Proposed Experiment to Estimate the Mixing Free Energy of Polymers

Eugene Helfand

Bell Laboratories, Murray Hill, New Jersey 07974. *Received October 11, 1977*

ABSTRACT: It is proposed to estimate the thermodynamic properties of polymer mixtures (which need not even be stable thermodynamic states) by measuring the chemical potential of oligomers of polymer A in AB copolymers. The measurements may be performed by determination of oligomer solubility or by partitioning the oligomer between the copolymer and a coexistent solvent phase.

Polymer blends are the object of considerable research interest at this time. Efforts toward correlating the vast body of data would be greatly advanced if more information was available on the degree of relative repulsion or attraction between polymeric pairs, as embodied in the free energy of mixing.

Several factors make difficult the determination of the thermodynamic properties of polymer mixtures. One is that in many cases the polymeric pair does not form a true mixture except in very dilute solutions, and one must speak of a hypothetical state in a sense clarified below. A second is that, due to the sluggishness of mixing, heat of mixing experiments are usually of limited value.[1]

Small angle neutron scattering is a valuable technique for determining mixing properties which is just beginning to be exploited.[2] It is most conveniently applied to the determination of the second virial coefficient of one polymer in another. More work has been done utilizing light scattering,[3] but it is usually necessary to bring the polymer mixture into dilute solution, and the solvent interactions must be subtracted off.

This paper is devoted to an examination of the virtues and some of the shortcomings of another method of estimating polymer mixing thermodynamic functions. It involves the use of an AB copolymer system as a model of an A and B mixed polymer environment. The simulated environment is then probed by measurement of the chemical potential of A oligomers in these surrounding. Possible methods of making such chemical potential measurements are by solubility determinations or by a study of partitioning between phases.

The present proposal involves elements of methods which have received previous attention. For example, the phase diagrams of oligomer mixtures (sometimes plus solvent) have been measured.[4] The deficiencies of such an approach include: (1) the need to rely heavily on theoretical mixing equations of state to interpret the data; (2) the difficulty of independently varying temperature and composition; and (3) the limited range of compositions which can be studied in this way.

Stockmayer, Moore, Fixman, and Epstein[5] proposed a measurement which also used copolymers, viz., the comparison of properties such as radius of gyration, osmotic second virial coefficient, and intrinsic viscosity of copolymers with those of the constituent homopolymers. Deviations from simple interpolations arise from the relative forces between unlike units. Subsequent workers have looked also at Θ temperature.[6] The method, while quite useful, has the following shortcomings: (1) the "probe" is an A or B unit on a copolymer molecule rather than on a homopolymer; (2) the interpretation of the data relies heavily on theoretical models; and (3) the AB interactions are assumed to be independent of the type or concentration of solvent (indeed the polymer is frequently dilute in this scheme, although recently moderately concentrated polymer solutions have been studied).[6] By the standards of precision which have been achieved in this field to date the assumptions listed above still seem to yield reasonably consistent results, in spite of the difficulties mentioned.

We defer the critical appraisal of the present proposal to section V.

I. Basic Ideas

Flory and Huggins[7] introduced the idea of dividing the free energy or chemical potential of mixing into a combinatorial term, associated with the number of ways of placing the molecules into the mixed environment, and a residual (contact or interchange) term which depends only on the local environment of each unit of polymer. We assume that such a separation is correct. The present proposal is based on the premise that the local environment of a homopolymer of A placed in a system of AB copolymer is a close approximation to the local environment of that A homopolymer in a solution of A and B having the same chemical composition. Thus the residual chemical potential of that A molecule is the same in the two media, and measurements in one may be substituted for measurements in the other. When the residual mixing free energy is positive, the mixture may be thermodynamically unstable. Nevertheless, the quantitative measure of this thermodynamic property is important for predicting blend properties, driving force toward the phase separation, interfacial properties, thermodynamics of block and graft copolymers, etc. In this case of positive free energy of mixing the required chemical potential of A homopolymer in AB copolymer can be determined by measurements of solubility of A in the copolymer.

On the other hand, when the residual mixing free energy is negative the solubility technique cannot be used. In its place one can substitute a study of the partition of a limited amount of oligomeric A between the copolymer medium and another phase (a poor solvent for AB). Scattering techniques may also be useful in this case, but they will not be discussed in this paper.

