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Mixing of a self-assembled supramolecular polymer and a covalent polymer in organic solutions[☆]

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Abstract

We report on a neutron scattering study of the molecular structure of a self-assembled supramolecular polymer composed of a bicopper complex within a solution of a covalent polymer (atactic polystyrene/*trans*-decalin). The study is achieved by putting two binary phases in contact and allowing for diffusion of both components in either phase. It is shown that the one-dimensional bicopper filaments are compatible to a high extent with the atactic polymer. These results are discussed in the light of a recently devised encapsulation process of the bicopper filaments within the fibrils of a physical network of isotactic polystyrene.

Keywords: Covalent polymer; Self-assembling; Supramolecular polymer

1. Introduction

In recent papers, it has been shown that the one-dimensional filaments produced from the piling of bicopper complex molecules of the type shown in Fig. 1 can be encapsulated within a polymer sheath [1,2]. This is achieved through a heterogeneous nucleation process in which the filaments act as heterogeneous nuclei for the growth of fibrils of an isotactic polystyrene physical network in *trans*-decalin [1]. The heterogeneous nucleation phenomenon has been particularly evidenced through an increase of the gelation temperature up to a certain fraction of bicopper complex. To be sure, at higher bicopper fraction the gelation temperature levels off, an effect which has been assigned to an additional liquid–liquid phase separation. The occurrence of such a type of phase separation is not surprising as the system consists of a mixture of two polymers [3,4]: a *covalent polymer* (iPS) of infinite lifetime, and a *self-assembled supramolecular polymer* of finite lifetime [5,6] (the bicopper complex filaments). Note that, in addition to the scission-recombination characterizing the self-assembled supramolecular polymer, namely filaments are ceaselessly broken while new ones form, the 1D filament state is metastable as it transforms gradually into 3D crystals.

With the aim of grasping the details of the encapsulation process Lopez and Guenet [7] have attempted to differentiate the phase separation effect from the gelation process. They have studied the bicopper structure by small-angle neutron scattering in solutions of atactic polystyrene (aPS), a polymer which does not produce physical gel in the solvent used, and accordingly does not encapsulate the bicopper complex filaments. In particular, they expected to find out to which extent the covalent polymer and the self-assembled supramolecular polymer could be compatible. By starting from ternary systems at high temperature, from which homogeneous solutions can be obtained, these authors faced insuperable difficulty. Due to the fact that the kinetics of total demixing into two macroscopic phases occurs too slowly the growth of bicopper complex three-dimensional crystals took over and so hampered a study under near-equilibrium conditions. Only experiments carried out after minimum ageing on microscopically phase separated systems were worth interpreting. From these it was inferred that compatibility was probably quite

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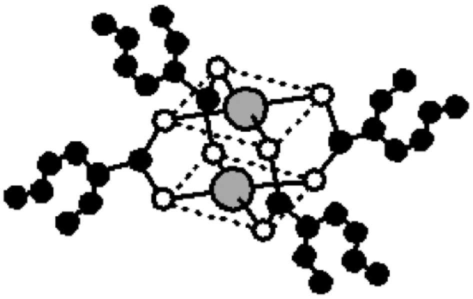

Fig. 1. Chemical structure of the bicopper complex molecule (copper II2-ethyl-hexanoate): grey = copper atom, white = oxygen atom, black = carbon atom. Hydrogen atoms are not represented for the sake of clarity.

important at least in one phase but it could not be told which phase was involved.

The purpose of this paper is to report on neutron scattering investigation of the molecular structure of the bicopper complex mixed with a covalent polymer, namely aPS, by using another experimental approach. Instead of starting from one homogeneous ternary system, two binary solutions are put into contact, and the diffusion process of each component in either phase is allowed to take place. After some time, a near-equilibrium is reached while two macroscopic phases are still observable. No 3D crystals are seen to grow so under these conditions so that a measure of the amount and the determination of the molecular structure of the state of the complex in each phase can be achieved.

2. Experimental

2.1. Materials

Deuterated atactic polystyrene was synthesized by classical anionic polymerization. The different moments of the molecular weight distribution were determined by SEC in THF at 25 °C. The following values were obtained for the weight-averaged molecular weight and the index of polydispersity: $M_w = 1.57 \times 10^5$ g/mol with $M_w/M_n = 1.2$.

