cases of $y = 3$ or 5 and $x = 14$.

Liquid crystallinity is observed in those poly(ester amides) exhibiting at least two endotherms during heating. The larger the number of such transitions, the clearer the mesomorphic behavior. This is seen as birefringence in cross-polarized light coexisting with polymer mobility. Of the polymers given in Figures 3 and 4, optically observable liquid crystallinity in the form of birefringence coupled with spontaneous fluidity is evident in the cases where $y = 3$ and $y = 5$. Birefringence is also observed but associated with slow mobility when $y = 9$. No such optically observable mesomorphic behavior is observed in the studied polymers when $y = 2$ and $y = 4$. Thus, we are led to the conclusion that when mobility at the ester (αy) site is restricted, as is the case for $y = 2$ and $y = 4$, the polymers melt in a single step at relatively high temperatures. However, when the αy carbon is more mobile, as is the case in $y = 3$, $y = 5$, and probably $y = 9$, then libration occurs in several small increments covering a broad temperature interval.

These results indicate a relationship between mesomorphic behavior in poly(ester amides) and molecular dynamics in the ester moiety. This suggests that liquid crystallinity is coupled to the molecular dynamics of the ester portion and effectively decoupled from the segmental motion present in the amide and aromatic portions of the polymer chain.

Comparison with Related Systems. It is of interest to compare these results with those previously reported in related studies[12,25–27] of polyesters. Horii and co-workers[25] examined a series of terephthalic acid polyesters above T_g via traditional high-resolution NMR methods. When the nomenclature adopted here is used, these polymers have the general structure [COC$_6$H$_4$COO(CH$_2$)$_y$O] and are analogous to the aromatic and y fragments of poly(ester amides). They found that, in the mobile isotropic phase above T_g, motion at the aromatic, αy, and iy sites was dependent upon the choice of y. This is the case for poly(ester amides), even below T_g. Further, motion at the aromatic site was greater than at αy. This is the same as our finding when x is long (Figure 4). There are two interesting points here. The first is that different degrees of localized motion, analogous to those observed here for poly(ester amides), also exist in polyesters. The second involves the fact that the motional heterogeneities observed by Horii and co-workers[25] above T_g were also observed by Jelinski and co-workers[12,26,27] on these and related glassy polymers below T_g, suggesting that the motional behavior that predominates below T_g persists above T_g. Unfortunately, our work on poly(ester amides) was limited to the semicrystalline solid state below T_g. However, it is interesting to speculate that these motions may also persist into the thermotropic liquid-crystalline phase. This speculation clearly mandates the need for further study.

Conclusions

It has been demonstrated that the molecular dynamics of poly(ester amides) are internally heterogeneous and dependent upon the length of the amide (x) and ester (y) alkylene chains. Mobility at the amide site was shown to be high relative to the rest of the molecule and largely independent of (y,x). Motion at the aromatic and ester sites, on the other hand, depends upon (y,x). This dependence includes an intriguing odd–even behavior for the ester moiety, revealing that motion at the ester site is more restricted for even values of y. These observations are discussed in terms of a dynamic model for poly(ester amides) and their relationship to related systems.

Registry No. Poly(ester amide) ($y = 2$, $x = 4$), 114677-81-5; poly(ester amide) ($y = 3$, $x = 4$), 114677-89-3; poly(ester amide) ($\gamma = 4$, $x = 4$), 114678-01-2; poly(ester amide) ($y = 5$, $x = 4$), 114678-10-3; poly(ester amide) ($y = 9$, $x = 4$), 114678-21-6; poly(ester amide) ($y = 2$, $x = 14$), 114677-84-8; poly(ester amide) ($y = 3$, $x = 14$), 114677-97-3; poly(ester amide) ($y = 4$, $x = 14$), 114678-08-9; poly(ester amide) ($y = 5$, $x = 14$), 114678-18-1; poly(ester amide) ($y = 9$, $x = 14$), 114678-25-0; poly(ester amide) ($y = 3$, $x = 8$), 114677-93-9.

