Hybrid Ising Mean Field Theories of Crystalline Polymer Melt Processes

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ABSTRACT: A third-order and a fourth-order Ising mean field theory have been developed to describe melt transitions in crystalline polymeric materials. These theories along with simpler Ising models are applied to crystalline polymethylene and polytetrafluoroethylene. Inclusion of interchain interactions is essential for the existence of a first-order phase transition in each of our theories. Moreover, the realistic prediction of transition temperature and heat capacity behavior is extremely sensitive to the model chosen for interchain crystalline breakdown. Near quantitative agreement has been achieved between theory and experiment in the application of our theories to polymethylene and Teflon, suggesting that our representation of molecular interactions probably incorporates the essential features of the melt process.

In a previous paper[2a] we reported an attempt at a first-principle statistical mechanical theory and energy calculation to describe the conformational and intermolecular configurational aspects of the melt process in dense chain molecular fluids. The molecular energetics were determined using molecular orbital theory in which only the valence bond geometry and a rough estimate of lattice packing were specified. The only arbitrary constant present in one of the statistical mechanical models was chosen in a prescribed manner independent of experimental results. Good quantitative agreement with the experimental melt transition properties of linear high-density crystalline polyethylene was achieved when the specific model adopted was an Ising mean field representation with a linear interchain melt correction term. This model does not include the excluded volume effects of the short-range interaction directly, but instead recognizes that while certain chain conformations and configurations (intermolecular wise) are energetically unfavorable, they can nevertheless occur. As a result long-range effects appear which cause crystal breakdown and melt. It is the long-range nature of these interactions which supports use of the mean field to describe the interchain interaction. The choice of mean field may appear to be similar in spirit to the mean field calculations of liquid crystals of Humphries et al.[2b] and Marcělja;[3] the similarity, however, is only superficial, as our theory depends on complete interchain energetics for each of the possible nearest-neighbor, interchain bond configurations.

Since a goal of our work is to produce an analytical solution for the melt transition, the inclusion of a detailed description of the molecular organization prior to, during, and after melting has been incorporated in a simple model which retains only the essential features of the real system. A significant part of our investigation focuses upon maximizing the quantity of detailed molecular structural information in a partition function which can be analytically evaluated. Neither the number of conformational and configurational states incorporated into the theory, nor the estimation of the corresponding molecular energetics represented as critical a limiting factor in the development of a realistic melt-transition model as the treatment of the interchain organization during melting.

In this paper we report the results of an exploration of a variety of melt transition models which have been applied to both polymethylene and polytetrafluoroethylene crystals. We have endeavored to identify how specific structural assumptions and simplifications inherent in each of the models manifest themselves in the predicted melt properties of each of the polymer fluids. Our hope is to optimize an analytic description of both the intra- and inter-molecular geometries of the polymer fluids before, during, and after the melt process so as to yield a set of melt properties in quantitative agreement with experiment. In turn, we may be able to put forth some propositions concerning the spatial organization of the chain molecules during the melt process by an examination of the form of the transition model that yields the best results.

High-density linear polyethylene is near enough to an ideal polymer fluid to use in our transition modelling work in that its crystal structure is well known and undergoes, essentially, a single melt transition.[4] Polytetrafluoroethylene, on the other hand, exhibits a more complex melt behavior[5] which requires a modification of the original theory to describe its melt properties. The polymer exists in two helical conformations which may be described as twisted ribbons in which the linear zigzag, 2_1-ribbon conformation is distorted to have a 180° twist in 13 CF_2 units in the more stable (low temperature) form. Above 19 °C this form is replaced by a slightly untwisted conformation with 15 CF_2 units per half-twist. Above 19 °C the x-ray diffraction pattern shows diffuse streaks suggesting small angular displacements of molecular segments about their long axes. Above 30 °C, more diffuseness occurs in the x-ray pattern which increases as the temperature is raised to, and above, the melting point at approximately 327 °C. The additional diffuseness is attributed to loss of molecular chain orientation and corresponding crystallinity.[5] The multiple sub-melt transitions that take place prior to melt makeeee it very difficult to assign molecular geometry, i.e., chain conformation and packing configuration, to the solid from which the molecular energy terms can be deduced. To circumvent this problem we have computed the molecular energetics for polytetrafluoroethylene for the low temperature, and presumably, most stable crystal structure and use these quantities directly in our transition theory. In other words, we have neglected the sub-melt transitions. The consequences of this simplification cannot be reasonably estimated since both internal energy and entropy are altered in competing directions. It is not clear which factor is dominant over temperatures in the melt range.