The bicopper complex used in this study, designated as CuS8, was prepared from the sodium salt of *2-ethyl-hexanoic acid* through the following reaction [8]:

$$2CuSO_4 + 4C_8H_{15}O_2^-Na^+ \rightarrow [Cu(C_8H_{15}O_2)_2]_2 + 2Na_2SO_4$$

The reaction was achieved in water where the bicopper complex, once formed, is insoluble. After recrystallization in heptane, the bicopper complex was filtered and dried under vacuum. Elementary analysis has given the following weight fractions (theoretical values are given in brackets): C = 54.83% (54.91%); Cu = 17.75% (18.16%); H = 8.65% (8.64%).

Hydrogenous *trans*-decahydronaphthalene (designated as TdecaH in what follows) was purchased from Aldrich while the deuterated *trans*-decahydronaphthalene (designated as TdecaD in what follows) was obtained from Eurisotop (Saclay, France). Both solvents were used without further purification.

2.2. Techniques

2.2.1. UV–visible spectrometry

Determination of the bicopper complex concentration and the polymer concentration in the different phases was performed by UV–visible spectrometry (Shimadzu UV-2101 PC spectrometer) at room temperature. The systems were studied in quartz cells of 0.1 cm optical path. The absorbance A of the bicopper complex was determined in the range 400–800 nm (absorption at 670 nm) and that of atactic polystyrene in the range 200–400 nm (absorption at 259 nm). Calibration was achieved with pure solutions of bicopper complex or deuterated polystyrene. The actual concentrations in each phase were then determined through the relation:

$$A = \log I/I_o = \varepsilon l C_i \tag{1}$$

where I/I_o is the transmission, ε_i and C_i the absorption coefficient and the concentration of species I, and l the optical path.

2.2.2. Small-angle neutron scattering

The experiments were performed on V4 camera at BENSC-Hahn-Meitner Institut (Berlin FRG). Neutrons were selected from the 'white' beam by means of a mechanical chopper. They were characterized by a wavelength distribution function of full width at half maximum, FWHD = $\Delta\lambda/\lambda_m \approx 10\%$ and a nominal neutron wavelength of $\lambda_m = 0.6$ nm. Counting was achieved with a ^{3}He-built-in two-dimensional sensitive detector composed of 64×64 cells of 10×10 mm^2 area (further details are available at website http://www.hmi.de/bensc). By changing the sample-detector distance (S-D = 5 and 1.4 m) the q-range made available was $0.1 < q$ (nm^{-1}) < 2.5 where $q = (4\pi/\lambda_m)\sin(\theta/2)$, θ being the scattering angle.

In order to match the coherent scattering amplitude of the deuterated polymer the solvent mixture contained a high fraction of deuterated solvent, namely 91% tdecaD/9% tdecaH in v/v. Under these conditions, the only remaining coherent scattering is that of the bicopper complex, $I_{CuS8}(q)$, which is written after empty cell subtraction, normalization by the totally incoherent scattering of hydrogenous water and proper calibration:

$$I_{CuS8}(q) = \left[I_s(q) - (1-\varphi)I_o - 8.65\varphi \frac{N_p}{V_{CuS8}} \right] \frac{1}{K} \tag{2}$$

where $I_s(q)$ is the total intensity scattered by the sample, I_o the intensity scattered by a aPS/0.91-trans-decaD/0.09-trans-decaH, φ the bicopper complex volume fraction (due to normalization $I_s(q)$ and I_o are dimensionless). The third term in brackets, which stands for the incoherent background scattered by the hydrogenous bicopper complex, is calculated by means of the relation determined experimentally by

Fazel et al. [9]. N_p is the number of protons in the molecules (here 60) and V_{CuS8} is the molar volume of the bicopper complex. Finally, K is a constant which reads:

$$K = \frac{4\pi B_x^2 \delta_w T_w N_A}{g(\lambda_m)(1 - T_w)m_i^2} \quad (3)$$

in which T_w the transmission of the light water sample of $\delta_w = 0.1$ cm thickness, m_i the molecular weight of the scattering unit, N_A Avogadro's number, and $g(\lambda_m)$ a dimensionless constant (= 1.76) which is camera-dependent and was measured by using Cotton's method [10]. B_x is the scattering amplitude of the complex with respect to the solvents, i.e. the mixture of deuterated and hydrogenous decalins. K is expressed here in cm^3/g^2 and the intensity $I_{CuS8}(q)$, expressed in g^2/cm^3, accordingly. This is so because $I_{CuS8}(q) = C\mu P(q)$ where C is a concentration in g/cm^3, μ some molecular weight and $P(q)$ a dimensionless structure factor.

