Encapsulation of Magnetic Self-assembled Systems in Thermoreversible Gels

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Summary: We describe two different ways of encapsulating within the fibrils of thermoreversible polymer gels the filaments of a supermolecular polymer formed by self-assembly of a bicopper complex. Heterogeneous nucleation is brought about with gels made from isotactic poly(styrene) while compound formation occurs with gels made from poly(hexyl isocyanate). These ways depend upon the interaction between the wings of the supermolecular polymer and the side groups of the polymer. In all cases, the filaments retain their 1-D structure. Preliminary results from magnetic susceptibility measurements show a striking difference between the pure and the encapsulated supermolecular polymer.

Keywords: encapsulation; gelation; gels, magnetic properties, supermolecular polymers

Introduction

By a self-assembling process, copper (II) tetra-2-ethylhexanoate (see Figure 1) forms viscous jellies consisting of long, rigid 1-D filaments.[1,2] These systems are referred to as *supermolecular polymers*. Unlike covalent polymers, the threads of supermolecular polymers continuously break up, while new ones are formed with a typical lifetime of less than 1s.[2] To stabilize the filaments, i.e., to yield filaments of "infinite" lifetime, we have used physical methods that produce encapsulation within the fibrils of thermoreversible gels, either from isotactic polystyrene,[3] or from poly(hexyl isocyanate).[4] These gels possess a network morphology made up of interconnected fibrils[3,4] with a mesh size in the micron range, while the fibrils possess cross-section radii in the *nanometre* range. A composite material is thus produced wherein filaments of the bicopper complex are encapsulated inside *nanosized* polymer fibrils.[5] In addition, owing to the presence of copper atoms, these materials are liable to exhibit unusual magnetic properties. In this paper, we give a short outline of these systems.

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The Self-assembling System: Copper (II) tetra-2-ethylhexanoate

Solutions of copper (II) tetra-2-ethylhexanoate (designated as CuS8) in organic solvents such as *trans*-decalin or *n*-octane are highly viscous. As shown in Figure 2, their rheological behaviour can be represented by a Maxwell relation:[2,6]

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

This behaviour can be described by Cates' theory[6] in which the characteristic time is $\tau = \left(\tau_{rep}\tau_{break}\right)^{1/2}$ where τ_{break} is associated with the *scission-recombination* process of the filaments and τ_{rep} is the characteristic *reptation* time.

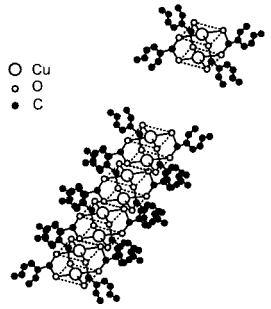

Fig. 1. The chemical structure of the bicopper complex (copper (II) tetra-2-ethylhexanoate) and the way it self-assembles to produce long filaments. The fit between two adjacent molecules occurs through the interaction of a copper atom with an oxygen atom.

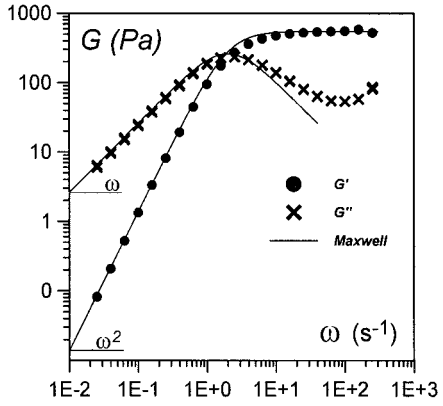

Fig. 2. Typical variation of G' and G'' as a function of frequency ω in oscillatory experiments[2] in *trans*-decalin solutions. The characteristic slopes for $\omega \rightarrow 0$ ($G' = \omega^2$ and $G'' = \omega$) are shown.

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This rheological behaviour is consistent with very long filaments, some of which are longer than 1 μm.[2] It also implies that the filaments have a finite lifetime.