Theory

As in our earlier publication[2a] we take as our starting point the statistical mechanics of a single polymer chain. The lengths of all carbon–carbon bonds are assumed fixed, as are the included angles between adjacent pairs of carbon atoms; only the torsional angles, θ_1 and θ_2, of the rotation about these bonds within a trimeric unit are treated as variables to describe the conformational potential energy.

The Hamiltonian is thus of the form

$$\mathcal{H}_0 = \int\int V(\theta_1,\theta_2)n(\theta_1,\theta_2)\,\mathrm{d}\theta_1\,\mathrm{d}\theta_2$$

with $n(\theta_1,\theta_2)$ the joint probability distribution of adjacent

Table I
Relationship between the Greek Parameters Used in the Implicit Equations for *M* and the Energy Parameters Obtained in the Inter- and Intrachain Interaction Calculations[a]

$\phi = \frac{1}{2}(V_{gg} - V_{tt} - kT \ln [2(\alpha_t/\alpha_g)^{1/2}])$
$\epsilon = \frac{1}{2}(W_{gg} - W_{tt}) + \phi$
$\eta = -\frac{1}{16}(6W_{tg} + 5W_{tt} + W_{gg}) + \phi$
$\sigma = \frac{1}{16}(5W_{gg} - 2W_{gt} - 3W_{tt}) + \phi$
$\rho = \frac{1}{2}(2W_{tg} - W_{gg} - W_{tt})$
$\delta = \frac{1}{8}(2W_{tg} + 5W_{gg} - 7W_{tt})$
$\zeta = \frac{1}{16}(13W_{gg} - 2W_{gt} - 11W_{tt})$

For Polytetrafluoroethylene

$V_{tt} = 0.0$ kcal/mol
$V_{gg} = 1.75$ kcal/mol
$V_{tg} = 0.70$ kcal/mol
$W_{tt} = -0.62$ kcal/mol
$W_{gg} = -0.44$ kcal/mol
$W_{gt} = 0.60$ kcal/mol
$\alpha_t = 0.87$ cal/(deg of rotation)^2
$\alpha_g = 0.43$ cal/(deg of rotation)^2

[a] Also listed are the numerical values used in the application of the models to polytetrafluoroethylene.

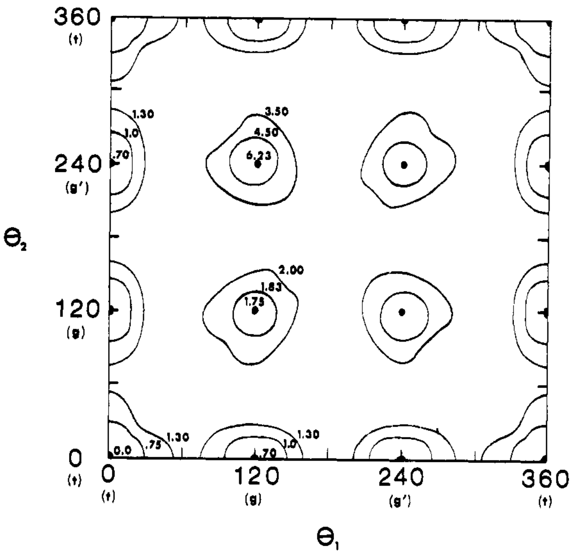

Figure 1. Iso–energy contour maps for the interchain interaction in polytetrafluoroethylene as a function of nearest-neighbor torsional angles θ_1 and θ_2. Energies are given in kcal/mol.

torsional angles and $V(\theta_1,\theta_2)$ the potential-energy function described in ref 2a. Interactions between monomeric elements separated by more than three other carbon atoms are thus neglected in this essentially one-dimensional model.

The core of the problem of the melt transition lies in the nature of the interchain interactions, without which phase transitions cannot occur. While a variety of possible models might be suggested, we restrict ourselves to a particular tractable subset in which the interchain potential energy is simply a functional of the probability distribution $n(\theta)$ of the torsional angle θ. This hypothesis may be thought of as a generalization of the van der Waals or mean field model of the gas–liquid system. It is the most detailed model for which an analytic solution may be found using currently available techniques.