2.2.3. Sample preparation and investigation procedure

Bicopper solutions and polymer solutions were prepared separately in mixtures of deuterated *trans*-decalin and hydrogenous *trans*-decalin. Dissolution was achieved at 150 °C for the bicopper complex and at 20 °C for the polymer. For both UV and neutron experiments, the bicopper complex solution was introduced first in a quartz cell of 0.1 cm optical path, and then the polymer solution was added slowly on top of it. Equivalent volumes of solution were used. The measurements were performed by illuminating either the lower bicopper phase (designated as *copper-rich* phase) or the upper polymer phase (designated as *polymer-rich* phase) as portrayed in Fig. 2. UV beam and neutron beam cross-sections were adjusted so as to make sure that only one phase was studied at a time. All the experiments were carried out at 20 ± 1 °C after allowing phase interdiffusion for 72 h (see Section 3). UV and neuton scattering experiments were carried out on the same type of samples, namely deuterated polymer and mixture of deuterated and hydrogenous *trans*-decahydronaphthalene.

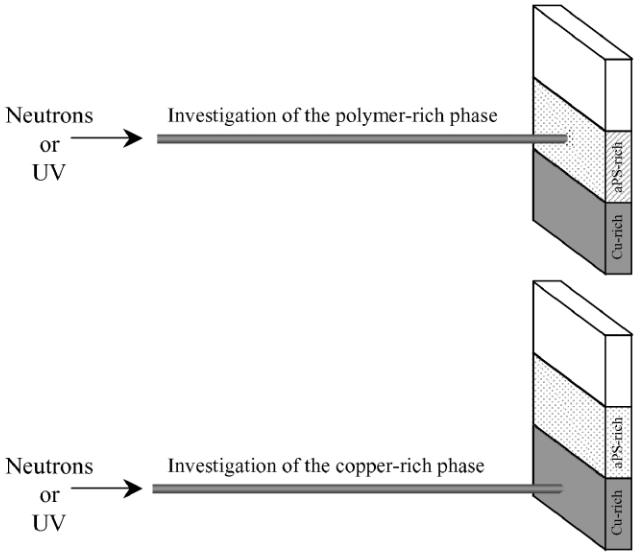

Fig. 2. Sketch of the way UV and neutron scattering experiments were carried out. The *polymer-rich* phase is always on top of the *copper-rich* phase.

Two types of samples have been investigated: Type I where the concentration of the polymer-rich phase is kept constant ($C_{aPS} = 0.04$ g/cm^3) and the concentration of the copper-rich phase varies from $C_{CuS8} = 0.02$ g/cm^3 to 0.06 g/cm^3, and Type II where the concentration of the copper-rich phase is kept constant ($C_{CuS8} = 0.04$ g/cm^3) and the concentration of the polymer-rich phase varies from $C_{aPS} = 0.02$ to 0.06 g/cm^3. Note that *trans*-decalin is a θ-solvent for aPS at 20 °C. The current concentrations are larger than C^*($C^* \approx 0.012$ g/cm^3) if one estimates C^* from the mass of the polymer contained in a sphere of radius $\langle s^2 \rangle^{1/2}/2$ where $\langle s^2 \rangle^{1/2}$ is the chain average end-to-end distance and which equals to ≈30 nm in the present case [11].

3. Results and discussion

3.1. Concentrations of the different components in either phase as studied by UV

A typical time-evolution of the bicopper complex concentrations in the two phases is shown in Fig. 3 where the UV-absorbance is plotted as a function of time. The concentrations level off after 45–72 h. As a result, all the experiments were carried out after allowing the bicopper complex and the polymer to diffuse for 72 h.

