would be detectable by surface decoration. On the other hand, slow crystallization as takes place at 77–78 °C might produce the highly regular folding, which is the possible cause for the high dissolution temperature of crystals grown in this temperature range. This issue is currently receiving further attention.

At this point an important general issue arises about crystal dissolution temperatures: namely, its concentration dependence. It has become customary to quote a single T_d value when referring to dilute polymer solutions (<1%). The approximation of a constant T_d is justified in the latter case due to the fact that the local concentration within the polymer coil becomes independent of the bulk concentration at sufficient dilution.[18] However, in the present case, neither is the molecular weight high enough nor is the concentration low enough to warrant a concentration independent T_d. The crystallization at 78 °C illustrates this point clearly (see Figure 7): while folded chain crystals start appearing relatively early, they do not surpass ca. 10% crystallization even after $t_c \simeq 3$ h. Only after the appearance of extended chain nuclei does crystallization take off toward completion. This indicates that for the initial concentration used (3.85%) T_d of the folded form was initially sufficiently above 78 °C for nucleation and crystal growth to occur, while after only 10% of the alkane had crystallized, i.e., after the concentration decreased to ca. 3.5%, T_d was reduced sufficiently to cause virtual cessation of further chain-folded crystal growth. Thus, it should be noted that all dissolution temperatures quoted in the present work refer only to the 3.85% concentration used and cannot be taken as concentration independent. We plan to expand on this issue in a subsequent publication; the present note is intended merely to indicate the problem and qualify our definition of T_d.

Conclusion

The present work reaffirms the principal results on melt crystallization in the case of crystallization from solution, with several additions. Thus, the quantized variation of the dissolution temperature as a function of crystallization temperature corroborates the previously established quantized variation in fold length. Furthermore, crystal thickening (chain-folded to chain-extended transformations) is observed in solution, in contrast to the behavior of polyethylene where isothermal crystal thickening in solution never occurs. Most significantly, however, the minimum in crystallization rate with increasing supercooling was reaffirmed, in an even more conspicuous form than previously observed in melt crystallization. Thus, strong additional support is lent to the concept of surface "self-poisoning" apparently unique to chain-folded crystallization. The latter effect pertains both to primary nucleation and crystal growth but, as shown in the present study, to a greater extended to the former. This effect thus provides a unique insight into the crucial processes at the growing edge of a polymer crystal or nucleus with corresponding implications for theories of crystallization of long-chain molecules.

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Registry No. $C_{198}H_{398}$, 98812-29-4.

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Deconvolution of the Excess Heat Capacity of the Brill Transition in Nylon 66

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ABSTRACT: The Brill transition in nylon 66, crystallized from solution, is a small, diffuse endotherm extending between roughly 130 and 230 °C. We have been able to deconvolute the excess heat capacity in this region using established methods of statistical mechanics. As have been found for the unfolding transitions in several globular proteins, the data can be characterized by a model having two energy states within 5% of their fractions. The transition appears to involve a mass corresponding to about 25 chemical repeat units or about five stems in a folded-chain crystal. This is much smaller than the size of the crystals calculated from small- and wide-angle X-ray data.

Background of the Brill Transition

In 1942, Brill[1] reported that the two strongest peaks in an X-ray diffraction pattern from nylon 66, the (100) reflection and the (010,110) doublet, merge into a single peak at 160 °C. At this transition, the triclinic unit cell changes to a pseudohexagonal form. The latter is actually still

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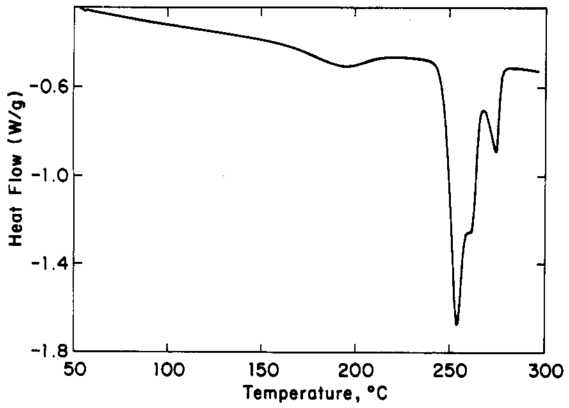

