 to 120°.[8] From this we extrapolated to liquid polyethylene at 140° and calculated the rate of change of the total entropy with volume from the relation $(\partial S/\partial v)_T = \alpha/\beta$, where α is the thermal expansivity and β is the compressibility. The details of this are described in the Appendix. The result is a value for $(\partial S/\partial v)_T$ that changes linearly with volume, from 0.69 J/°K cc at the volume of the liquid at 140° and atmospheric pressure (1.262 cc/g) to 2.12 J/°K cc at the volume of the crystal (1.050 cc/g). The total entropy change on compressing the liquid back to the crystalline volume at 140° is then

$$\int_{\text{liq}}^{\text{cryst}} (\partial S/\partial v)_T \, dv = -0.30 \text{ J/°K g}$$

Combining with the entropy of fusion at constant pressure (0.711 J/°K g) gives 0.41 J/°K g for the entropy of fusion at constant volume. (Of course, the liquid could not be compressed back to the crystal volume at 140° without its tending to crystallize. Indeed, there is probably no reasonable condition of temperature and pressure at which the crystal and liquid are both in equilibrium with each other and have the same density.) The entropy of fusion at constant volume thus represents only about 75% of the configurational entropy existing in the melt at atmospheric pressure. In other words, approximately 25% of the configurational entropy of the melt is lost on compressing the melt to the volume of the crystal.

Acknowledgment. We wish to express appreciation to our colleagues and former colleagues at the General Electric Research and Development Center for helpful discussions during the course of this work. We especially wish to thank R. E. Barker, F. E. Karasz, A. A. Miller, and J. M. O'Reilly, each of whom contributed importantly at particular stages of the work.

Appendix

Change in Entropy with Volume at Constant Temperature. To estimate the rate of change of entropy with volume for liquid polyethylene we will use the pressure–temperature–volume data from the *n*-paraffins, extracting out the contribution of the methylene portion from the methyl ends. By manipulating thermodynamic relations it is possible to find that the rate of entropy change with volume at constant temperature equals

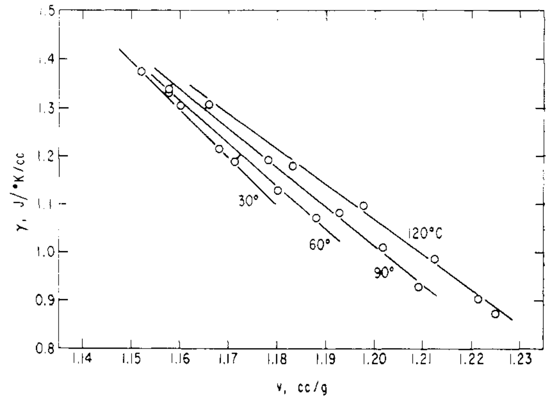

Figure 3. $\gamma = \alpha/\beta$ *vs.* volume for polyethylene. The points were obtained by extrapolating from data on *n*-nonane and *n*-hexadecane and the lines represent the least-squares fit.

$$\left(\frac{\partial S}{\partial v}\right)_T = -\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p \Big/ \frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T \tag{1}$$

$$= \alpha/\beta = \gamma \tag{2}$$

where α is the thermal expansivity and β the compressibility.

Assuming that the *n*-paraffins can be treated as simple mixtures of noninteracting methyl ends and methylene middles, the volumes, expansivities, and compressibilities of the *n*-paraffins can be written as

$$v_\nu = 2v_{\mathrm{CH_3}} + (\nu - 2)v_{\mathrm{CH_2}} \tag{3}$$

$$\begin{aligned} \alpha_\nu = {} & \frac{1}{v_\nu}\left[2\frac{\partial v_{\mathrm{CH_3}}}{\partial T} + (\nu - 2)\frac{\partial v_{\mathrm{CH_2}}}{\partial T}\right] = \\ & \frac{1}{v_\nu}\left[2\frac{v_{\mathrm{CH_3}}}{v_{\mathrm{CH_3}}}\frac{\partial v_{\mathrm{CH_3}}}{\partial T} + (\nu - 2)\frac{v_{\mathrm{CH_2}}}{v_{\mathrm{CH_2}}}\frac{\partial v_{\mathrm{CH_2}}}{\partial T}\right] = \\ & v_\nu^{-1}[2v_{\mathrm{CH_3}}\alpha_{\mathrm{CH_3}} + (\nu - 2)v_{\mathrm{CH_2}}\alpha_{\mathrm{CH_2}}] \end{aligned} \tag{4}$$