The form of the interchain interaction will be taken to be:

$$\mathcal{H}_1 = \int W_1(\theta)n(\theta)\,d\theta + \int\int W_2(\theta_1,\theta_2)n(\theta_1)n(\theta_2)\,d\theta_1\,d\theta_2 + \int\int\int W_3(\theta_1,\theta_2,\theta_3)n(\theta_1)n(\theta_2)n(\theta_3)\,d\theta_1\,d\theta_2\,d\theta_3 + \int\int\int\int W_4(\theta_1,\theta_2,\theta_3,\theta_4)n(\theta_1)\ldots n(\theta_4)\,d\theta_1\ldots d\theta_4 + \ldots$$

These integrals may be given a physical interpretation in terms of the nature of the interactions between neighboring polymer chains. The integral involving $W_1(\theta)$ contains only a single probability distribution function $n(\theta)$ and thus does not represent a true interaction between chains and will be omitted. The integral involving $W_2(\theta_1,\theta_2)$ is bilinear in the $n(\theta)$, and thus does represent an interaction capable of leading to a phase transition under appropriate conditions. This term is somewhat analogous to the interaction in the Curie–Weiss theory of ferromagnetism[6] in which a contribution to the energy is postulated that is proportional to the square of the magnetization.

The third-order term represents a more subtle effect, in that the interaction strength between a pair of chains is itself modified by the distribution $n(\theta)$. This may be thought of as an attempt to allow for the three-dimensional nature of the system and to include an attenuation of the interchain interaction as the temperature rise causes the misalignment of neighboring chains. This type of model ha however, the property that at very high temperatures, where $n(\theta)$ approaches a constant and the chains are totally misaligned, some interchain interaction remains. It is not clear whether this is a correct representation of the real physical system. This difficulty may be circumvented by obliging this contribution to vanish at high temperatures through a particular form of a third-order term. This was the approach adopted in ref 2a, and which will also be reapplied in the present work. It carries with it a new problem, however, in that a constant which would normally be arbitrary must now be fixed, and the physical criterion for fixing the constant is not clearly known. Thus it is desirable to consider also the fourth-order term W_4, from which these problems may be arranged to be absent. In the present study the form of W_4 was chosen to be

$$W_4(\theta_1,\theta_2,\theta_3,\theta_4) = W_2(\theta_1 + \theta_3,\theta_2 + \theta_4)$$

which gives an interaction similar to the bilinear term but with W_2 replaced by its two-dimensional convolution with $n(\theta)$. At low temperatures where $n(\theta)$ is approximately a δ function, the W_4 interaction is nearly identical with the W_2 interaction, whereas at high temperatures, where $n(\theta)$ goes to a constant, the interchain interaction is also attenuated to a constant.

The solution for the free energy of this set of models follows closely the approach of ref 2a, and only the broad outline will be repeated here. The form of the potential function $V(\theta_1,\theta_2)$ restricts θ to be close to the trans, gauche, or gauche′ values of 0, 120, and 240°, and hence $V(\theta_1,\theta_2)$ may be approximated by the form

$$V(\theta_1,\theta_2) = V_{ij} + \alpha_i(\theta_1 - \theta_i)^2 + \alpha_j(\theta_2 - \theta_j)^2$$
$$i,j = \text{trans, gauche, and gauche}'$$

Consequently the integrations were replaced by summations over these three conformations. The partition function was then found by considering the effect of the mean field term on the free energy of a single chain described by the Hamiltonian $\mathcal{H}_0$.

The characteristic interaction energy terms for polyethylene are reported in ref 2a, along with a description of the method[7] used in their computation. Table I contains the energy parameters for polytetrafluoroethylene which were computed in the same manner as those for polymethylene. Briefly, the intrachain energetics have been determined by a complete conformational analysis of dimeric and trimeric fluoroethylene units for fixed valence bond geometries appropriate for tetrafluoroethylene chains.[5] The conformational energies have been determined by application of the PCILO (perturbation of configurational interactions using localized orbitals) method.[8] The resulting potential energy function $V(\theta_1,\theta_2)$

Table II
Comparison of Theory to Experiment for Polymethylene and Polytetrafluoroethylene[a]

