Nano-Structured, Semicrystalline Polymer Foams

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SYNOPSIS

Semicrystalline polymers gelled from thermally quenched semidilute solutions can, in some cases, be supercritically dried to produce nano-structured foams of exceedingly high specific surface area. This article investigates the nano-morphology of these semicrystalline foams. The common morphological feature that these systems display in small-angle scattering can be described by uncorrelated lamellar platelets. The morphological details, which can be obtained using microscopy and small-angle scattering, indicate that these low-density systems occupy a morphological niche between polymeric crystallites from dilute solutions, and spherulitic crystals derived from concentrated solutions and melts. Because these crystalline morphologies occur in concentration ranges between dilute and concentrated, they may offer simple insight into the mechanisms available for distortion of ideal, dilute-solution-derived crystallites as polymer concentration is increased. Several mechanisms for the observed distortions are proposed. © 1996 John Wiley & Sons, Inc.

Keywords: nano-structured foams \bullet semicrystalline polymers \bullet small-angle scattering \bullet platelet model

INTRODUCTION

This article pertains to an overview of the structure of low-density polymer foams produced from semicrystalline polymer gels using supercritical solvent extraction. The focus of this article is to compare the morphology in several systems in order to argue that all of these systems have as their morphological basis uncorrelated lamellar crystallites. In some cases, particularly in some olefin foams, this is without a doubt the case as evidenced by electron micrographs, as discussed below. It is believed that a treatment of these systems as a class can elucidate such a morphological basis over currently held views that some of these systems, particularly polyacrylonitrile (PAN) and isotactic polystyrene (IPS) foams, are based on domains of liquid-liquid phase separation that aggregate into, or are initially formed as mass-fractal morphologies similar to inorganic aero- and xero-gels. Such mass-fractal morphologies are certainly the basis of some amorphous polymer foams such as the resorcinol-formaldehyde (RF) foams.

Nano-structured, low-density polymer foams were developed in the early 1990s for several technological uses such as precursors to low-density battery electrodes and targets for fusion reactors.¹⁻ ⁶ The systems most intensely studied were isotactic polystyrene (IPS) and polyacrylonitrile (PAN), both of which are known to display significant degrees of crystallinity. In the production of these nano-structured foams, thermal quenching of semidilute polymer solutions in conventional solvents leads to gelation. If the gels are dried from these conventional solvents either a powder (from fast drying) or a collapsed solid (from slow drying) result. In parallel work on sol-gel-based silicates (et seq.),^{6,7} the collapse of nano-porous morphologies in conventional solvents was overcome by solvent exchange with supercritical solvents, namely, supercritical CO₂. Because supercritical fluids do not have surface tension, solvent removal does not lead to nano-pore collapse and monolithic silica with densities close to that of air can result. The same supercritical solvent

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exchange route was adapted to produce aerogel-like, nano-scale polymer foams in IPS, PAN, isotactic polypropylene (IPP), and a number of other olefinbased systems.

There are inherent disadvantages to the solvent exchange route in industrial scale-up.⁹ One way to alleviate this situation is to gel the semidilute polymer solution in a supercritical solvent.⁹⁻¹⁵ Ehrlich et al.⁹⁻¹⁵ used supercritical propane and a variety of olefin based polymers to produce nano-structured foams in this way. Mandelkern and collaborators, among others, have also made significant contributions to this area.¹⁶⁻¹⁹

In addition to semicrystalline nano-structured foams, amorphous organic foams have been produced using chemical crosslinking^{6,20,21} and supercritical solvent exchange. Pekala et al.^{7,20,21} introduced the resorcinol-formaldehyde system for these studies and has produced nano-structured foams of high surface area using this approach. The morphology of these systems resembles more closely that of the silica aerogels mentioned above.