and similarly for β, where ν is the number of carbon atoms in the paraffin. Then for $\gamma = \alpha/\beta$ we have

$$\gamma_\nu = \frac{2v_{\mathrm{CH_3}}\alpha_{\mathrm{CH_3}} + (\nu - 2)v_{\mathrm{CH_2}}\alpha_{\mathrm{CH_2}}}{2v_{\mathrm{CH_3}}\beta_{\mathrm{CH_3}} + (\nu - 2)v_{\mathrm{CH_2}}\beta_{\mathrm{CH_2}}} \tag{5}$$

which can be rearranged to give

$$\gamma_\infty = \gamma_\nu + [2\gamma_\nu/(\nu - 2)](1 - \gamma_2/\gamma_\nu)X_\beta \tag{6}$$

where $\gamma_\infty = \alpha_{\mathrm{CH_2}}/\beta_{\mathrm{CH_2}}$ is the quantity that describes polyethylene, $\gamma_2 = \alpha_{\mathrm{CH_3}}/\beta_{\mathrm{CH_3}}$, and $X_\beta = (v_{\mathrm{CH_3}}/v_{\mathrm{CH_2}})\cdot(\beta_{\mathrm{CH_3}}/\beta_{\mathrm{CH_2}})$. The unknowns are γ_∞, γ_2, and X_β. The knowns are the γ_ν's and the ν's. Equation 6 should be fit statistically to data from many of the longer *n*-paraffins or, at least, to data from three *n*-paraffins to take care of the three unknowns. Unfortunately, because of the lack of consistent data, we cannot even do the latter. Instead we must fit eq 6 to the data obtained by Boelhouwer[8] on the two paraffins, *n*-nonane and *n*-hexadecane. (Boelhouwer has also obtained data on *n*-dodecane; but these data turn out to be inconsistent with the other data in the second differences, which are involved in fitting the data).

To eliminate the third unknown we will assume that

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(8) J. W. M. Boelhouwer, *Physica*, 26, 1021 (1960).

γ_ν changes slowly enough with ν for $(1 - \gamma_2/\gamma_\nu)$ to be virtually independent of ν. This assumption will lead to a lower limit for γ_∞. Considering two paraffins with the number of carbon atoms ν_1 and ν_2 we then get for liquid polyethylene

$$\gamma_\infty = (\nu_1 - \nu_2)\gamma_{\nu_1}\gamma_{\nu_2}/[(\nu_1 - 2)\gamma_{\nu_2} - (\nu_2 - 2)\gamma_{\nu_1}] \quad (7)$$

and

$$v_\infty = v_{\mathrm{CH_2}} = (\nu_1 + {}^1/_7)v_{\nu_1} - (v_2 + {}^1/_7)v_{\nu_2} \quad (8)$$

where the v's are in units cubic centimeters per gram and the ${}^1/_7$ comes from changing the units from cubic centimeters per mole to cubic centimeters per gram.

Using Boelhouwer's data for *n*-nonane and *n*-hexadecane at the temperatures 30, 60, 90, and 120°, we get the points shown in Figure 3. These data have been fitted to an equation with the form

$$\gamma_\infty = A_0 + A_1v + A_2T + A_3vT \quad (9)$$

which yields

$$\gamma_\infty = (\partial S/\partial v)_T\ \mathrm{J/^\circ K\ cc} = 13.47 - 10.51v - 0.0303T + 0.0268vT \quad (10)$$

where v has the units cc/g and T the unit °C. (The standard deviation of the fit is 0.013 J/°K cc.)

One test of eq 10 is to compare it with the measured values at 140° and atmospheric pressure where the volume is 1.262 cc/g. The value computed from eq 10 is 0.69 J/°K cc, which compares well with the values of 0.68 J/°K cc quoted by Quinn and Mandelkern[9] and 0.71 J/°K cc quoted by Starkweather and Boyd.[10]

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[9] F. A. Quinn, Jr., and L. Mandelkern, *J. Amer. Chem. Soc.*, **80**, 3178 (1958).