Figure 1. DSC Scan for nylon 66 crystallized from solution. Heating rate: 10 °C/min.

triclinic, but the projection on a plane normal to the c-axis is metrically hexagonal. The situation is most simply described in terms of the reciprocal unit cell parameters.

$$a^* = b^*, \qquad \gamma^* = 120°$$

In nylon 66, the hydrogen-bonded sheet corresponds to the (010) plane. The interchain separation in the hydrogen bond direction, $a \sin \beta$, is almost independent of temperature from room temperature to 250 °C.[2] The interchain separation between the hydrogen-bonded sheets, $b \sin \alpha$, is initially smaller but increases with temperature until the two separations become equal at the Brill transition. When nylon is quenched rapidly from the melt, only one strong peak is seen in a diffraction pattern taken at room temperature.[3] The triclinic pattern is resolved only after the material has spent some time in the pseudohexagonal form above the Brill transition.

The changes in the unit cell parameters and the corresponding changes in the volume of the unit cell with temperature[4] suggest a first-order thermodynamic transition. One would expect to find an endothermal peak in a DSC scan corresponding to a well-defined latent heat, but this is not usually found in samples crystallized from the melt. However, a broad endotherm has been observed in samples crystallized from a variety of solvents.[2]

A representative DSC scan is shown in Figure 1. A powder was formed by disolving nylon 66 in methanol under autogenous pressure and cooling in a shaker tube. The sample had been dried by heating for 15 min at 240 °C. The heating rate for this scan was 10 °C/min. In addition to the endotherm for the Brill transition centered at 192 °C, there appear to be three melting peaks at 254, 261, and 279 °C. Earlier work[2,4] has also shown evidence for two or more melting peaks. The total latent heat for the melting interval, 24.45 cal/g, corresponds to 54% crystallinity based on our previously determined heat of fusion of 45 cal/g for the crystalline phase.[4] The excess heat capacity for the Brill transition obtained by subtracting the base line from the DSC curve is plotted in Figure 2.

Deconvolution Procedures

Our procedures are derived from those of Freire and Biltonen[5,6] who used DSC data to characterize transitions in biopolymers such as the thermal unfolding of globular proteins.

Given a system having a reference state and n higher energy states, the partition function is

$$Q = 1 + \sum_{i=1}^{n} \omega_i \exp(-\Delta G_i/RT) \tag{1}$$

where ω_i is the degeneracy of the ith state and ΔG_i is its Gibbs energy in excess of that of the reference state.

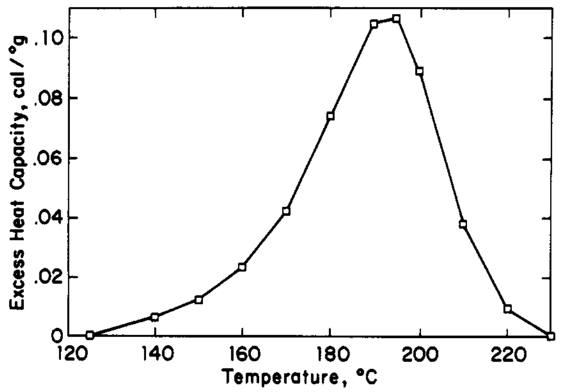

Figure 2. Excess heat capacity in the region of the Brill transition.

The fraction of units in the ith state is

$$F_i = \frac{\omega_i \exp(-\Delta G_i/RT)}{Q} \tag{2}$$

The excess enthalpy relative to the reference state is

$$\langle \Delta H \rangle = \sum_{i=0}^{n} \Delta H_i F_i = \frac{\sum_{i=0}^{n} \Delta H_i \omega_i \exp(-\Delta G_i/RT)}{Q} \tag{3}$$

where $\Delta H_i = (H_i - H_0)$ is the difference in enthalpy between the ith state and the initial state.

