2044 *Macromolecules* **1999,** *32,* 2044−2050

Computation of Heat Capacities of Liquid Polymers[†]

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Received October 23, 1998; Revised Manuscript Received January 25, 1999

ABSTRACT: The liquid heat capacities at constant pressure of a series of linear polymers have been computed as the sum of vibrational, external, and conformational contributions. Most of the heat capacity of liquid macromolecules arises from vibrational motion. The external contribution is assumed to approach zero at constant volume. The conformational contribution, finally, is calculated using a fit of experimental heat capacities, as available from the ATHAS data bank, to a one-dimensional Ising-type model with two discrete, degenerate states. A stiffness and a cooperativity parameter permit the representation of the experimental data for polyethylene, polypropylene, poly(methyl methacrylate), poly(*n*-butyl methacrylate), and polystyrene. Agreement between computation and experiment lies within a few percent, close to the experimental precision.

Introduction

While the heat capacity of solid macromolecules at constant volume, C_v, can be described fully based on an approximate vibrational spectrum,[1] the description of the heat capacity of liquid macromolecules is more complicated. Empirically it was found, however, that the heat capacity of liquid polymers is often a linear function of temperature. Furthermore, an empirical addition scheme based on group contribution of the constituent chain segments could be derived within the framework of the advanced thermal analysis system (ATHAS).[2]

There is no fully adequate and simple microscopic theory of polymeric liquids. Lattice theories are used frequently for the representation of liquid structures.[3−5] Flory,[6−8] Sanchez,[9] and Simha[10−12] developed the intermolecular interactions as an external contribution. Furthermore, a flexibility parameter was introduced by Prigogine[13] and then used by Flory,[6] Sanchez,[9] and Simha[10] to describe effect of the intramolecular interactions as a conformational contribution. Extensive calculations for the conformations of macromolecules were carried out by Flory and co-workers.[14] O'Reilly[15] considered the external and conformational contributions to the heat capacity of liquid polymers for a larger number of polymers using the rotational isomers model without cooperative effect. Both the external and conformational contributions to heat capacity were also considered by Gibbs and DiMarzio.[16,17] They described the vibrational contribution with an Einstein term with changes of frequencies during the glass transition. This accounted, however, only for 20% of the measured change. In an earlier paper we described how the vibrational contribution, as estimated from an approximate vibrational spectrum for the solid, added to external and conformational contributions, can be used to evaluate the heat capacity of liquid polyethylene (PE).[18] This approach serves as a starting point for our present analysis.

Calculation Scheme

The advanced thermal analysis system for the computation of liquid macromolecules is based on the evaluation of[18,19]

$$C_p = C_{\text{vib}} + C_{\text{conf}} + C_{\text{ext}} \qquad (1)$$

with C_p representing the liquid heat capacity at constant pressure, C_{vib} the vibrational heat capacity at constant volume, C_{ext} the external heat capacity, and C_{conf} the conformational heat capacity. For the heat capacities of solids, eq 1 is reduced to the first two parts (C_{vib} and C_{ext}) since the chain conformation is largely fixed. The major part of the total heat capacity comes from vibrational motion for both the solid and the liquid. It is calculated as[1]

$$C_{\text{vib}} = C_v(\text{group}) + C_v(\text{sk})[\Theta_1,\Theta_2,\Theta_3] \qquad (2)$$

where C_v(group) is the heat capacity based on an approximate group vibrational spectrum, derived from infrared or Raman spectra and normal mode calculations, and C_v(sk) is the heat capacity for the skeletal vibrations, estimated using the various Debye approximations, as developed in the ATHAS scheme.[2,20,21] The parameters Θ_1, Θ_2, and Θ_3 represent the characteristic one-, two-, and three-dimensional Debye frequencies for continua, expressed in kelvin ($\Theta = h\nu/k_B$). Since the heat capacities of glasses and crystals are similar,[2] it is assumed that the liquid has, at least close to the glass transition, also largely the same vibrational contribution to the heat capacity, C_{vib}, as the solid. The internal rotation which is involved in the conformational motion changes its heat capacity only very slowly from the limit of torsional oscillation ($R = 8.314$ J K^{-1} mol^{-1}) to free rotation ($C_v = R/2$).

Generally, the external contribution of the heat capacity C_{ext} in eq 1 is calculated from the standard thermodynamic relationship:[22]

$$C_p(\text{exp}) - C_v \approx C_{\text{ext}} = TV\alpha^2/\beta \qquad (3)$$

where V is the volume, α the thermal expansivity, and β the compressibility, to be taken as a function of

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[†] Presented in part at the 26th NATAS Conference in Cleveland, OH, Sept 13−15, 1998.

10.1021/ma9816620 CCC: $18.00

temperature over the full range of calculation. Since often values α and β are not available, one can only use the Nernst–Lindemann approximation,[23] as modified for polymers:[24]

$$C_p(\exp) - C_v = 3RA_0\frac{C_p^{\,2}(\exp)}{C_v}T/T_m \qquad (4)$$

where A_0 is a universal constant (≈0.0039 K mol J^{-1}), T the temperature, T_m the melting temperature, and R the gas constant.

