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

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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:

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

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

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to test its applicability to crystalline polymers, particularly PTBD.

The work to be described below had the following objectives:

(1) to predict the value for the interchain spacing in crystalline PTBD forms I and II by finding the minimum potential energy as a function of interchain spacing using a Scott–Scheraga function[8] (this has the simultaneous effect of testing the function for representing the potential energy of this system); (2) to compute the mean lattice vibration frequencies (Einstein frequencies) for the above lattices using the calculated energies; (3) to compute E, S, and A as functions of temperature for the form I and II lattices having the potential energies and mean lattice frequencies computed above; (4) to compute the heat, entropy, and temperature of transition for the change from form I to II; and (5) to adapt the method of generalized frequencies of Dobratz[7] to compute the heat capacity.

Calculation Methods

1. Energy Functions. The nonbonded potential energy function chosen for the present work was that given by Scott and Scheraga[8] and is a Lennard-Jones potential function.

$$V_{ij} = -a/(r_{ij})^6 + b/(r_{ij})^{12} \tag{4}$$

where r_{ij} is the distance between the ith and jth atoms. The parameters for this function are as follows:

Atom pair	a, kcal A^6 mol^{-1}	b, kcal A^{12} mol^{-1}
H···H	46.7	4 460
C···H	128	205 000
C···C	370	286 000

The threefold sinusoidal torsion potential energy function used in this study is:

$$E_{\text{tor}} = (V_0/2)(1 + \cos(3\omega)) \tag{5}$$

where $V_0 = 1.98$ kcal/mol[9] and ω is the dihedral angle.

2. Generalized Frequency Method. Use of the generalized frequency method to calculate C_v, S_{vib}, and E_{vib} for crystalline polymeric solids requires certain changes in the Dobratz equation (eq 3); these are the addition of terms representing the Einstein contribution from generalized lattice vibrations and torsional vibrations and the omission of the terms for translation, rotation, and internal rotation.

The generalized frequency equation representing C_v as modified for a crystalline polymer is therefore as follows:

$$C_v = 4C_{\bar{\nu}_1} + aC_{\nu_{\text{tor}}} + \Sigma n_i C_{\nu_i} + \left[\frac{3n - 4 - a - \Sigma_i n_i}{\Sigma_i n_i}\right] \sum_i n_i C_{\delta_i} \tag{6}$$

The four terms account for lattice, torsion, stretching, and bending vibrations, respectively. It is assumed that the three translational and one rotational lattice vibrations can be represented by the same generalized lattice frequency, $\bar{\nu}_1$, calculated as outlined below. In eq 6 the symbol a is the number of torsional vibrations in the repeat unit, n_i is the number of times the ith bond type appears in the repeat unit, and n is the number of atoms per monomer repeat unit. In counting the number of torsional vibrations it is reasonable to assume that those in the main chain are combined with skeletal bending vibrations. For the torsional vibrations remaining a frequency of 250 cm^{-1} was derived using:

$$\nu_{\text{tor}} = \frac{1}{2\pi c}(GF)^{1/2} \tag{7}$$

where G is the Wilson G matrix element[10] for torsional vibration around a C–C bond and F is the force constant given for hydrocarbon torsion barriers by Neto and diLauro.[11] Equation 7 was derived on the assumption that at reasonably high temperatures the low-frequency torsion vibrations in alkyl branches can be separated from the higher frequency bending and stretching modes. At this level of approximation the vibrational secular equation, Det $|GF - E\lambda| \equiv 0$, decomposes into a matrix equation for the stretching and bending motion and into a one-dimensional equation for each branch torsion vibration.

In order to obtain lattice vibration frequencies force constants can be calculated using the empirical potential energy function (eq 4) as outlined in the following. Taking E_0 as the energy per monomer unit at equilibrium, then the force constant resulting from the displacement of this monomer unit as a rigid body in the x direction is given by:

$$k_x = \left(\frac{\partial^2 E_0}{\partial x^2}\right)_{x_0} - k_x{}^0 = \sum_{i=j}^{n} \sum_{j=n+1}^{N\ \text{lattice}} \times \left[\left(\frac{\mathrm{d}^2V}{\mathrm{d}r_{ij}{}^2}\right)\left(\frac{x_{ij}}{r_{ij}}\right)^2 + \left(\frac{r_{ij}{}^2 - x_{ij}{}^2}{r_{ij}{}^3}\right)\left(\frac{\mathrm{d}V}{\mathrm{d}r_{ij}}\right)\right]_{x_0} - k_x{}^0 \tag{8}$$

