hexane (A) and -1-hexadecyne (B), which are the first examples of block copolymerization of substituted acetylenes.

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Registry No. $MoOCl_4$, 13814-75-0; Bu_4Sn, 1461-25-2; EtOH, 64-17-5; $ClC{\equiv}C(CH_2)_5CH_3$ (homopolymer), 100858-77-3; $ClC{\equiv}C(CH_2)_3CH_3$ (homopolymer), 100858-76-2; $ClC{\equiv}C(CH_2)_7CH_3$ (homopolymer), 100858-79-5; $ClC{\equiv}C(CH_2)_{13}CH_3$ (homopolymer), 108711-62-2; $ClC{\equiv}CPh$ (homopolymer), 81953-16-4; $(ClC{\equiv}C(CH_2)_{13}CH_3)(ClC{\equiv}C(CH_2)_3CH_3)$ (block copolymer), 121029-94-5.

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Starlike Micelles: Their Growth in Homopolymer Solutions

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Diblock copolymers may be considered as the macromolecular counterpart of ordinary, "monomeric" surfactants. Yet, polymeric surfactants exhibit features having no direct analogue among monomeric surfactants. In the following we focus on one such trait. It concerns the behavior of micelles formed by *neutral* diblock copolymers in a selective solvent of low molecular weight. In particular, *addition of homopolymer* to certain types of micellar solutions results in an increase of the average aggregation number. This effect involves only *starlike micelles*, i.e., micelles endowed with extended coronas. Micelles having thin coronas are not affected. This phenomenon is somewhat reminiscent of the effect of added electrolyte on the size of micelles formed by charged monomeric surfactants.[1] It has, however, no analogue among micelles consisting of neutral, low molecular weight amphiphiles.

Consider micelles formed by flexible A-B diblock copolymers consisting of N_A A monomers and N_B B monomers. The micellization takes place in a highly selective low molecular weight solvent, that is, a good solvent for the A blocks but a poor one for the B blocks. The micelles thus formed are spherical, comprising two concentric regions: An inner core, consisting of immiscible B blocks in a meltlike state, and an outer corona of soluble A blocks swollen by the solvent. For a highly selective solvent the A-B junctions are localized at the sharp core-corona boundary. In effect both A and B blocks are thus grafted to the interface, i.e., attached to the surface by an end group only. This is an important point, as the deformations resulting from dense grafting play a central role in the determination of the micelle's equilibrium structure. For solutions well past the critical micelle concentration (cmc) but prior to the onset of micelle overlap, micellar properties are determined by F, the free energy per chain of a single micelle. F of a micelle consisting of f A-B coils is calculated with respect to the free energy of a free, nonaggregated chain. We approximate F as a sum of three contributions due to the core, the corona, and the interface between them:[2,3]

$$F/kT = (\gamma a^2/kT)f^{-1/3}{N_B}^{2/3} + f^{2/3}{N_B}^{-1/3} + f^{1/2}\ln{(R_{core} + L)/R_{core}} \quad (1)$$

The first term, $F_{interface}$, is the free energy per chain associated with the core-corona interface. For a melt of B blocks the core volume scales as fN_Ba^3 where a is a characteristic monomer size. The core surface area is accordingly proportional to $f^{2/3}{N_B}^{2/3}a^2$, thus leading to $F_{interface}$ as given. γ, the associated surface tension, is independent of f and N_B for highly selective solvents. As this term is a decreasing function of f, it favors micellar growth. However, the incorporation of extra chains in the micelle results in an increase of the grafting density and in stronger deformations of the grafted blocks. The accompanying free energy penalties arrest the aggregation process. Two such penalties are involved, F_{core} and F_{corona}, due, respectively, to the deformations of the core and coronal blocks. The second term in (1) is due to F_{core}. To obtain a core of radius R_{core} larger than ${N_B}^{1/2}a$, it is necessary to stretch some of the B blocks. This follows because the B blocks are grafted and subject to a constant density constraint, i.e., the necessity to "fill" the core's center. The associated free energy penalty per chain scales as ${R_{core}}^2/N_Ba^2$. While this form was originally justified by a uniform stretching assumption,[3] it also obtains when a full self-consistent-field calculation is carried out.[4] F_{corona} gives rise to the final contribution to F. The coronal blocks are stretched because of the balance between the osmotic pressure and the chains' elasticity. To obtain F_{corona}, we exploit the similarity between micelles and star polymers:[2] In both systems chains are grafted to spherical cores. A useful description of the corona is accordingly given by the Daoud-Cotton model for star polymers.[5] In it the corona is divided into f identical, radially aligned, and close-packed truncated cones. A coronal block is grafted to the narrow base of each of these virtual capillaries. The cone's walls set the blob size, $\xi(r)$, at a distance r from the micelles center so that $\xi(r) \approx r/f^{1/2}$. F_{corona} is then given by the kT per blob ansatz.[6] F_{corona}/kT thus obtained is proportional

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to[2b] $f^{-1}\int_{R_{\text{core}}}^{R_{\text{core}}+L}\zeta^{-3}r^2\,\mathrm{d}r \approx f^{1/2}\ln{(R_{\text{core}}+L)/R_{\text{core}}}$ where L is the thickness of the corona. Strictly speaking, the Daoud–Cotton model is applicable only to micelles endowed with thick coronas, $L \gg R_{\text{core}}$. Nevertheless, this approach recovers the Alexander–de Gennes results in the limit of $L \ll R_{\text{core}}$ when the corona is essentially a flat grafted layer. This, however, is not crucial to our discussion as F_{corona} is negligible in this limit.