Calculation of the conformational contribution to the liquid heat capacity of the linear macromolecules, C_{conf} of eq 1, is based on the following simplifying assumption: The conformational states of the bonds, repeating units, or flexible segments of the polymer can occur in only two discrete states, a ground state and an excited state, and a (to be determined) ratio of degeneracies. When applied to simple chains, this assumption is similar to the rotational isomers model.[25–27] For polymethylene, for example, the two states are the rotational isomers of the trans and gauche conformation with a ratio of degeneracies of gauche-to-trans equal to two. In the present analysis, the degeneracy of the conformational states is, however, determined by a fit to the experimental heat capacity. Furthermore, the energy difference between the two states is represented by two parameters, as in a one-dimensional Ising model.[28] The parameters, A and B, have the meaning of stiffness and cooperativity. The total conformational energy of the macromolecule with a total of N rotatable bonds is then fixed by the following summation:

$$E_1 = A\sum_{j=1}^{N} m_j m_{j+1} + B\sum_{j=1}^{N} m_j \qquad (5)$$

where B (≥ 0) is the energy difference between the independent excited and ground states. This energy of B is modified by A, depending on the state of the next neighbor, so that the parameter A accounts for the cooperative interaction between sequential states. It may be positive or negative. The conformation number $m_j = 0$ applies to the ground state with energy zero and degeneracy g_0. The conformation number $m_j = 1$ corresponds to the excited state with energy B and degeneracy g_1. Their ratio $\Gamma = g_1/g_0$ will enter into the computation.

Knowing E_I, as given by eq 5, one can calculate the partition function Ξ and the free energy F_{conf}, per bond using the transfer-matrix method:[28]

$$F_{conf} = -k_B T \ln \Xi = -k_B T \ln[\mathrm{Tr}\; e^{-E_I/k_BT}] \qquad (6)$$

where

$$\Xi = \sum_{m_1,m_2,\ldots m_N} \prod_{j}^{N} [e^{-E_I/k_BT}] \qquad (7)$$

The result has the form

$$F_{conf} = -k_B T \ln P_{max} = -k_B T \ln\frac{1}{2}[(1 + ab\Gamma) + [(1 + ab\Gamma)^2 - 4\Gamma(ab - b)]^{0.5}] \qquad (8)$$

where the parameters a and b are defined by the relationships $a = \exp[-A/(k_BT)]$ and $b = \exp[-B/(k_BT)]$, with k_B being the Boltzmann constant. The expression $\mathrm{Tr}\exp[-E_I/(k_BT)]$ in eq 6 denotes the trace of the matrix.

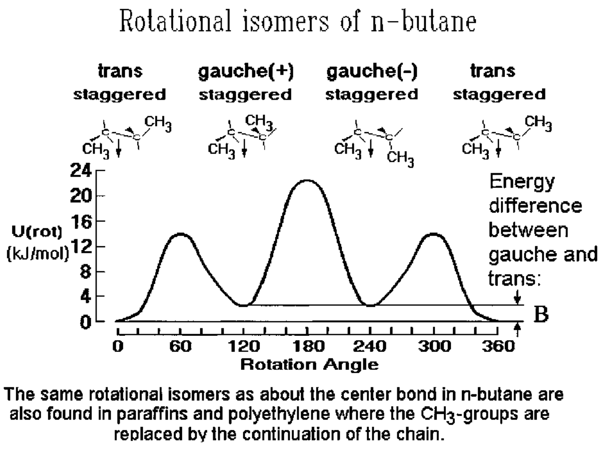

Figure 1. Potential energy versus rotation angle for n-butane.

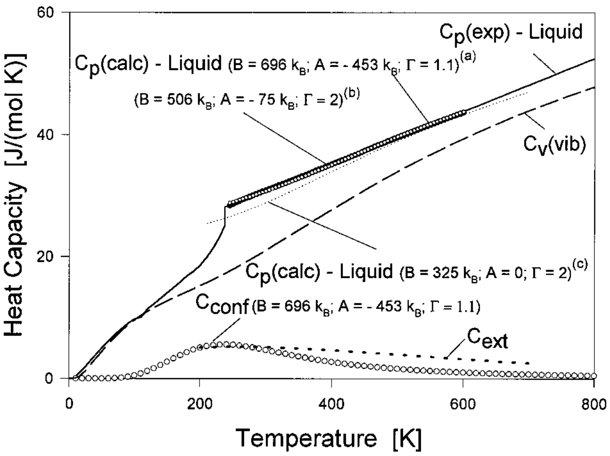

Figure 2. Comparison of the experimental and computed heat capacity of liquid polyethylene.

Next, the free energy F_{conf} from eq 8 can be used to calculate the conformational heat capacity:

$$C_{conf} = \frac{dU_{conf}}{dT} \qquad (9)$$

$$U_{conf} = -k_B T^2 \frac{d(F_{conf}/k_BT)}{dT} = -k_B T^2 \frac{d(\ln \Xi)}{dT} \qquad (10)$$

where U_{conf} is the total conformational energy per assumed bond of the system under consideration.