The excess enthalpy can be evaluated from the excess heat capacity, $\langle C_p \rangle$, which was found by subtracting the base line from a DSC curve.

$$\langle H \rangle = \int_{T_0}^{T} \langle C_p \rangle \, dT \tag{4}$$

The error from taking T_0, the temperature at which all units are in the reference state, as the point at which the DSC curve becomes tangent to the base line (rather than absolute zero) is very small. One must also consider whether there are differences in the heat capacities of the various states. If the base line is tangent to substantial segments of the DSC curve below and above the transition, this can be neglected.

Equation 1 can be rewritten in differential form as

$$d(\ln Q) = \frac{\langle \Delta H \rangle}{RT^2} \, dT \tag{5}$$

Thus, the partition function can be evaluated through numerical integration.

$$\ln Q = \int_{T_0}^{T} \frac{\langle \Delta H \rangle}{RT^2} \, dT \tag{6}$$

The fraction of units in the lowest energy state is given by

$$F_0 = \frac{1}{Q} = \exp\left(- \int_{T_0}^{T} \frac{\langle \Delta H \rangle}{RT^2} \, dT \right) \tag{7}$$

By analogy, the fraction in the highest energy state is given by

$$F_n = \exp\left(- \int_{T}^{T_n} \frac{(\Delta H_n - \langle \Delta H \rangle)}{RT^2} \, dT \right) \tag{8}$$

where ΔH_n is the overall enthalpy of the transition and T_n is the temperature at which all of the units are in the highest energy state. The fraction of units in intermediate states is thus

$$F_I = 1 - (F_0 + F_n) \qquad (9)$$

It happens to be the case (see below) that the Brill transition can be described quite well with the simplest construction, an essentially two-state model. When a transition is characterized by negligible populations of intermediate states, the quantity F_I is close to zero. Interestingly, this has been found to be a good approximation for the complex thermal unfolding transitions in globular proteins such as ribonuclease, lysozyme, chymotrypsin, cytochrome c, and myoglobin.[5-8]

A two-state transition will obey a simple van't Hoff relationship where

$$\Delta H_n = -R\frac{\mathrm{d}\ln(F_n/F_0)}{\mathrm{d}(1/T)} \qquad (10)$$

The fractions, F_0 and F_n, will also obey the following relationships:

$$F_0 = 1 - \frac{\langle\Delta H\rangle}{\Delta H_n} \qquad F_n = \frac{\langle\Delta H\rangle}{\Delta H_n} \qquad (11)$$

The version of eq 3 having only two terms, i.e., $i = 0$, n, leads to the following equation:

$$\langle C_p\rangle_{\max} = \frac{(\Delta H_n)^2}{4RT_{\max}^{\ 2}} - R \qquad (12)$$

where $\langle C_p\rangle_{\max}$ and $T_{\max}$ are the value and temperature of the maximum in the excess heat capacity. The second term in eq 12 is very small (less than 0.2% of the first term in the present case) and has been omitted in the literature.[6] This equality applies within about 5% for the thermal unfolding transitions in globular proteins.[6]

A special problem arises when one seeks to apply this treatment to synthetic polymers. Transitions involve quantities which are smaller than a molecule but larger than a repeat unit. The enthalpies and heat capacities in the previous equations are molar quantities while DSC presents these quantities on the basis of the sample weight. If c and h_n are the heat capacity and the enthalpy of the transition per gram

$$\langle C_p\rangle = cM \qquad \text{and} \qquad \Delta H_n = h_nM \qquad (13)$$

where M is the molecular weight of the characteristic quantity of the transition. By substituting these relationships in the simplified form of eq 12, one can obtain M.

$$M = \frac{4RT_{\max}^{\ 2}c_{\max}}{h_n^{\ 2}} \qquad (14)$$

If M is very small, $c_{\max}$ will also be small, and the transition will be very diffuse in temperature. This may be the reason why the Brill transition has usually not been recognized in DSC scans of samples crystallized from the melt.

Another approach is based on the recognition that the integrals in eq 7 and 8 will be equal when $F_0 = F_n = 0.5$. Having obtained these fractions as functions of temperature, a check for consistancy with the two-state model can be performed through eq 9–11 and 14.