Before stating these ideas in quantitative terms we introduce some notation and definitions. Let us use the subscript A to denote units of type A in general or total, a to denote A homopolymer, and α to denote units of A on copolymer. Similarly define B, b, and β. The subscript C will denote copolymer. Thus we shall consider mixtures of N_a molecules of homopolymer A of degree of polymerization Z_a (we consider only monodispersed polymers in this paper) and N_b molecules of B with Z_b mers each. The total number of mers is respectively n_a (= N_aZ_a) and n_b. The choice of what to pick as units is somewhat arbitrary, but we feel that there are advantages in using conventional monomers. The final formulas are independent of the arbitrary choice of chemical units.

We will also be considering a system of N_C molecules of AB copolymer, consisting of n_α mers of A and n_β of B. There will be present too N_a homopolymer molecules so that the total number of A units is $n_A = n_a + n_\alpha$.

The mole fraction of K units (K = A or B) is

0024-9297/78/2211-0682$01.00/0

$$x_{\mathrm{K}} = n_{\mathrm{K}}/(n_{\mathrm{A}} + n_{\mathrm{B}}) \tag{I.1}$$

but it is also useful to define what we will call v^* fractions

$$\phi_{\mathrm{K}} = n_{\mathrm{K}}v_{\mathrm{K}}^*/(n_{\mathrm{A}}v_{\mathrm{A}}^* + n_{\mathrm{B}}v_{\mathrm{B}}^*) \tag{I.2}$$

(Flory[8] calls these "segment fractions" because he defines segments in such a way that they all have equal v_{K}^*. We consider this inconvenient because: (1) this definition of segment varies from system to system; and (2) it is based on a parameter, v_{K}^*, which depends on approximate theory for its definition, and has not been extensively measured.) There is some uncertainty as to what is the most appropriate v_{K}^*. Flory et al.[8] have suggested as a value the "core volume" of a segment, which they propose to approximate on the basis of their theory of the equation of state of the pure polymer. The use of volume fraction for ϕ_{K}, i.e., the substitution for v_{K}^* of $v_{0\mathrm{K}}$, the specific volume of the pure polymer, may be more convenient and in the present case still useful. Uncertainty as to the proper v_{K}^* leads to an uncertainty in the combinatorial entropy terms, but as we shall see the net effect may not be extreme.

We assume that the Gibbs free energy of mixing of the homopolymers A and B is (in this case $n_{\mathrm{a}} = n_{\mathrm{A}}$)

$$\Delta G(N_{\mathrm{a}},N_{\mathrm{b}}) = RT(N_{\mathrm{a}} \log \phi_{\mathrm{a}} + N_{\mathrm{b}} \log \phi_{\mathrm{b}}) + \Gamma(n_{\mathrm{A}},n_{\mathrm{B}}) \tag{I.3}$$

with $\Gamma(n_{\mathrm{A}},n_{\mathrm{B}})$ being the residual free energy of mixing, and with pressure, p, and temperature, T, being left as implicit variables. R is the gas constant. Here it is assumed that the overall concentration of A is large enough so that the interactions of a unit on the oligomer with other units on that molecule are a negligible part of all AA interactions. Also the deviations from random mixing predictions observed by Kleintjens, Koningsveld, and Stockmayer[9] and by Bieringer, Breitenbach, and Wolf[10] will not enter. One could write Γ in the form $RT\chi_{\mathrm{AB}}n_{\mathrm{A}}\varphi_{\mathrm{B}}$ frequently employed,[11] with a temperature and concentration dependent χ. Little is gained because derivatives of χ will be introduced into most standard equations (e.g., those for the coexistence curve) and explicit solutions will not be possible. For clarity of presentation we temporarily neglect polymer end effects in eq I.3; because they may be important we will discuss them later in this section. The chemical potential of a mer of A is

$$\Delta\mu_{\mathrm{a}} = \mu_{\mathrm{a}} - \mu_{\mathrm{a}}^0 \tag{I.4}$$

$$\Delta\mu_{\mathrm{a}} = (\partial\Delta G/\partial n_{\mathrm{a}})_{p,T,n_{\mathrm{b}}} \tag{I.5}$$

where μ_{a}^0 is the chemical potential of a mer of pure A. By this we really mean

$$\Delta\mu_{\mathrm{a}} = (1/Z_{\mathrm{a}})(\partial\Delta G/\partial N_{\mathrm{a}})_{N_{\mathrm{b}}} \tag{I.6}$$

(In principle one could make measurements with two different length oligomers, giving a literal interpretation of eq I.5. This would change some of our formulas below, but the interested reader should be able to make these modifications.)