The final result of the conformational heat capacity can be expressed in closed form as

$$C_{conf} = R\frac{(g_1/g_0)[B/(k_BT)]^2 e^{-B/(k_BT)}}{(g_1/g_0)e^{-B/(k_BT)}}[1 + \vartheta(A,B,\Gamma,T)] \qquad (11)$$

where the expression $\vartheta(A,B,\Gamma,T)$ is too extensive to be shown in detail. Instead, we illustrate the results in Figures 2–6 for several of the fitted values of the parameters of the assumed models.

For the case of noncooperative statistics ($A = 0$), the conformational contribution to the heat capacity of eq

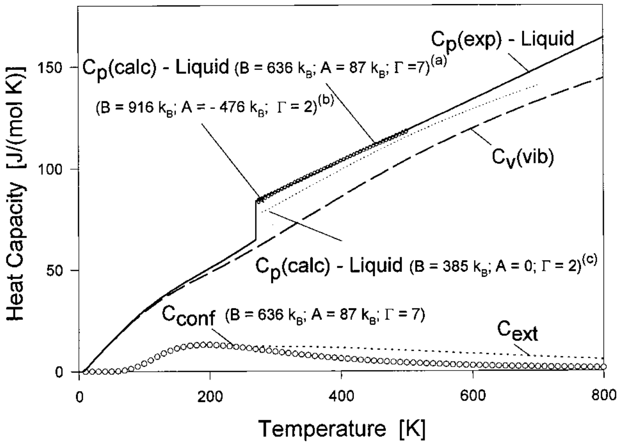

Figure 3. Comparison of the experimental and computed heat capacity of liquid polypropylene.

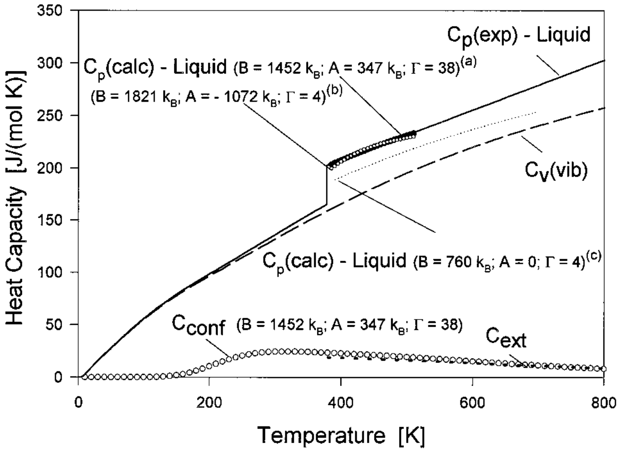

Figure 4. Comparison of the experimental and computed heat capacity of liquid poly(methyl methacrylate).

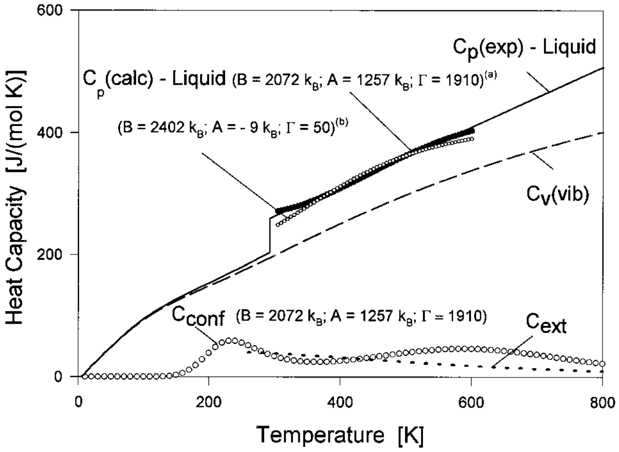

Figure 5. Comparison of the experimental and computed heat capacity of liquid poly(n-butyl methacrylate).

11 is identical to the rotational isomers model:[15,22,27]

$$C_{\mathrm{conf}}\,(\mathrm{RI\ model}) = R\frac{(g_1/g_0)[B/(k_BT)]^2 \mathrm{e}^{-B/(k_BT)}}{(g_1/g_0)\mathrm{e}^{-B/(k_BT)}} \tag{12}$$

An example to which eq 12 was first applied is liquid polyethylene.[29] Its rotational isomers and their energies can be modeled on n-butane, as shown in Figure 1. [27]

The population of the excited conformational states is given by

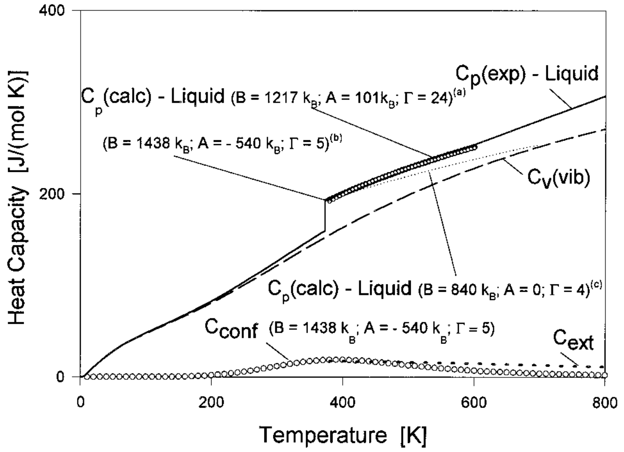

Figure 6. Comparison of the experimental and computed heat capacity of liquid polystyrene.