It is, in general, very difficult to invert heat capacity data to reveal a complex series of energy states. However, the availability of several independent checks for a simple two-state system offers one some confidence in that case. It is thought that this approach should not be applied to typical melting processes in polymers because of the well-known complications due to superheating and/or partial melting and recrystallization. In the region of the Brill transition, on the other hand, the material seems to remain much closer to equilibrium.

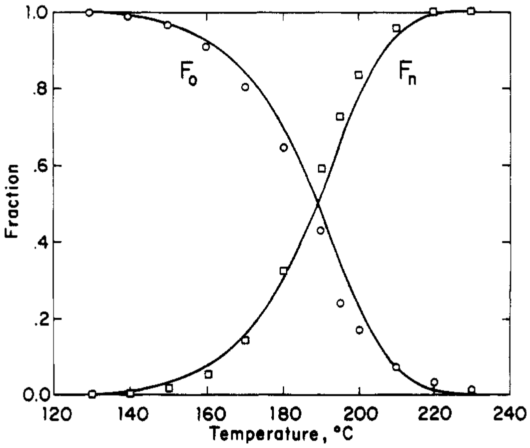

Figure 3. Dependence on temperature of the fractions of the low- and high-energy forms in nylon 66 in the region of the Brill transition. Points from eq 7 and 8. Line from eq 11.

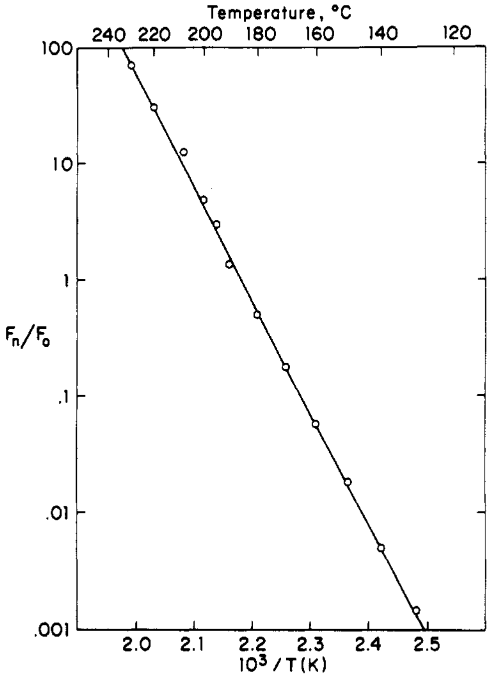

Figure 4. van't Hoff plot of the energy states of the Brill transition in nylon 66.

Application to the Brill Transition

The excess heat capacity had a maximum value of 0.1093 cal deg^{-1} g^{-1} at 465 K. Correcting for 54% crystallinity gives 0.2024 cal deg^{-1} g^{-1} for the crystalline phase. The latent heat of the transition was 7.834 cal g^{-1} for the crystal. Inserting these values in eq 14 gives $M = 5668$ which corresponds to 25 repeat units of molecular weight 226.

The fractions of the low- and high-temperature forms, F_0 and F_n, calculated from eq 7 and 8 using this value of M are plotted against temperature in Figure 3. The sum $(F_0 + F_n)$ remains equal to unity within 5% as was found for the thermal unfolding transitions in proteins.[5-8] The curves were plotted according to eq 11. They agree with the points to within 5% on the fraction scale and 2–3 °C on the temperature scale. These values of F_0 and F_n were used to construct the van't Hoff plot in Figure 4. The slope corresponds to ΔH_n = 43.8 kcal/mol and a value of M equivalent to 26 repeat units. Thus, by all tests, the

Brill transition appears to be characterized by two energy states and to occur in a space corresponding to about 25 chemical repeat units.

The Size of the Crystals in Nylon 66

Having shown that the elemental unit involved in the Brill transition contains about 25 chemical repeat units or 50 amide groups, it is of interest to compare this quantity with the size of the crystals.