From eq I.1 we find

$$\Delta\mu_{\mathrm{a}} = \frac{RT}{Z_{\mathrm{a}}} \log \phi_{\mathrm{a}} + RT\left(\frac{1}{Z_{\mathrm{a}}} - \frac{v_{\mathrm{A}}^*}{v_{\mathrm{B}}^*Z_{\mathrm{B}}}\right)\phi_{\mathrm{b}} + \gamma_{\mathrm{A}}(x_{\mathrm{A}}) \tag{I.7}$$

$$\gamma_{\mathrm{A}}(x_{\mathrm{A}}) = (\partial\Gamma/\partial n_{\mathrm{A}})_{p,T,n_{\mathrm{B}}} \tag{I.8}$$

It follows from the linear homogeneous nature of Γ that the residual chemical potential γ_{A} is a function only of composition variable x_{A}, the overall fraction of A.

Next consider the system of homopolymer A in an AB copolymer. The Gibbs free energy of mixing is

$$\Delta G(N_{\mathrm{C}},N_{\mathrm{a}},y_\alpha) = RT(N_{\mathrm{a}} \log \phi_{\mathrm{a}} + N_{\mathrm{C}} \log \phi_{\mathrm{C}}) + \Gamma(n_{\mathrm{A}},n_{\mathrm{B}}) \tag{I.9}$$

where y_α is the fraction of A units on the copolymer and

$$\phi_{\mathrm{C}} = \frac{n_\alpha v_{\mathrm{A}}^* + n_{\mathrm{B}}v_{\mathrm{B}}^*}{n_{\mathrm{A}}v_{\mathrm{A}}^* + n_{\mathrm{B}}v_{\mathrm{B}}^*} \tag{I.10}$$

The chemical potential of a mer on the A homopolymer is

$$\Delta\mu_{\mathrm{a}} = \frac{RT}{Z_{\mathrm{a}}} \log \phi_{\mathrm{a}} + RT\left(\frac{1}{Z_{\mathrm{a}}} - \frac{\mathrm{N}_{\mathrm{C}}v_{\mathrm{A}}^*}{n_\alpha v_{\mathrm{A}}^* + n_{\mathrm{B}}v_{\mathrm{B}}^*}\right)\phi_{\mathrm{C}} + \gamma_{\mathrm{A}}(x_{\mathrm{A}}) \tag{I.11}$$

Thus, if the assumptions hold, the γ_{A} which appears in the AB mixture chemical potential appears also in the μ_{a} of an A molecule in an AB copolymer system. The residual mixing free energy may be determined by integration.

Because of the finite length of the oligomer it may be necessary to introduce a term to account for oligomer end effects. In the free energy this term would have the form $+(1/Z_{\mathrm{a}})\Gamma_{\mathrm{e}}(n_{\mathrm{A}},n_{\mathrm{B}},N_{\mathrm{A}})$. We have explicitly introduced a prefactor of $1/Z_{\mathrm{a}}$ to indicate that this term is of $0(1/Z_{\mathrm{a}})$ smaller than the Γ term. With this change the chemical potential of A oligomer in AB copolymer would be

$$\Delta\mu_{\mathrm{a}} = \frac{RT}{Z_{\mathrm{a}}}[\log(\phi_{\mathrm{a}}) + \phi_{\mathrm{C}}] + \gamma_{\mathrm{A}}(x_{\mathrm{A}}) + \frac{1}{Z_{\mathrm{a}}}\gamma_{\mathrm{eA}}(x_{\mathrm{A}},x_{\mathrm{ea}}) \tag{I.12}$$

where x_{ea} is the mole fraction of a ends. In many practical cases the oligomer end concentration will be low enough to ignore end–end interaction; i.e., set $x_{\mathrm{ea}} = 0$ in eq I.12. Then we will write $\gamma_{\mathrm{eA}}(x_{\mathrm{A}},x_{\mathrm{ea}} = 0) \equiv \gamma_{\mathrm{eA}}(x_{\mathrm{A}})$. We cannot rigorously rule out a term with Z_{a} to a fractional power, such as might arise from excluded volume effects. We doubt that such a term would be of major import in the concentrated systems considered here where the screening length for excluded volume will be fairly short.