$$\langle \textstyle\sum m_j \rangle = \frac{\mathrm{d}F_{\mathrm{conf}}}{\mathrm{d}B} \tag{13}$$

Insertion of the conformational free energy of eq 8 leads to the result of the Ising model:[28]

$$\langle \textstyle\sum m_j \rangle = \frac{1}{2} + \frac{1}{2}\frac{ab\Gamma - 1}{[(1 + ab\Gamma)^2 - 4\Gamma(ab - b)]^{0.5}} \tag{14}$$

For the case of noncooperative statistics (when $a = 1$) the population $\langle\sum m_j\rangle$ reduces to the fraction predicted by the rotational isomers model:[28]

$$\langle \textstyle\sum m_j \rangle = \frac{1}{2} + \frac{1}{2}\frac{b\Gamma - 1}{b\Gamma + 1} \tag{15}$$

The liquid heat capacity of polymers is next estimated as the sum of the vibrational, external, and conformational contributions. The experimental conformational contributions are assessed by subtraction of the vibrational and external contributions (eqs 2 and 3) from the total liquid heat capacity. The experimental conformational heat capacity is then fitted to eq 11 of the Ising model to obtain the parameters Γ, A, and B for the polymers.

Results

The heat capacity of the liquid above the glass transition temperature of the following polymers has been analyzed: polyethylene (PE), polypropylene (PP), poly(methyl methacrylate) (PMMA), poly(n-butyl methacrylate) (PnBMA), and polystyrene (PS). The data resulting from the fitting parameters have been compared with the experimental heat capacities of the liquid polymers, available from the ATHAS Data Bank.[2] The results are presented in Figures 2–6, respectively. The parameters are listed in Tables 1 and 2.

The vibrational heat capacity C_{vib} for all analyzed polymers was calculated, as before,[20,21] using the ATHAS Data Bank[2] for the experimental C_p of the solid polymers (glassy or crystalline). For the external heat capacity, C_{ext}, of the presented polymers, eq 3 was used with data derived from the respective equations of state.[18,30–32] The molar volume of the liquid (V, in m^3 mol^{-1}), the expansivity (α, in K^{-1}), and the compressibility (β, in Pa^{-1}) were available for PE, PP, PMMA,

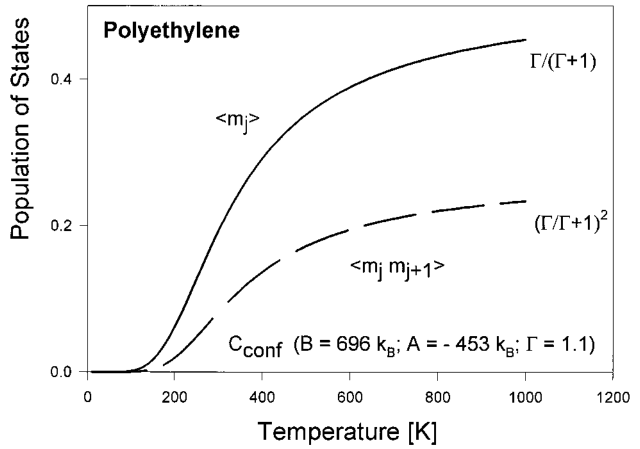

Figure 7. Population of bonds in the excited state as a function of temperature for liquid polyethylene.

Table 1. Parameters for Eqs 16 and 17 To Calculate the External Heat Capacity C_{ext}

polymer	$V_0 \times 10^{-5}$ [m^3 mol^{-1}]	$\alpha \times 10^{-4}$ [K^{-1}]	$b_0 \times 10^{-10}$ [Pa^{-1}]	$b_1 \times 10^{-3}$ [K^{-1}]
PE[18,30]	1.284	7.806	1.418	4.661
PP[31]	4.875	6.7	1.8793	4.177
PMMA[30]	7.080	5.30	2.307	4.146
PS[32]	8.4095	5.13	1.6669	3.31
PnBMA[30]	13.28	6.05	0.917	5.344