where V is the empirical potential energy function. The summation in j is carried out from $n + 1$ since the r_{ij} distances within the monomer unit which is rigid are independent of its displacement. The symbol x_0 indicates that this derivative is evaluated at the equilibrium values of x for each atom i and j. The term $k_x{}^0$ in eq 8 is given by:

$$k_x{}^0 = \sum_{i=j}^{n} \sum_{j=n+1}^{N} \left[\left(\frac{\mathrm{d}^2V}{\mathrm{d}r_{ij}{}^2}\right)\left(\frac{x_{ij}}{r_{ij}}\right)^2 + \left(\frac{r_{ij}{}^2 - x_{ij}{}^2}{r_{ij}{}^3}\right)\left(\frac{dV}{dr_{ij}}\right)\right]_{x_0} \tag{9}$$

This represents the difference between the force constant computed for a monomer unit and that for a rigid polymer chain moving relative to the rest of the lattice. Following the aforementioned procedure reduces edge effects which would be introduced if eq 8 were applied to the chain typically used in the computed experiments with $k_x{}^0 = 0$.

The vibration frequency can be obtained from the force constant by the equation:

$$\nu = \frac{1}{2\pi c}(k_x/M)^{1/2} \tag{10}$$

where M is the molecular weight of one repeat unit in the polymer. These calculations were also carried out for k_y and k_z and for the corresponding frequencies; an average frequency, $\bar{\nu}_1$, viz., $(\nu_x + \nu_y + \nu_z)/3$, was obtained for use in calculating C_p, S_{vib}, and E_{vib}.

For a polymer system, at or near room temperature, for which a mean lattice force constant and frequency are not available, to a good approximation, a value of R can be taken as the contribution of each lattice mode to C_{ν_1}, since the frequencies of such modes are usually small. The generalized stretching, ν_i, and bending, δ_i, frequencies used were taken from the literature and are given in Table I.

3. Molecular and Lattice Geometries. The bond lengths and bond angles describing the PTBD repeat unit are the same as those used by Stellman et al.[3] In form I the -CHCH$_2$- dihedral angle is 109° and in form II it is 80°.

The equal and opposite dihedral angles of the PTBD chains give the molecule translational symmetry so that the polymer chain can be generated through a series of unit translations of the initial monomer unit along the molecular symmetry axis. The unit of translation is the same as the molecule's fiber period, which is computed from the molecular geometry. The unit cell is generated from an initial monomer unit by a series of translational, rotational, and reflection operations.

To generate the monoclinic lattice the operations are applied to a PTBD chain containing five monomer units yielding

Table I
Generalized Frequencies for Various Bond Types

Bond type	ν, cm^{-1}	δ, cm^{-1}	Ref
C—H (arom)	3045	1318	12
C—H (aliph)	2914	1247	12
C—C (aliph)	989	390	12
C—C (arom)	989	390	12
C=C (aliph, assym)	1664	421	12
C=C (aliph, sym)	1618	599	12
C=C (arom)	1618	844	12
C—O	1030	205	7
C=O	1700	390	7

a stack of five unit cells. The lattice is then generated by a series of simple translations of the unit cell stack in the *xy* plane as shown in Appendix A. To simplify force and torque constant computations, the lattice is oriented so that the chains are perpendicular to the *xy* plane.

To generate a "hexagonal" lattice of chains, after the method of Stellman,[13] a chain consisting of five monomer units is subjected to a series of simple translations in the *xy* plane, as described in Appendix A.

Results

Prediction of Crystal Lattice Constants. The conformational energies of the form I and form II monoclinic and of the "hexagonal" form II lattices were calculated as functions of σ, the interchain distance, using eq 4 and 5. The data are plotted as $U - E_{\text{tor}}$ vs. σ in Figure 1; E_{tor} was omitted since it is constant for each form. The form I minimum occurs at σ = 4.60*A* which is the same as the experimental value given by Suehiro and Takayanagi at 20 °C.[2] The monoclinic form II lattice has a minimum at 4.85*A*; however, if it is assumed that 4.85*A* is the value at 20 °C and the coefficient of thermal expansion for form II given by Suehiro and Takayanagi[2] (viz., 2.8×10^{-4} °C^{-1}) is applied, a value of 4.92*A* for the interchain spacing at 75 °C is obtained. The Scott–Scheraga parameters are derived from van der Waals radii which comes from crystallographic data. At temperatures well below a transition the van der Waals radii have nearly constant values.[14a] The minimum energy of the form II "hexagonal" lattice occurs at 5.10*A*; correction for thermal expansion yields a value of 5.18*A* at 75 °C. Experimentally, σ for form II at 75 °C has been reported as 4.88 Å[1] and 4.95 Å[2].