Note that we shall use in what follows the terms *copper-rich* phase for the starting pure solution of bicopper complex and *polymer-rich phase* for the starting pure polymer solution. As will be seen these terms are not strictly valid once diffusion has taken place but are convenient for designating the lower and upper phases.

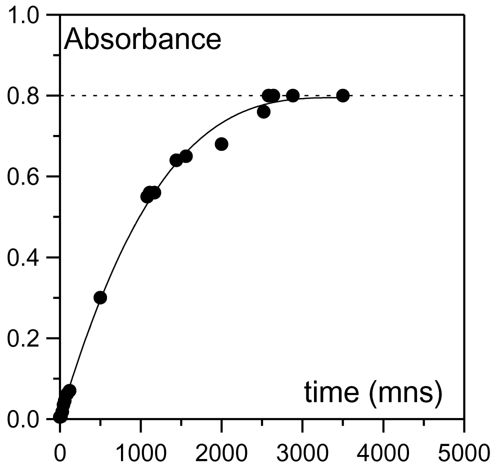

Fig. 3. Absorbance of bicopper complex at λ = 670 nm vs time. The solid line is a guide for the eyes.

The values of the concentration in the different phases and for the different components are gathered in Tables 1–3. The following issues are worth stressing.

(i) Keeping the bicopper complex concentration constant in the *starting copper-rich* phase while varying the polymer concentration in the *starting polymer-rich* phase entails, within experimental uncertainties, the diffusion of a constant amount of bicopper complex into the polymer-rich phase. Also, the partition of the bicopper complex in either phase is virtually a constant.
(ii) The bicopper complex concentration in the *polymer-rich* phase after interdiffusion has taken place decreases with increasing the bicopper complex concentration in the *starting copper-rich* phase while keeping the polymer concentration constant in the *starting polymer-rich* phase. Here, the partition of the bicopper complex in either phase decreases quite markedly with increasing the concentration of the *copper-rich* phase.
(iii) Surprisingly, there is almost equipartition of the polymer in both phases.

These results show that large amounts of bicopper complex can coexist with a covalent polymer.

It is worth again stressing that, unlike covalent polymer, the filaments of bicopper complex have a finite lifetime: they ceaselessly break while new ones form. Diffusion of the bicopper complex into the polymer phase can certainly not be regarded the same as that of a covalent polymer. Isolated bicopper complex molecules can diffuse in the polymer phase and once there form long filaments. Diffusion can thus be more rapid than would be expected if two covalent polymers were allowed to diffuse into one another.

To find out whether the bicopper complex is still able to form filaments can be achieved by a small-angle neutron scattering investigation.

3.2. Molecular structure of the bicopper complex

It has been shown in previous publications that the neutron scattering curve in the present q-range (namely for $qL > 1$) can be fitted with a prolate cylinder model whose equation is written [1,2,7,12]:

$$q^2 I_A(q) = C_{CuS8}\mu_L \frac{4J_1^2(qr_c)}{q^2 r_c^2}\left[\pi q - \frac{2}{\langle L\rangle}\right] \qquad (4)$$

in which μ_L and r_c are the mass per unit length, the cross-sectional radius, and $\langle L\rangle$ the mean-length of the bicopper complex filaments, respectively, and J_1 is the Bessel function of first kind and order 1. Typically, the cross-sectional radius of these filaments is $r_c \approx 0.9 \pm 0.1$ nm and $\mu_L \approx 1500 \pm 300$ g/nm mol. This implies that filaments are obtained through the one-dimensional piling of bicopper complex molecules.

Although these systems are dynamic, self-assembled systems [5,6], it has been previously concluded that the length distribution function might depart significantly from a Boltzmann type [7] in this solvent. Rather, the solutions are likely to consist in a mixture of short filaments ($\langle L\rangle$ being about 10–15 nm) and of very long filaments. The existence of the latter is inferred from rheological experiments [13].

Here too, in spite of using polymer-containing solutions as a matrix, the ratio signal/noise is quite high (see Fig. 4). Also, the use of a mixture of deuterated and hydrogenous solvents allows one to match to a very large extent the coherent signal of the polymer as ascertained by the virtually flat signal of the matrix. Note that the flat, incoherent signal of the bicopper complex (3rd term in bracket in relation (2) represents approximately 10% of the total background for the case shown in Fig. 4.

