the large diameter of the bead and suffice for an analysis of experimental data for ordinary flexible chains. It has been shown that the effect of the finite volume cannot be ignored as far as the behavior of $[\eta]$ of flexible chains in the oligomer region is concerned. We have shown the two examples of flexible chains for which the behavior of $[\eta]$ may be better explained by the helical wormlike chain than by the ordinary wormlike chain or Gaussian chain, if the experimental data in the oligomer region are included.

In previous papers,[4,5] we evaluated various kinds of equilibrium properties on the basis of the HW model. From a comparison of these theoretical results with numerical results for the rotational isomeric state model or with experimental data, we showed that the HW chain can mimic the equilibrium conformational behavior of real polymer chains (both flexible and stiff) on the bond length or somewhat longer scales, and determined the HW model parameters of various polymers (see Table 1 of ref 4). The present analysis leads to the model parameters consistent with those previously determined, and we believe that $[\eta]$ is also a useful quantity for their determination. Therefore, a further experimental study of the behavior of $[\eta]$ of flexible chains over a wide range of the molecular weight including the oligomer region is required to clarify the local structure of flexible chains in solutions.

Registry No. Poly(methyl methacrylate), 9011-14-7.

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Thermotropic Polypeptides. 5. Temperature Dependence of Cholesteric Pitches Exhibiting a Cholesteric Sense Inversion

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ABSTRACT: The cholesteric pitches were determined for the thermotropic cholesteric mesophases of poly[(γ-benzyl L-glutamate)-*co*-(γ-dodecyl L-glutamate)] with the dodecyl content of 58% in the wide temperature range from 100 to 250 °C. The pitches in an initial temperature range 100–130 °C are comparable to the wavelength of visible color and increase with rising temperature. After the pitches diverge at 195 °C, they decrease as temperature is raised further. In contrast to this anomalous behavior of pitches, the reciprocal pitches (measuring the twisting angles) vary smoothly with the temperature along a curve. The curve exhibits a remarkable variation of twisting angle at lower temperature and seems to approach a constant value at higher temperature, passing through zero at 195 °C. The latter indicates the cholesteric sense inversion. The results are discussed in terms of existing theories.

Introduction

The cholesteric mesophase is generally regarded as a distorted form of the nematic mesophase and characterized by a macrohelical twist of pseudonematic layers. The existence of a finite pitch, thus, is a common feature of all cholesteric mesophases. The mutual twist of pseudonematic layers results from the microscopic structure of molecules and the nature of intermolecular interactions. According to the potential model based on the quadrapole–dipole interaction as well as the dipole–dipole one, Goossens[1] reached a conclusion that chirality is the major cause of the macroscopic twist. Unfortunately, Goossens also offered another conclusion that the pitch is insensitive to the temperature variation.

In actual situations, the pitch of cholesterics invariably depends on the temperature. Taking notice of this point, Keating[2] proposed the forces opposing the twist to be anharmonic in the chiral systems, so that a macroscopic twist results from the ensemble-averaging process. The theory predicts the pitch decreasing with the increasing temperature, which is in qualitative agreement with the experimental observation on most cholesterics.

There are, however, certain exceptional cases on the temperature variation of pitch. In one of them, the pitch increases with temperature. Also in another case, the pitch diverges, after which the helicity reverses and the pitch decreases as temperature is raised further. Such cases are hard to understand in terms of Keating's model.

The lyotropic cholesteric mesophases of polypeptides exhibit a temperature variation of pitch corresponding to the latter case as reviewed by Uematsu and Uematsu.[3] The typical example can be seen in the lyotropic systems of

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poly(γ-benzyl L-glutamate) (PBLG) in *m*-cresol or trichloropropane, in which the reciprocal pitch changes linearly with temperature and the inversion of helical sense from the right- to the left-handed twist takes place at a certain temperature.[4,5] The helical sense of PBLG cholesteric mesophases also depends on the supporting solvent so that it undergoes an inversion by altering the solvent composition in appropriate binary solvent mixtures.[6-9] These unusual phenomena activated the theoretical studies.[10-12] Kimura et al.[10] theoretically concluded that the thermally induced sense inversions can occur in a system of chiral rods such as α-helical polypeptides. On the other hand, Samulski and Samulski[11] and Osipov[12] emphasized the significance of the solvent dielectric constant on the helical sense. Some speculation has been also given for a relation between average side-chain conformation and helix inversion.[13]

In this paper, we represent a typical temperature dependence of pitch observed in novel thermotropic cholesteric mesophases of polypeptides,[14-17] in which an effect of solvent can be neglected. The pitches were widely detected over a range of more than 300 nm and the helical sense was carefully determined. The results exhibit the same inversion of helical sense as in the lyotropic system, although there is a somewhat different situation in the temperature dependence of pitch between lyotropic and thermotropic systems.