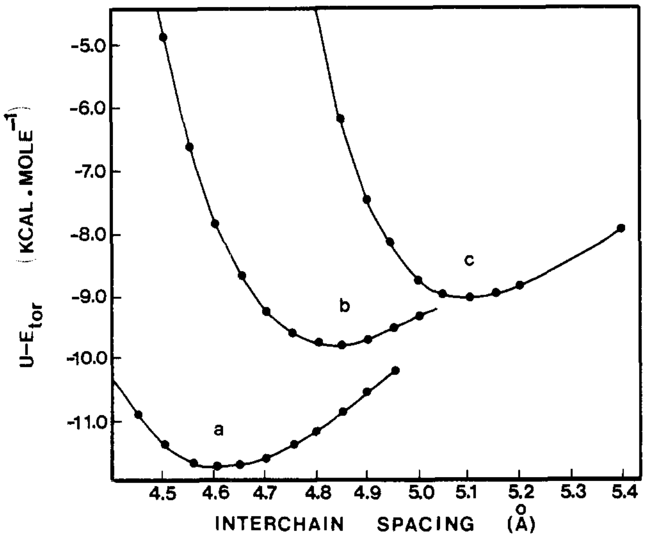


Figure 1. Energy vs. interchain spacing for PTBD: (curve a) monoclinic form I, (curve b) monoclinic form II, (curve c) hexagonal form II.

Table II
Calculated Lattice Vibrational Frequencies for PTBD

T, °C	σ, Å	$\bar{\nu}_x$	$\bar{\nu}_y$	$\bar{\nu}_z$	$\bar{\nu}_1$	Comment
20	4.60	43	96	45	61	Form I—Exptl and calcd
75	4.67	31	85	46	54	Form I—Exptl
75	4.92	28	70	35	44	Form II—calcd Monoclinic
75	4.95	26	65	32	41	Form II—exptl

Mean Lattice Vibrational Frequencies. Values for the force constant, k_x, were calculated using eq 6; values for k_y and k_z were obtained from similar equations. The force constants were then used to calculate the lattice vibration frequencies listed in Table II for monoclinic lattices having various experimental and computed σ values.

Thermodynamic Quantities. E_{vib}, TS_{vib}, and A were computed for monoclinic lattices having the theoretical and experimental σ values, using the mean lattice vibration frequencies listed in Table II assuming the system to be an Einstein solid. To simplify the calculation the conformation energies U were held constant at the value corresponding to the 75 °C interchain spacings and the contributions of internal vibrations were not included. In these calculations $E_0(\text{I}) = -11619$ cal mol^{-1} and $\Delta E_{\text{tor}} = -1325$ cal mol^{-1}. Two $E_0(\text{II})$ values were used; for σ = 4.92 Å, $E_0(\text{II}) = -9652$ cal mol^{-1} and for σ = 4.95 Å, $E_0(\text{II}) = -9511$ cal mol^{-1}. For the theoretical transition, viz., ($\sigma = 4.67A$, $\phi = 109°$) → ($\sigma = 4.92A$, $\phi = 80°$), T_{tr} is found to be 107 °C. ΔA vs. T data calculated from the experimental lattice geometries, viz., ($\sigma = 4.67A$, $\phi = 109°$) → ($\sigma = 4.95A$, $\phi = 80°$), yielded a T_{tr} value of 80.4 °C. ΔH_{tr} ($\Delta E_{\text{vib}} + \Delta U$) was calculated for both sets of lattice geometries. The values obtained and values of ΔS_{tr} are compared in Table III with experimental values for various PTBD preparations. All of the samples but H63MR were prepared by crystallization from dilute solution. The sample designation indicates the solvent used (H = heptane, T = toluene, and B = benzene) and the precipitation temperature. Sample H63MR is a melt-crystallized sample. In addition, the values calculated by Stellman et al.,[3] assuming a hexagonal lattice and using a Kitaigorodsky function,[17,18] are also given in Table III; the two values given are for $\sigma(\text{I})$ = 4.60 Å to $\sigma(\text{II})$ = 4.90 Å (SWS-I) and $\sigma(\text{I})$ = 4.60 Å to $\sigma(\text{II})$ = 4.97 Å (SWS-II).