[10] H. W. Starkweather, Jr., and R. H. Boyd, *J. Phys. Chem.*, **64**, 410 (1960).

Low-Temperature Relaxations in Polyurethans

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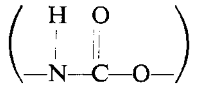
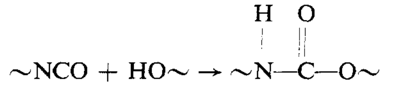
ABSTRACT: A study has been made of the relaxation phenomena in three series of glassy polyurethans in the temperature range from −190 to −100° and at various frequencies up to 110 Hz using dynamic mechanical and dielectric relaxation. The structures of the repeat units of the three series are given in eq 1–3. Several overlapping relaxation peaks are discernible in the temperature and frequency region investigated. All of these relaxations arise largely from motion in the amorphous phase. The following assignments of the various relaxation peaks to specific molecular motions have been made on the basis of comparisons both within and among the three series. (1) The δ relaxation (−160°, 110 Hz) (4M series only) arises from hindered rotation of the methyl group attached to the 4 position of the benzene ring. (2) The γ_3 relaxation (−150°, 110 Hz) (H series only) arises from motions of methylene sequences in the diisocyanate part of the repeat unit. (3) The γ_2 relaxation (−140°, 110 Hz) arises from motions of methylene sequences, including oxygen, in the diol part of the repeat units of all three series. (4) The γ_1 relaxation (−120°, 110 Hz) arises from motions of methylene sequences including nonhydrogen bonded ester groups, and is active in all three series.

The term polyurethan refers to a large class of synthetic organic polymers having the common feature of containing the urethan linkage



$$\left(\begin{array}{c}\mathrm{H}\ \ \mathrm{O}\\ |\ \ \ \|\\ -\mathrm{N}-\mathrm{C}-\mathrm{O}-\end{array}\right)$$

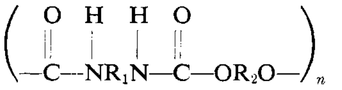
The urethan linkage is not necessarily the only functional group present in the polymer nor is it necessarily the preponderant functional group. Polyurethans may be prepared by a variety of methods most of which involve the reaction of isocyanate (NCO) and hydroxyl (OH) groups to produce the urethan linkage according to



$$\sim\mathrm{NCO} + \mathrm{HO}\!\sim\ \rightarrow\ \sim\overset{\mathrm{H}}{\underset{}{\mathrm{N}}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{O}\!\sim$$

The polyurethans utilized in the present study were obtained by the step growth polymerization of a diisocyanate with a diol. Schematically

$$n\mathrm{OCNR_1NCO} + n\mathrm{HOR_2OH} \rightarrow$$



$$\left(-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\overset{\mathrm{H}}{\mathrm{N}}\mathrm{R_1}\overset{\mathrm{H}}{\mathrm{N}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{OR_2O}-\right)_n$$

Three different diisocyanates were used, namely, 1,6-hexamethylene diisocyanate, 4,4′-diphenylmethane diisocyanate, and 4-methylmetaphenylene diisocyanate. The diols used ranged from 1,2-ethanediol to 1,10-decanediol. The structures of the repeat units of the polyurethans obtained by this procedure are given in eq 1–3. For convenience, in what follows the various series will be referred to as H-1,*n*, DP-1,*n*, and 4M-1,*n*, where *n* refers to the number of methylene units in the diol part of the repeat unit.

Polyurethans of the general structural type of the three series shown above have been investigated using the dynamic mechanical technique by several groups.[1–4] All of these polymers show three main relaxation regions and these are usually labeled α, β, and γ in order of decreasing temperature. It has been established that (1) the α relaxation is associated with the

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[1] G. W. Becker and H. Oberst, *Kolloid Z.*, **152**, 1 (1957).

[2] K. H. Illers and H. Jacobs, *Makromol. Chem.*, **39**, 234 (1960).

[3] H. Jacobs and E. Jenckel, *ibid.*, **43**, 132 (1961); **47**, 72 (1961).

[4] For a review of the mechanical data on polyurethans through 1965, see N. G. McCrumb, B. E. Read, and G. Williams, "Anelastic and Dielectric Effects in Polymeric Solids," John Wiley & Sons, Inc., New York, N. Y., 1967, Chapter 12.