Table 2. Fitting Parameters Used for the Calculation of Conformational Heat Capacities

polymer	*B* [K]	*A* [K]	Γ	comments
PE (a)	696	−453	1.1	*A*, *B*, Γ fitting
PE (b)	506	−75	2	*A*, *B* fitting; Γ set = 2
PE (c)	325	0	2	ref 15
PP (a)	636	87	7	*A*, *B*, Γ fitting
PP (b)	916	−476	2	*A*, *B* fitting; Γ set = 2
PP (c)	385	0	2	ref 15
PMMA (a)	1452	347	38	*A*, *B*, Γ fitting
PMMA (b)	1821	−1072	4	*A*, *B* fitting; Γ set = 4
PMMA (c)	760	0	4	ref 15
PS (a)	1217	101	24	*A*, *B*, Γ fitting
PS (b)	1438	−540	5	*A*, *B* fitting; Γ set = 5
PS (c)	840	0	4	ref 15
PnBMA(a)	2072	1257	1910	*A*, *B*, Γ fitting
PnBMA (b)	2402	−9	50	*A*, *B* fitting; Γ fixed

PnBMA, and PS as a function of temperature:

$$V(T)_{p=0} = V_0 \exp(\alpha T) \tag{16}$$

$$\beta(T) = b_0 \exp(b_1 T) \tag{17}$$

where values for the all constants V_0, α, b_0, and b_1 are presented in Table 1 with the appropriate references. The results of the changes in population of the bonds in the excited state for PE are presented in Figure 7. The conformational energies, U_{conf}, for PE and PP are illustrated in Figures 8 and 9, respectively.

The fitting of $C_{conf}(T,B,A,\Gamma)$ to the experimental conformational contributions followed the outline above. In the general case, all three characteristic parameters, *B*, *A*, and Γ, were obtained. In case one or two of the parameters are known, abbreviated fits were attempted. Next, the conformational heat capacity was calculated with the known values for *B*, *A*, and Γ. Finally, using vibrational and external heat capacities, the total heat capacity above the glass transition was computed, as illustrated in Figures 2−6. Note that *A* and *B* are written in terms of Θ temperatures, given in kelvin (i.e., $B = \Theta_B k_B$, for energy in J mol^{-1} multiply Θ with the gas constant $R = 8.314$ J K^{-1} mol^{-1}). The Θ temperatures permit a direct comparison with the data in the ref 18 and give a measure of the degree of excitation of the conformational motion.

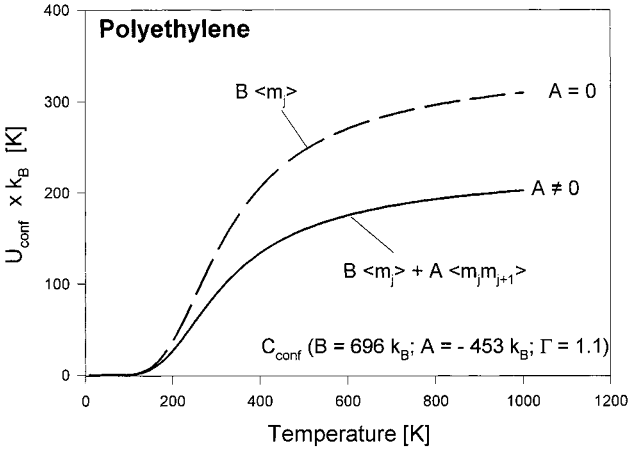

Figure 8. Comparison of the total conformational energy U_{conf} with ($A \neq 0$) and without cooperative effect ($A = 0$) for polyethylene.

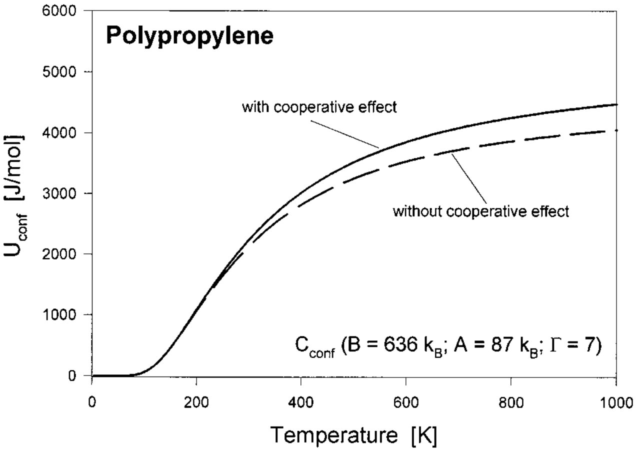

Figure 9. Comparison of the total conformational energy U_{conf} with ($A \neq 0$) and without cooperative effect ($A = 0$) for polypropylene.

The optimization method used to obtain *B*, *A*, and Γ is based on minimizing the chi-square statistics function (χ^2):

$$\chi^2 = \sum \left[\frac{[C_{conf}(\exp)(T_i) - C_{conf}(\mathrm{calc})(T_i,B,A,\Gamma)]}{\sigma_i} \right]^2 \tag{18}$$

where σ_i is the standard deviation of the experimental data taken at the temperatures T_i. Low optimal values of χ^2 correspond to a better fitting of the calculated heat capacity to the experimental data. The numerical minimization is conveniently performed within the programming language of Mathematica 3.0. Figure 10 presents an example of the comparison of the experimental and calculated conformational contributions to the heat capacity for PE after fitting with three parameters *B*, *A*, and Γ (see Figure 10a) and on fitting of only parameter *B* with fixed *A* and Γ (see Figure 10b). The latter calculation duplicates the method of ref 18. The root-mean-square deviations of the experimental data from the calculated values of the liquid heat capacity