At least two paradigms for the morphology of nano-structured, semicrystalline foams currently exist:

1. A mass-fractal model, which is related to liguid-liquid phase separation and perhaps aggregation, leading to a ramified network/ cluster morphology. This model is essentially based on the structure of the RF foams and silica aerogels. Aerogels are wet gels that have been supercritically dried and are usually composed of inorganic materials such as silica.⁷ (Xerogels are similar gels dried by normal evaporation.) Silica based aerogels, on a nano-scale, are well described by mass-fractal models in which primary particles of close to 50 Å in diameter form loosely branched aggregates with close to 20 primary particles per aggregate.^{6,7} Mass-fractal models describe these ramified morphologies both in gels,²² in xerogels and in supercritically dried aerogels.^{6,7} Similar nano-scale morphologies are seen in xerogels rapidly dried from normal solvents. Xerogels are typically powders, whereas aerogels are typically monoliths. In addition, mass-fractal morphologies are known in pyrolyticly produced fumed silica and other silicates and titanates formed in nonequilibrium processes.⁷ No clear mechanism for the formation of mass-fractal morphologies in semicrystalline foams has been proposed in the literature.

2. A model based on uncorrelated, lamellar platelets, which form a niche between dilute solution crystallized polymer platelets and melt crystallized spherulites. This article presents arguments in support of this second model for the entire class of semicrystalline, nano-structured foams.

While the amorphous, RF based foams of Pekala and co-workers fall directly into the line of massfractal based nano-morphologies,^{6,20,21} the morphologies of the semicrystalline gelled systems are somewhat more perplexing. The initial understanding of these morphologies was based on several facts. (1) Micrographic evidence for the first systems extensively investigated, PAN and IPS, failed to display conventional crystalline features.¹⁻⁶ (2) Smallangle scattering failed to display a long-period peak corresponding to the expected correlation between lamellar units.⁶ (3) The extensive studies of silica based aerogels and RF-based polymer foams indicated that the morphological details of these systems might be based on mass-fractal morphologies. (4) The initial systems studied appeared to display liquid-liquid phase separation.¹⁻⁶

Aubert^{1-3,16,17} proposed that the morphology in these semicrystalline systems on a micron to submicron scale fell into the conventional liquid-liquid phase separation category. Spinodal-like morphologies were reported, under certain solvent and quench conditions, which Aubert associated with spinodal decomposition between polymer-rich and solvent-rich domains. Additionally, spherical domains could also be produced, which Aubert associated with nucleation and growth domains. Aubert's "phase diagram" displayed the expected symmetry associated with liquid-liquid phase separation. The issue of the significant crystallinity in these systems, measured by XRD and DSC, was explained as a secondary feature that occurred after the primary micron to submicron morphology was defined. In some cases, Aubert's nucleation and growth domains displayed features that resembled crumpled paper.

At the opposite extreme, work on high-density polyethylene $(HDPE)^{9-15}$ gelled in supercritical propane displayed quite a different morphology from that of PAN and IPS. In HDPE foams, there was strong microscopic evidence for crystalline-driven phase separation, which resulted in extremely large lamellar platelets clustered in spherical domains. In this work there was some evidence for correlations between the lamellae from HDPE foams. Foams of ultrahigh molecular weight polyethylene (UHMWPE) formed in supercritical propane also displayed clear lamellar domains. The lamellae in PE foams displayed extensive distortions under certain solvent/quench conditions. These were associated with spherical tertiary structures (micron-scale) such as spherulites rather than with nucleation and growth domains of Aubert's liquid-liquid phase separation model. More recently, Ehrlich and Stein have produced gels and foams in isotactic polypropylene, IPP. This system results in spherical domains that resemble the "nucleation and growth" domains reported by Aubert in IPS and PAN.

The dominant morphological evidence presented to date on these systems involves microscopy. In the PE foams this has lead to unequivocal support of a lamellar model. Microscopy has been less successful in other systems such as IPS, PAN, and IPP, where more complicated, overlapping and finer features are present. For these systems a technique, such as small-angle scattering, which probes 3D structure is more appropriate. Scattering probes morphological scaling over a wide range of size scales. Distinct transitions between regimes of structure have lead to the concept of "structural-levels." In scattering, a structural level corresponds to a regime of exponential decay in intensity and an associated powerlaw regime. In this article the crystalline morphology of polymers will be discussed in terms of these levels of morphology using the unified equation.^{20,22,23-27} A lamellar platelet is described, in this approach, by two structural levels. The smallest pertains to the lamellar thickness and the Porod surface scattering regime. The largest pertains to the overall lamellar size and the two-dimensional scaling regime between the lamellar thickness and overall size.

