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Behavior of a Self-Assembling Bicopper Complex in Organic Solutions

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ABSTRACT: The structure of a self-assembling system, *bicopper ethyl-2-hexanoate*, producing filaments in organic solvents, has been studied as a function of temperature, of solvent type, and in polymer solutions. While the rheological behavior in organic solvents can be accounted for by Cates' theory, the neutron scattering data rather suggest a two-population system: very long filaments and short filaments. Raising temperature or increasing polymer fraction both seem to promote the appearance of a significant fraction of individual bicopper complex molecules. These findings are discussed by considering side-by-side aggregation of short filaments.

Introduction

In the past few years, we have been involved in the study of a self-assembling system, namely a bicopper complex (bicopper ethyl-2-hexanoate, see Figure 1), in organic solvents.[1−3] It was concluded that the system could be described to a first approximation by Cates' theory,[4,5] although determination of the plateau modulus as a function of temperature had revealed an unexpected transition reminiscent of a first-order transition.[3] It was then suggested that filaments joined through limited side-by-side aggregation, thus producing longer threads. The resulting hypothetical junctions were thought to be responsible for the first-order transition on melting.

More recently, we have reported on and discussed a method for encapsulating the filaments of the bicopper complex in polymer sheaths.[6] This method relies upon the effect of heterogeneous nucleation: the self-assembling system, namely filaments of a bicopper complex (see Figure 1), acts as the nucleating agent for the formation of isotactic polystyrene fibrils under gelling conditions in *trans*-decalin. We have observed that, beyond a given molar fraction of bicopper complex, some liquid−liquid phase separation occurs. Gelation and phase separation are concurrent so that it was felt that a deeper understanding of the ternary system could be gained by using a nongelling polymer. This task can be easily achieved in the present case by using atactic polystyrene, which does not form gels in the solvent used.[7]

The purpose of this paper is to report on the determination of the structure of the bicopper complex as a function of temperature and when embedded in a polymer solution.

To the best of our knowledge, the study of a "living" polymer in a classical polymer has never been performed so far. It is worth emphasizing that the bicopper complex considered here is certainly a more appropriate candidate for this type of study than giant micelles used so far for testing theories developed for "living" polymers.[8,9]

Experimental Section

Materials. The bicopper complex (copper(II) 2-ethylhexanoate), designated as CuS8 herein, was synthesized and purified by a method devised by Martin and Waterman.[10] Hydrogenous solvents (*trans*-decalin and *cis*-decalin) were purchased from Aldrich while their deuterated counterpart as well as deuterated styrene was obtained from Eurisotop (Saclay, France). The solvents were distilled and kept under argon atmosphere in order to prevent from water contamination. Deuterated atactic polystyrene (aPS) was synthesized by means of anionic polymerization after proper purification of the monomer. The weight-average molecular weight as determined by SEC in THF at 25 °C was $M_w = 155\ 000$ g/mol with $M_w/M_n = 1.2$.

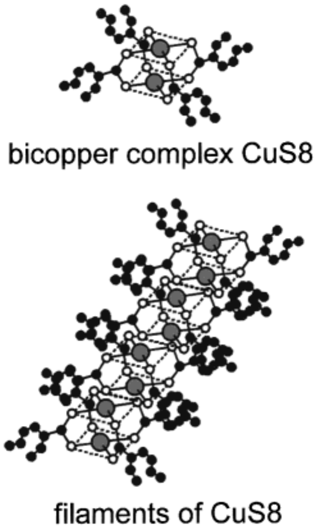

Figure 1. Schematic drawing of a bicopper complex molecule, namely bicopper ethyl-2-hexanoate (left), and the way these molecules pile up to form long filaments (right). Gray-filled circles stand for copper atoms, open circles for oxygen atoms, and black circles for carbon atoms. For the sake of clarity, hydrogen atoms are omitted.

Small-Angle Neutron Scattering. The experiments were performed on the PAXE camera located at the Laboratoire Léon Brillouin (LLB) (CEN Saclay, France). A wavelength of $\lambda_m = 0.6$ nm was used with a wavelength distribution characterized by a full width at half-maximum, $\Delta\lambda/\lambda_m$, of about 10%. Neutron detection and counting were achieved with a built-in two-dimensional sensitive detector composed of 64 × 64 cells (further details are available on request at LLB). The sample−detector distance was set at 5 m so that the q range spanned from 0.1 to 0.8 nm^{-1} where $q = (4\pi/\lambda)\sin(\theta/2)$, θ being the scattering angle.