Experimental Section

Material. Poly[(γ-benzyl L-glutamate)-*co*-(γ-dodecyl L-glutamate)] with a dodecyl content of 58% and a degree of polymerization of 2.5×10^2, as designated by BD-1-58 in a previous paper,[16] was used for the present study. The polymer exhibited the mesophase above 104 °C and invariably took up the right-handed α-helical conformation in the experimental temperature range from 25 to 250 °C as detected by IR spectra.[16]

Methods. The cholesteric pitches in the range 300–700 nm were determined by circular dichroism (CD) using a JASCO automatic recording spectrometer (J-20). For this measurement, the liquid crystals with a thickness less than 20 μm were prepared between glasses. In these thin samples, the Grandjean texture, as clarified by a microscopic observation, was easily attained with the cholesteric helical axis perpendicular to the glass surface, since the rigid molecules prefer to orient parallel to the glass surface. On irradiation of light perpendicular to the glass surface, thus, cholesteric pitch, P, was determined from the wavelength of maximum reflectivity of CD, λ_m, according to the equation[18]

$$\lambda_m = nP \qquad (1)$$

where the average refractive index $n = 1.51$ as measured at room temperature by an Abbe refractometer.

The cholesteric pitches larger than 1 μm were determined by observation of the striation lines due to an Olympus BH-2 polarizing microscope. Since the striation lines can be most clearly seen in a view perpendicular to the helical axis, the mesophase specimens were prepared so as to have the polydomain structure, which preferentially arised for the sample with a thickness of more than 1 mm. In this case, the spacing between lines corresponds to a half-pitch.

The helical sense of cholesterics was clarified from the sign of the CD and optical rotational dispersion (ORD) curves by using J-20.

In order to satisfy the equilibrium condition, all the measurements were performed for the mesophases which were kept at a respective temperature for more than 4 h and in an atmosphere of nitrogen.

Results

A. Temperature Dependence of Cholesteric Pitch.

Figure 1 shows the typical CD and ORD curves observed for the cholesteric mesophase at 120 °C. The CD curve, appearing sharp, has the negative value and at the maximum position of CD the optical rotation (OR) changes its sign from the positive to the negative on increasing wavelength. Both are expectable for the right-handed cholesteric helix.[18]

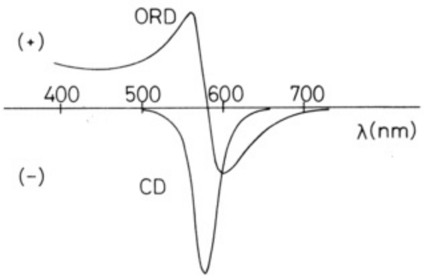


Figure 1. CD and ORD curves for the cholesteric mesophase of BD-1-58 at 120 °C.

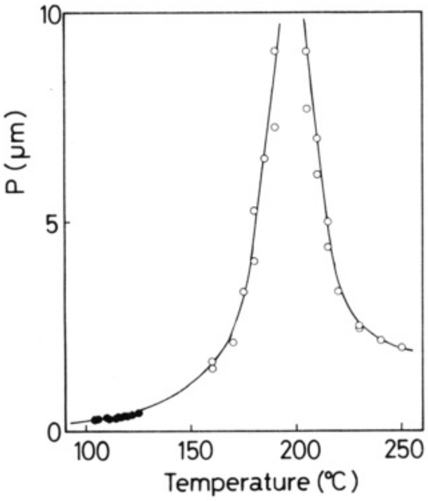
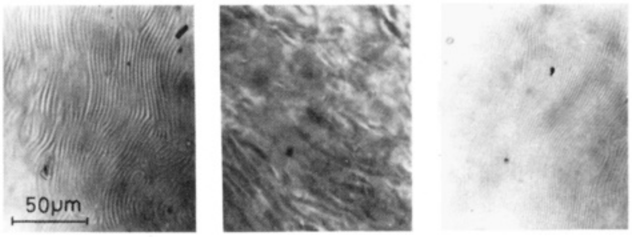


Figure 2. Variation of pitches with temperature for the cholesteric mesophases of BD-1-58. The closed and open circles indicate the data obtained by CD and microscopic observations, respectively (see text).