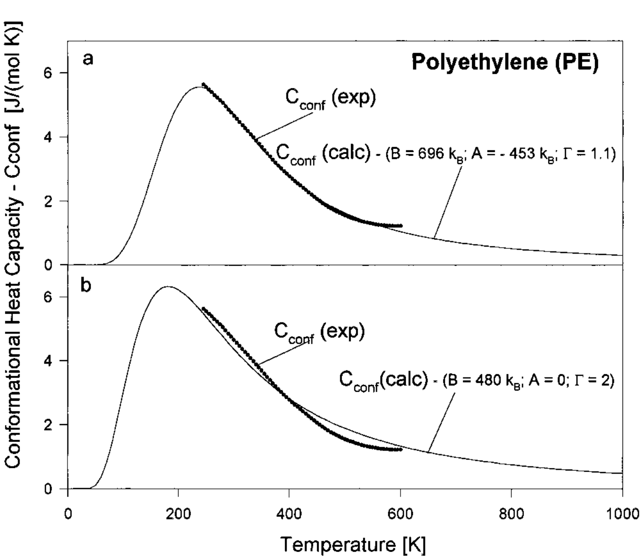

Figure 10. Comparison of the quality of fit of the conformational heat capacity with and without cooperativity.

are always less than ±2% and depend on the temperature range.

Discussion

Inspection of the results in Figures 2−6 establishes that a description of the heat capacity of liquids based on eq 1 is feasible. The observation that most heat capacities of macromolecular liquids increase linearly with temperature[2] can easily be explained as resulting from a superposition of the three nonlinear terms of eq 1, as suggested earlier.[18] Although a unique triple of the parameters A, B, and Γ gives the best fit of the experimental data, considerable concerted changes of the three are possible without moving out of the typical range of experimental precision of 1−3%. Still, some earlier proposed calculations are not credible.[15]

The error introduced by representing the external contribution by $C_p - C_v$ was discussed earlier and shown to be small.[18] To have the best possible set of experimental conformational heat capacities, only data that could be treated with the thermodynamic eq 3 have been detailed in this paper. The empirical Nernst−Lindemann approximation of eq 4 has proven useful for the evaluation of the heat capacity of solids,[2] but for the higher temperatures of the liquid state, possible errors could become more serious. The assumption that the vibrational contribution to the liquid and solid heat capacities is identical should be acceptable, particularly when discussing heat capacities of liquids close to the glass transition region. The group vibrations of eq 2 are known from spectroscopy to a precision far higher than needed for the thermodynamic discussion. The small change of the group vibrations with temperature is negligible for heat capacity calculation. The approximation of the skeletal vibrations with one to three Θ temperatures was shown to lead also to a unique set of values for each polymer.[21] The need of the use a combination of Θ_1 and Θ_3 for linear macromolecules,[2] Θ_2 and Θ_3 for layer crystals,[33] and Θ_3 alone for three-dimensionally connected solids[22] supports its significance. Only the skeletal vibrations are expected to change their frequency in going from the solid to the liquid state. At the glass transition of most polymers their contribution to the heat capacity is, however, already almost fully excited;[2] i.e., a change in frequency due to the larger expansivity of the liquid and changes in conformation cannot cause significant changes in C_{vib}. One anticipates thus a rather reliable experimental conformational heat capacity for the chosen polymers.

The best studied liquid polymer is PE. The experimental heat capacities are based on results from many laboratories[2] and cover the temperature range from about 250 to 600 K. Earlier attempts at computation of its heat capacity were successful. Using the simple rotational isomers model without cooperativity along the chain, i.e., the excited and ground states are the gauche and trans conformational isomers, respectively, as shown in Figure 1 for the butane model compound, all parameters could be supported by independent evidence ($A = 0$, $B = 480$ K $= 4.0$ kJ mol^{-1}, and the degeneracy ratio $\Gamma = 2$).[18] In the same paper an attempt was made to partially include cooperativity between successive backbone bonds, as known from the pentane effect which severely hinders two successive gauche conformations with opposite rotation directions. Using the interaction energies generally accepted,[34] no improvement was found, indicating possible flaws in the more detailed conformational-isomers calculation.

In the case of the present three-parameter fitting, the effective energy difference between the gauche and trans states $B + A = (696 - 453)R = 2.0$ kJ mol^{-1}, compared to the 4.0 kJ mol^{-1} suggested above, and Γ is also not close to 2. Since the degeneracies g_1 and g_0 must be an integer for each bond, the $\Gamma = 1.1$ from the fitting with three parameters must be interpreted such that only every 11th trans state has easy availability of two gauche states. All others have only one. The change of the population of C−C bonds in the gauche state ($\langle m_j \rangle$) is a monotonic function of temperature, as is shown in Figure 7. As expected, at low temperature this contribution to the heat capacity becomes negligible. At high enough temperature, the population of the gauche state is independent of B; it depends only on the ratio of degeneracies $\langle m_j \rangle = 1/(\Gamma + 1) = 0.524$ and follows the law of equipartition. Almost half of the gauche conformations are paired, which causes the lower total conformational energy, shown in Figure 8. No independent evidence of sufficient experimental precision seems presently available to support these differences in conformational statistics.