It ought to be stressed that such a behaviour holds as long as the solution is not aged. For ageing times longer than 2 days, the 1-D filament structure is not stable and the bicopper complex eventually forms 3-D crystals.

Although the theory of Cates can describe these systems to a first approximation,[6] the length distribution function may not be exactly given by a Boltzmann distribution.[7] In fact, the intensity scattered by the CuS8 solutions can be fitted by considering a solid prolate cylinder model of cross-sectional radius r_c and mean length $<L>$ (see Figure 3). For $q<L> > 1$ and $<L> > r_c$, the theoretical scattering intensity is written:[8]

$$q^2 I(q) \propto C_{Cu}\mu_L \times \frac{4J_1^2(qr_c)}{q^2 r_c^2} \times \left[\pi q - \frac{2}{< L >}\right] \qquad (2)$$

in which μ_L is the mass per unit length and C_{cu} the bicopper complex concentration. The cross-section radius r_c was found to be r_c= 0.8 nm, a value consistent with one molecule per cross-sectional area. $J_1(x)$ is the cylindrical Bessel function of of 1st kind and 1st order.

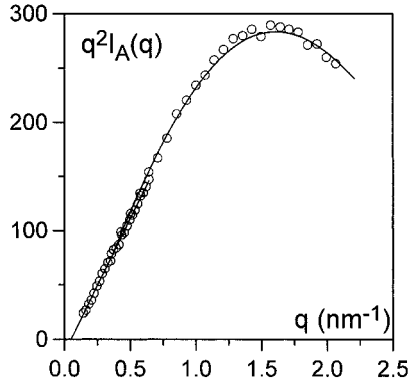

Fig. 3. Kratky-representation ($q^2 I_A(q)$ *vs* q) of the scattered intensity for self-assembled CuS8 in *trans*-decalin solutions. The full line is a best fit through equation (2).

The scattering curve therefore suggests a system made up of rod-like entities of about 10-15 nm in length . Although scattering is rather sensitive to the smallest rods ($<L>$ in equation 2 corresponds to the first moment of the distribution) the value $<L> \approx$ 10-15 nm derived from the scattering curve seems to be in conflict with the rheological data, which are more consistent with far longer filaments. A model that can reconcile both types of experiment consists in considering the presence of a small percentage of very long filaments, thus accounting for the

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rheological behaviour, and a high fraction of small rod-like structures, which explain the scattering curve.[7]

Encapsulation in iPS: Heterogeneous Nucleation Process

Isotactic polystyrene produces thermoreversible gels in *trans*-decalin. These gels display a fibrillar structure with a typical mesh size of about 0.1-1μm and fibrils possessing cross-sections in the nanometer range.[3]

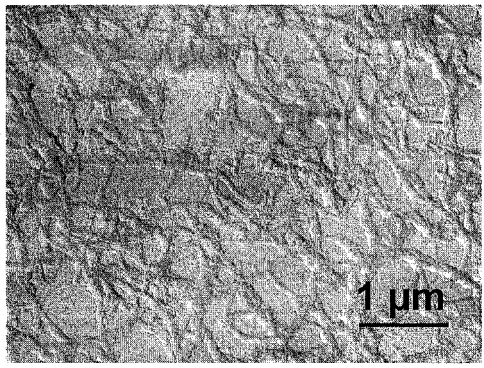

Fig. 4. Electron micrograph of an iPS xerogel.[3] Scale as indicated.