II. Measurement for Positive Residual Free Energy of Mixing

When the residual free energy of mixing is positive the chemical potential of oliomer A in copolymer AB may be determined by a solubility measurement. Let the degree of polymerization of the copolymer be high. In this case the solubility of the copolymer in the oligomer rich phase is negligible. The chemical potential of the oligomer in copolymer at saturation v^* fraction, $\phi_{\mathrm{a}}^{\mathrm{s}}$, equals the chemical potentials of the coexistent pure oligomer, so $\Delta\mu_{\mathrm{a}} = 0$. From eq I.12 we find

$$0 = \frac{RT}{Z_{\mathrm{a}}}[\log(\phi_{\mathrm{a}}^{\mathrm{s}}) + \phi_{\mathrm{C}}^{\mathrm{s}}] + \gamma_{\mathrm{A}}(x_{\mathrm{A}}^{\mathrm{s}}) + \frac{1}{Z_{\mathrm{a}}}\gamma_{\mathrm{eA}}(x_{\mathrm{A}}^{\mathrm{s}},x_{\mathrm{ea}}) \tag{II.1}$$

or

$$\gamma_{\mathrm{A}}(x_{\mathrm{A}}^{\mathrm{s}}) = -\lim_{Z_{\mathrm{a}}\to\infty} \frac{kT}{Z_{\mathrm{a}}}[\log \phi_{\mathrm{a}}^{\mathrm{s}} + (1 - \phi_{\mathrm{a}}^{\mathrm{s}})] \tag{II.2}$$

Note that eq II.2 is not really dependent on the somewhat uncertain choice of reduction volumes v_{K}^* used to define ϕ_{a}. That is because

$$\frac{1}{Z_{\mathrm{a}}} \log \phi_{\mathrm{a}} = \frac{1}{Z_{\mathrm{a}}} \log \frac{n_{\mathrm{a}}}{V} + \frac{1}{Z_{\mathrm{a}}} \log \frac{v_{\mathrm{A}}^*V}{n_{\mathrm{A}}v_{\mathrm{A}}^* + n_{\mathrm{B}}v_{\mathrm{B}}^*} \tag{II.3}$$

where V is the volume, and the second term on the right is $0(1/Z_{\mathrm{a}})$ as compared with the first (n_{a}/V goes to zero exponentially). In practice, however, this requires Z_{a} to be quite large.

To develop a better understanding of this technique let us make some simple, order-of-magnitude estimates based on the Flory–Huggins theory, ignoring end effects, using the molar volume v_{0K} as reduction parameters, and letting the copolymer have infinite molecular weight. The residual chemical potential is given by

$$\gamma_A = \alpha k T v_{0A} \left(\frac{n_A v_{0A}}{n_A v_{0A} + n_B v_{0B}}\right)^2 \qquad \text{(II.4)}$$

Let $n_A = n_B$, and let pure A and B both have specific volumes of 10^{-4} m^3/mol. Take $\alpha = 10^3/\text{m}^3$, which corresponds to a difference of solubility parameter of $1.56 \times 10^3 (\text{J/m}^3)^{1/2} = 0.76$ $(\text{cal/cm}^3)^{1/2}$ at 20 °C (if χ is defined as $\chi \equiv \alpha(v_{0A}v_{0B})^{1/2}$, then $\chi = 0.1$). Then, according to eq II.1, $\phi_a{}^s = 0.12$ for $Z_a = 50$.