The specific heat of crystalline PTBD was computed as a function of temperature between 50 and 139 °C. The mean lattice vibration frequency obtained for a form II monoclinic lattice with σ = 4.95 Å was used to compute the lattice vibrational contribution to the partition function. The values of each term in eq 9 for PTBD II at 80 °C are shown in Table IV. The calculated specific heat, C_{v}, as a function of temperature for form II of PTBD, is compared in Figure 2 with experimental curves for C_{p} in the 50–110 °C range given by Stellman et al.[3]

To test the general utility of the generalized frequency method it was applied to the calculation of heat capacities at a single temperature for several polymers using the frequencies in Table I. A contribution of 1.9872 cal mol^{-1} deg^{-1} was assumed for each of the four degrees of lattice vibrational freedom. The calculated C_{v}'s for these polymers are given in Table V along with experimentally determined C_{p} values from the literature. In all cases the literature value given is for crystalline material. Three polymers containing atoms other than C and H are included. Conversion of C_{v}(calcd) values to C_{p}(calcd) values involves knowledge of the coefficient of cubical expansion, α, and the compressibility, β, for the polymers listed in Table V. Since this information is not readily available, C_{p}(calcd) values were obtained from C_{v}(calcd) by addition of 4% of the C_{v}(calcd) value. Perusal of available data

Table III
Phase Transition Thermodynamic Properties of Several Preparations of Crystalline PTBD

Sample	ΔH, cal. g^{-1}	ΔS, cal. g^{-1} deg^{-1}	T_{tr}, °C	Ref
Case I	12.3	0.032	107	Calcd
Case II	14.4	0.041	80.4	Calcd
H60	27.5			15
H43	19.5			15
H18	23.0			15
H63MR	27	0.079	71	16
H63	26	0.075	73	16
T23	19	0.058	55	16
B8	18	0.053	65	16
SWS I	43.5			3
SWS II	59.8			3

Table IV
The Heat Capacity of PTBD Computed at 80 °C by the Method of Generalized Frequencies[a]

n_i	Type	$\bar{\nu}_i$, cm^{-1}	C_i cal mol^{-1} deg^{-1}
6	ν_{CH}	2914	0.012
1	$\nu_{C=C}$	1664	0.104
3	ν_{CC}	989	1.783
6ϕ	δ_{CH}	1247	3.095
ϕ	$\delta_{C=C}$	599	1.979
3ϕ	δ_{CC}	390	7.760
4	ν_1	41	7.930

$$C_p(\text{total}) = 22.663 \text{ cal mol}^{-1} \text{ deg}^{-1} = 0.419 \text{ cal g}^{-1} \text{ deg}^{-1}$$

[a] Monomer formula (-$CH_2CH_2CH{=}CH$-): $n = 10$, $a = 0$, $\phi = (3n - 4 - \Sigma n_i)/\Sigma n_i = (3 \times 10 - 4 - 10)/10 = 1.6$.

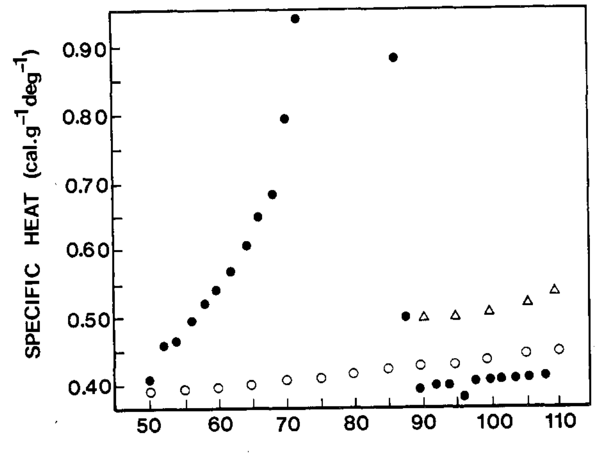


Figure 2. Comparison of C_v(calcd) (○) and C_p(exptl)[3] (●, △) at various temperatures for PTBD.

for α and β for various glassy and partially crystalline polymers suggests that this correction is a reasonable one;[14b] the C_p(calcd) values are listed in Table V.