The origin of this morphology lies in the worm-like chain conformation taken by iPS chains in *trans*-decalin solutions.[3] The persistence length in these solutions is about 4 times longer than that in the unperturbed state, which clearly prevents chains from folding during crystallization. As a result, the growth of chain-folded crystals is hindered and fibrils form instead. The reason that the persistence length is enhanced to such an extent is related to the helical structure. The specific solvent, owing to its matching size, is capable of stabilizing the 3_1 helical structure of this polymer, thus reducing the number of accessible conformations.[9]

Gel formation occurs at a well-defined gelation threshold T_{gel} : below T_{gel} fibrillar gels are formed, while above T_{gel} spherulitic structures (i.e, assemblies of chain-folded crystals) grow.[10] There is a significant gap between the gelation threshold and gel melting. The origin of this hysteresis may arise from the fact that gelation occurs through a *homogeneous nucleation* process. This gives birth to a significant undercooling effect, as required for the formation of stable nuclei. Finding appropriate heterogeneous nuclei may thus promote gelation at a much higher temperature by *heterogeneous nucleation*. As gelation occurs through bunching of rigid chains, it can be surmised that rigid, rod-like entities, such as the above

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bicopper complex, may be good candidates for use as a heterogeneous nucleus. This is especially so as the bicopper complex molecules are dispersed at high temperature and are thus compatible with isotactic polystyrene in *trans*-decalin solutions, but also because the filaments form at a higher temperature than the gelation threshold, the latter being at about T= 20°C.[3] One can therefore expect to have long, compatible rigid bicopper complex filaments within the iPS/*trans*-decalin solution while the latter is still disordered.

Calorimetric experiments are well suited for determining the gelation threshold as a function of the content of bicopper complex. In particular, the gelation temperature can be measured as a function of the cooling rate. After proper extrapolation to zero cooling rate, this gives the gelation threshold. Results obtained in this way are shown in Figure 5.[5]

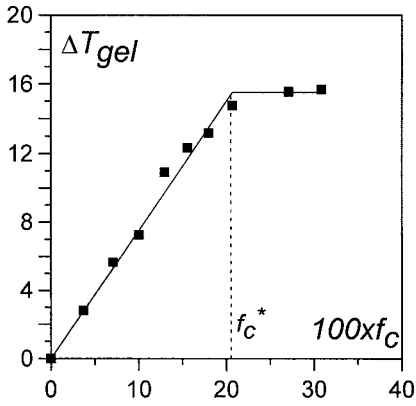

Fig. 5. Variation of the gelation threshold as a function of the composition in bicopper complex (mole fraction of bicopper complex with respect to the polymer) in iPS/*trans*-decalin solutions. Starting polymer concentration C_{pol}= 0.04 g/cm^3.

Although there is a significant increase of the gelation threshold, the gel melting point and the gel melting enthalpy remain virtually constant with increasing bicopper fraction. These findings clearly point to a heterogeneous nucleation effect. The consequence of the occurrence of this phenomenon is that the bicopper complex filaments should be encapsulated within a polymer sheath.[5]

Beyond a given mole fraction of bicopper complex the gelation threshold becomes constant. This is most probably due to the formation of an additional phase into which the bicopper complex is rejected and which is of no further use for nucleation purposes. This point will receive support from the investigation into the molecular structure.

The molecular structure of the polymer and of the bicoppper complex can be determined with

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small angle neutron scattering, by varying the isotopic composition of the solvent and by using deuterated polystyrene and a protonated bicopper complex. In an isotopic mixture of *trans*-decalin (TdecaD/TdecaH= 8/92 v/v) the coherent scattering of the bicopper complex can be matched, thus giving access to the molecular structure of the polymer. Correspondingly, in a TdecaD/TdecaH= 9/91 v/v mixture the reverse situation is obtained, namely the matching of the coherent scattering of the polymer, which gives access to the molecular structure of the bicopper complex. Scattered intensities for both situations are displayed in Figure 6.