The micelle's equilibrium structure is determined by minimizing F with respect to f. To simplify the algebra, we approximate the logarithmic factor in (1) as a constant. This yields the scaling behavior of the equilibrium f and thus of R_{core} and L. Two extreme micellar types are distinguishable: (i) micelles with thin coronas, $L \ll R_{\text{core}}$, for which F_{core} is the dominant penalty term; and (ii) starlike micelles endowed with extended coronas, $L \gg R_{\text{core}}$, where the major penalty term is F_{corona}. The scaling behavior of f is different in the two limits:[2]

$$f \sim N_{\text{B}} \qquad L \ll R_{\text{core}} \tag{2i}$$

$$f \sim N_{\text{B}}^{4/5} \qquad L \gg R_{\text{core}} \tag{2ii}$$

So far we have considered the equilibrium structure of micelles in a pure low molecular weight solvent. Addition of A homopolymers to the solution does not affect F_{core} and $F_{\text{interface}}$ but does modify F_{corona}. In turn, the effect on F_{corona} is important only for starlike micelles. For brevity we will thus consider the effect of immersion in a solution of A homopolymers consisting each of N_{A} monomers on starlike micelles. Such solutions, of concentration $c > c^*$, may be considered as a melt of "concentration blobs". Each blob consists of $n_{\text{b}} \approx (ca^3)^{-3/4}$ monomers and is of size $\xi_{\text{c}} \approx (ca^3)^{-3/4}a$. The presence of homopolymers in the solution results in increased screening of excluded volume interactions in the corona. Within the Daoud–Cotton model this effect is accounted for by distinguishing two coronal regions:[5] an interior region where the star structure is preserved (i.e., $\xi \approx r/f^{1/2}$) and an exterior region where the coronal blocks assume bulk structure (i.e., $\xi \approx \xi_{\text{c}}$). The crossover between the two zones occurs when the size of the coronal blobs equals that of the concentration blobs, $\xi \approx \xi_{\text{c}}$. This takes place at a distance $\chi \approx (ca^3)^{-3/4}f^{1/2}a$ from the micelle's center. In this case F_{corona}, as obtained by the blob counting ansatz, is given by

$$F_{\text{corona}}/kT \approx f^{1/2}\ln{\chi/R_{\text{core}}} + (N - N_{\text{i}})/n_{\text{b}} - N/n_{\text{b}} \tag{3}$$

where N_{i} is the number of monomers per block in the inner, starlike region (i.e., $r < \chi$). The extent of the starlike region, χ, and the magnitude of F_{corona} diminish with the growing homopolymer concentration c. This process is associated with an increase of the aggregation number f. However, the growth in f is eventually arrested by the second penalty term, F_{core}. Altogether, the aggregation number of starlike micelles grows from $f \sim N_{\text{B}}^{4/5}$ in a pure low molecular weight solvent to $f \sim N_{\text{B}}$ in an A homopolymer solution of concentration $c \sim N_{\text{B}}^{-2/9}a^{-3}$. At this stage f and R_{core} of the starlike micelles scale exactly as those of micelles with thin coronas. The overall dimensions of the two micellar types remain, however, different because the coronal contribution to the diameter of starlike micelles is always significant.[5] The effect considered is only observable if the micelles attain their equilibrium structure. To ensure that, care should be taken to operate above the glass temperature of the core blocks. Also, N_{B} should not be too large as the relevant relaxation times scale as[7] $\exp(\gamma a^2 N_{\text{B}}^{2/3}/kT)$.

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NMR Characterization of Molecular Motions in Liquid-Crystalline Poly(ester amides) below Their Glass Transition

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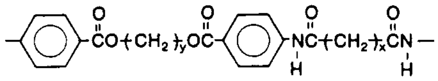
Introduction

A new family of poly(ester amides) has been recently synthesized and shown to exhibit thermotropic liquid crystallinity.[1] These poly(ester amides) are highly regular, strictly alternating, and interchain hydrogen bonded, with the generic structure given below:



When $y = 2$, the transition from semicrystalline solid to isotropic melt occurs in a single step. However, for $y \geq 3$ this transformation occurs in several steps, during some of which the polymers were found to exhibit thermotropic liquid crystallinity.[1,2] These steps are first-order phase transitions, the number and magnitude of which depend on the lengths of x and y.[2]

Many of the structural details of this system have been elucidated through a combination of solid-state nuclear magnetic resonance (NMR), infrared (IR), and X-ray diffraction (XRD) studies.[1-3] IR results reveal that the amide groups are hydrogen bonded in the crystalline, glassy, and mesomorphic states while XRD results suggest that the hydrogen bonds exist between chains and are not present as intrachain bonds. By a combination of NMR and XRD, it was determined that the conformation of the x methylenes is exclusively trans but that the y segments include both trans and gauche states. The gauche bonds allow the chains to adopt an overall zigzag configuration and are associated with the existence of liquid crystallinity.[3]

Previously inaccessible information such as amorphous-phase structure and polymer-chain dynamics can often be readily obtained through a variety of NMR methods.[4,5] One of the strengths of solid-state NMR is its ability to probe molecular motion at specific individual nuclear sites along a polymer chain. This is often done by measuring $T_{1\rho}$(C), or ^{13}C spin-lattice relaxation in the rotating frame.[6,7] Studies of $T_{1\rho}$(C) have provided valuable information on molecular dynamics in semicrystalline polymers such as polyesters and in glassy polymers such as polycarbonates and polystyrenes. The purpose of this report is to document our findings on motional behavior in poly(ester amides) in their semicrystalline solid state below their glass transition temperature, T_g. In addition,

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