A practical question is how long might it take to achieve equilibrium between an oligomer and a copolymer phase. Rhee, Ferry, and Fetters[12] have reported diffusion constants of the order of $D = 10^{-11}$ m^2/s for a polybutadiene oligomer of number average molecular weight 1600 in various rubbery polymers. For characteristic distances required to achieve equilibrium of $l = 1$ mm, the characteristic time of the experiment is $l^2/D = 10^5$ s, about a day. It should be possible to design experiments with much shorter characteristic distance and time. It is clear, however, that diffusion is too slow to use this method to study glassy systems.

One may wish to add a small to moderate amount of solvent to the system in order to speed up equilibration. The effect of this added solvent on the thermodynamic properties can be removed using formulas akin to those to be developed in the next section.

III. Chemical Potential by Partition between Phases

The solubility technique is only employable when a saturation value can be reached. For negative residual free energy of mixing this is not the case, so another technique must be used. When there is positive residual free energy of mixing other techniques may also be valuable, working at concentrations of oligomer below saturation.

Even for fairly short oligomers the vapor pressure will probably be too small to be useful in determining the chemical potential. This means, in essence, that the "solubility" of oligomer in vacuum is very low. But one could replace the vacuum with a solvent.

Choose a rather poor solvent for A and especially B, one that is not miscible in all proportions with the oligomer–copolymer mixture. Call this solvent s. We are now considering two coexistent phases: phase 1 is a C-rich phase, containing also a and s; phase 2 is an s-rich phase, containing a but almost no C because of the copolymer's high molecular weight. The object of study is the partition of oligomer a between the two phases, $x_a{}^{(1)}$ and $x_a{}^{(2)}$. Equilibrium demands that

$$\mu_a(x_a{}^{(1)}, x_C{}^{(1)}) = \mu_a(x_a{}^{(2)}) \qquad \text{(III.1)}$$

The difference between the chemical potential of oligomer in the solvent and that of pure oligomer can be determined by measurements of the chemical potential of the solvent using the Gibbs–Duhem equation.

With $\mu_a(x_a{}^{(1)}, x_C{}^{(1)}) - \mu_a{}^0$ known it is necessary to remove the solvent from the chemical potential of the oligomer in phase 1. Here a Maxwell relation is of value:

$$\mu_a(n_a, n_C, n_s) = \mu_a(n_a, n_C) + \int_0^{n_s} \left[\frac{\partial \mu_s(n_a, n_C, n_s')}{\partial n_a}\right]_{p, n_C, n_s'} \mathrm{d}n_s' \qquad \text{(III.2)}$$

so again only the chemical potentials of the solvent need be determined. If it is not possible to get a sufficient quantity of oligomer into the system to measure $(\partial \mu_s/\partial n_a)$ accurately one may fall back on the idea of changing the A content of the copolymer instead, exercising care to account for differences in the combinatorial terms.

As a guide to the magnitude of quantities in a partitioning experiment imagine that we have a system composed of oligomer, copolymer, and solvent such that the A and B mers and the solvent all have equal specific volume. Take $\chi_{AB} = -0.1$, $\chi_{As} = 0.6$, and $\chi_{Bs} = 1.0$. To five parts by volume of 55% B copolymer add ten parts solvent and one part oligomer with $Z_a = 50$. Using the Flory–Huggins theory we find that there will be a copolymer–solvent–oligomer phase with volume fractions $\phi_a = 0.037$, $\phi_A = 0.27$, $\phi_B = 0.29$, and $\phi_s = 0.44$. This will coexist with a solvent–oligomer phase in which the volume fraction of oligomer will be $\phi_a = 0.10$.

IV. A Test of the Basic Hypothesis

Before embarking on extensive measurements along the lines suggested so far it may be well to conduct a simple test of the degree of validity of the basic hypothesis we have made, i.e., that a copolymer environment is similar to a mixture environment. The simplest way to test this idea is to prepare a mixture of two miscible polymers and also a copolymer of the same composition. Then measure the chemical potential in the two media of some small molecule with a significant vapor pressure (perhaps low molecular weight oligomer a).