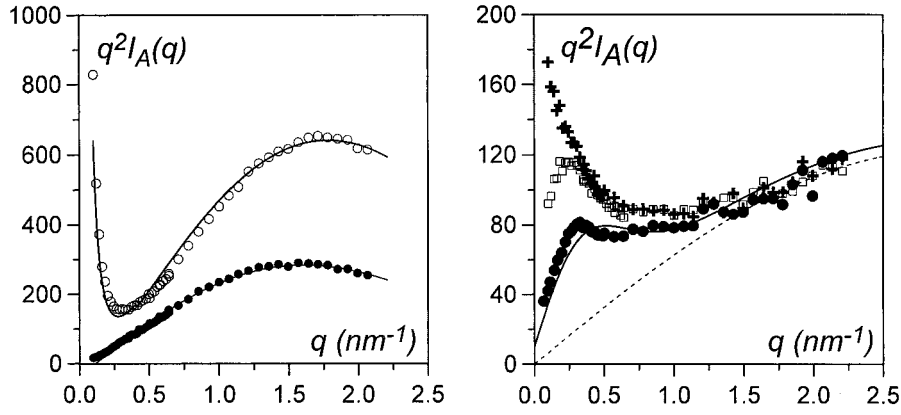

Fig. 6. *left*: Intensity scattered by the polymer in a Kratky representation, $q^2I(q)$, for f_{Cu}= 0 (+), f_{Cu}= f_c^*= 0.2 (□) and f_{Cu}= 0.35 (•); C_{pol}= 0.04 g/cm^3. Full line is the best fit to equation 4, while the dotted line is the single chain behaviour calculated from eq. 2 with $<L>$= ∞, r_H= 0.45 nm and μ_L= 520 g mol^{-1} nm^{-1} *right*: Intensity scattered by the bicopper complex in a Kratky representation, $q^2I(q)$, for C_{pol}= 0.04 g/cm^3 and f_{Cu}= f_c^* = 0.2 (•) and f_{Cu}= 0.35(○). Fits were made with equation 2 for f_{Cu}= f_c^* and equation 5 for f_{Cu}= 0.35.

The intensity scattered by the polymer is sensitive to the fibril cross-section at small q. It reveals that the fibril cross-section decreases with increasing bicopper complex content. Conversely, at large q the single chain behaviour is recovered. The decrease in fibril cross-section is consistent with a heterogeneous nucleation effect. Lopez and Guenet have further fitted the scattered intensity for structure f_{Cu}= 0.35 with a model in which four worm-like chains wrap around one bicopper complex filament.[5] To produce a satisfactory fit of the entire scattering curve, frozen fluctuations of the distance between chains about the most probable value l_o must be considered. The following distribution function was used:

$$w(r) = l\,exp\left(-l^2 / 2l_o^2\right) \tag{3}$$

from which an analytical solution for the scattered intensity can be derived by integrating from 0 to ∞:

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$$q^2 I(q) = \pi \mu_L C_p q \times \frac{4J_1^2(qr_H)}{q^2 r_H^2} \times \left[1 + exp(-q^2 l_o^2) + 2\,exp(-q^2 l_o^2/2)\right] \qquad (4)$$

Relation (4) gives the best fit shown in Figure 6 *left* with $l_o = 2.4$ *nm*, taking $r_H = 0.45$ *nm*.

The intensity scattered by the bicopper complex can still be fitted by equation 2 for $f_{Cu} = f_c^*$, which indicates that the one-dimensional state is preserved in the encapsulated state (and correspondingly that the filaments are encapsulated within a polymer sheath). For $f_{Cu} > f_c^*$ a strong upturn is observed at small q, of the form $1/q^4$. The scattered intensity can be then fitted by the following equation:

$$I(q) \propto X\frac{S}{Vq^4} + (1-X)C_H \mu_L \times \frac{4J_1^2(qr_c)}{q^4 r_c^2} \times \left[\pi q - \frac{2}{<L>}\right] \qquad (5)$$

The first term in equation 5 indicates that 3-D objects of volume fraction X, of surface area S and volume V are now present in the system. These objects are probably bicopper complex crystals that have grown in the additional phase, the existence of which was deduced from the calorimetric experiments. As the excess bicopper complex rejected into this phase is of no use for nucleation purposes, and therefore cannot be encapsulated, it forms 3-D crystals.