(a) (b) (c)

Figure 3. Optical microphotographs taken for the cholesteric mesophases of BD-1-58 at (a) 180, (b) 195, and (c) 220 °C. Here, the observations were made in crossed polarizers.

The sharp CD allows the precise determination of cholesteric pitches according to the eq 1. The variation of pitches with temperature thus obtained is illustrated as closed circles in Figure 2. In the temperature range from 100 to 130 °C, in which CD spectra can be detected, the pitch increases with increasing temperature. In other words, the pitch changes over a whole wavelength range of visible color in a temperature span of 30 °C; this trend can be qualitatively recognized from visual observation of beautiful reflection colors changing from blue to red.

With a further increase of temperature, the pitches get larger so that they appear visible as fine striation lines under an optical microscope. The photomicrographs exhibiting these lines are shown in Figure 3. By measuring the spacings between lines from these photographs, the

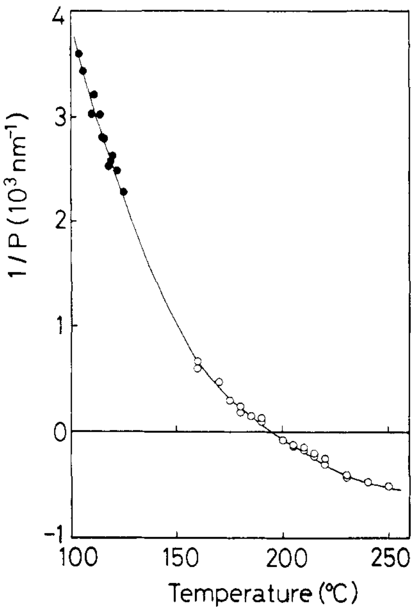


Figure 4. Variation of the reciprocal pitches with temperature for the cholesteric mesophases of BD-1-58. The closed and open circles indicate the data obtained by CD and microscopic observations, respectively.

pitches were determined in the temperature range from 150 to 250 °C and are plotted against temperature as open circles in Figure 2. Interestingly, the pitch increases still substantially with the increase of temperature from 150 °C and diverges at around 195 °C. Then it decreases as the temperature is raised further. This trend can be obviously seen in comparison of the microphotographs of Figures 3; the fine striation lines observed at 180 °C (Figure 3a) disappear at 195 °C (Figure 3b) and again appear at 220 °C (Figure 3c).

B. Temperature Dependence of Twisting Angle. The twisting angle, θ, can be determined from the pitch and the thickness of the pseudonematic layer, d, according to the equation

$$\theta = 2\pi d/P \tag{2}$$

The reciprocal pitch, hence, is proportional to the twisting angle between the pseudonematic layers under an assumption that the thickness of each layer is independent of temperature. This assumption is qualitatively satisfied in this case, since the molecular spacing (corresponding to the layer thickness) thermally expands only with a small expansion factor (d ln $d/\mathrm{d}T$) on the order of 10^{-4} °C^{-1}.

We, thus, obtained a plot of the reciprocal pitch measuring the twisting angle against the temperature in Figure 4. The overall data points fall on a smooth curve passing through zero at 195 °C. This indicates that the twisting angle changes continuously with the temperature if the helicity reverses at around 195 °C. At lower temperature the remarkable variation of twisting angle is observed whereas at higher temperature the curve indicates less variation and seems to approach a constant value.