The intensity scattered by the bicopper complex molecules was obtained after proper subtraction of a flat background.

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This background consisted of the signal scattered by the matrix (solvent or a mixture of polymer + solvent) plus a term standing for the incoherent signal scattered by the hydrogenous bicopper complex. The latter was calculated from an experimental relation established by Fazel et al.[11]

The position sensitive detector was calibrated by means of hydrogenous *cis*-decalin, which gives off only incoherent scattering. Under these conditions the absolute intensity, $I_A(q)$, is written

$$I_A(q) = I_N(q)/K \tag{1}$$

in which $I_N(q)$ is the intensity obtained after background subtraction, transmission corrections, and detector normalization, and K is a constant which reads

$$K = \frac{4\pi(a_{Cu} - ya_s)^2 \delta_{dec} T_{dec} N_A}{g(\lambda_m)(1 - T_{dec}) m_{Cu}^{\;2}} \tag{2}$$

in which a_{Cu} is the coherent scattering amplitude of the bicopper complex, a_s is the scattering coherent amplitude of the solvent mixture, δ_{dec} and T_{dec} are the thickness and the transmission of the calibration *cis*-decalin sample, m_{Cu} is the molecular weight of the bicopper complex, and $g(\lambda_m)$ is a constant which is camera-dependent and was measured by using Cotton's method.[11]

Sample Preparation. Samples were prepared directly in sealable quartz cells from HELLMA of optical paths of 1 and 2 mm, depending upon the mixture's transmission. After introduction of the appropriate constitutents, the system was heated to 150 °C to obtain homogeneous solutions.

In the case of the ternary systems, CuS8/aPS/solvent, the solvent mixture contained a high fraction of deuterated solvent, namely 91% tdecaD/9% tdecaH in v/v, for matching the coherent scattering amplitude of the deuterated polymer. As a result, the only remaining coherent scattering is that of the bicopper complex.

Results and Discussion

I. Binary Systems: Effect of Solvent Conformer and of Temperature. 1. CuS8/*trans*-Decalin.

As is known from previous studies, the bicopper complex molecules pile up in several organic solvents[1] so as to form a monomolecular filament with a persistence length far larger than 15 nm (see Figure 1). The rheological properties of the resulting "jellies" can be accounted for in the framework of Cates theory developed for "living" polymers.[4,5] In particular, the variation of the storage modulus G' and the loss modulus G'' as a function of frequency ω in oscillatory experiments is very close to a Maxwell-type relaxation model where only one characteristic time τ is involved (see Figure 2):

$$G' = G_0 \frac{\omega^2\tau^2}{1 + \omega^2\tau^2} \qquad G' = G_0 \frac{\omega\tau}{1 + \omega^2\tau^2} \tag{3}$$

in which G_0 is the plateau modulus. In Cates' theory τ is, under these conditions, expressed as follows:

$$\tau = (\tau_{rep}\tau_{break})^{1/2} \tag{4}$$

where τ_{rep} is the characteristic time associated with the reptation process and τ_{break} the characteristic time associated with the breaking process of the filaments.

This means that a given filament only exists for a finite time because the binding energy between bicopper complex molecules is of the order of kT. Much of the stress relaxation process occurs therefore through a scission–recombination mechanism.[2] Cates' theory predicts that the distribution in length of the filaments should obey Boltzmann statistics[4] at thermodynamic equilibrium, which gives the following expression for the average length $\bar{L}$ of the filaments:

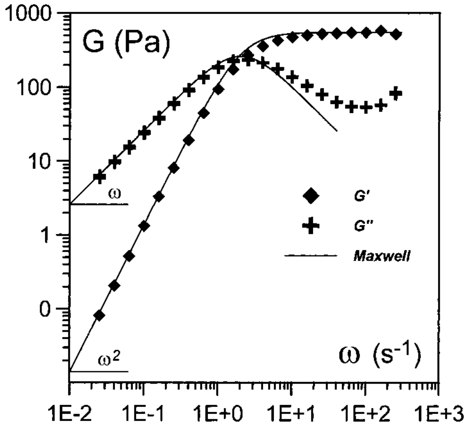

Figure 2. G' and G'' as a function of frequency ω in oscillatory experiments (from ref 3). CuS8 in *trans*-decalin, C = 0.04 g/cm^3, T = 20 °C. The characteristic slopes at low frequency $G' = \omega^2$ and $G'' = \omega$ are shown.

$$\bar{L} \propto \varphi^{\alpha} \exp\left(\frac{E_{scis}}{2kT}\right) \tag{5}$$

in which E_{scis} is the scission energy and φ the filaments volume fraction. α is an exponent which depends on the long-range statistics of the filaments.