	SC[b]	SC + 2d order	SC + 3d order	SC + 4th order	Exptl
			(a) Polymethylene		
1st-order transition?	No	No	Yes	Yes	Yes
Peak in heat capacity, °K	169.5	443.8	390.3	382.6	415.5
ΔS, cal/(mol °K)			1.63	2.39	$\Delta S = 2.32$ $(\Delta S)_V = 1.73$

	SC	SC + 2d order	SC + 3rd order	SC +4th order	Revised SC + 3rd order	Revised SC + 4th order	Exptl
				(b) Polytetrafluoroethylene			
1st-order transition	No	No	No	Yes	Yes	Yes	Yes
Peak in heat capacity, °K	279.5	684.7	630.4	611.3	585.9	571.2	600
ΔS, cal/(mol °K)				2.06	0.58	2.16	$\Delta S = 1.14$ $(\Delta S)_V = 0.76$

[a] Theories shown are the results for a single chain with no interchain interaction, a chain with an interchain interaction with no crystal breakdown correction (second order), a linear disorder breakdown of interchain interaction (third order), and a convolution of the interchain interaction with $n(\theta)$ (fourth order). For polytetrafluoroethylene the third- and fourth-order theories are also shown for the revised energetics where only 90% of the monomer units were assigned to the trans state at 0 K. Our ΔS values should correspond to the experimental $(\Delta S)_V$ since we have no volume dependence in the energy calculations. [b] SC = single chain.

which combines the intrachain nearest-neighbor and second-nearest-neighbor monomeric interactions as a function of the included torsional angles θ_1 and θ_2 is represented by the isoenergy contour map shown in Figure 1. The nearest-neighbor interchain interactions have been computed by carrying out configurational energy calculations similar to those used by Hopfinger[9] to estimate hydration shell parameters. The molecular species chosen were two identical trimeric fluoroethylene units both of which are held rigidly in one of the nine low-energy conformational states defined by the respective intrachain torsional rotation angles. The configurational energy was subsequently minimized as a function of the seven degrees of intermolecular freedom.

As was done for polymethylene, the gauche and gauche′ states are considered degenerate for polytetrafluoroethylene. Accordingly the summation over conformations was limited to a sum over the two conformations trans and gauche with the appropriate factor 2^{n_g} included in the partition function to describe the degeneracy. Here n_g is defined as the fraction of units near the g conformation. For the third-order model the arbitrary constant was chosen such that the average intrachain energy vanishes when all states are equally occupied.

The maximum of the partition function is found for the three different terms of $\mathcal{H}_1$ that are being modeled, and in each case the result can be expressed in an implicit equation for the quantity $M = n_t - n_g$. The form of the equation with the W_2 term is

$$M = M_0(\epsilon + \rho M)$$

For the modified W_3 term one finds

$$M = M_0(\eta + \delta M + 9\rho M^2/8)$$

and for W_4 the implicit equation is

$$M = M_0[\sigma + \zeta M + 9\rho(M^2 + M^3)/8]$$

where $M_0(\psi)$ is the negative derivative of the Helmholtz free energy per spin for the Ising spin ½ chain, with respect to the applied field ψ.[2a] The Greek constants are defined in Table I.

Results

Table II contains the results of applying a variety of melt transition models to chain molecular fluids of polymethylene and polytetrafluoroethylene. Clearly, semiquantitative agreement with experimental data is only possible when detailed interchain organization is built into the theory. Only the Ising mean field third- and fourth-order models, which consider the most interchain information, yield melt temperatures and entropies in reasonable agreement with experimental data for both polyethylene and polytetrafluoroethylene.

It is interesting to note that both the third- and fourth-order models underestimate the observed melt temperature of polyethylene, suggesting the calculations are underestimating the order in the crystalline phase or overestimating the order in the melt phase, or a combination of both factors. The third- and fourth-order models applied to the fluorinated species, on the other hand, yield too high a melt temperature. This is probably indicative of assigning too much order to the crystalline state in view of the two polymorphic phase transitions in which chain orientation and, correspondingly, order decrease prior to melting. The loss in crystallinity is estimated to be about 10% for these solid-state transitions.[5] We have attempted to model this structural modification in our calculations by assigning the trans conformation ($\theta = 0°$) an energy equivalent to the case where only 90% of the monomer units are in the trans state. Thus 100% trans now essentially corresponds to the case where there is already 10% loss of crystallinity.The results are part of Table II. Figure 2 contains plots of the fraction in the trans conformation vs. temperature for polytetrafluoroethylene using the various transition models. These curves are, model by model, of the same respective shapes as those for polymethylene reported in ref 2a. Interchain interactions again drastically sharpen the melt transition curves and are necessary for the existence of a theoretical first-order transition.