V. Critique of the Assumptions

In this section we will try to appraise how serious the various assumptions may be, and how they might be improved. The basic assumption is that a homogeneous mixture and a copolymer environment closely resemble each other. This assumption is inherent in the method of measuring AB interactions by the study of copolymers in solution described earlier.[5–6,13–15] In that case it is generally[5,6,13,14] (but not always)[15] reported that the value of χ_{AB} depends on the solvent, which it should not. If the method is valid this indicates an intrinsic failure of our basic assumption. Kotaka, Tanaka, and Ohnuma[13] prefer an interpretation of the data in which neighboring pairs along the chain are taken as the basic units of interaction. For the purpose of appraisal of the basic assumption, still, we would prefer to see the more straightforward experiment suggested in section IV performed. In any event our method may yield results of some utility. Besides, there are steps which can be taken to increase the validity of the basic assumption. One is to increase the blockiness of the copolymer, not going so far as to induce microdomain formation. Another is to work at equal volume for the copolymer and mixture instead of equal pressure. (However, if the mixture is only hypothetical then a volume may not be known.) The pressure is surely more convenient, especially since the copolymer will probably be more dense. The effect should not be large.[16]

The second major assumption is that the configurational entropy is as given by Flory and Huggins, and the reduction volumes, $v_K{}^*$, are known. We discussed in section 2 how part of this error may be extrapolated out.

The last assumption is that oligomer end effects can be extrapolated out. Except for highly incompatible polymers where the work would be confined to the use of very short oligomers this should not be difficult.

Perhaps we should add to the list the assumption that the copolymers can be synthesized and the measurements of sufficient accuracy can be made. Certainly some very interesting copolymers are easily synthesized and are even commercially available. The accuracy attainable in experiments remains a challenge to the experimentalist.

References and Notes

(1) G. L. Slonimskii, *J. Polym. Sci.*, **30**, 625 (1958); G. Allen, G. Gee, and J. P. Nicholson, *Polymer*, **2**, 8 (1961), studied heats of mixing of oligomers.

(2) W. A. Kruse, R. G. Kirste, J. Haase, B. J. Schmitt, and D. J. Stein, *Makromol. Chem.*, **177**, 1145 (1976).

(3) A. J. Hyde in "Light Scattering from Polymer Solutions", M. B. Huglin, Ed., Academic Press, New York, N.Y., 1972.

(4) T. R. Paxton, *J. Appl. Polym. Sci.*, **7**, 1499 (1963); G. Allen, G. Gee, and

J. P. Nicholson, *Polymer*, **1**, 56 (1960); N. A. Rounds, Doctoral Dissertation, University of Akron, 1971; D. McIntyre and N. A/ Rounds, private communication.

(5) W. H. Stockmayer, L. D. Moore, Jr., M. Fixman, and B. N. Epstein, *J. Polym. Sci.*, **16**, 517 (1955).

(6) D. J. Goldwasser and D. J. Williams, *Macromolecules*, **6**, 353 (1973). Reference to other, dilute studies is contained therein.

(7) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.

(8) P. F. Flory, R. A. Orwell, and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507 (1964); P. J. Flory, *Discuss. Faraday Soc.*, **49**, 7 (1970).

(9) L. A. Kleintjens, R. Koningsveld, and W. H. Stockmayer, *Br. Polym. J.*, **8**, 144 (1976).

(10) H. F. Bieringer, *Ber. Bunsenges. Phys. Chem.*, **81**, 996 (1977); J. W. Breitenbach and B. A. Wolf, *Makromol. Chem.*, **108**, 263 (1967).

(11) S. Krause, A. L. Smith, and M. G. Duden, *J. Chem. Phys.*, **43**, 2144 (1965).

(12) C. K. Rhee, J. D. Ferry, and L. J. Fetters, *J. Appl. Polym. Sci.*, **21**, 783 (1977).

(13) T. Kotaka, T. Tanaka, and H. Ohnuma, *Polym. J.*, **1**, 245 (1970).

(14) A. Dondos and H. Benoit, *Makromol. Chem.*, **118**, 165 (1968).

(15) W. Mächtle, *Angew. Makromol. Chem.*, **10**, 1 (1970).

(16) J. A. R. Renuncio and J. M. Prausnitz, *J. Appl. Polym. Sci.*, **21**, 2867 (1977).