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Comments on "Temperature-Dependent Changes in the Structure of the Amorphous Domains of Semicrystalline Polymers"

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Received April 11, 1989;
Revised Manuscript Received April 12, 1989

The premelting phenomenon is a spontaneous growth of the amorphous domains of semicrystalline polymers at the expense of the crystalline layers as the temperature

0024-9297/89/2222-3810$01.50/0

rises (e.g., consult ref 1 and references cited therein). One of us has published a theoretical explanation of this phenomenon.[2] Unfortunately, mistakes were made in the derivation given in that publication. In this paper we publish a corrected version of the theory.

The physical arguments behind the theory of premelting are as follows: Transport (via the α relaxation or other mechanisms; consult ref 2 for details) is possible between the two phases of at least some semicrystalline polymers, notably polyethylene. At any temperature below T_m, a thermodynamic driving force exists tending to draw chains out of the amorphous domains and into the crystallites. That the material does not crystallize completely, given the existence of transport between the phases, implies the existence of another thermodynamic force opposing the first. The inability of these systems to completely crystallize has always been attributed to their entangled nature; however, the only way an entangled network can give rise to a net thermodynamic force is through rubber elasticity deformations. The amorphous domains of semicrystalline polymers should be viewed, therefore, as deformed rubbers. The tug-of-war between these two forces accounts for the premelting phenomenon. For example, if the temperature is lowered, the drive to crystallize increases and material is drawn into the crystallites. The crystallites thicken at the expense of the amorphous domains, which become more anisotropic as they become thinner. This increased anisotropy leads to stronger rubber elasticity forces, which eventually become strong enough to balance the increased crystallization drive. At any temperature, a metastable equilibrium can be established, with lower temperatures favoring thinner, more anisotropic domains. This model, although similar, differs from earlier models of this effect.[3-6]

A polymer chain having N backbone bonds whose ends are constrained to lie at a relative separation R has statistical weight

$$W(\mathbf{R}) = AZ^N N^{-3/2} \exp\left(\frac{-3R^2}{2Na^2}\right) \tag{1}$$

Here a^2 is the square statistical segment length, Z^N is the partition function of the chain with unconstrained ends, and A is a normalization factor. It follows that an ensemble of chains whose ends are constrained to follow a distribution characterized by the moment $\langle R^2 \rangle$ has free energy per chain given by

$$\beta G_{ch} = -\ln A - N \ln Z + {}^3\!/_2 \ln N + \frac{3\langle R^2 \rangle}{2Na^2} \tag{2}$$

Here G_{ch} is the free energy of the chain, and β is $(kT)^{-1}$. In most rubber elasticity applications, N is constant, and one can neglect all but the last term above, as was done in ref 2. This is a mistake, however, in the present application, since N is not constant. To be correct, our model must include all the terms shown above. For example, one of us has shown how such terms produce interesting bifurcation phenomena when chains are permitted to reptate through slip links.[7]

The derivation continues in ref 2 by dividing eq 2 above by N and considering contributions on a per bond basis. On the surface, that step seemed inoccuous but in fact generates errors. The correct approach is given here.

For reasons given in ref 2, we take $\langle R^2 \rangle = a^2(2N_0 + N^2/N_0)/3$. We also assume that the complete amorphous phase of the system is comprised of ν such chains, each of length N, for ν a constant. We also write $\beta g_m = -\ln Z$, where g_m represents the free energy per bond of the bulk melt. Then if G_a represents the free energy of the amorphous phase, we obtain from eq 2

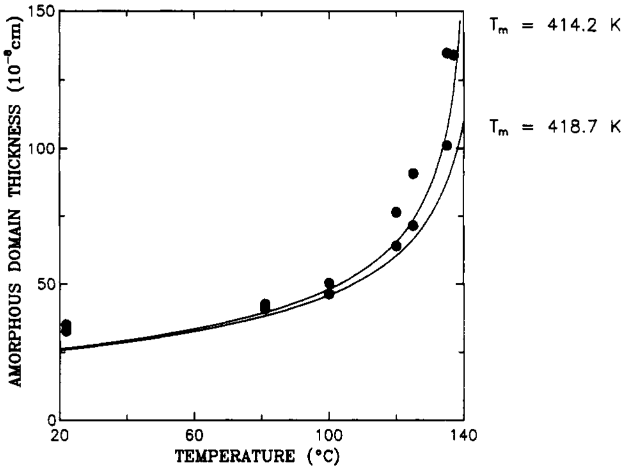

Figure 1. Fit of eq 7 to the amorphous domain thickness of semicrystalline polyethylene crystallized at 125 °C. Experimental data are from ref 1.