$S_{139°} - S_{73°}$ for PTBD was computed by the method of generalized frequencies and was found to be 0.077 cal deg^{-1} g^{-1}. The mean specific heat (C_p) of PTBD-II measured by Stellman and co-workers[3] was 0.45 cal g^{-1} deg^{-1}. The value of $S_{139°} - S_{73°}$ derived from this works out to be 0.079 cal deg^{-1} g^{-1} in close agreement with the value calculated in this work.

Discussion

The present study shows that by assuming the lattice of form II to be monoclinic and using a Scott–Scheraga potential function to represent the nonbonded interactions, close agreement is found with experiment for the value of the interchain spacings of both forms I and II. On the other hand, the hexagonal lattice of Stellman et al.[3] in conjunction with the Scott–Scheraga function leads to poor agreement for the form II lattice constant. Apparently, generation of this lattice by simple translation of the PTBD chain is unrealistic because it leads to unfavorable steric interference between methylene hydrogens lying in common planes. The calculations of Stellman et al.[3] using the Scott–Scheraga function yielded a different σ value for form I than that found in this work. This discrepancy is apparently due to the use of an incorrect b_{HH} constant in the earlier work. A specific crystallographic space group for form II of PTBD has not been obtained to date, although the value of the interchain spacings is known.[1,2] The agreement of the computed σ value assuming a monoclinic lattice with the experimental one, therefore, may be fortuitous.

The calculated transition temperatures for monoclinic lattices, having the calculated and experimental interchain spacings, are 107 and 80.4 °C, respectively. The first is quite high when compared to the experimental values for melt crystallized PTBD (viz., 71 to 75 °C);[16,40,41] however, the transition with T_{tr} = 80.4 °C bears closer examination. The theoretical thermodynamic properties correspond to those of a perfectly crystalline material undergoing a transition. Even the most carefully prepared crystals contain defects which tend to lower the value of T_{tr} and ΔH so that a T_{tr} of 80.4 °C is consistent with the experimental value which is somewhat lower. However, the ΔH_{tr} calculated at T_{tr} = 80.4 °C is not larger than the experimental values, as should be the case, but is significantly smaller. This is probably due to the choice of functions used to calculate E_0 and E_{tors} and the fact that ΔH_{tr} is obtained by subtraction of these two relatively large numbers. Also, in this calculation internal vibrations were treated as invariant between forms I and II, whereas Raman spectroscopy shows this not to be entirely the case.[42]

Because the method employed herein to calculate E_{vib}, S_{vib}, and C_v assumes the Einstein harmonic oscillator approximation several limitations must be observed. First, the motions of the molecules should approximate harmonic oscillations. Second the equilibrium potential energies of the molecules composing the substance in question should not be changing; therefore, the method should not be used to compute specific heats of substances which are approaching phase transitions. The method cannot be used at low temperatures. Finally, the method is limited by the availability of generalized frequencies which can be applied to the system of interest.

The calculated specific heat vs. temperature curve for PTBD form II is found to fall between the two sets of results given by Stellman et al.[3] (see Figure 2). The generalized frequency method therefore does represent the results satisfactorily. The close agreement between the computed ΔS for the change from 73 to 139 °C and that obtained from the mean specific heat given by Stellman et al.[3] is a consequence of the agreement in the specific heat values. The generalized frequency method also appears to be applicable for estimation of heat capacities of a number of crystalline hydrocarbon polymers at 25 °C (see Table V). It is seen that in all cases for the hydrocarbon polymers except PTBD C_p(calcd) exceeds C_p(exptl) by 1–2 cal/mol deg. This is due at least partially to the fact that the contribution by the four lattice modes was assumed to be 4R cal/mol deg. The actual contribution of the lattice modes would depend on the lattice vibration

Table V
Comparison of Theoretical and Experimental Heat Capacities for Various Polymers[a]