Computation of the Thermodynamic Properties of Poly(*trans*-1,4-butadiene)

H. Evans and A. E. Woodward*

Department of Chemistry, City College of the City University of New York, New York, New York 10031.

Received July 11, 1977

ABSTRACT: Calculations of the lattice conformational energy vs. interchain spacing using a Scott–Scheraga function carried out for monoclinic form I and form II lattices of PTBD yielded interchain spacings at 75 °C in close agreement with experiment upon taking thermal expansion into account. Values for the enthalpy, entropy, and temperature of transition were calculated using mean Einstein lattice vibration frequencies, the lattice conformation energy, and the torsional potential energy. The method of generalized frequencies due to Dobratz was adopted for calculation of the heat capacity, C_v, of crystalline polymers. C_v and ΔS as a function of temperature were calculated for PTBD form II.

The availability of crystal structure data for both the low (I) and high (II) temperature forms of crystalline poly(*trans*-1,4-butadiene), PTBD,[1,2] provides an opportunity to relate the macroscopic properties of PTBD to its microstructure. In an effort to predict the most stable structure for the two forms, Stellman, Woodward, and Stellman[3] minimized the total conformational energy per monomer unit, with respect to the *a* and *b* lattice parameters in form I and with respect to the interchain spacing in form II in which a hexagonal array of chains was assumed. The procedure met with considerable success in predicting the constants of form I but was less successful when applied to the proposed hexagonal chain structure for form II. The thermodynamic properties associated with the phase transition, namely the enthalpy change, ΔH_{tr}, and from that the entropy change, ΔS_{tr}, were computed and found to be too high. The heat capacity for form II of PTBD was computed from the conformational energy change with temperature yielding a value lower than the experimental by three- to fourfold.

A possible thermodynamic formulation for a crystalline hydrocarbon polymer can be given in terms of the Helmholtz free energy,

$$A = E_0 + E_{tor} + E_{vib} - TS_{vib} = U + E_{vib} - TS_{vib} \quad (1)$$

E_0 is the sum of all pairwise interactions of the atoms of one monomer unit with all atoms where the pairs are separated by at least four covalent bonds. E_{tor} is the energy arising from ethanelike torsion barriers[4] present in the monomer unit. E_{vib} and S_{vib} are the energy and entropy resulting from internal and lattice vibrations of the molecules and can be calculated from the vibrational partition function for the crystal.

For the transformation of one crystalline form to another the expression for ΔA is:

$$\Delta A = \Delta U + \Delta E_{vib} - T\Delta S_{vib} \quad (2)$$

At equilibrium, $\Delta A = 0$, and T become the transition temperature, T_{tr}.

If the temperature is high enough then it is reasonable to assume that the vibrational partition function becomes independent of the exact nature of the frequency distribution;[5] therefore, almost any distribution with the same mean frequency as the true distribution should give satisfactory results. Under these circumstances it should be possible to use the Einstein approximation.

For gaseous hydrocarbons above 250 K the method of generalized frequencies has met with considerable success in the calculation of the heat capacity as a function of temperature. This method, which should also be applicable to calculations of E_{vib} and S_{vib}, assumes the Einstein approximation to be valid for each type of vibration. This method was first introduced by Bennewitz and Rossner[6] for use with ideal organic gases and was later modified by Dobratz[7] to give more accurate results. The Dobratz equation is:

$$C_p^\circ = 4R + \frac{aR}{2} + \sum_i n_i C_{\nu_i} + \frac{(3N - 6 - a - \Sigma n_i)\ \Sigma_i n_i C_{\delta_i}}{\Sigma_i n_i} = R + C_v^\circ \quad (3)$$

The first term in the above equation includes the rotational and translational contribution to C_p; a is the number of internal free rotations in the molecule; ν_i and δ_i are generalized frequencies of bond stretching and bending, respectively, associated with the ith bond type; N is the total number of atoms in a molecule; n_i is the number of times the ith bond type appears in the molecule; C_{ν_i} and C_{δ_i} are the Einstein contributions of frequencies ν_i and δ_i, respectively, to the heat capacity; and the summations are carried out over the different bond types in the molecule, e.g., CH, CC, C═C. Due to the relative simplicity of this method it was believed of interest

0024-9297/78/2211-0685$01.00/0