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Models of the Structural Phase Transition in Poly(butylene terephthalate)

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ABSTRACT: Two alternative models are investigated of the structural phase transition in poly(butylene terephthalate) (PBT). In model I, benzene rings from neighboring chains are constrained to remain in registry while in model II benzene rings from neighboring chains can slide past each other. The models have been studied by using mean-field analysis and Monte Carlo simulations. Model I yields better agreement with experiment than model II.

1. Introduction

Poly(butylene terephthalate) (PBT) has been found to exhibit a structural phase transition from the crystalline α-phase to the crystalline β-phase on the application of uniaxial stress.[1-3] X-ray studies[4-6] indicate that both crystalline phases have a triclinic unit cell, the main difference in the two crystal forms being in the length of the lattice period in the chain-axis, or *c*-axis, direction. This period is longer in the β-phase than in the α-phase. On removal of a modest stress, all the β-phase material reverts to the α-form, and in this sense the transition is said to be reversible. It is generally believed[1-3] that this phase transition occurs as a consequence of a conformational change in the tetramethylene segment, which is crumpled in the α-form and extended in the β-form.

In this paper, we present two alternative models for the structural phase transition in PBT. In one model benzene rings from neighboring chains are constrained to remain in registry, while in the other this constraint is absent. The scheme of this paper is as follows: Section 2 contains a description of the two models, while results for the mean-field versions of these models and a discussion of their significance are presented in section 3.

2. Description of the Models

The main aim of our studies has been to investigate the influence of the interchain interaction in the structural phase transition in PBT. In particular, we are interested in deciding whether longitudinal motion of one chain is possible within the matrix represented by neighboring chains. As a starting point, we ignore any interactions between tetramethylene segments along a chain, since these are separated by bulky and fairly rigid terephthalate residues. Further, we assume that interchain interactions are limited to those occurring between terephthalate residues belonging to neighboring chains, and ignore interchain interactions between the tetramethylenes or between benzene rings and tetramethylene segments. This is a reasonble starting approximation, given that the lateral dimensions of a benzene ring are larger than those of a tetramethylene segment. However, the planar nature of the terephthalate residue may dictate some modification of this hypothesis for the α-form of PBT.

The main question to which we address ourselves is the nature of the atomic displacements that take place during the α–β transition. Are the relative motions of atoms on neighboring chains always small on the scale of a lattice spacing, as in the case of martensitic transitions, or do we have large-scale diffusive motions of atoms? To answer this question we have studied two alternative models. In model I benzene rings from neighboring chains are constrained by elastic bonds to remain in registry, while in model II the rings are permitted to slide past each other. The interchain interaction in both cases is modeled by assuming simple but realistic forms for the interchain potential. These models represent a first step toward a more complete analysis of the mechanics of the α–β phase transition in PBT than has been possible in some of the very simplified systems considered in the past.[2,7]

2.1. Model I. In this model benzene rings belonging to neighboring chains are constrained to remain in registry through the agency of interchain van der Waals interactions modeled as Hookean springs, as shown schematically in Figure 1. In the simplest version of this model, the length of a tetramethylene segment can take only two values—l_α in the crumpled α-form and l_β in the extended β-form. The Hamiltonian for the system can then be written as

$$\mathcal{H} = \tfrac{1}{2}K \sum_{i,j,k} \{(l_{i,j,k} - l_{i+1,j,k})^2 + (l_{i,j,k} - l_{i,j+1,k})^2\} - F \sum_{i,j,k} l_{i,j,k} + \sum_{i,j,k} E_{i,j,k} \quad (1)$$

Here $l_{i,j,k}$ is the length of the tetramethylene segment at site (i,j,k) and takes on one of the two values l_α and l_β, with corresponding energy $E_{i,j,k}$ equal to E_α or E_β. The spring constant for interchain attraction between terephthalates is K, and F is the applied stress expressed as a force per unit chain backbone.

The two-valued nature of l makes this Hamiltonian equivalent to that of the Ising model of ferromagnetism. If we define

$$\tfrac{1}{2}(l_\beta - l_\alpha) \equiv b \qquad \tfrac{1}{2}(E_\beta - E_\alpha) \equiv e$$

then the Hamiltonian becomes

$$\mathcal{H} = Kb^2 \sum_{i,j,k} (\sigma_{i,j,k}\sigma_{i+1,j,k} + \sigma_{i,j,k}\sigma_{i,j+1,k}) + (e - Fb) \sum_{i,j,k} \sigma_{i,j,k} + \text{constant} \quad (2)$$

where $\sigma_{i,j,k}$ takes on the values ± 1 according to whether $l_{i,j,k}$ is l_β or l_α, respectively.