In a recent paper, it was shown that the usual rheological parameters (modulus, viscosity, etc.) when studied as a function of temperature displayed a sharp transition, an effect not predicted by the theory.[3] All happened as if a first-order transition occurred. Dammer and co-workers attributed this effect to some kind of physical gel structure that melted once reaching a well-defined temperature.[3]

Also, the "jelly" of filaments is not stable as aging for several days at room temperature eventually produces a suspension of CuS8 crystals. This clearly means that three-dimensional aggregation, as occurs in crystals, is more stable than one-dimensional aggregation.

The intensity scattered by the "jellies" of CuS8 filaments in the usual scattering range can be fitted by considering a solid, prolate cylinder model of cross-section radius r_c and mean length $\langle L\rangle$ (see Figure 3). For $q\langle L\rangle > 1$ and $\langle L\rangle > r_c$, the theoretical scattering intensity is written[13]

$$q^2 I(q) \propto C_{Cu}\mu_L \frac{4J_1^{\;2}(qr_c)}{q^2 r_c^{\;2}} \left[\pi q - \frac{2}{\langle L\rangle}\right] \tag{6}$$

in which μ_L is the mass per unit length and C_{Cu} the bicopper complex concentration. The cross-section radius r_c has been found to be r_c = 0.8 nm, a value consistent with one molecule per cross-sectional area.

The q range of interest in this paper is such that $qr_c \ll 1$ so that (6) reduces to

$$q^2 I(q) \propto C_{Cu}\mu_L \left[\pi q - \frac{2}{\langle L\rangle}\right] \tag{7}$$

The intensity, when plotted as $q^2 I(q)$, varies linearly as

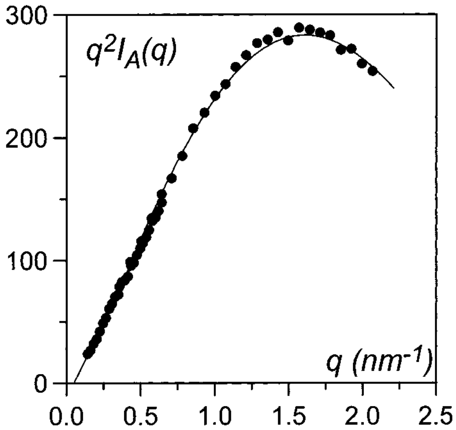

Figure 3. Scattering curve in a Kratky representation ($q^2I_A(q)$ vs q) for self-assembled CuS8 in *trans*-decalin ($C_{Cu} = 0.07$ g/cm^3). The continuous line has been calculated through eq 6.

a function of q, and the length $\langle L\rangle$ is simply given through

$$\langle L\rangle = \frac{2}{\pi q_0} \tag{8}$$

in which q_0 is the intercept with the q-axis for $q^2I(q) = 0$.

It is clear that rheological data and neutron scattering findings are in apparent conflict: rheology implies very long filaments while neutron scattering suggests the presence of short filaments. Short filaments would never give the variation of G' and G'' as seen in Figure 2. Although neutron scattering data are more sensitive to the number-average distribution (first moment of the distribution), a distribution as given in relation 5 is not supposed to give such a short mean length. Note that neutron scattering experiments and rhoelogical experiments are carried out on the same time scale, i.e., about 1 h. The conflict does not therefore arise from structures that would grow on different time scales. Also, X-ray data obtained at the very onset of the bicopper jelly formation (unpublished data not shown here) exhibit the same scattering pattern as those recorded by neutron scattering on longer counting times.