$$\beta G_a = -\nu \ln A + \nu N \beta g_m + \frac{3\nu}{2} \ln N + \frac{\nu N_0}{N} + \frac{\nu N}{2N_0} \tag{3}$$

The complete free energy of the system is written as a sum of contributions from the crystal and amorphous domains and the interfacial region: $G = G_a + G_c + G_i$. We assume $G_c = N_c g_c$, for g_c the free energy per backbone bond of the bulk crystal. We let $N_a = N\nu$ represent the number of backbone bonds in the amorphous domains. N, N_a, and N_c are permitted to vary but are subject to the constraints $N_a/N = \nu =$ constant and $N_a + N_c =$ constant. Therefore, we write

$$\beta G = \beta N_c g_c - \nu \ln A + \nu N \beta g_m + \frac{3\nu}{2} \ln N + \frac{\nu N_0}{N} + \frac{\nu N}{2N_0} + \beta G_i \tag{4}$$

as the total free energy of the system.

We now assume that, at any given temperature, N_a is allowed to adjust until eq 4 is minimized. Remembering that $\partial N_c/\partial N_a = -1$ and $\partial N/\partial N_\alpha = 1/\nu$ yields the condition[8]

$$O = \frac{\partial \beta G}{\partial N_a} = -\frac{N_0}{N^2} + \frac{3}{2N} + \frac{1}{2N_0} + \beta \Delta g \tag{5}$$

where $\Delta g = g_m - g_c$. We solve the above for N to obtain

$$N = N_0[{}^3\!/_4 + ({}^{17}\!/_{16} + N_0 \beta \Delta g)^{1/2}]^{-1} \tag{6}$$

or

$$d = d_0[{}^3\!/_4 + ({}^{17}\!/_{16} + N_0 \beta \Delta g)^{1/2}]^{-1} \tag{7}$$

This replaces the originally published expression:[2]

$$d = d_0(N_0 \beta \Delta g - 1)^{-1/2} \tag{8}$$

In these expressions Δg is the free energy difference per backbone bond between the bulk melt and the bulk crystal and is calculated as explained in ref 2. d_0 and N_0 are adjustable parameters. N_0 should be comparable,[2] if not equal, to the critical number of backbone bonds for the formation of entanglements in a bulk melt, about 300. Equation 7 adequately fits the experimental data of Tanabe et al.[1] with reasonable values of the adjustable parameters. Figure 1 displays a comparison between eq 7 and the experimental data for crystallization at 125 °C. The curves on Figure 1 are drawn for these values of the adjustable parameters: $(d_0, N_0) = (374\ \text{Å}, 400)$. Large variations in N_0 and d_0 can be permitted as long as $N_0 d_0^{-2}$ is held constant. Equally adequate fits are obtained for the remainder of the Tanabe et al.[1] data. We omit them here to conserve space. We have drawn curves for two different values of T_m, the equilibrium melting point of polyethylene, since the exact value is a matter of controversy.[9]

One important difference between eq 7 and 8 needs to be mentioned. Equation 8 has no real solutions when $N_0\beta\Delta g < 1$. This fact led to speculation about a melting point depression.[2] Since eq 7 has a root for any $\Delta g \geq 0$, melting point depression is not expected to occur.

Any completely rigorous mathematical treatment of the premelting phenomenon would require exact mathematical expressions for each of the two thermodynamic forces discussed above. Unfortunately, approximations only are available for either. Equation 17 of ref 2 represents the crystallization force, but it is only valid for small ΔT. Likewise, classical rubber elasticity theory is already an approximation when applied to bulk networks. We undoubtedly introduce additional approximations when we apply it to the thin amorphous domains of semicrystalline polymers. One should not expect complete accuracy from the present model.