C. Confirmation of Helical Sense Inversion. de Vries[18] proposed that the optical rotation ($\mathrm{d}\psi/\mathrm{d}z$) of the light with a wavelength λ, produced by the cholesteric helical arrangement of pseudonematic layers, is written as

$$\mathrm{d}\psi/\mathrm{d}z = 2\pi\alpha^2/8P\lambda'^2(1 - \lambda'^2) \tag{3}$$

where $\lambda' = \lambda/nP$, $\alpha = \Delta n/n$, $\Delta n = n_{\parallel} - n_{\perp}$. If $\lambda \ll P$, eq 3 is simplified as follows:

$$\mathrm{d}\psi/\mathrm{d}z = 2\pi P\Delta n^2/8\lambda^2 \tag{4}$$

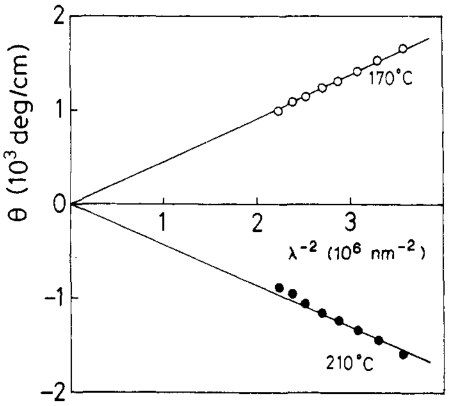


Figure 5. Plots of optical rotation versus $1/\lambda^2$ according to eq 4, for the cholesteric mesophases with a thickness of around 10 μm at (○) 170 and (●) 210 °C.

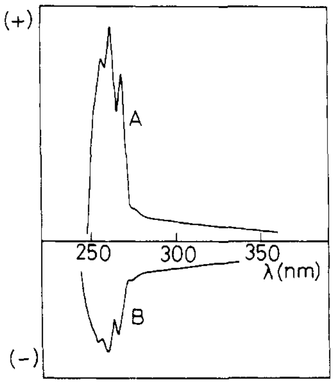


Figure 6. CD curves induced for the phenyl groups at the end of side chain of the benzyl L-glutamate unit. Curves A and B were observed for the cholesteric mesophases at 170 and 210 °C, respectively.

The equation indicates the linear relationship between optical rotation and $1/\lambda^2$. The sign of the slope clarifies the sense of the cholesterics; a positive slope indicates the right-handed helix whereas a negative the left-handed one.

Equation 4 was applied for the cholesterics in the range 150–250 °C. The representative results are shown for the cholesteric mesophases at 170 and 210 °C in Figure 5. Each datum satisfies the linearity between $\mathrm{d}\psi/\mathrm{d}z$ and $1/\lambda^2$ and, as found in comparison of data at 170 and 210 °C, the sign of slope changes from positive to negative at around 195 °C, at which the twisting angle becomes zero in Figure 4. Thus, the inversion of cholesteric sense from right to left handed on heating is obvious. The former right-handed helix in a lower temperature range has been confirmed above from the negative CD curve of Figure 1.

The helix inversion reflects also on the induced CD of around 260 nm which arised for the phenyl groups at the end of side chain of the benzyl L-glutamate unit because of their helical arrangement enforced by the cholesteric structure.[19] As found in Figure 6, the induced CD also changes its sign at an inversion temperature of 195 °C. In this case, however, it should be noted that the positive CD appears for the right-handed cholesterics, a situation which is the reverse of that in the CD caused by the selective reflection of light due to the cholesterics.

The thermotropic mesophase of a polypeptide, thus, indicates the same inversion of cholesteric sense as the lyotropic mesophase, dictating that a certain property of the solvent is not essential to cause the thermally induced inversion. For the system composed of L isomers, the sense inversion from the right to the left on heating is normal and no exceptional data have been so far observed.[16,20] An

IR study displays that the right-handed α-helix of the main chain remains unchanged throughout the mesophase temperature range. Thus, the cholesteric sense is not simply dictated by the sense of helical conformation of constituent molecules. Further, DSC thermograms and the temperature variation of molecular spacing or specific volume offer no significant transition at the temperature of helix inversion. This also exhibits no drastic change of the force field around α-helical molecules on inversion.