Polymer[b]	Monomer unit	Temp, °C	C_v (calcd)	C_p (calcd)[c]	C_p (exptl)	Ref
Polyethylene (l)	$(-CH_2CH_2-)$	25	13.64	14.2	12.44	19–26
Poly-1-butene (i, c)	$CH_2CH(CH_2CH_3)-)$	25	24.10	25.1	23.91	27, 28
Polystyrene (i, c)	$(-CH_2CH(C_6H_5)-)$	25	30.41	31.6	30.37	27, 29, 30
Poly(4-methyl-1-pentene) (i, c)	$(CH_2CH(CH_2CH(CH_3)_2))$	25	34.55	35.9	34.70	31, 32
Polypropylene (i, c)	$CH_2CH(CH_3))$	25	18.87	19.6	18.00	29, 30
Polypropylene (s, c)	$CH_2CH(CH_3))$	25	18.87	19.6	18.15	29, 33, 34
Poly(1,4-*trans*-butadiene) (c)	$(CH{=}CHCH_2CH_2)$	80	22.66	23.6	23.	3
Poly(ethylene terephthalate)	$(OCH_2CH_2OCOC_6H_4CO)$	0	43.97	45.7	50.66	35, 36
Polyoxytrimethylene (c)	$(CH_2CH_2CH_2O)$	0	20.53	21.4	25.58	37
Polyoxymethylene	(CH_2O)	25	12.32	12.8	8.71	38, 39

[a] Units are in cal mol^{-1} deg^{-1}. [b] i = isotactic, c = crystalline, l = linear, s = syndiotactic. [c] C_p(calcd) = 1.04C_v(calcd) (see text).

frequencies for the particular polymer and would be less than $4R$ leading to better agreement between the calculated and experimental values of C_p. For oxygen-containing polymers much poorer agreement is found between C_p(calcd) and C_p(exptl), the two values differing by ±4 to 5 cal/mol deg.

Conclusions

(1) The Scott–Scheraga nonbonded potential energy function predicts the correct interchain spacing for PTBD-I at 20 °C and in conjunction with the coefficient of thermal expansion given by Suehiro and Takayanagi[2] only slightly underestimates (4.92A compared to 4.95A) the interchain spacing in form II at 75 °C when monoclinic lattices are considered.

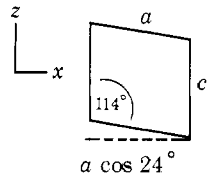
(2) The "hexagonal" lattice overestimates σ for form II of PTBD by 0.23A when the Scott–Scheraga function is used. This probably results from methylene steric interference.

(3) Assuming the system to be an Einstein solid, calculation of the heat capacity and entropy change for form II yielded agreement with experimental values.

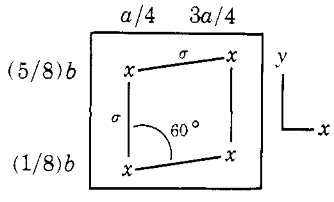
Appendix A

Translation operations for generating monoclinic and "hexagonal" lattices

A and B depict xz and xy projections of the unit cells used to



A



B

generate the monoclinic lattices used in the computer experiments. The crosses in B show the positions of the four PTBD chains. The a and b parameters are related to σ by

$$a = 2\sigma \frac{\cos 30°}{\cos 24°}, \quad b = 2\sigma$$

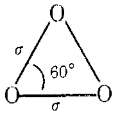
c is the fiber period and is equal to the distance between atom 1 and atom $n + 1$ for monomer unit oriented with its symmetry axis coincident with the z axis. Atom $n + 1$ is an auxiliary atom. n is the number of atoms per monomer unit. The translations applied to the unit cell are given below in terms of simple integers

$$U_x = n_x a \cos 24°$$

$$U_y = n_y b$$

$$U_z = n_z c - n_x a \sin 24°$$

C defines the translations needed to generate the "hexagonal" lattice. The translations are applied to a chain of n_{chain} monomer units whose symmetry axis coincides with the z axis. These translations are given in terms of σ below.