Figure 3 contains plots of heat capacity vs. temperature for polytetrafluoroethylene, again using the various transition models. The respective shapes of the heat capacity curves are again similar to those of polymethylene. We could not find experimental heat capacity curves published for polytetrafluoroethylene. However, transition entropies at constant volume are available for both polytetrafluoroethylene and polymethylene.[10] On the assumption that the 95–90% trans crystal approximation is a more realistic representation of the immediate pre-melt structure of Teflon than the 100% trans, we observe that the third-order model yields a better quantitative prediction of transition entropy for both polymeric materials than the fourth-order model.

Lastly it is to be noted that the 100% trans polytetrafluo-

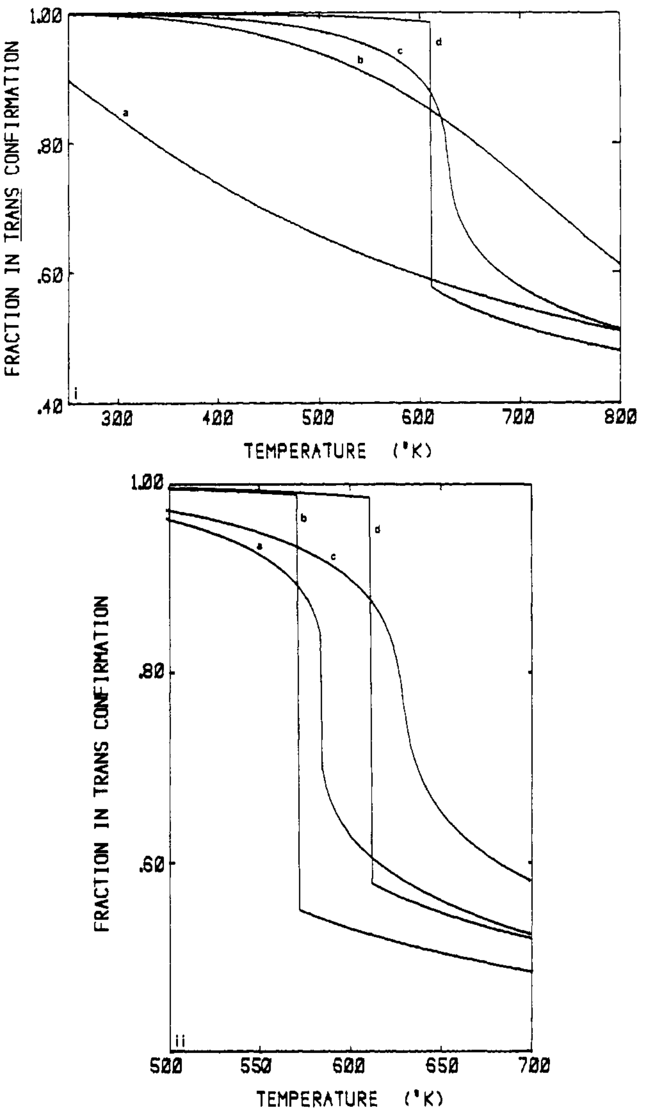

Figure 2. (i) Fraction in the trans conformation for (a) single chain, (b) second-order interchain interaction, (c) third-order interaction, and (d) fourth-order interaction. No pre-melt transitions are taken into account. (ii) Fraction in the trans conformation for (a) third-order and (b) fourth-order theories with no pre-melt transitions and (c) third-order and (d) fourth-order theories with revised 90% trans energetics. These curves are for tetrafluoroethylene.

roethylene crystal does not lead to a first-order transition for the third-order theory.

Discussion

A reasonable conclusion from this series of calculations is that the third- and fourth-order transition models coupled with the methods of conformational and configurational analyses provide a realistic semiquantitative means of predicting melt-transition properties of crystalline polymer materials. Put another way, given the primary structure of the polymer and a reasonable estimate of type and extent of interchain packing, it is possible to make meaningful predictions of the values of several thermodynamic melt transition properties of crystalline polymeric materials.