When the PE data are fitted with a fixed $\Gamma = 2$, the prior analysis based on the rotational isomers model is practically recovered.[18] The effective energy is 431 K, close to the value also expected from spectroscopic data (400−450 K).[34] The small amount of cooperativity is negative (−75 K), while the pentane effect would cause a positive cooperativity. The new data would, thus, support advantageous conformations for successive gauche bonds instead of steric hindrance. Figure 2 includes also the earlier calculation performed in ref 15 with $B = 325$ K (2.7 kJ mol^{-1}), $A = 0$ K, and $\Gamma = 2$. This combination of parameters does not fit the experimental data as well.

The calculated and experimental liquid heat capacities of polypropylene (PP) in Figure 3 demonstrate a good fit with three and two parameters over the full measured range of temperatures from 270 to 500 K. It is interesting to note that the fitting with two parameters using $\Gamma = 2$ gives an effective energy of $B + A =$ 440 K (3.7 kJ mol^{-1}), which is not far from the value suggested in ref 15. The curve (c) without cooperativity

Table 3. Results of Residual Entropy Calculations

polymer	$S_0^{\text{residual}\ a}$ [J K^{-1} mol^{-1})]	S_{ext} at $T_g{}^b$ [J K^{-1} mol^{-1}]	S_{conf} at $T_g{}^c$ [J K^{-1} mol^{-1}]	S_{vib} at $T_g{}^d$ [J K^{-1} mol^{-1}]	$T_0{}^e$ [K]	$T_g{}^f$ [K]
PE	−5.2 (+3.0)	8.5	2.7	18.4	52.5	237
PP	−23.7 (+5.2)	20.3	11.1	68.4	70.4	270
PMMA	−42.7 (+7.1)	40.9	15.0	180.0	70.5	378
PS	−34.1 (+4.4)	30.7	16.8	162	65.0	373

[a] Residual entropy at absolute zero calculated using the heat capacities of fit a in Table 2. The value in parentheses is the residual entropy at absolute zero using the experimental heat capacities of the liquid and glass in eq 19. Note that the extensive data refer to 1 mol of CRU, i.e., PE is calculated per chain atom, the other polymers per two chain atoms. [b] External entropy, integrated from 0 K to T_g. [c] Conformational entropy, integrated from 0 K to T_g. [d] Vibrational entropy from, integrated 0 K to T_g. [e] Temperature where the calculated liquid entropy reaches the value zero when it is integrated from the melt toward 0 K. [f] Glass transition temperature.

parameter,[15] in contrast, does not agree well with the experimental heat capacity.

From the three-parameters fitting, the total numbers of states for PP is eight or multiples of the ratio 7/1. Fitting for B, A, g_1, and g_0 instead of the ratio Γ leads to values of g_1 and g_0 close to 7 and 1, respectively, rather than 14/2. The meaning of the degeneracy 1 of the backbone may be linked to the preference of the low-energy, helical gauche−trans sequences in the backbone. The seven higher-energy conformations account then for most of the additional conformations of the rotational isomers model (3 × 3). The energetics of PP is similar to PE, except that the (small) positive cooperativity increases the total conformational energy, as shown in Figure 9. The population of repeating units in excited states at high temperature is 0.875. To better describe the conformational behavior of PP, multilevel models should probably be considered.

For PMMA (Figure 4), PnBMA (Figure 5), and PS (Figure 6) relatively good agreement is also achieved between calculation and experiment. For these three polymers with complex side chains Γ is rather large when obtained from the three-parameter fit. Reasonable, but not as good, fits were also obtained with fixed, smaller values of Γ and a fit of the experimental data for A and B. The smaller values for Γ were suggested in the literature,[15] except for PnBMA where a guess was made to achieve similar results. The higher values of Γ are, however, not necessarily unreasonable when one estimates the total number of different rotational isomers possible, assuming three isomers per rotatable bond, and counting $-CH_3$ and the carboxyl group as single entities (PMMA, 81; PnBMA, 729; PS, 27).

The effective difference in energy between the two states for PMMA ($B + A = 749$ K; 6.2 kJ mol^{-1}) is similar to the choice in ref 15, where $B = 760$ K and $A = 0$. Similarly for PS with a fixed value of five for Γ, the effective energy ($B + A = 898$ K; 7.5 kJ mol^{-1}) is similar to 840 K, as chosen in ref 15, again neglecting the rather large nearest-neighbor influence. For PnBMA it should be noted that despite the very high value of Γ, the effective value for three-parameters fit of $B + A = 3329$ K (27.7 kJ mol^{-1}) is about 4 times higher than the value suggested in the literature for PMMA.[14,15]

To summarize, the new method of calculating the conformational contribution to the heat capacity of liquids leads to good agreement between experiment and calculation. The fitting leads to two or three parameters that can be linked to some degree to the rotational isomers model but points to improvements that must be developed. In all examples presented, the general observation can be made that introducing a cooperative effect in describing the conformational contribution to the heat capacity of the liquid of linear polymers leads to a better agreement to the experimental data. Larger side groups lead, furthermore, not unexpectedly, to larger degeneracy. To some degree energetics and degeneracy are coupled in the fitting procedure. The new approach also gives a more realistic picture of the conformational behavior in linear macromolecules with longer side chains than is presently possible with the rotational isomers model. The one-dimensional Ising model may further open the way to handle intermolecular cooperativity.