Equation 2 describes an assembly of independent two-dimensional Ising nets.[8] While a complete analytical solution is not available for this problem, extensive numerical solutions are available, and exact results are known for the critical temperature T_c and for some critical exponents.[9] We may, for instance, immediately note that

$$T_c = 2Kb^2/0.881k_B \quad (3)$$

with k_B Boltzmann's constant. The exact treatments, however, do not allow us to estimate the hysteresis in the stress–strain behavior of PBT, a quantity that is of considerable interest experimentally.

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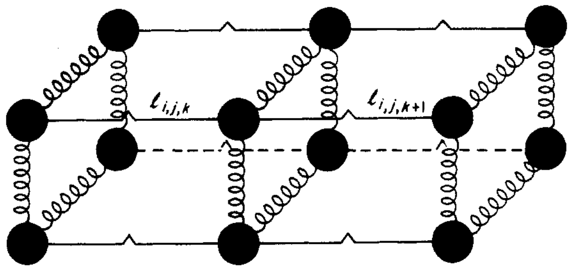

Figure 1. Schematic representation of model I of the PBT lattice. The solid circles denote benzene rings joined to neighbors along the c axis by bistable connections that can assume only two lengths, l_α and l_β. Each benzene ring is connected to other near neighbors by Hookean springs.

In order to obtain an estimate of the hysteresis in the stress–strain behavior we make a mean-field approximation and replace the Hamiltonian of eq 2 by

$$\mathcal{H}_{\rm MF} = -2NKb^2\langle\sigma\rangle^2 + N(e - Fb)\langle\sigma\rangle \quad (4)$$

with N the total number of monomer units in the crystal. If we define p as the fraction of tetramethylene segments in the β-form, so that $\langle\sigma\rangle = 2p - 1$, then

$$\mathcal{H}_{\rm MF} = N[-2Kb^2(2p-1)^2 + (e - Fb)(2p - 1)] \quad (5)$$

The entropy will be given by the expression

$$S = -Nk_{\rm B}[p \ln p + (1-p)\ln(1-p)] \quad (6)$$

The equilibrium distribution is found by minimizing the free energy, $\mathcal{H}_{\rm MF} - TS$, by differentiation with respect to p. One finds

$$-8Kb^2(2p-1) + 2(e - Fb) + k_{\rm B}T \ln[p/(1-p)] = 0$$

from which

$$p = \{\exp[(1/k_{\rm B}T)(-8Kb^2(2p-1) + 2(e - Fb))] + 1\}^{-1} \quad (7)$$

The solution to eq 7 yields the strain as a function of applied stress F and temperature T. The existence of multiple solutions in eq 7 indicates the presence of metastable states and leads to hysteresis in the stress–strain behavior. The critical temperature in the mean-field approximation is

$$T_{\rm c} = 4Kb^2/k_{\rm B} \quad (8)$$

Another quantity of interest is the width of the hysteresis loops as a function of temperature. Below $T_{\rm c}$, eq 7 yields an unstable region in the stress–strain curve which demarcates the limits of metastability, and consequently yields the widths of the hysteresis loops. This can be seen more easily by rewriting eq 7 in the form

$$\langle\sigma\rangle = \tanh[(4Kb^2\langle\sigma\rangle - (e - Fb))/k_{\rm B}T] \quad (9)$$

or

$$F = (1/b)[k_{\rm B}T \operatorname{arctanh}(\langle\sigma\rangle) - 4Kb^2\langle\sigma\rangle] + e/b \quad (10)$$

The unstable region lies between the two roots of $\mathrm{d}F/\mathrm{d}\langle\sigma\rangle = 0$

$$k_{\rm B}T/(1 - \langle\sigma\rangle^2) - 4Kb^2 = 0 \quad (11)$$

Denoting these roots by $\langle\sigma\rangle_{\rm uns}$ we get

$$\langle\sigma\rangle_{\rm uns}{}^2 = 1 - T/T_{\rm c} \quad (12)$$

The width ΔF of the stress–strain curves along the stress axis is then

$$\Delta F = (1/b)[8Kb^2(1 - T/T_{\rm c})^{1/2} - 2k_{\rm B}T \operatorname{arctanh}(1 - T/T_{\rm c})^{1/2}] \quad (13)$$