One way of reconciling rheological properties and neutron scattering data is to consider a two-population system: a fraction $(1 - Y)$ of very long filaments (most probably possessing wormlike statistics) and a fraction Y of very short filaments. On condition that $l_p \geq \langle L\rangle$, where l_p is the persistence length of the very long wormlike filaments, and ignoring intermolecular terms, the intensity is written

$$q^2I(q) \propto C_{Cu}\mu_L\left(\pi q - \frac{2Y}{\langle L\rangle} + \frac{2(1 - Y)}{3l_p}\right) \tag{9}$$

since the scattered intensity for a wormlike chain is written for $ql_p > 1$:

$$q^2I(q) \propto \mu_L\left[\pi q + \frac{2}{3l_p}\right] \tag{10}$$

In the limiting case where $l_p = \langle L\rangle$

$$\langle L\rangle = \frac{2(2Y + 1)}{3\pi q_0} \tag{11}$$

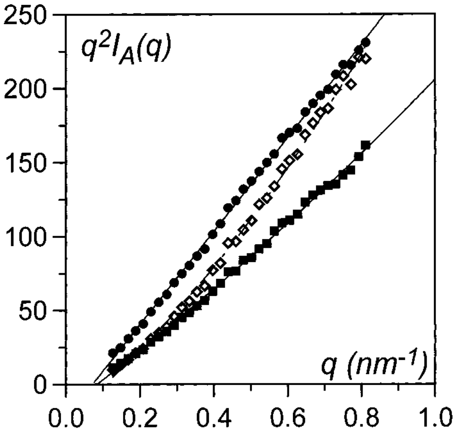

Figure 4. Scattering curve in a Kratky representation ($q^2I_A(q)$ vs q) for self-assembled CuS8 in *trans*-decalin limited to the domain wherein eq 7 applies. (●) C_{Cu}= 0.07 g/cm^3, $T = 20$ °C; (■) C_{Cu}= 0.07 g/cm^3, $T = 90$ °C; (◇) $C_{Cu} = 0.147$ g/cm^3 + $C_{aPS} = 0.08$ g/cm^3, $T = 90$ °C. Solid lines are best fits using eq 13.

The value of $\langle L\rangle$ would be underestimated. It is, however, likely that $l_p \gg \langle L\rangle$ prevails in which case a value close to the actual value of $\langle L\rangle$ is determined by measuring q_0. The assumption $l_p \gg \langle L\rangle$ rests on the fact that long filaments cannot be more flexible than the shortest ones since they are made up with the same bicopper complex.

As can be seen in Figure 4, the intensity for bicopper complex "jellies" in *trans*-decalin at $T = 20$ °C obeys relation 7. A typical mean length $\langle L\rangle = 8.4$ nm and a mass per unit length $\mu_L = 1515 \pm 160$ g/(mol nm) are found. We note that the value of $\langle L\rangle$ differs little from previous values obtained at much lower concentrations.[3]

Note that the presence of intermolecular terms[14] arising from a correlation length ξ (terms in $1/q^2$) would also lead one to underestimate $\langle L\rangle$. To be sure the overlap concentration C^* of the shortest segments, i.e., those entities that contribute most to the scattering signal, can be calculated through

$$C^* = \frac{6\mu_L}{\pi\langle L\rangle^2 N_A} \tag{12}$$

which gives by introducing the above values of $\langle L\rangle$ and μ_L, $C^* \approx 0.06$ g/cm^3. We therefore conclude that effect of intermolecular terms on the value of $\langle L\rangle$ can be ignored to a first approximation.

At higher temperature and/or higher polymer concentration, $q^2I(q)$ no longer varies linearly with q (see Figure 4). Rather, it can be fitted with a quadratic function (parabola). Such a behavior can be accounted for by considering a simple model where filaments coexist with nonaggregated bicopper complex molecules. Under these conditions the scattered intensity can be written

$$q^2I(q) \propto C_{Cu}\left[X\mu_L\left(\pi q - \frac{2}{\langle L\rangle}\right) + (1 - X)M_{Cu}q^2P_{Cu}(q)\right] \tag{13}$$

in which X is the fraction of filaments; M_{Cu} and $P_{Cu}(q)$ are the molecular weight and the form factor of a bicopper complex molecule. In the investigated q range, $P_{Cu}(q) \approx 1 - q^2r^2/3 \approx 1$ because of the small bicopper complex radius of gyration ($r \approx 0.4$ nm). (To be sure,