We shall now examine the molecular structure of the bicopper complex for each type of samples and in both phases.

3.2.1. Molecular structure in Type I samples (starting polymer phase of same concentration)

The scattering curve in the *copper-rich* phase reported in Fig. 5 is virtually identical to that observed in the binary system copper complex/*trans*-decalin [7], namely filaments created through the one-dimensional piling of bicopper complex molecules. As a matter of fact, the fit by means of relation (4) gives the same parameters as those reported earlier (namely $\mu_L = 1500 \pm 500$ g/nm mol, $r_c = 0.9 \pm 0.01$ and $\langle L\rangle = 13 \pm 2$ nm, for further details see Table 1). The molecular structure turns out to be independent of the starting bicopper complex concentration.

Table 1
Type I samples; polymer concentration is kept the same in the *starting polymer phase* while bicopper complex concentration varies in the *starting copper phase*. The variation of the concentrations of the bicopper complex in the different phases is given after 72 h diffusion. The partition P of the bicopper complex in the *copper-rich* phase is given through $P = C_{CuS8}(CR)/C_{CuS8}$ and through $1 - P = C_{CuS8}(PR)/C_{CuS8}$ in the *polymer-rich* phase

C_{aPS}, $t = 0$ (g/cc)	C_{CuS8}, $t = 0$ (g/cc)	Copper-rich phase			Polymer-rich phase		
		$C_{CuS8}(CR)$, $t = 72$ h	μ_L (g/nm mol)	P	$C_{CuS8}(PR)$, $t = 72$ h	μ_L (g/nm mol)	$1 - P$
0.04	0.02	0.009 ± 0.001	1900 ± 300	0.45	0.011 ± 0.001	1200 ± 300	0.55
0.04	0.04	0.032 ± 0.002	2200 ± 300	0.8	0.009 ± 0.001	1600 ± 300	0.2
0.04	0.06	0.052 ± 0.002	1900 ± 250	0.87	0.008 ± 0.001	–	0.13

Table 2
Type II samples; bicopper complex concentration is kept the same in the *starting copper phase* while polymer concentration varies in the *starting polymer phase*. The variation of the concentrations of the bicopper complex in the different phases is given after 72 h diffusion. The partition P of the bicopper complex in the *copper-rich* phase is given through $P = C_{\mathrm{CuS8}}(\mathrm{CR})/C_{\mathrm{CuS8}}$ and through $1 - P = C_{\mathrm{CuS8}}(\mathrm{PR})/C_{\mathrm{CuS8}}$ in the *polymer-rich* phase

C_{aPS}, $t = 0$ (g/cc)	C_{CuS8}, $t = 0$ (g/cc)	Copper-rich phase			Polymer-rich phase		
		$C_{\mathrm{CuS8}}(\mathrm{CR})$, $t = 72$ h	μ_L (g/nm mol)	P	$C_{\mathrm{CuS8}}(\mathrm{PR})$, $t = 72$ h	μ_L (g/nm mol)	$1 - P$
0.02	0.04	0.032 ± 0.002	2100 ± 300	0.8	0.008 ± 0.001	1600 ± 300	0.2
0.04	0.04	0.032 ± 0.002	2100 ± 300	0.8	0.008 ± 0.001	1800 ± 300	0.2
0.06	0.04	0.033 ± 0.002	2300 ± 300	0.825	0.008 ± 0.001	–	0.175

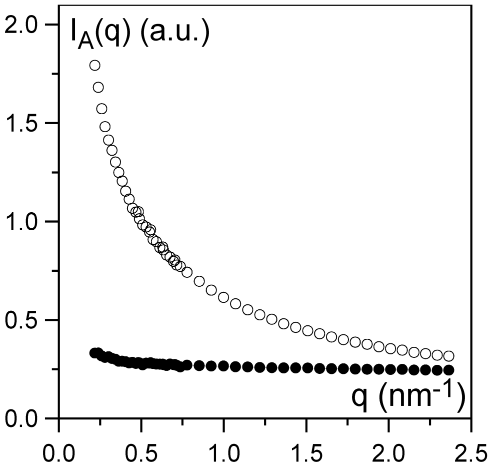

Fig. 4. Scattered intensity in arbitrary units for a bicopper sample $C_{CuS8} = 0.02$ g/cm^3 (○) and the corresponding matrix *aPS/0.91tdecaD/0.09tdecaH* (●).