The unified equation,²³⁻²⁷ (1), presents four general parameters for each level of structure in a material. These parameters can be specified according to morphological details as assumed in a model for the system that may be based on micrographs. The unified function is given by²³⁻²⁵

$$\begin{split} I(q) &\approx \sum_{i=1}^{n} \left(G_{i} \exp\left(\frac{-q^{2} R_{gi}^{2}}{3}\right) \right. \\ &+ B_{i} \exp\left(\frac{-q^{2} R_{g(i+1)}^{2}}{3}\right) \left(\frac{1}{q_{i}^{*}}\right)^{P_{i}} \right), \quad (1) \end{split}$$

where the summation is over the number of structural levels in a material. Here, level 1 is the largest structural level. There are four free parameters for each level of structure in the most general case, the contrast factor, G_i , the radius of gyration, R_g , the power-law prefactor B_i , and the power-law slope $-P_i$. For lamellar platelets the contrast factor for the largest level,^{28,29} level 1, is $I_e N V^2 \Delta \rho^2$. I_e is the scattering factor for a single electron, N is the number of platelets in the scattering volume, V is the volume of a platelet which for a circular platelet is $\pi R^2 t$, $\Delta \rho$ is the electron density difference between the platelet and the matrix material. If the platelets are somewhat concentrated but not regularly arranged, G_1 will also include a function of the form $\phi_p(1-\phi_p)$, where ϕ_p is the volume fraction of platelets.²⁸ G_1 can be taken as a free parameter for the platelet fit or it can be calculated. Here it is used as a free parameter. For the largest structural level of a disk platelet of radius R and thickness t, R_{g1} is defined as³⁰

$$R_{g1}^2 = \frac{R^2}{2} + \frac{t^2}{12} \,. \tag{2}$$

 B_1 for the 2D regime between R_{g1} and the thickness is given by $^{\rm 23-26,28}$

$$B_1 = \frac{2G_1}{R^2} \,. \tag{3}$$

For the first structural level, P_1 is 2 for the 2D level.²³⁻²⁵

For the second structural level, the platelet thickness level, G_2 is given by²³⁻²⁷

$$G_2 = G_1 \left(\frac{t}{2R}\right)^2. \tag{4}$$

 R_{g2} for the platelet thickness level is given by t/2.^{23–27,28} Assuming that the platelet has smooth sharp interfaces, $P_2 = 4$ following Porod's law.^{28,29} Porod's law also describes B_2 as^{28,29}

$$B_2 = 2\pi I_e N_2 \rho^2 S = 4G_1 \frac{(t+R)}{(t^2 R^3)}, \qquad (5)$$

where ρ is the electron density of a platelet, and S is the surface area of a platelet. Equations (2) to (5) describe all eight general parameters in the unified platelet model in terms of G_1 , t, and R.

For randomly arranged platelets an exact calculation using an integral equation²⁸ is possible and can be compared with eqs. (1) to (5) (Fig. 1). For both calculations three parameters are used: G_1 , R, and t. In the integral calculation, monodispersity in thickness leads to structural oscillations in the scattering pattern at high-q. The average features of the



Figure 1. Comparison of an integral calculation for a platelet and the unified function using the same three parameters. Oscillations in the parallelipid calculation at high-q are due to monodispersity in the thickness. Generally, sample thicknesses are sufficiently polydisperse to not display these oscillations.

integral calculation are evident in the unified calculation. Absent are the high-q oscillations, which are due to monodispersity of the platelet thickness. Because the exact calculation involves an integral, and because of the oscillations at high-q, it is difficult if not practically impossible to use this function to fit data using a least-squares minimization. The unified function can be easily used to fit data modeled as randomly arranged platelets. The unified calculation is more representative of real systems because the oscillations at high-q are usually absent from experimental data due to polydispersity in thickness.

The platelet model, described above, is generally limited to randomly distributed platelets. Correlation of platelets leads to the long-period peak commonly observed in SAXS from melt crystallized polymers. Such correlations can be accounted for in this approach if they are observed.²³⁻²⁷ Long-period correlations are absent from scattering in the nanostructure polymer foams investigated here. Disorganized, concentration effects, in these semidilute systems, can be accounted for in the contrast factor G_1 , as mentioned above.

A number of scattering instruments with different q-ranges must be used to fully describe complex morphologies over a wide range of size. In investigating nano-structured foams, combined data from SALS, USAXS, SAXS, and XRD has been used, as

well as complementary SANS experiments to obtain a "structural-spectrum" over up to seven orders in size. Through comparison with microscopic evidence, certain scattering features are associated with structural levels in scattering. Additionally, comparison between different semicrystalline systems can be used to determine trends in morphological features which can indicate unknown features.