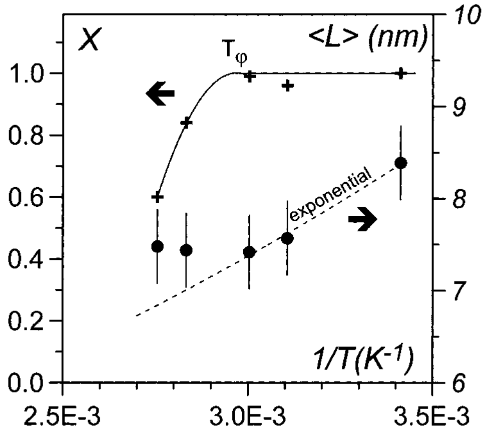

Figure 5. Variation of the fraction of filaments X (+) and their mean length $\langle L\rangle$ (●) as a function of the reciprocal of the temperature. T_φ indicates the temperature at which some transition is taking place. The full line is a guide for the eye, while the dotted line stands for an exponential decay.

Table 1. Variation of the Mean Length $\langle L\rangle$, the Fraction of Filaments X as a Function of Temperature for a CuS8/*trans*-Decalin Solution ($C_{\mathrm{Cu}} = 0.07$ g/cm^3); M_{Cu} Is the Molar Mass Determined for the Presumably Nonbonded Bicopper Complex Molecules

T (°C)	$\langle L\rangle$ (nm)	X	M_{Cu} (g/mol)
20	8.4	1	
49	7.6	0.96	
60	7.4	0.99	
80	7.5	0.84	
90	7.5	0.6	1180

the scattering at high temperature of a bicopper complex solution is flat.) Relation 13 reduces to

$$\frac{q^2 I(q)}{C_{\mathrm{Cu}}} = \left[-\frac{2X\mu_{\mathrm{L}}}{\langle L\rangle} + X\mu_{\mathrm{L}}\pi q + (1 - X)M_{\mathrm{Cu}}q^2\right] \quad (14)$$

which is the equation of a parabola $Aq^2 + Bq + C$. Since μ_{L} is known and the same for all the samples, we have $X = B/\pi\mu_{\mathrm{L}}$, $\langle L\rangle = -B/\pi C$, and $M_{\mathrm{Cu}} = A/(1 - X)$.

The different values are gathered in Table 1 and plotted in Figure 5 ($\langle L\rangle$ and X as a function of $1/T$). As can be seen, the value of X drops abruptly beyond $T_\varphi = 333$ K (60 °C) while the value of $\langle L\rangle$ is little affected and even seems to level off beyond T_φ. The transition for X at T_φ corresponds within experimental uncertainties to that reported by Dammer et al. on the basis of rheological parameters,[3] in particular the drop of plateau modulus (note that X is not affected whether l_{p} is virtually equal to or larger than $\langle L\rangle$). This together with the virtually nonvariant value of $\langle L\rangle$ suggests that parts of the longest filaments "melt", thus producing shortest filaments and randomly dispersed bicopper complex molecules. The presence of these randomly dispersed bicopper complex molecules is further borne out by the experimental value of $M_{\mathrm{Cu}} \approx 1180$ g/mol, which is in close agreement with the actual value (760 g/mol).

The mechanism involved in the transition process cannot be totally elucidated from these experiments. Yet, the results remain consistent with the melting of junctions zone constituted by filaments interacting side by side on a limited distance as proposed by Dammer at al.[3] (see Figure 6). It is a possibility to explore that under these conditions junction melting yield individual bicopper complex molecules (Figure 6). The reason why these individual molecules do not re-form new filaments remains puzzling. Cates' theory may eventually not pertain to these systems at high temperature because the specific interactions with the solvent molecules are ignored. For instance, a strong solvation effect may prevent further aggregation.

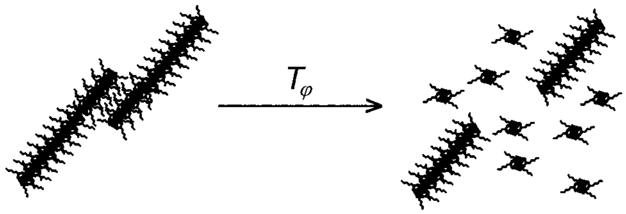

Figure 6. Schematic drawing of a possible molecular mechanism occurring at T_φ for explaining both the increase of the fraction of bicopper complex molecules not engaged in the formation of filaments and the drop of elastic modulus as observed by Dammer et al.