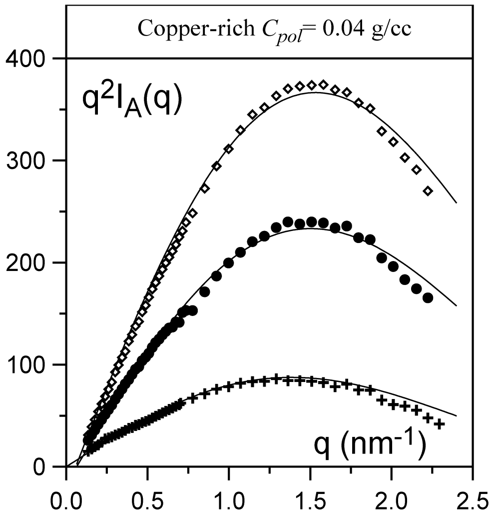

Fig. 5. Scattering curves for bicopper molecules located in the *copper-rich* phase (in g^2/cm^3 nm^2). Samples of Type I: constant concentration of the *starting polymer-rich* phase ($C_{\mathrm{aPS}} = 0.04$ g/cm^3) and variable concentration of the *starting copper-rich* phase. $C_{\mathrm{CuS8}} = 0.02$ g/cm^3 (✚); $C_{\mathrm{CuS8}} = 0.04$ g/cm^3 (●); $C_{\mathrm{CuS8}} = 0.06$ g/cm^3 (◇). The solid lines represent best fits with relation (4) with $r_c = 0.09 \pm 0.005$ nm and $\langle L \rangle = 12 \pm 2$ nm. Values of μ_L are gathered in Table 1.

Concerning the *polymer-rich* phase (Fig. 6) only the domain where $qr_c < 1$ has been studied because only the determination of μ_L was of interest. Under these conditions relation (4) of the scattered intensity reduces to:

$$q^2 I_A(q) \approx C_{\mathrm{CuS8}}\mu_L\left(1 - \frac{q^2 r_c^2}{4}\right)\left[\pi q - \frac{2}{\langle L \rangle}\right]$$
$$\approx C_{\mathrm{CuS8}}\mu_L\left[\pi q - \frac{2}{\langle L \rangle}\right] \quad (5)$$

In a Kratky-representation ($q^2 I_A(q)$ vs q) a straight line is therefore obtained. For $C_{\mathrm{CuS8}} = 0.02$ and 0.04 g/cm^3 a linear variation is observed so that the same conclusions as above are reached. Conversely, for $C_{\mathrm{CuS8}} = 0.06$ g/cm^3 a significant upturn occurs at low q-values while the linear domain seems to reappear at larger q. This suggests the presence of 3D objects, most probably CuS8 crystals, together with CuS8 filaments. For $qr_c < 1$. The scattered intensity can indeed be fitted with [2,7]:

$$q^2 I_A(q) = (1 - X)C_{\mathrm{CuS8}}\frac{2\pi\rho S}{Vq^2} + XC_{\mathrm{CuS8}}\mu_L\left[\pi q - \frac{2}{\langle L \rangle}\right] \quad (6)$$

where X is the fraction of filaments, $(1 - X)$ the fraction of crystals, S and V the crystals surface and volume, and ρ their density in g/nm^3 mol. Taking $\mu_L \approx 1500$ g/nm mol, one obtains $1 - X \approx 0.6$.