However, we cannot at this stage infer too much about the mechanisms of melting from the theory. We might ask how the two principal formulations, i.e., the third- and fourth-order models, differand how these differences translate into thermodynamic melt behavior. Succinctly, the third-order model introduces a linear disorder-dependent term in the mean field interchain interaction. This forces the interchain energetics to decrease uniformly in magnitude from the low-temperature energy values W_2, to zero as the disorder of the system increases from zero at the low-temperature limit to complete disorder at the high-temperature limit. The magnitudes of the interaction energies decrease for increasing disorder at the same rate for all chain conformations. In the fourth-order model both the relative magnitudes of the interaction energies for different chain conformations as well as the disorder dependence are not linear, but rather a function of the chain populations of respective conformational states. Obviously, these are only two examples of a large number of third- and fourth-order theories that could be postulated. However, it is noteworthy that both models perform reasonably well in quantitative predictions. Contrasting polymethylene with polytetrafluoroethylene, it would appear that the lattice breakdown corresponds to a nearly linear loss in interchain energy interactions. However, significant excursions from a linear loss in interchain energetics, as exemplified by the fourth-order model, do not produce correspondingly drastic changes in the melt temperature but do alter in a major way the entropy of fusion. It would seem at first sight that we

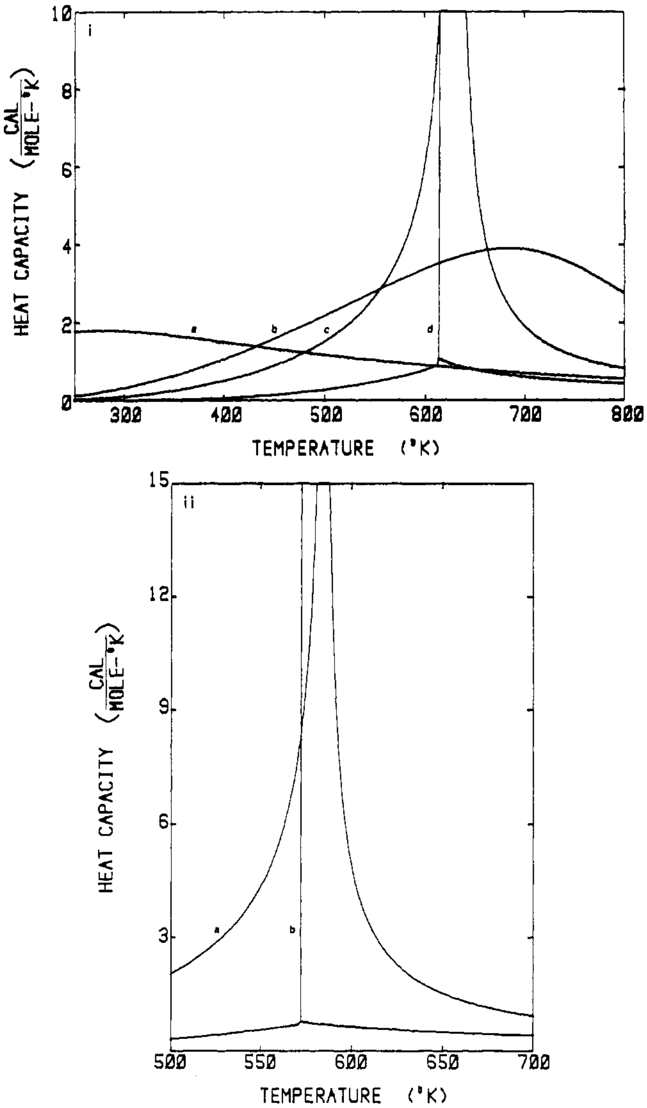

Figure 3. (i) Heat capacity of polytetrafluoroethylene vs. temperature for (a) single chain, (b) second-order interchain interaction, (c) third-order interaction, and (d) fourth-order interaction. No pre-melt transitions are taken into account. (ii) Heat capacity vs. temperature for (a) third-order and (b) fourth-order theories with the revised 90% trans energetics.

might be able to decide on the "best" model in describing lattice breakdown by matching predicted and observed entropy changes in several different polymeric solids. However, one can argue that the experimental values of ΔS are of sufficiently high uncertainty to negate this expectation. Variations in degree of crystallinity and crystalline homogeneity of the samples can lead to significant variation in experimental values of ΔS.