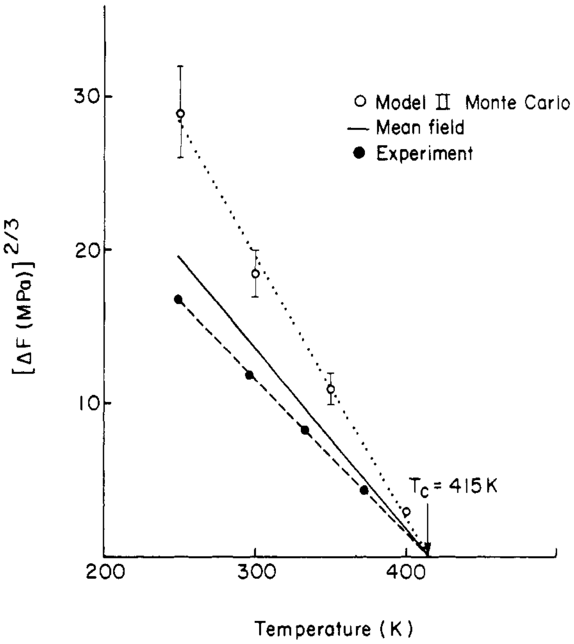

Figure 2. Variation of $(\Delta F)^{2/3}$ with temperature, where ΔF is the width of the hysteresis loops. The solid circles denote experimental points from ref 2, while the dashed line is drawn to guide the eye. The solid line is the mean-field approximation to model I. The open circles are obtained from the computer simulations of model II, the dotted line through them being a fit to the open circles.

In the vicinity of $T_{\rm c}$ the width varies as the $^3/_2$ power of the deviation of the temperature from its critical value, and

$$\Delta F = (4k_{\rm B}T_{\rm c}/3b)(1 - T/T_{\rm c})^{3/2} \quad (14)$$

2.2. Model II. In this model the Hookean forces between benzene rings on neighboring chains are absent, and large-scale longitudinal motion is possible. The interchain potential experienced by a benzene ring is then assumed to have the form

$$V = V_0[p \cos k_\beta x + (1-p)\cos k_\alpha x] \quad (15)$$

where x denotes the position of a benzene ring along a chain, p is the fraction of tetramethylene segments in the β-form, $k_\alpha = 2\pi/l_\alpha$, $k_\beta = 2\pi/l_\beta$, and V_0 is a parameter which represents the interaction between benzene rings. The potential of eq 15 has two competing periodicities and is similar to a Frenkel–Kontorova potential. It represents, in a mean-field manner, the potential due to an ensemble of chains, a fraction p of which are in the β-form and a fraction $1 - p$ in the α-form.

The total energy of a single chain of M monomer units placed in the above potential is

$$\mathcal{H} = V_0 \sum_{m=2}^{M} \{p \cos k_\beta(\sum_{i=1}^{m} l_i) + (1-p)\cos k_\alpha(\sum_{i=1}^{m} l_i)\} - F\sum_{i=1}^{M} l_i + \sum_{i=1}^{M} E_i \quad (16)$$

where, as in model I, l_i is the length of a tetramethylene segment and can take the value l_α or l_β, with corresponding energy E_i equal to E_α or E_β.

In order to study the thermodynamics of a system with the above Hamiltonian we have performed Monte Carlo simulations[10] at fixed F and T. The Monte Carlo simulations were done on a chain of 20 monomer units by using the Metropolis[11] algorithm. In this procedure an initial guess is made for p so as to specify the potential in eq 15. The Monte Carlo method then efficiently samples the phase space of a chain of N monomer units in this potential at a given value of F and T, to yield a new value for p. This