C

$$U_x = 2n_x\sigma \cos 60° + n_y\sigma \sin 60° = (n_x + \tfrac{1}{2}n_y)\sigma$$

$$U_y = n_y\sigma \sin 60°$$

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Thermodynamics of Polymer Compatibility

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ABSTRACT: A simple form of the Prigogine–Flory solution thermodynamics has been used to discuss the thermodynamics of compatible polymer mixtures which are contrasted with polymer–solvent systems and mixtures of oligomers. The treatment is similar to, but simpler than, that of McMaster (*Macromolecules*, **6**, 760, 1973), facilitating estimation of the trends the χ parameter may be expected to show as a function of temperature and pressure. The free volume contribution, depending on a difference in thermal expansion coefficients of the components, is positive, i.e., unfavorable to mixing. For a compatible high molecular weight system, this is balanced at low T by a small favorable interactional or contact energy term ($X_{12} < 0$) due to hydrogen bonding or charge transfer which decreases with increase of T bringing about phase separation. This LCST has, typically, a considerable positive dependence on pressure (~0.2 K atm^{-1}) which may become negative for a mixture of a cohesive (high P^*) but flexible (low T^*) polymer of lower cohesion and flexibility.

Recent reviews[1,2] testify to increasing interest in the thermodynamics of polymer–polymer interactions and the causes of polymer compatibility or incompatibility. The basic treatment by Scott[3] and Tompa[4] applied the Flory–Huggins theory of polymer solution thermodynamics which is mainly concerned with the positional or combinatorial entropy of mixing the two components. More recently, the Flory–Huggins theory has been extended through the introduction of free volume or equation of state effects giving the Prigogine–Flory theory,[5] and this has proved very useful for polymer–solvent systems. McMaster[6] has now applied the Prigogine–Flory theory to the thermodynamics of polymer mixtures and finds that free volume effects are of importance in polymer–polymer as well as in polymer–solvent systems. However, the equations developed by McMaster are extremely complex, partly because he has generalized the Prigogine–Flory theory at the same time as applying it to polymer mixtures.

We believe it is useful to apply the original Prigogine–Flory theory in a simple but adequate approximation which has been extensively used to treat phase diagrams in polymer–solvent systems at ordinary pressure[7] and at higher pressure.[8] Our aim is to review and give an intuitive understanding of some of the main effects in polymer–polymer thermodynamics. Numerical predictions are similar to those of McMaster, but our general impression is that free volume is less important in these systems than one might infer from his paper. For instance, he made the important and correct prediction that phase separation in a compatible polymer–polymer system normally takes place on raising the temperature at a Lower Critical Solution Temperature (LCST). We believe that the primary cause of this LCST does not lie in an increasingly unfavorable free volume effect, as in the usual polymer–solvent system, as suggested by McMaster. We prefer to place the emphasis on the favorable interaction between the polymers which stabilize the mixtures at low T but which fall off at higher T.

We do not believe that the Prigogine–Flory theory is capable of explaining the detailed shape of binodals such as the double peaks recently found by Koningsveld[1] and others. Koningsveld and Stepto have suggested[9] that these may reflect a new interaction between the polymers which would be outside the scope of the present Prigogine–Flory theory. It should also be noted that Sanchez and Lacombe[10] have recently developed a new theory of liquid mixtures which allows for free volume effects, and they have applied it to polymer mixtures. Predictions should be similar to those of the Prigogine–Flory theory, and a detailed comparison could be of interest at a later date.

Review of Thermodynamic Contributions in the Prigorine–Flory Theory

The Interactional or Contact Energy Term.[11] This arises from the weakness or strength of unlike 1–2 contacts in the mixture relative to the like 1–1 and 2–2 contacts in the pure components. In the usual case of dispersion forces, the unlike contacts are relatively weak and there is a positive, endothermic contribution in ΔH_M, or in the Flory nomenclature, X_{12} is positive. Although in principle there is an accompanying positive contribution in ΔS_M, this is small and the net effect in ΔG_M and the χ parameter is positive, i.e., unfavorable to mixing. However, in the rare case of a specific interaction between the components, i.e., a hydrogen bond or a weak charge transfer complex, it is possible to have a negative or exothermic contribution in ΔH_M and X_{12} is negative. This is important here since only through such specific interactions can a stable mixture of high polymers be obtained. Various groups are known which should interact in this way, e.g., an aromatic with an ether. Unfortunately, an exothermic contribution in ΔH_M may be overcome by an unfavorable negative contribution in ΔS_M making difficult the prediction of compatible pairs of polymers.

The Free Volume Term.[11] Two liquid components will generally have different free volumes or degrees of thermal expansion. A liquid polymer has extremely low free volume because of chain connectivity. The chain segments are linked by strong covalent bonds which decrease the number of "external", expansion-promoting degrees of freedom/segment. Thus the difference in free volume between a polymer and a typical solvent will be large. However, even two polymeric

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