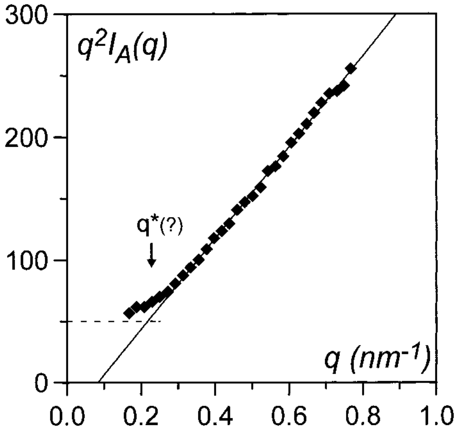

Figure 7. Scattering curve in a Kratky representation ($q^2 I_{\mathrm{A}}(q)$ vs q) for self-assembled CuS8 in *cis*-decalin limited to the domain wherein eq 7 applies ($C_{\mathrm{Cu}} = 0.08$ g/cm^3). There is a noticeable departure from linearity for $q < 0.25$.

2. CuS8/*cis*-Decalin. The existence of specific interactions is best illustrated when either conformer of decalin is used (*cis*- or *trans*-decalin). The macroscopic behavior of CuS8/*cis*-decalin systems, in particular the rheological properties, differ markedly. While viscous "jellies" are obtained for concentrations as low as 0.005 g/cm^3 in *trans*-decalin, concentrations above 0.07 g/cm^3, namely 10 times larger, are needed in *cis*-decalin to reach similar viscosities.[15]

As can be seen in Figure 7, the scattering curve in *cis*-decalin ($C_{\mathrm{Cu}} = 0.08$ g/cm^3) does not differ dramatically from that observed in *trans*-decalin; in particular, the mean length $\langle L\rangle$ is virtually the same ($\langle L\rangle \approx 9-10$ nm). Worth noting, however, is a change of behavior for $q < 0.25$ nm^{-1}. Since the rather low viscosity of these solutions suggests a very low content, or even the absence, of long filaments, this behavior may arise from the presence of small aggregates (CuS8 "crystals"). A study at much lower q should allow one to settle this point.

If the occurrence of long filaments in these solvents arises effectively from a side-by-side aggregation, then this process appears to be impeded for low-concentrated *cis*-decalin solutions. In other words, the melting of these "junctions" as portrayed in Figure 6 takes place at a lower temperature in *cis*-decalin than in *trans*-decalin. That viscous "jellies" are obtained by increasing the concentration would simply mean that these "junctions" become more stable, which makes sense in the

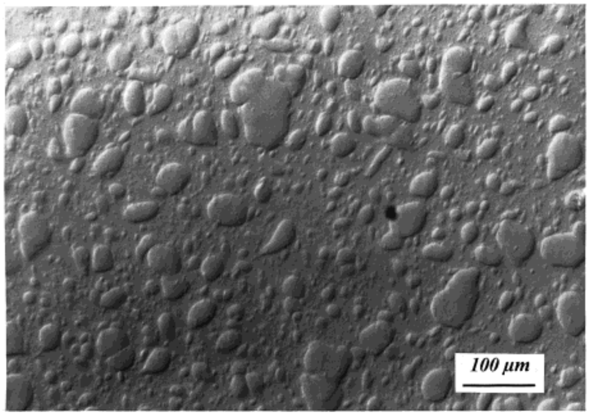

Figure 8. Optical micrograph of a ternary mixture C_{Cu}= 0.04 g/cm^3 + C_{aPS} = 0.07 g/cm^3 at room temperature. Scale as indicated.

case of a first-order transition (the higher the concentration, the higher the melting point).

II. The Ternary System CuS8/aPS/*trans*-Decalin. 1. **Phase behavior of the Ternary System CuS8/aPS/*trans*-Decalin.** At high temperature (T > 120 °C) atactic polystyrene and the bicopper complex form clear solutions, which suggests a high degree of compatibility. This does not come as a surprise since at this temperature bicopper complex molecules are nonaggregated and randomly dispersed. On cooling, turbidity sets in due to phase separation as confirmed by optical microscopy (see Figure 8). The kinetics of phase separation turns out to be rather slow since the formation of two macroscopic phases takes several hours. Thanks to this retarded phase separation process, neutron scattering experiments can be carried out as they just require counting times of about 1 h. To be sure, two consecutive measurements did not show any noticeable discrepancies. Of further note is the crystallization of the bicopper complex after macroscopic phase separation has taken place.