Table 3
Variation of the concentrations of the polymer in the different phases after 72 h diffusion

C_{aPS}, $t = 0$ Polymer-rich phase	C_{CuS8}, $t = 0$ Copper-rich phase	C_{aPS}, $t = 72$ h Polymer-rich phase	C_{aPS}, $t = 72$ h Copper-rich phase
0.04	0.02	0.015 ± 0.001	0.025 ± 0.002
0.04	0.04	0.02 ± 0.002	0.02 ± 0.002
0.04	0.06	0.018 ± 0.002	0.022 ± 0.001
0.02	0.04	0.009 ± 0.001	0.011 ± 0.001
0.06	0.04	0.032 ± 0.002	0.028 ± 0.002

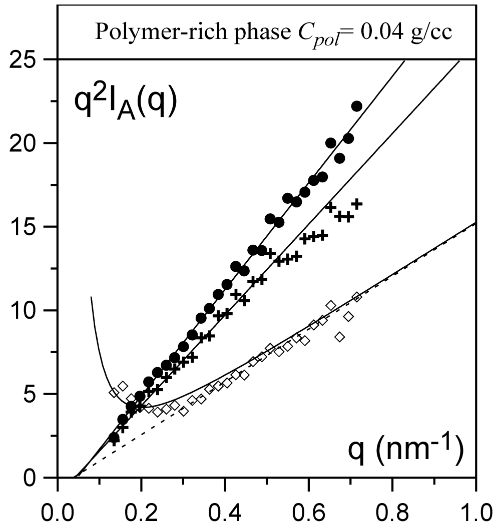

Fig. 6. Scattering curves for bicopper molecules located in the *polymer-rich* phase (in g^2/cm^3 nm^2). Samples of Type I: constant concentration of the *starting polymer-rich* phase ($C_{aPS} = 0.04$ g/cm^3) and variable concentration of the *starting copper-rich* phase. $C_{CuS8} = 0.02$ g/cm^3 (✚); $C_{CuS8} = 0.04$ g/cm^3 (●); $C_{CuS8} = 0.06$ g/cm^3 (◇). The straight lines represent a best fit with relation (5) while the curved line stands for a fit with relation (6). Again, $\langle L\rangle = 12 \pm 2$ nm. Values of μ_L are gathered in Table 1.

3.2.2. *Molecular structure in Type II samples (starting bicopper complex phase of same concentration)*

The scattering curves can be also fitted with straight lines for the results obtained from the *copper-rich* phase (see Fig. 7). Data obtained from relation (5) and gathered in Table 2 show again that bicopper complex filaments are dealt with, independent of the polymer concentration of the polymer-rich phase.

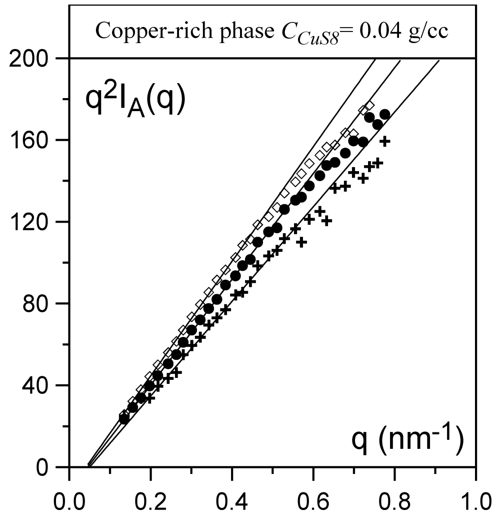

Fig. 7. Scattering curves for bicopper molecules located in the *copper-rich* phase (in g^2/cm^3 nm^2). Samples of Type II: constant concentration of the *starting copper-rich* phase ($C_{CuS8} = 0.04$ g/cm^3) and variable concentration of the *starting polymer-rich* phase. $C_{aPS} = 0.02$ g/cm^3 (✚); $C_{aPS} = 0.04$ g/cm^3 (●); $C_{aPS} = 0.06$ g/cm^3 (◇). The straight lines represent a best fit with relation (5). Again, $\langle L\rangle = 12 \pm 2$ nm. Values of μ_L are gathered in Table 2.