RESULTS/DISCUSSION

Figure 2 contains data from a nano-structured, semicrystalline PAN foam, which shows the available range of q using conventional scattering instruments. At low-q, 0.00001 to 0.005 Å⁻¹, small-angle light scattering (SALS) reflects micron-scale structures, which in this case correspond to "struts" associated with "spinodal" features by Aubert.¹⁻³ At intermediate q, 0.0005 to 0.001 Å⁻¹ ultrasmall-angle x-ray scattering (USAXS) reflects a 2D morphology between the lamellar platelet's overall radius of gyration, R_g , and the thickness of the platelet. At highq, 0.001 to 0.6 Å⁻¹ conventional small-angle x-ray scattering (SAXS), describes the platelet thickness and the Porod regime for the surface scattering of the platelets. At highest q, 0.6 to 10 Å⁻¹, x-ray diffraction (XRD) describes the substantial degree of crystallinity in these PAN samples. The unified fit



Figure 2. Scattering data from polyacrylonitrile foam. SALS, USAXS, SAXS, and XRD data. SALS data has been scaled to match the intensity of the USAXS curve. Others are in absolute intensity. For the 3 parameter fit t = 86 Å and R = 1953. Portions of the combined data set were previously published.²³

in Figure 2 (dashed curve) is based on three parameters, the thickness, lateral dimension, and contrast factor for the platelet model. This fits the data over three decades of q with XRD features dominating at highest q and the micron strut morphology dominating at lowest-q. The strut morphology can be included in this fit as shown with the solid curve, but this introduces three additional parameters associated with a third structural level in (1). These added parameters are not necessary, because the strut morphology can often be observed in the optical microscope.¹⁻³

Lozenge-crystallites formed in dilute solution are considered an ideal structure that is modified under semidilute conditions.^{31,32} Such lozenge-crystallites display 2D scaling between the lamellar thickness and the lateral dimension of the lamellae and no large-scale, tertiary structures. The PAN foam of Figure 2 is morphologically similar to dilute solution crystallites except for the large-scale (low-q) tertiary structure. In all lamellar crystallites, the lamellar thickness is thermodynamically governed by asymmetry between surface energies of the chain fold and lateral crystallite faces according to Hoffman-Lauritzen theory.^{33,34} A thermodynamic balance between the energy of crystallization and these surface energies leads to an inverse relationship between the lamellar thickness and the quench depth. The thickness of lamellar crystallites, from the Hoffman-Lauritzen Theory, is generally between 50 and 150 A for typical quench depths. The lateral dimension of dilute solution crystallites is only limited by the local availability of polymer in the dilute solution and extremely large aspect ratios (100 to 1000) are commonly observed. The thickness of the PAN crystallites from the fit in Figure 2 is 86 Å, which is conventional. The aspect ratio of 45 is similar to dilute solution crystallites but slightly lower. This might be due to slower diffusion, the presence of entanglements, or a smaller screening length for enthalpic interactions, as discussed below.

Melt crystallized polymers can be considered the opposite extreme of lamellar growth. The nanostructured PAN foam, of Figure 2, can be compared with the morphology for a melt crystallized polymer (Figure 3). In Figure 3, data for melt-crystallized HDPE shows several striking differences with the data for the PAN foam. First, the long-period stacking peak at $q \approx 0.025$ Å⁻¹ in Figure 3 is completely lacking in Figure 2. The thickness Guinier regime and following Porod regime are present in both Figures 2 and 3. In Figure 3, this corresponds to the weak knee at ≈ 0.07 Å⁻¹ and above. (The stacking peak corresponds to stacking of the lamellar thick-



Figure 3. Scattering data for conventional melt crystallized polymers, HDPE with fibrillar, and platelet secondary morphologies.