Both the calorimetric experiments and the structural investigation are consistent with a heterogeneous nucleation effect, and correspondingly show that bicopper complex filaments are encapsulated in iPS microfibrils in such a way that *one and only one filament* lies right in the centre of the fibrils. To some extent, the new nanocomposite material can be regarded as a nanowire.

Encapsulation in PHIC: Solid-solid Phase Separation

Unlike isotactic polystyrene, poly(hexyl isocyanate) (PHIC) is an intrinsically rigid polymer, as has been shown from light scattering experiments[11] and also by small angle neutron scattering[4] (see e.g., Figure 7). The persistence length is certainly much larger than 17 nm, so that chain-folded crystals can never be produced. In solution this entails that only a fibrillar gel structure similar to that of iPS can be obtained. To be sure, PHIC possesses side groups that are reminiscent of the wings of the bicopper complex. Compatibility between filaments of the bicopper complex and PHIC is therefore expected, in contrast to isotactic polystyrene.

As with iPS there is an effect of the solvent type. In *n*-heptane a polymer-solvent compound is formed, unlike what is observed in *n*-octane. As a result, the molecular organization is higher in gels produced from *n*-octane than in those produced from *n*-heptane.

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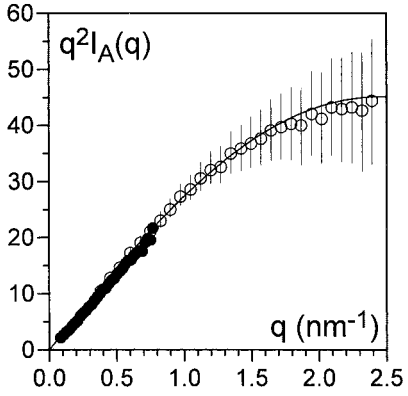

Fig. 7. Small-angle neutron scattering of PHIC in n-octane at 70°C. The best fit is obtained with equation 2 with μ_L= 581±20 g/nmxmol and r_H= 0.55±0.15 nm. These parameters are consistent with a conformation close to an 8_3 helical form.[12]

Unlike what was observed in iPS/Cus8 systems, no heterogeneous nucleation effect occurs in PHIC/CuS8/*n*-octane or in PHIC/CuS8/*n*-heptane. In particular, both the gelation threshold and the gel melting point decrease with increasing bicopper complex content, as shown in Figure 8.

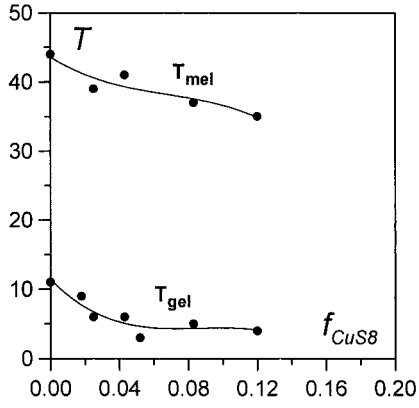

Fig. 8. Gelation threshold (T_{gel}) and gel melting temperature (T_{mel}) as a function of the mole fraction of bicopper complex with respect to the polymer, as prepared from PHIC/CuS8/*n*-octane ternary systems.

These thermodynamic results are more consistent with the occurrence of either a *solid solution* or a PHIC/CuS8 *complex*. X-ray diffraction experiments shown in Figure 9 for PHIC/CuS8 systems, obtained from *n*-octane, support the notion of a complex. As can be seen, the diffraction spectrum for PHIC/CuS8 systems differs from a simple superposition of the

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diffraction spectra of each component. On the contrary, new reflections are observed, which suggests another organization.