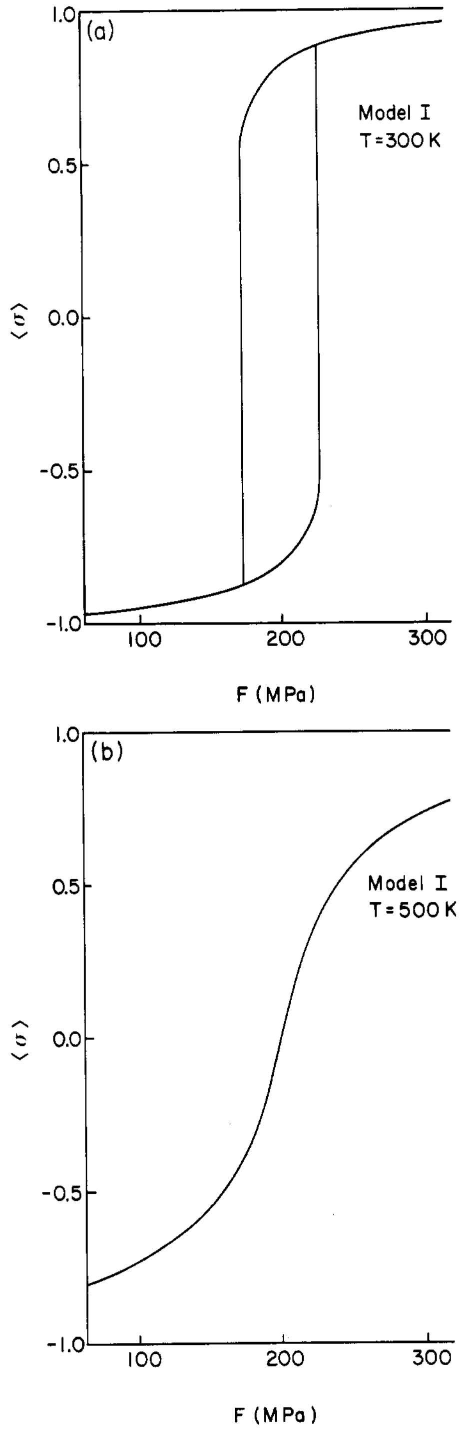

Figure 3. Stress–strain behavior from model I. Here $\langle\sigma\rangle = 2p - 1$ is plotted as a function of applied stress for one temperature below T_c (a) and one above T_c (b).

procedure is repeated until the desired convergence is reached. Multiple solutions for p at a given value of applied stress and temperature indicate the existence of metastable states and lead to hysteresis.

3. Results and Discussion

In attempting to make a comparison between theory and experiment, we are hindered by the fact that not all the relevant parameters can be estimated with any great accuracy. While values for l_α and l_β and for E_α and E_β may be found in the literature, the interchain force parameters represented by K in model I and V_0 in model II can only be conjectured from conformational energy calculations of poor precision. Accordingly, we treat these parameters as adjustable constants chosen to make the critical temperature T_c of the model agree with experiment. The test of the model then lies in the closeness of the fit of the theoretical value of the width ΔF of the hysteresis loop to its measured value at temperatures below T_c. Because model II does not yield an analytic prediction for the width of the hysteresis loops as a function of temperature, we use the results of model I as the basis for our comparison between theory and experiment.

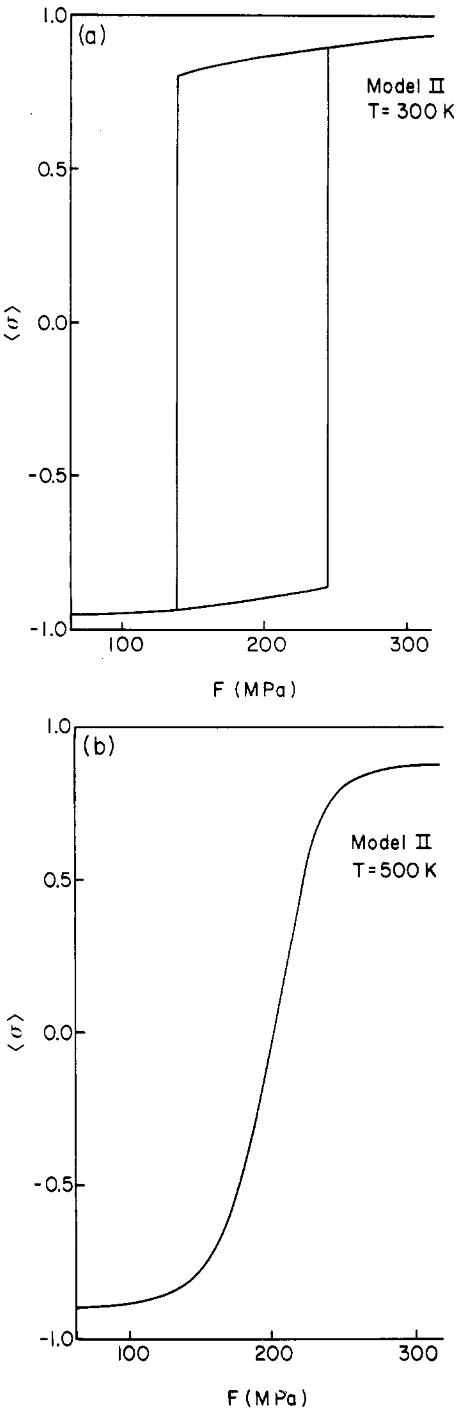

Figure 4. Stress–strain behavior for model II: (a) $T < T_c$, (b) $T > T_c$.