In the polymer-rich phase straight lines are also observed for $C_{pol} = 0.02$ g/cm^3 and 0.04 g/cm^3 while significant departure from linearity takes place for $C_{pol} = 0.06$ g/cm^3 (Fig. 8). This result is similar to that reported by Lopez and Guenet [7] and suggests that the bicopper complex is under two states: filaments and individual molecules. As a matter of fact, under such circumstances the scattered intensity can be written for $qr_c < 1$ (see Ref. [2]):

$$q^2 I_A(q) = C_{CuS8}\left[-\frac{2X\mu_L}{\langle L\rangle} + X\mu_L\pi q + (1-X)M_{CuS8}q^2\right] \qquad (7)$$

in which X is the fraction of filaments and $1 - X$ the fraction of individual molecules whose molecular weight is M_{CuS8}. Relation (7) therefore indicates that the scattering curve is a parabola. From a fit with relation (7), X is found to be about $X \approx 0.63 \pm 0.06$ and $M_{CuS8} \approx 1150 \pm 200$ g/mol (theoretical value for one bicopper complex molecule $M_{CuS8} = 700$) (Table 4).

4. Concluding remarks

The outcomes from this series of experiments are manifold.

(i) The fraction of bicopper complex in the polymer-rich phase can be quite large.
(ii) There is no detectable difference as long as the molecular structure is concerned between bicopper complex in organic solutions and bicopper complex in polymer solutions. To be sure, what can be concluded

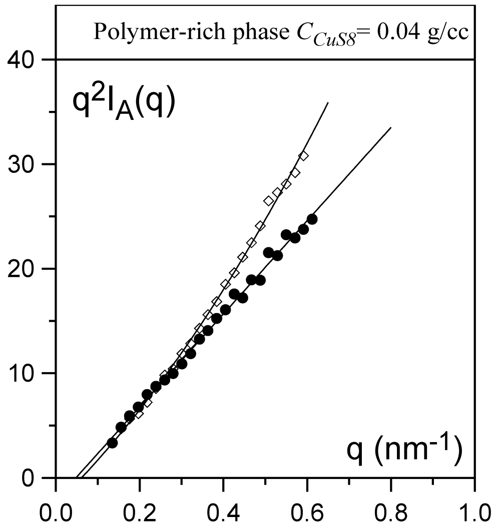

Fig. 8. Scattering curves for bicopper molecules located in the *polymer-rich* phase (in $g^2/cm^3 \times nm^2$). Samples of Type II: constant concentration of the *starting copper-rich* phase ($C_{CuS8} = 0.04$ g/cm^3) and variable concentration of the *starting polymer-rich* phase. $C_{aPS} = 0.04$ g/cm^3 (●); $C_{aPS} = 0.06$ g/cm^3 (◇). The straight line represents a best fit with relation (5) and the curved line with relation (7). Again, $\langle L\rangle = 12 \pm 2$ nm. Values of μ_L are gathered in Table 2.

Table 4
Summary of the structure of the bicopper complex vs polymer and bicopper complex concentrations

Sample type	C_{CuS8} (g/cm^3)	C_{aPS} (g/cm^3)	Copper-rich phase	Polymer-rich phase
Type I, C_{CuS8} varies, $C_{\mathrm{aPS}} = \mathrm{Const}$	0.02	0.04	Filaments	Filaments
	0.04	0.04		
	0.06	0.04	Filaments	Filaments + crystals
Type II, C_{aPS} varies, $C_{\mathrm{Cu}} = \mathrm{Const}$	0.04	0.02	Filaments	Filaments
	0.04	0.04		
	0.04	0.06	Filaments	Filaments + isolated molecules

from the present experiments is the presence of rod-like filaments of about 10–15 nm. As has been highlighted in Section 1, the existence of exceedingly long filaments in binary organic solutions of bicopper complex has been inferred from rheological experiments. Clearly, rheological experiments cannot be carried out with the present samples, so that the occurrence of exceedingly long filaments in ternary systems remains a pending question.

(iii) Increasing the concentration of the *polymer-rich* phase or the *copper-rich* phase entails the appearance of either individual bicopper complex molecules or of crystals of bicopper complex molecules. This is consistent with previous results by Lopez and Guenet [7] which were carried out on samples microscopically phase-separated.

(iv) That a large fraction of bicopper complex filaments can coexist with a covalent polymer in organic solutions accounts for why they behave as a powerful nucleating agent for the growth of the fibrils of isotactic polystyrene thermoreversible gels [1]. These filaments are therefore dispersed within the covalent polymer solution to be gelled and represent a large density of heterogeneous nuclei. As is usual with heterogeneous nuclei, they are encapsulated right in the center of the structure of which they promoted the growth.

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