nesses so that the peak occurs to the left of the thickness Guinier knee in the scattering plot, i.e., the packing distance is by definition larger than the thickness which is correlating.) The power-law regime between the overall lamellar size and the thickness shows variability in conventional melt crystallized HDPE between -1 for fibrillar lamellar bundles and -2 for 2D platelets. In Figure 2 only a 2D morphology is observed. A similar 2D morphology has been observed in micrographs for dilute solution crystallized polymers.^{31,32} The micron scale structure is spherulitic in Figure 3 and is a prominent feature of the data at low-q. A corresponding tertiary structure is less prominent in the PAN foam of Figure 2 and displays some degree of flexibility in its details for these systems.¹⁻³ The XRD regime at very high q is similar for Figures 2 and 3, indicating semicrystalline morphologies with a significant degree of crystallinity in both cases.³⁵

The morphology of nano-structured semicrystalline foams can be considered a distortion of ideal, dilute-solution crystallites discussed above. It is expected that some systematic constraints lead to distorted crystalline morphologies in both semidilute and concentrated (melt crystallized) systems:

1. The lateral dimension of lamellar crystallites in melt crystallized polymers is thought to be limited by a balance between the diffusion rate (and concentration) of noncrystallizing components in the melt and the crystalline growth rate. In concentrated systems, the

concentration of noncrystallizing components can be different in different growth directions as crystallization progresses leading to asymmetric growth, e.g., fibrillar growth, Figure 3 power-law -1. In some cases this situation can be mitigated leading to 2D growth, Figure 3 power-law -2. This kinetic balance is described by Keith and Padden theory.^{36,37} The Keith and Padden "\delta"-parameter describes a limiting size-scale for lateral growth, $\delta = D/G$ where D is the diffusion coefficient for noncrystallizing components and G is the linear, crystalline, growth rate. The noncrystallizing components may be chain branches, noncrystallizable chains or simply dirt in the melt state. Keith and Padden's diffusion theory can give some insight into the mechanism for asymmetric fibrillar growth in melt crystallized polymers, as well as symmetric limitations of lateral growth in nano-structured foams.

- 2. On increasing the concentration above the critical overlap concentration, 38,39 entanglements between chains are expected to become a constraint on crystallite growth. The state of entanglement is not expected to effect equilibrium thermodynamic considerations but will have a dramatic effect on kinetic phenomena. Because of this, entanglements are not expected to effect the Hoffman-Lauritzen thickness but may dramatically effect the Keith-Padden dimension, $^{31,32,36,37} \delta$, as well as the degree of constraint on lamellae, which may lead to distortion on drying. The extreme degree of entanglement present in the melt, coupled with highly asymmetric lateral growth, may play some role in regular stacking of lamellae which leads to the long period peak of Figure 3.
- 3. On increasing the concentration in a polymer solution from dilute to the semidilute regime enthalpic interactions that drive crystallization are expected to become limited to a shorter range due to screening.^{38,39} For the concentrated regime and for polymer melts this limiting length for interactions is close to the size of a monomer unit. Different morphologies might be expected to result from this change in the screening length. In general, finer features might be expected to result from a decreasing screening length with increasing concentration.
- 4. The regime of crystallization^{40,41} will play an important role in the development of mor-

phology in semidilute solutions. At the current time, data on the growth rates in semidilute solutions is insufficient to give a detailed analysis of the regime of crystallization, and here it is assumed that all growth occurs in regime II, for simplicity, although this certainly is an important feature for further investigation. Additionally, because conventional spherulitic morphologies are not present, a new description of the growth regime equations might be required. In general, all quench depths are at an intermediate level that supports the assumption of regime II growth.

The nano-structured, semicrystalline foams, investigated here, can be categorized as to mechanisms for distortion of ideal, dilute-solution crystallized:

Thick (Non-Hoffman-Lauritzen), Semicorrelated Lozenges of Conventional Aspect Ratio

The HDPE foams produced by Ehrlich et al.⁹⁻¹⁵ in supercritical propane display extremely large platelets that organize into spherical, tertiary structures. Some degree of lamellar stacking can be seen in the excellent micrographs of Ehrlich.9-15 The large and symmetric lateral lamellar radius, R, for these systems may be a result of a high diffusion coefficient for impurities, which leads to a large δ . Low degree of entanglements may play a role in the loose stacking of lamellae in Ehrlich's spherical structures. The thickness of these lamellae is much larger than the expected range for Hoffman-Lauritzen thickness^{33,34} mentioned above. The scattering patterns from HDPE foams have not been investigated because there is clear evidence of the morphology from microscopy.