The long period determined by small-angle X-ray diffraction on three samples crystallized from solution in methanol varied from 61 to 69 Å, corresponding to 5.0 ± 0.3 repeat units along the chain.[2] These results are consistent with those of Hinrichsen[9] who studied the dependence of the long period on the temperature of crystallization from solution. He reported 53-54 Å for crystallization temperatures of 60-130 °C, 55.5 Å for 140 °C, and 60 Å for 147 °C.

Estimates of the lateral dimensions can be calculated from the breath of the (100) and (010) peaks in the wide-angle diffraction pattern obtained for an earlier study using the Sherrer equation. This method gives minimum values because there may be other causes of broadening. The underlying amorphous diffraction is a complicating factor. The estimated sizes at room temperature are about 130 Å in the hydrogen bond direction and 85-125 Å normal to the hydrogen-bonded sheets, corresponding to widths of 29 and 23-34 chains, respectively. Above the Brill transition, there is a single, relatively sharp peak in this region which becomes more narrow as the temperature is increased. The apparent crystal size increases from 170 Å or 40 chain widths at 202 °C to 290 Å or 68 chain widths at 240 °C. Thus, it can be estimated that the number of repeat units in a crystal is of the order of 4000 at room temperature and much more at higher temperatures. The important point is that it is much larger than the active quantity of 25 repeat units deduced by deconvoluting the excess heat capacity for the Brill transition. This means that the transition does not involve a cooperative motion of an entire crystal but only a quantity equivalent to about five stem segments traversing the relatively thin nylon crystals. We conclude that the Brill transition occurs point by point involving small groups of adjacent stems.

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Registry No. Nylon 66, 32131-17-2.

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Synthesis and Characterization of Poly(methylphenylphosphazene)-*graft*-polystyrene Copolymers[1]

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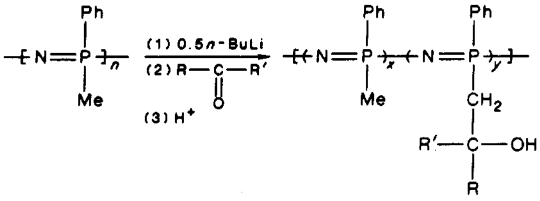
ABSTRACT: The polymeric anion formed by the deprotonation of poly(methylphenylphosphazene) was used to initiate the anionic polymerization of styrene to form new polyphosphazene-*graft*-polystyrene copolymers with compositions ranging from 65 to 90% polystyrene. These new materials were characterized by elemental analyses, ^{1}H and ^{31}P NMR spectroscopy, dilute solution techniques (size exclusion chromatography, membrane osmometry, and viscosity), and thermal analysis (differential scanning calorimetry and thermal gravimetric analysis).

Introduction

While the preparation of block and graft copolymers comprised of very different polymers has been widely used in organic polymer chemistry to develop new materials with optimum properties, relatively few copolymers have been reported that contain the class of inorganic polymers known as polyphosphazenes, $[R_2P{=}N]_n$. Polyphosphazenes have a number of useful properties, such as flame retardancy and unusual thermal and radiation stability, that could substantially enhance more commonly used organic materials and are, therefore, useful candidates for block or graft formation. Some work has been directed toward the preparation of polyphosphazene/polysiloxane graft and block copolymers,[2] and a recent paper[3] reports the preparation of polystyrene/polyphosphazene grafted systems using a radical initiation process. These reports have made use of ring opening reactions of $[Cl_2P{=}N]_3$ or poly(aryloxyphosphazene) products of the ring opening/substitution method.

Recent work in our laboratory[4] has demonstrated that the deprotonation of a polyphosphazene prepared by a condensation polymerization, $[Ph(Me)P{=}N]_n$,[5] is easily accomplished by treatment with BuLi. Subsequent quenching of the resulting anion sites along the polymer backbone with various electrophiles (e.g., eq 1) has pro-



$$[N{=}P(Ph)(Me)]_n \xrightarrow[(3)\ H^+]{(1)\ 0.5n\text{-BuLi};\ (2)\ RC(O)R'} [(N{=}P(Ph)(Me))_x(N{=}P(Ph)(CH_2C(OH)RR'))_y] \quad (1)$$

duced several new derivatized polyphosphazenes in which

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