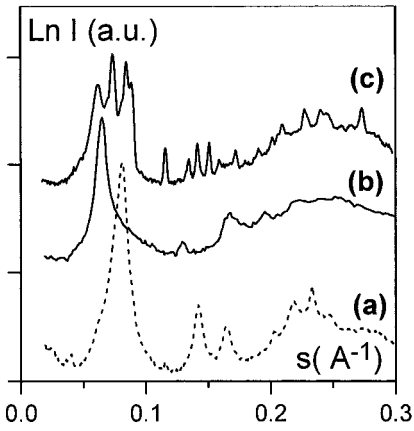

Fig. 9. Diffraction patterns (a) bicopper complex CuS8; (b) PHIC dried from PHIC/*n*-octane gels; (c) PHIC/CuS8 dried from PHIC/CuS8/*n*-octane gels.

Unlike encapsulation produced from heterogeneous nucleation, where one filament is wrapped in a polymer sheath, PHIC fibrils may contain several filaments parallel to their long axis.

Magnetic Properties of the Encapsulated Systems

The magnetic susceptibility χ_M was measured as a function of temperature in a SQUID device for the as-prepared CuS8 powder and for the encapsulated material (Figure 10). In the case of the CuS8 powder the experimental data can be fitted by a Bleaney-Bowers expression[13] for an isolated two spin $^1/_2$ model, where the magnetic exchange coupling constant J corresponds to a Hamiltonian of the form $\mathcal{H} = -2JS_1S_2$, where S_1 and S_2 are the spins of each copper atom (i.e., $\pm 1/2$). This expression is based upon the rationale that two states exist at high temperature for the bicopper complex molecule, i.e., the spins of the two copper atoms in the same direction and in opposite directions. Upon cooling the former state gradually vanishes, leaving only the state where spins are in the opposite direction (antiferromagnetism). As a result, the magnetic susceptibility goes to zero. The slight upturn observed at low temperature arises from a small amount of paramagnetic impurities.

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The Bleaney-Bowers expression is:

$$\chi_M = \frac{N_A g^2 \mu_B^2}{kT} \frac{2\exp(2x)}{1+3\exp(2x)} \quad with \quad x = \frac{J}{kT} \tag{6}$$

where N_A is Avogadro's number, g is the number of unpaired electrons in the molecule and μ_B is the Bohr magneton. Here $-2J = 202$ cm^{-1}.

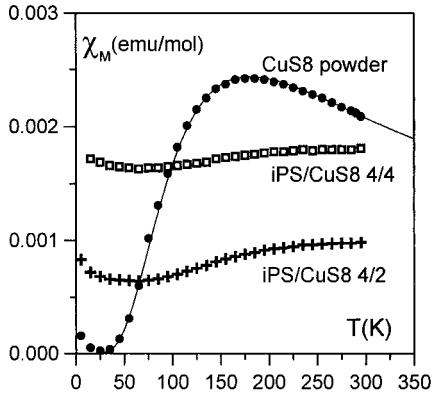

Fig. 10. Magnetic susceptibility measured as a function of temperature. Systems as indicated. The full line is a least squares fit to relation 6.

Conversely, in the case of the encapsulated materials, the magnetic susceptibility has a finite value whose magnitude depends upon the bicopper complex content. So far we have no straightforward explanation for this effect. It may be due to the interaction between adjacent bicopper complex molecules in the encapsulated state: the piling may proceed through Cu-Cu interactions instead of the Cu-O interactions reported so far. Under these conditions, a stronger coupling between copper atoms may exist, which is liable to alter the magnetic properties.

Concluding Remarks

Encapsulation of self-assembling systems can be achieved by using simple physical methods. The major finding is that the 1-D structure of the filaments can be preserved, and correspondingly that their lifetime becomes infinite. Nanocomposite materials are obtained into which the dispersion of self-assembled filaments can be controlled by the physical process: heterogeneous nucleation implies one filament per fibril cross-section while solid-solid phase separation entails several filaments per fibril cross-section. That magnetic properties are altered

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when the bicopper complex filaments are encapsulated makes these nanocomposites systems promising materials.

It is clear that the encapsulation in fibrils from thermoreversible gels can be extended to all sorts of self-assembling systems that exhibit a 1-D structure, provided these form filaments in appropriate solvents.

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