Discussion

A. On Helix Inversion. First we recall the helix inversion phenomena in lyotropic system. Lyotropic cholesteric mesophases of polypeptides exhibit both thermally and solvent induced sense inversions of the helix. The latter indicates that the cholesteric sense depends on the supporting solvent as well as temperature and so the sense inversion is observed in an appropriate binary solvent mixture as reported by Dupre et al.[8] and Uematsu et al.[3,5,9]

Samulski and Samulski[11] first took notice of the significance of the solvent on the helix sense and developed a theory of solvent-induced compensation of the cholesteric twist in polypeptide solutions, taking into account van der Waals forces between macromolecules in a dielectric medium. The theory showed that the average angle between two polypeptide molecules changes its sign when the dielectric constant of the medium is increased by altering the solvent composition. It also explained the observed influence of the dielectric constant of alkyl chloride solvents on the cholesteric sense and pitch of PBLG mesophases.[9] It, however, should be noted that the temperature dependence of the cholesteric pitch is not included in this theory.

On the other hand, Kimura et al.[10] proposed a statistical theory of the thermally induced sense inversion in the system of chiral rods considering both van der Waals attraction of Goossens type[1] and repulsion of hard core[21] with a shape of a twisted rod like that of an α-helical polypeptide molecule. According to this, the twisting angle is given by

$$\theta = 2\pi d/P = (B - Cmk_BT/d)/(A + \gamma m(1 - \langle P_4\rangle/\langle P_2\rangle)k_BT) \quad (5)$$

where A and B are constants introduced by Goossens,[1] m is the density of molecular number, C is the steric factor which is simply proportional to the deflection angle between twisted rods closely in contact, and γ is the factor related to the shape of the rods. The different temperature variation between repulsion and attraction causes the inversion of cholesteric senses.

More recently, Osipov[12] obtained a further detailed expression for the chiral dispersion as a function of the anisotropic permittivity and optical activity of the polypeptide molecule and of the solvent dielectric constant. Combining the chiral dispersion force with the repulsion as in the theory by Kimura et al.[10] Osipov arrived at the following expression for the cholesteric twisting angle

$$\theta \propto (J_0(\epsilon_m) - \kappa k_BT) \quad (6)$$

where $J_0(\epsilon_m)$ is the coupling constant of the chiral interaction between polypeptide molecules and κ is the factor related to the molecular shape. Since the first and second terms are functions of the solvent dielectric constant ϵ_m and temperature T, respectively, the sign of θ can be altered by the variation of ϵ_m and T. The equation, thus, offers the possibility of thermally and solvent induced helix inversion, both of which have been observed in lyotropic polypeptide system.

The latter two theories predict that the existence of solvent is not essentially responsible for the thermally induced inversion of the cholesteric helix and so the inversion may arise even in the thermotropic system of a polypeptide. They also prophesy that no abrupt change of the force field around molecule is included on inversion. These predictions indeed correspond to our present data in thermotropic cholesteric system of polypeptides.

B. On Temperature Variation of Pitch. Theories also predict the linear relationship between $1/P$ and T. For example, Kimura et al.[10] suggested that the denominator of eq 5 is always positive and increases only slightly with temperature due to the factor $\gamma m(1 - \langle P_4\rangle/\langle P_2\rangle)k_BT$—although they give no evident reason for the latter point. Hence, the twisting angle may change somewhat linearly with temperature. Also, Osipov's eq 6 exhibits a linear relationship between twisting angle and T. These in practice have explained the experimental data so far observed in the lyotropic system of polypeptide and cellulose derivatives, which have been expressed by an empirical equation[3,22]

$$1/P = b(1 - T/T_N) \quad (7)$$

where b is a constant factor for a given polymer–solvent concentration and T_N in kelvin is defined as the temperature of helix inversion. In the present thermotropic system, however, a nonlinear relationship of T and $1/P$ is obvious as was seen in Figure 4. On this point, it is thus presumed that there may be a different situation beween lyotropic and thermotropic systems.

According to the theory by Kimura et al.,[10] we can give two possible explanations for the significant deviation from the linear relationship. One explanation can be given by considering the temperature variation of the C factor in eq 5. In the theory, C is treated as a constant (which is positive in this particular case), but in actual situation it may depend on the chiral geometry produced by side chains on the exterior of the α-helical main chain and, hence, vary more or less with temperature. Possibly, C may decrease on heating since it is apparent that the side-chain structure becomes more disordered and so the chiral geometry disappears gradually with rising temperature. This explains the experimentally observed deviation from linearity. Another way to interpret the deviation comes from the consideration of temperature dependence of the denominator in eq 5. As mentioned above, Kimura et al.[10] have assumed that the denominator of eq 5 has less temperature dependence. However, if there is a significant temperature dependence in the denominator so that it cannot be ignored, the eq 5 can be rewritten in the form

$$1/P = t(1/(T - u) - 1/(T_N - u)) \quad (8)$$

where $T_N = 468$ K. This equation also explains the trend of experimental data. By curve fitting, we have elucidated 0.357 nm^{-1} K and 319 K for t and u, respectively, and seen good agreement of the solid calculated curves with the observed data in Figure 7.