Figure 2 is a plot of $(\Delta F)^{2/3}$ as a function of temperature, where ΔF is the width of the hysteresis loops. The solid circles denote the experimental results of Brereton et al. and these are seen to lie on a straight line. This indicates that the power law behavior predicted by mean-field theory (eq 14) is obeyed. The dashed line drawn through the experimental points intercepts the temperature axis at 415 K. With this value for T_c we determine the spring constant

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in model I (eq 8) to be $K = 184$ kJ mol^{-1} nm^{-2}. Taking values of the lattice spacings l_α and l_β in the two phases from ref 4 and 12, we set $l_\alpha = 1.16$ nm and $l_\beta = 1.30$ nm. The mean-field prediction for ΔF (eq 14) is shown as the solid line in Figure 2. We see that the mean-field prediction lies close to the experimental result.

Figure 3 shows the behavior of the stress–strain curves obtained from the mean-field approximation to model I, i.e., the stable and metastable solutions to eq 7. The considerable hysteresis predicted at low temperatures diminishes with increase in temperature, vanishing at the critical point. In plotting Figure 3, we took the values of the conformational energies E_α and E_β from the calculation of Yokouchi et al.,[6] who found $E_\alpha = -6.60$ kJ mol^{-1} and $E_\beta = -1.21$ kJ mol^{-1}, and the stress F expressed per unit polymer backbone was divided by the average cross-sectional area of a unit cell (taken to be 0.28 nm^2) in order to convert it to conventional units.

Figure 4 is a plot of the stress–strain curves for model II at one temperature below T_c and at one temperature above T_c. The parameter V_0 appearing in model II was fixed by requiring that the critical temperature equal 415 K. This leads to a value of V_0 equal to -3.34 kJ mol^{-1}.

Although model II is considerably more complex than model I, it nevertheless also has the character of a mean-field model and yields similar values for the critical exponents. We thus find that model II also produces a straight-line plot in Figure 2, where points from the Monte Carlo simulations are shown as open circles. The slope of this line, however, is in considerably poorer agreement with experiment than is the case for model I.

The highly simplified models of PBT that we have studied allow us to understand qualitatively the nature of the atomic displacements during the α–β structural transition. The results presented here show that model I yields better agreement with experiment than model II, suggesting that benzene rings from neighboring chains remain in registry during the transition.[13] In future work, we propose to refine these models to include the structure of the tetramethylene segment and to take into account more realistic van der Waals interactions between benzene rings.

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(13) We would like to point out here that the conformational energy parameters appearing in the two models do not play a role in determining the widths of the hysteresis loops. The results presented above are therefore valid in spite of the uncertainties in the conformational energies. A refinement of the conformational energy calculations would however lead to a better prediction of the critical stress.

Separating Polymer Solutions with Supercritical Fluids

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ABSTRACT: The high-pressure phase behavior of mixtures consisting of random poly(ethylene-*co*-propylene), a mixed organic solvent, and a light supercritical fluid additive is experimentally investigated. The amount and type of supercritical fluid additive (methane, ethylene, propylene, and carbon dioxide) have a dramatic effect on the shape and location of the phase border curves of the polymer solution. In particular it is demonstrated that the lower critical solution temperature (LCST) curve can be shifted by more than 100 °C to lower temperatures by introducing a supercritical fluid additive to the polymer solution. The effect of pressure, over a range of 2.76–31.02 MPa, on the LCST curve is also determined.

Introduction

The possibility of designing novel, energy-efficient separation processes using supercritical fluids (SCF's) has generated an increased number of high-pressure phase behavior studies within the past decade.[1,2] However, very little work has been done in applying SCF technology to the problem of separating polymer solutions. For certain solution polymerization processes an extremely costly process step occurs when the polymer is separated from its solvent. In some instances the cost of this separation can amount to approximately 10% of the final cost of the product.[3] Currently, the most common technique for separating polymer from solvent is to devolatilize the solvent from solution by steam stripping. This type of separation technique can be very energy intensive since the solvent can amount to 90–95% (w/w) of the solution.

Inducing a polymer–solvent phase split offers an alternative to steam stripping as a separation technique.[3-6] This phase splitting technique is based on the experimental observation first made by Freeman and Rowlinson[7] that a miscible polymer solution will split into two liquid phases if the system temperature approaches the critical tem-

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