Both third- and fourth-order theories allow a given chain to interact with a variable number of neighboring chains. For polymethylene we found that each chain interacted with slightly more than two other chains in order to yield a realistic melt temperature.[11] The same is true for polytetrafluoroethylene. When the chain is set up energetically to interact with four chains instead of two chains, the melt temperature changes from 586 to 832 K for the third-order theory and from 571 to 823 K for the fourth-order theory. How this apparent interaction of a given chain with only two of its neighbors is produced in the actual melt process is not clear. It would suggest that polymethylene and polytetrafluoroethylene crystals melt out via similar if not identical mechanisms. It would also appear that while several chains maintain close contact in the crystalline states this proximity is not reflected in the energetics of the melt process.

At this point, a question can be raised concerning effects of the approximations made in going from the continuum model to the discrete two-level model. The answer to this question is the goal of our current research. Solving the continuum model directly poses difficulties and computer-dependent numerical techniques need to be employed rather than analytic equations as is the case with the discrete two-level system. Once the initial work is done, the models presented here can be tested in the continuum case, and also other models will be tested to determine how one might better describe lattice breakdown.

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(11) Figure 4 of our first paper[2a] is mislabeled; curve b is with two interacting chains, and curves c, d, and e are four, six, and eight interacting chains, respectively.

Brillouin Scattering from Poly(vinylidene fluoride)–Poly(methyl methacrylate) Mixtures

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ABSTRACT: Brillouin scattering has been observed from poly(vinylidene fluoride) (PVF_2)-poly(methyl methacrylate) (PMMA) mixtures in the temperature range 20–200 °C. The mixtures are shown to be homogeneous in the melt, and to quench to an amorphous film. A single glass–rubber relaxation region is observed for the quenched mixtures, indicating a compatible polymer mixture. The PVF_2 crystallizes from the mixture at temperatures between T_g and T_m. These measurements demonstrate the usefulness of Brillouin scattering in the study of melting in polymers.

The polymer blend of poly(vinylidene fluoride) (PVF_2) and poly(methyl methacrylate) (PMMA) has been the subject of several recent studies.[1–3] This mixture has been shown to be compatible above the melting point of PVF_2 (170 °C).[2] Below T_m the PVF_2 may crystallize from the melt if the mixture is well above the glass–rubber relaxation temperature T_g.[3] Conversely, amorphous films of PVF_2/PMMA mixtures may be formed by rapid quenching from the melt.[3] In the present work, Brillouin scattering is employed to study the thermal behavior of PVF_2/PMMA films.

Theory

Brillouin scattering from longitudinal acoustic phonons in a homogeneous amorphous phase results in fully polarized peaks shifted in frequency by

$$\pm \frac{\Delta\omega_l}{\omega_0} = 2\tilde{n}\,\frac{V_l}{C}\sin\theta/2 \qquad (1)$$

where ω_0 is the incident frequency, $\tilde{n}$ is the refractive index, V_l is the longitudinal phonon velocity, C is the speed of light in a vacuum, and θ is the scattering angle in the scattering plane. Typical Brillouin splittings for polymers are of the order of 10^{10} Hz, so that the phonon velocity may differ considerably from the low-frequency velocity of sound.

The phonon velocity V_l is given by

$$V_l = \sqrt{\frac{3K + 4\mu}{3\rho}} \qquad (2)$$

where K is the modulus of compression, μ is the modulus of rigidity, and ρ is the density.

In the region of the glass–rubber relaxation, the moduli reflect the change from equilibrium behavior above T_g to nonequilibrium behavior below T_g. Thus there is a change in slope in the plot of $\Delta\omega_l$ vs. T at T_g.[4–6] The modulus of rigidity shows an enormous change in the glass–rubber relaxation region at very low frequencies, but at hypersonic frequencies there is no discontinuity in either K or μ at T_g.

At a melting transition, μ changes considerably, even at high frequencies. Thus, the Brillouin splitting is expected to be a sensitive probe of crystallization and melting in polymers. Another notable effect of crystallization in polymers is that the material becomes locally birefringent. This leads to de-