Finally, we mention that the experimental data could be also expressed in the form

$$1/P = \alpha((T_N/T)^\beta - 1) \quad (9)$$

where $\alpha = 9.72 \times 10^{-4}$ nm^{-1} and $\beta = 7.26$, as illustrated by the dashed curve in Figure 7. In this case, however, it should be noted that the equation has no theoretical base.

There are thus several ways to explain the nonlinear relationship between $1/P$ and temperature, and the best

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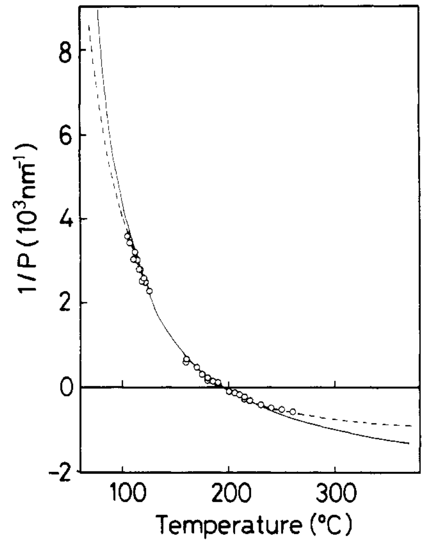

Figure 7. Comparison of the observed data (given by the circles) with the calculated curves. The solid and dashed curves are due to the calculations according to eq 8 and 9, respectively.

understanding of it seems to need further collection of data for other kinds of thermotropic polypeptides. The study is in progress.

Registry No. BD-1-58, 111291-00-0.

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Synthesis and Characterization of Hydrophobically Associating Block Polymers

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ABSTRACT: The influence of polymer composition and architecture on solution rheological properties of hydrophobically associating polymers was explored. The water-soluble block polymers were synthesized in two steps involving anionic polymerization of poly(*tert*-butylstyrene-*b*-styrene) followed by selective sulfonation of the styrene block. Viscometric measurements in distilled water clearly identified viscosity enhancement due to the presence of the hydrophobic *tert*-butylstyrene groups in a block architecture, while the presence of the same functionality in a random copolymer produced little effect on the solution properties. The block polymer solutions were also observed to solubilize toluene with a marked increase in the solution viscosity. These results were interpreted in terms of polymer intermolecular association through the hydrophobic blocks similar to micellization of surfactants.

Introduction

Block and random polymers comprised of *tert*-butylstyrene and styrenesulfonate as the hydrophobic and hydrophilic or water-soluble blocks, respectively, were synthesized to study the effects of polymer molecular architecture on aqueous solution behavior. All of the water-soluble, sulfonated polymer systems, including homopolymers, random and block polymers, were synthesized by functionalization via sulfonation of hydrocarbon-soluble polystyrene or poly(*tert*-butylstyrene–styrene) copolymers. Their aqueous solution behavior was studied as a function of hydrophobe block size, polymer molecular weight, molecular architecture of the polymer (block versus random configurations), and other solution effects such as hydrocarbon solubilization.

Viscosification of an aqueous solution can be achieved with linear ultrahigh molecular weight polymers.[1] The presence of ionically charged monomers along a randomly coiled polymer chain will expand the coiled polymer by charge repulsion (polyelectrolyte effect),[2] thereby increasing the effective hydrodynamic volume. However, the repulsions can be largely screened by salts in the aqueous solution ultimately lowering the viscosity.

An alternative approach to ultrahigh molecular weight and chain expansion for aqueous viscosification by polymers involves intermolecular aggregation in solution through hydrophobic association. Landoll reported[3] on the behavior of hydrophobically modified cellulosic ethers wherein the solution properties were explained in terms of interchain polymer associations resulting in aggregate

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