The parameters N_0 and d_0 supposedly characterize the initial isotropic state of the amorphous domains. However, this state is probably never achieved. It is entirely possible that the amorphous domains are already anisotropic at the moment of crystallization. At the very best, N_0 and d_0 characterize the isotropic state to which the system would extrapolate if it could be heated above the melting point.

The concept of premelting has never been completely accepted, presumably because spontaneous, reversible, partial melting many degrees below the melting point appears thermodynamically unsound. Many polymer scientists have adopted an alternative explanation for the observed crystallinity changes. It is argued that thinner crystals nucleate and grow within the amorphous domains at lower temperatures. These thinner crystals would melt at or near the temperature at which they formed and so would disappear upon reheating. However, no new nucleation can occur if, as we are asserting, the two phases are in metastable equilibrium at all temperatures, just as nucleation from the bulk melt cannot occur at the equilibrium melting temperature. Since this metastable equilibrium is the only way of reconciling the existence of transport between the phases with their coexistence at arbitrary temperature, we conclude that the concept of premelting is a sound one.

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Communications to the Editor

^{15}N T_1 Measurements of Semicrystalline Nylon 6

High-resolution solid-state NMR is becoming an important tool for characterizing polymer systems. Cross polarization and magic angle spinning (CP/MAS) along with high-power decoupling allow acquisition of high-resolution spectra of natural abundance ^{13}C nuclei with good sensitivity. Relaxation studies have identified noncrystalline regions poorly characterized by X-ray.[1] Recently, we have demonstrated that solid-state CP/MAS NMR of natural abundance ^{15}N is readily obtainable on solid polyamides.[2,3] In addition, ^{15}N CP/MAS peaks were shown to correlate with the two predominant crystal forms found in most solid polyamides, i.e., the α and γ crystal forms. Resonances were observed for other regions that could not be assigned to either crystal form. Further study by NMR and molecular modeling calculations showed nitrogen chemical shifts to be extremely sensitive to conformation about the amide group providing a tool for observing ordered region conformations in solid polyamides.[4]

Our interest in examining the previously unobserved noncrystalline and amorphous regions in polyamides by ^{15}N CP/MAS prompted us to prepare an isotopically enriched polyamide sample. We chose to prepare an ^{15}N-enriched sample of nylon 6 because it is an important commercial polyamide that has been thoroughly characterized in the solid state by many techniques (DSC, IR, X-ray) including solid-state ^{13}C NMR.[5,6] Nylon 6 was prepared by anionic polymerization of ε-caprolactam. Isotopic enrichment of the monomer was accomplished using commercially available ^{15}N-labeled hydroxylamine hydrochloride. Details of the polymer synthesis will be reported in a future paper. Here we report preliminary ^{15}N NMR characterization of nylon 6 including the first report of ^{15}N T_1 values for a solid polyamide.

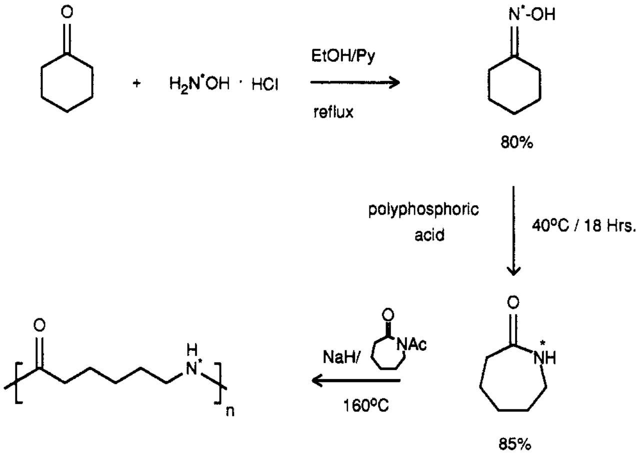

Figure 1. Reaction scheme for preparation of ^{15}N-enriched nylon 6.

Sample Preparation. Poly(ε-caprolactam) (20% ^{15}N enrichment) was prepared using the scheme outlined in Figure 1. The crude product was extracted with methanol to remove unreacted monomer. The extracted samples

0024-9297/89/2222-3812$01.50/0