It is worth emphasizing that both decalin isomers are Θ-solvents to atactic polystyrene at room temperature.[16]

2. **Self-Assembled Bicopper Complex Structure in the Polymer Solution.** The conspicuous effect when aPS is added to the binary system Cus8/*trans*-decalin is the decrease of X, namely the increase of nonaggregated bicopper complex molecules. Two cases are worth examining:

(*a*) *At Constant Bicopper Concentration* (C_{Cu} = 0.07 g/cm^3). X is seen to decrease as C_{aPS} increases. Unlike in the binary system, the decrease of X is rather monotonic with increasing temperature (see Figure 9). However, the gradient of X with temperature (dX/dT), which is negative for C_{aPS} = 0.04 g/cm^3 (as with C_{aPS} = 0), becomes positive for C_{aPS} = 0.08 and C_{aPS} = 0.16 g/cm^3. Any abrupt transition is definitely absent for the last two concentrations while there might be still one for C_{aPS} = 0.04 g/cm^3, although not as sharp as with the binary system.

For C_{aPS} = 0.04 g/cm^3 the mean length $\langle L\rangle$ slightly decreases and then levels off as with the binary system (Figure 10). Conversely, for C_{aPS} = 0.08 and C_{aPS} = 0.16 g/cm^3 the mean length decay appears to be exponential. Use of relation 5 yields E_{scis} = 5.7 kJ for C_{aPS} = 0.08 g/cm^3 and E_{scis}= 10 kJ for C_{aPS} = 0.16 g/cm^3. These values are of about 1 order of magnitude lower than those reported for giant micelles.[17]

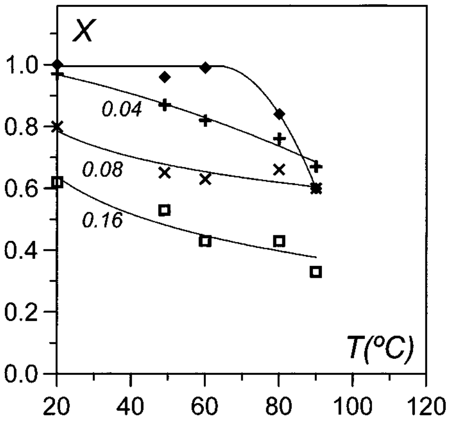

Figure 9. Variation as a function of temperature of the fraction of filaments in ternary mixture CuS8 + aPS + *trans*-decalin at constant bicopper complex concentration. (◆) C_{aPS} = 0; (+) C_{aPS} = 0.04 g/cm^3; (×) C_{aPS} = 0.08 g/cm^3; (□) C_{aPS} = 0.16 g/cm^3. Solid lines are guides for the eye.

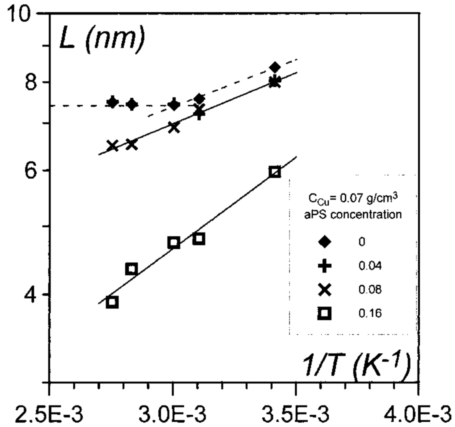

Figure 10. Variation as a function of the reciprocal of the temperature of the mean length of filaments in ternary mixture CuS8 + aPS + *trans*-decalin at constant bicopper complex concentration. (◆) C_{aPS} = 0; (+) C_{aPS} = 0.04 g/cm^3; (×) C_{aPS} = 0.08 g/cm^3; (□) C_{aPS} = 0.16 g/cm^3. The last two sets of results have been fitted with exponential functions (solid lines). Dotted lines are guides for the eye that highlight the transition at T_φ.

Again, the exponential decay of $\langle L\rangle$ as a function of the reciprocal of the temperature in the investigated temperature range is consistent with the absence of any first-order transition in the samples with the highest two polymer concentrations.