UHMWPE foams are similar to the HDPE foams and gels but display contortion of the lamellae so that they are not perfect platelets. Accordingly, the unified fit of Figure 2 does not work well with UHMWPE samples (Fig. 4). The slope in the structural-scaling regime is steeper than -2 indicating a higher dimension than that of flat platelets. Because the gels in supercritical propane could not be observed using scattering it is not clear if this crumpling distortion of the platelets occurs on supercritical drying or is a feature of the crystallization process in semidilute conditions. Evidence from the IPS foams, below, indicates that crumpling distortions may be related to the drying process even under supercritical conditions. The crumpling distortion may



Figure 4. Attempt to fit data from UHMWPE foam from supercritical propane using a 2D platelet model. Micrographs display extremely large crumpled platelets organized into microscale spherical tertiary structures. For the fit t = 354 Å, which agrees with micrographs. XRD peaks are seen at high-q.

be related to a higher degree of entanglement in UHMWPE when compared with HDPE. The scattering data shows no indication of correlations for these crumpled lamellae, i.e., no long period peak near the thickness R_g . Although these platelets are of extremely large thickness, 350 Å in Figure 4, they display close to conventional aspect ratios of between 40 and 50 when compared with platelets from dilute solution crystallization. The mechanism for large platelet thicknesses is not clear. Chain folding may be difficult due to entanglements leading to reduction in the asymmetry of crystallite surface energies.

Conventional (Hoffman-Lauritzen) Thickness, Uncorrelated Lozenges with Small Aspect Ratios

Several of the semidilute crystallized polymer foams and gels display Hoffman–Lauritzen thicknesses^{33,34} with small aspect ratios for 2D nano-morphologies. Because these platelets are 2D it is believed that diffusion is not a critical issue in the distortion of these lamellae. The clearest case of this type distortion occurs in the isotactic polypropylene (IPP) foams produced by Ehrlich, Stein et al.⁹⁻¹⁵ Micrographs of these foams show a tertiary structure of $\approx 10 \ \mu m$ diameter spheres but micrographic indication of the presence of lamellae within these spheres is weak. The spheres appear to display a



Figure 5. IPP foam from supercritical propane. For the Platelets: t = 108 Å, R = 208 Å. The Tertiary structure in the fit correlates with 0.5 μ m diameter spheres.

convoluted morphology with no indication of stacking between these convolutions. Figure 5 shows a typical scattering pattern from the IPP foams fit with the three-parameter platelet model. The thickness of 108 Å is typical for a Hoffman-Lauritzen thickness in this system. The aspect ratio in the absence of Keith-Padden restrictions is extremely small with an estimated circular diameter of 400 Å. This may indicate accommodation of the weak en-



Figure 6. Semidilute IPS gel in decalin. High-q peak reflects the liquid structure of decalin in the XRD regime. The fit uses three parameters with t = 65.2 Å and R = 327 Å. Data is over a smaller range of q than Figure 5.



Figure 7. Comparison of the same IPS gel and the corresponding supercritically dried foam. Increase in the slope of the 2D regime indicates densification of the structure. Foam data was previously published.²³

tanglements present in this system through small aspect ratios.

Similar to the IPP foams, gels of IPS in decalin display Hoffman-Lauritzen thicknesses with small aspect ratios. Figure 6 shows the scattering pattern from a typical case of these small aspect ratio platelets. The aspect ratio for this case is about 10, which is small compared with conventional dilute solution crystallized platelets reflecting the possibility of weak entanglement-interference with the lateral growth of lamellae. Although the platelets observed in IPS gels display similar morphology to those in IPP the supercritically dried foams display a highly distorted morphology (Fig. 7). Although the foam displays a similar platelet thickness, second Guinier knee, the scaling regime at sizes larger than this thickness (lower-q) is steeper indicating a densification of the structure. UHMWPE samples similarly display a denser state and a stronger slope for microscopically demonstrated crumpling. Crumpling appears to lead to partial lamellar collapse into a more compace (higher dimensional) condition as discussed theoretically by Nelson.42-45 In both IPS and UHMWPE samples surface tension is not expected to play a role in this crumpling distortion because supercritical fluids have no surface tension. It may be that there is some relationship between the inherent resistance of the lamellae to distortion, i.e., a lamellar modulus, and the extent of chain entanglement which drives the distortion. These issues must be resolved in a more careful study of the

mechanisms behind this lamellar crumpling distortion. From a crystallization perspective, IPS and IPP display a similar distortion mechanism in semidilute conditions. That is, they both display Hoffman-Lauritzen thicknesses with very low aspect ratios and symmetric lateral growth.