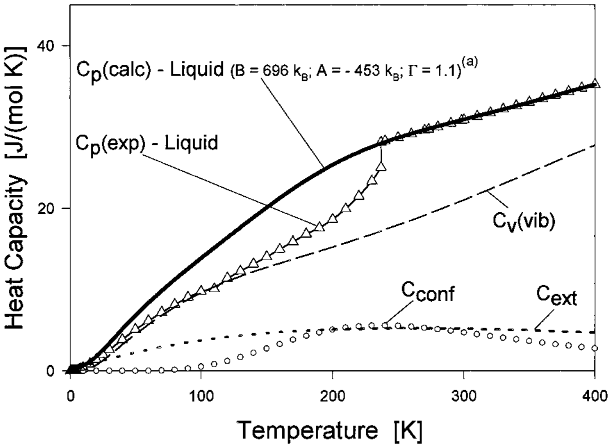

Figure 11. Extension of all contributions to the liquid heat capacity of PE to lower temperatures.

All three different contributions to the heat capacity of the liquid as expressed by eqs 2, 3 (on insertion of eqs 16 and 17), and 11 go to zero at absolute zero, as is indicated for the example of PE in Figure 11. One would expect, thus, that a more reasonable extrapolation of the heat capacity of the hypothetical liquid to temperatures below the glass transition is possible than with the empirical linear heat capacities. This extrapolation may shed some light on one of the key issues of the description of the liquid, the so-called Kauzmann paradox.[35] One finds that, on integration of the absolute entropy of the liquid to lower temperatures, an impossible, negative value is obtained before the absolute zero is reached. This observation was also the origin of a proposed “thermodynamic” glass transition which occurs when the entropy of the liquid approaches zero; i.e., the number of different conformations available to the liquid becomes very small.[16,17] This temperature was estimated to occur about 50 K below the glass transition temperature.

To calculate the residual entropy, $S_0{}^{\text{res}}$, the absolute entropy of the liquid above the melting temperature was established for the polymers that can be crystallized (PE, PP, PMMA, and PS), could be extrapolated to full crystallinity, and have reasonable estimates of the equilibrium heat of fusion and melting temperature.[2] From this high-temperature, absolute reference entropy,

$S^{\rm ref}$, the low-temperature values $S^{\rm res}$ were found using the calculated heat capacities of Figures 2−4 and 5:

$$S^{\rm res} = S^{\rm ref} - \int_{T_{\rm h}}^{T_{\rm l}} \frac{C_p(\text{calc})}{T}\,\mathrm{d}T \qquad (19)$$

Table 3 shows the results in column 2. Also listed in Table 3 are the residual entropies of the glass (in parentheses in column 2), determined with eq 19, but using the experimental heat capacities of the liquid and the glass as given in the ATHAS data bank.[2] Similarly, the increase in entropy from absolute zero to the glass transition temperature was integrated for the three contributions to the heat capacity. The results are listed in columns 3−5 of Table 3. Finally, T_0, the temperature where $S^{\rm res}$ reaches zero, is also listed in Table 3.

Inspection of Table 3 reveals first that all $S_0{}^{\rm res}$ are negative, leaving the Kauzmann paradox in tact. Next, one notices that T_0 occurs at a much lower temperature than the suggested $T_{\rm g} - 50$ K. The values for T_0 range from $T_{\rm g} - 184$ to 308 K. Finally, one can see that the estimate of the external contribution is probably too large (see also Figure 11). If the liquid, indeed, approaches a state of low entropy that prohibits conformational rearrangement, the external heat capacity contribution should decrease similarly quickly to zero as the conformational $S_0{}^{\rm res}$ part. Note that typically $C_{\rm p} - C_{\rm v}$ of the glass has reached values close to zero at about 200 K. This suggestion moves the temperature, T_0, even closer to zero, and for PE, it may even lead to a positive $S_0{}^{\rm res}$. Similar questions of the interpretation of various interpretations of calculations of the entropy of liquid polymers below the glass transition arose also out of computer simulations carried out recently.[36]

Acknowledgment. This work was financially supported by the Division of Materials Research, NSF, Polymers Program, Grant DMR-9703692, and the Division of Materials Sciences, Office of Basic Energy Sciences, DOE, at Oak Ridge National Laboratory, managed by Lockheed Martin Energy Research Corp. for DOE, under Contract DE-AC05-96OR22464.

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MA9816620