If we infer from what has been discussed above that the side-by-side aggregation is revealed by a sharp transition in the variation of $\langle L\rangle$ as a function of temperature; then increasing polymer concentration seems to suppress this type of interaction between filaments and correspondingly impedes the formation of the longest threads. In the presence of polymer chains the CuS8 filaments display a behavior as a function of temperature closer to that described by Cates' theory.[4]

(*b*) *At Constant Polymer Concentration.* The increase of bicopper complex concentration while keeping the atactic polystyrene concentration constant also entails a significant decrease of the fraction X of filaments with some leveling off (see Figure 11). The decay turns out to be stronger for the lowest polymer concentration. Correspondingly, the mean length $\langle L\rangle$ remains virtually constant. So, *increasing the proportion of bicopper complex in the ternary mixture does not enhance the fraction of filaments, but has an opposite effect.*

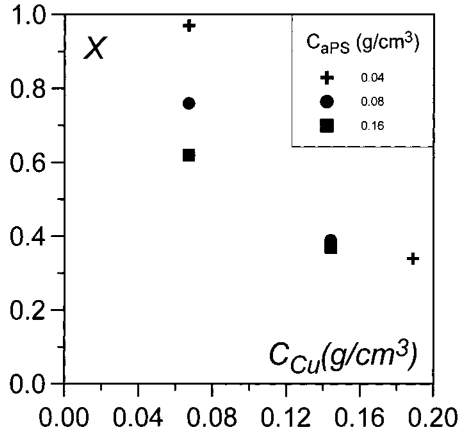

Figure 11. Variation of the fraction of CuS8 filaments in ternary mixtures as a function of the bicopper complex concentration. (+) $C_{aPS} = 0.04$ g/cm^3; (●) $C_{aPS} = 0.08$ g/cm^3; (■) $C_{aPS} = 0.16$ g/cm^3.

The increase of global concentration, namely the increase of the polymer fraction or of the bicopper complex fraction, entails the same effect: decrease of the fraction of bicopper complex molecules engaged in the filaments. This is possibly related to the fact that increasing the concentration of either component results in the increase of the proportion of one phase with respect to the other. This would mean that one phase houses the filaments while the other receives the nonaggregated bicopper complex molecules. That X decreases to lower values on adding bicopper complex (which increases the proportion of polymer-poor phase) than on adding polymer (which increases the proportion of polymer-rich phase) may suggest that the filaments are rather located in the polymer-rich phase. Additional experiments are clearly needed to settle this point.

Concluding Remarks

The results obtained as a function of temperature give further support to the model developed by Dammer et al. where limited side-by-side aggregation of the filaments is thought to occur. Also, the effect of solvent type on the side-by-side aggregation is highlighted. *trans*-Decalin seems to promote it unlike *cis*-decalin. Similar solvent type effects have been observed in the gelation or the crystallization habit of polymers and have been shown to arise from the formation of polymer−solvent compounds.[7] To put it simply, all happens as if the interactions between adjacent rods were mediated by the solvant. That the bicopper complex also forms differing compounds whether *trans*- or *cis*-decalin is used is quite possible but remains an open question. In principle, this could be checked by using highly concentrated systems and finding out by means of diffraction techniques whether the solvent molecules are intercalated between the CuS8 columns in the hexagonal phase.[18]

The results obtained for the ternary systems (aPS/CuS8/*trans*-decalin) suggest that CuS8 filaments are rather located within the polymer-rich phase. This is consistent with a recent report on the role of CuS8 filaments as a nucleating agent of isotactic polystyrene fibrils under gelling conditions.[6] We also note that in ternary solutions at 20 °C the mean length of the filaments is longer than what has been reported for the gelling system containing iPS instead of aPS. This is especially conspicuous for low polymer concentrations ($\langle L \rangle \approx 9$ nm vs 6 nm). This observation is again consistent with the nucleation role of CuS8 filaments as gelation sets in at higher temperature. The resulting encapsulation of the filaments within the polymer fibrils is expected to hamper their growth. We, however, note that no evidence was reported for the existence of isolated bicopper complex molecules (i.e., not engaged in the formation of filaments) for the gelling system. This is most puzzling but may be due to the fact that gelation impedes phase separation to proceed further. Clearly, the gelling system is out of equilibrium whereas the nongelling system is near equilibrium (actually metastable but for a sufficient time as to appear to be near equilibrium).

Evidently, a specific theory dealing with such ternary systems is much needed to throw some light on these results and provide clues for future experiments.

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