Hoffman-Lauritzen Thickness, Uncorrelated Lozenges of Conventional Aspect Ratio and Tertiary Structures

The final general case observed for crystallization distortions in semidilute conditions pertains to polyacrylonitrile (PAN) gels and foams, which have been extensively studied by Lagasse and Aubert.¹⁻⁶ Strut and ball morphologies are shown in Figures 2 and 8, respectively, as discussed above. The base morphology matches the lamellar model extremely well in both the gels and the supercritically dried foams for PAN systems (Figs. 2, 8, and 9). The thickness is 86 Å in Fig. 2 and the diameter is close to 3900 Å yielding a somewhat small, but close to conventional, aspect ratio of 45. The ball morphology of PAN foams displays similar fits with enhanced tertiary structural scattering at low q (Fig. 8). The Porod prefactor at high-q yields the specific surface area for these foams, which agrees closely with gas absorption measurements using BET theorv. about 300 m^2/g .

PAN gels (Fig. 9) can be investigated using neutron scattering and deuterated solvents. This data



Figure 8. PAN foam with Ball Morphology. Unified Platelet fit yields t = 121 Å, R = 2,700 Å. For a spherical ball tertiary structure the diameter of the balls is $0.76 \,\mu$ m. Portions of the combined data set were previously published.²³



Figure 9. PAN gels in deuterated solvents and PAN foam display similar morphologies. This indicates that there is little distortion on supercritically drying the PAN gels.

the foams is essentially identical to that of the gels from which they are supercritically dried (Fig. 9).

CONCLUSIONS

Nano-structured polymer foams can be made from semidilute polymer solutions via chemical crosslinking, such as in the RF aerogels of Pekala and co-workers,^{5,6} or via crystallization. The nanostructural details of these two types of systems are distinct and can be studied using scattering combined with microscopy. This article details the nanoscale morphological features that are observed when semicrystalline polymers are crystallized under semidilute conditions in the production of nanostructured polymer foams. Trends in the morphology of these systems has led to a generalized characterization based on uncorrelated lamellar platelets. Scattering data that span many decades in size can be fit with three parameters using this approach, the platelet thickness, t, the platelet lateral radius, R, and a contrast factor, G_1 . The surface area is of primary importance to these materials and the lamellar model yields a direct means of calculating the specific surface area (this will be detailed in later publications). Several general means of distorting the ideal crystallite morphology seen in dilute solution crystallization are observed in these systems: (a) thick (non-Hoffman-Lauritzen), semicorrelated lozenges of conventional aspect ratio: HDPE and UHMWPE from supercritical propane; (b) conventional (Hoffman-Lauritzen) thickness, uncorrelated lozenges with small aspect ratios: IPP and IPS gels; and (c) conventional (Hoffman-Lauritzen) thickness, uncorrelated lozenges of conventional aspect ratio: PAN foams and gels.

It is proposed that the semidilute condition removes constraints on crystallite growth seen in melt crystallized morphologies due to the Keith-Padden dimension, δ , allowing 2D growth. In most cases, except (a) above, the Hoffman-Lauritzen thickness is observed, so lamellar folding mechanisms are generally at play. It is believed that the primary mechanism for distortion from the dilute model is the slight amount of entanglements that are present under semidilute conditions. It has been proposed that a manifestation of these weak entanglements are restriction of lateral growth, as evidenced by small but symmetric aspect ratios, distortion of the lamellae into higher dimensional forms (UHMWPE, IPS), and in some cases failure of the lamellae to follow Hoffman-Lauritzen thickness laws (HDPE, UHMWPE).

Clearly, much work remains to be done on elucidating the mechanisms for crystallite distortion in semicrystalline polymers. It is hoped that this work will serve as a starting point for further studies in this regard. Several unanswered questions are obvious from this work, particularly pertaining to the universal absence of lamellar stacking in the semidilute crystallized polymers studied. Additionally, the fate of the amorphous component would appear to be critical to the accurate calculation of surface area of these materials, although, at least in the PAN foams the amorphous component does not seem to play a role in determination of the surface area.

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