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Encapsulation of a Self-assembling Bicopper Complex in Polymer Nanowires

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SUMMARY: We report on a new type of composite material where the filaments of a self-assembling bicopper complex (*copperII-2-ethylhexanoate*) are encapsulated in a polymer matrix. The encapsulation is achieved in the fibrils created during the formation of thermoreversible gels. Two gelling systems have been studied: *isotactic polystyrene/trans-decalin* and *poly[n-hexylisocyanate]/n-heptane*. In the former system, addition of bicopper complex trigger gelation by heterogeneous nucleation while in the latter formation of a solid solution is thought to occur. In both cases, however, the bicopper complex filaments are encapsulated in the polymer fibrils of the gel. Characterization by differential scanning calorimetry (thermodynamic study) and by atomic force microscopy (morphology study) will be presented.

Introduction

In a recent paper1) Lopez and Guenet have shown that a self-assembling bicopper complex (designated as CuS8 in what follows), which produces monomolecular filaments in dilute solutions2) (see fig. 1), can be encapsulated while nucleating the growth of the fibrils of a thermoreversible gel. The purpose for encapsulating these filaments is to give them an infinite lifetime which they do not possess otherwise in solution2). As a matter of fact the interaction between bicopper complex molecules within the filaments is of the order of *kT* so that filaments continously break up randomly while new ones are reformed. Typically the lifetime in solution is about *1s*.

The encapsulation process is carried out in a common solvent, namely trans-decalin, and occurs through a heterogeneous nucleation mechanism: *the filaments of bicopper complex nucleate the growth of the gel fibrils.* This conclusion is borne out by the increase of the gelation temperature upon addition of bicopper complex. On the basis of a neutron scattering study these authors conclude that the cross-section of the gel microfibrils diminishes upon

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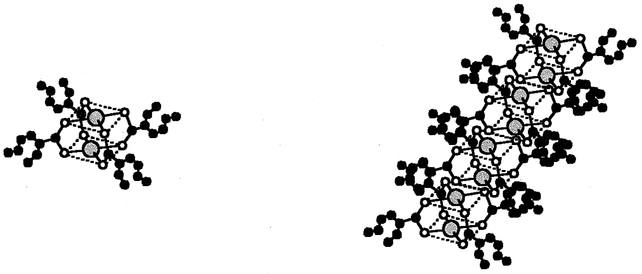
addition of CuS8, which is consistent with a heterogeneous nucleation process. We shall here report a preliminary study by AFM on such samples. Also, we will report on another way of encapsulating the bicopper complex filaments, namely by making a solid solution in poly[*n-hexyl isocyanate*], an intrinsically-rigid polymer[4,5)], whose side groups are chemically very similar to the aliphatic wings of the bicopper complex.

The bicopper complex.

The bicopper complex is obtained by reacting copper sulfate with 2-ethyl-hexanoate acid [3,6)]. Its chemical structure is represented in fig.1. In organic solvents, such as *trans*-decahydronaphthalene, molecules pile up to form long monomolecular threads. This process gives rise to the formation of a so-called "living" polymer because these long filaments have a finite lifetime. As highlighted in the introduction section, filaments constantly break up while new ones are reformed.



bicopper complex CuS8 filaments of CuS8

Fig. 1: The bicopper complex (*left*) is a 2-ethyl- hexanoate copper II complex. Its synthesis is described in *ref. 3*. It forms filaments in organic solvents by piling up in one dimension (*right*), the interaction between two consecutive molecules being established through the copper and oxygen atoms[2)].

This aspect is best illustrated by the rheological properties in the framework of Cates' theory [7,8)]. As shown in figure 2, the rheological properties can be accounted for using a Maxwell-type model where G' and G" are expressed as a function of the frequency:

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

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

The characteristic time τ is related to the reptation time and the breaking time through:

$$\tau = (\tau_R \tau_b)^{1/2} \tag{3}$$

Characteristic times of about *1s* are obtained. Clearly, if this material is to be used for application purposes, it cannot be processed under these conditions. Encapsulation in a polymer matrix is one possible approach to give an *infinite lifetime* to these filaments.

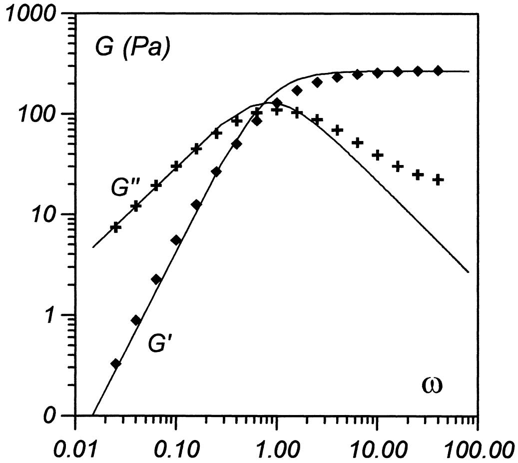


Fig. 2 : G' and G'' versus frequency for CuS8 in trans-decahydronaphthalene at room temperature.

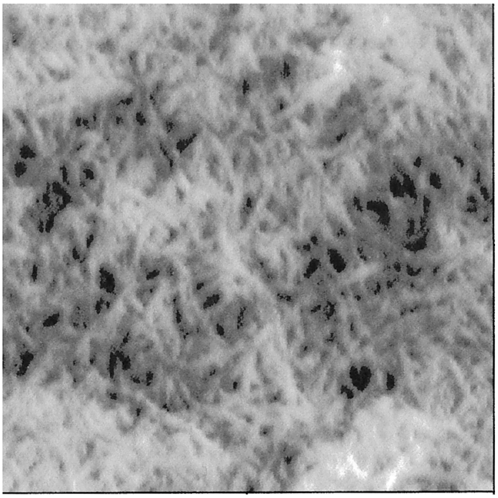


Fig. 3: AFM picture of a CuS8-nucleated gels after partial drying at room temperature in open atmosphere. The size of the image is 1.5x1.5 μm.. The AFM apparatus is TMX 2000 Explorer from TOPOMETRIX.

Encapsulation of the bicopper complex filaments by heterogeneous nucleation: *isotactic polystyrene/trans-decalin/CuS8.*

It is known that polymer crystallization can be triggered at higher temperature than usual through heterogeneous nucleation$^{9,10)}$ by using thread-like systems such as DBS (dibenzylidene sorbitol). Accordingly, chain-folded crystals grow onto these DBS threads that act as heterogeneous nuclei, and form shish-kebab structures where the DBS threads are located in the middle of the chain-folded crystals. While this process can be used for encapsulating filaments that already possess an infinite lifetime, it will not do with the bicopper complex under consideration. Indeed, the thread portions not housed inside chain-folded crystals will undergo breaking mechanism so that the original shish-kebab structure will gradualy transform into dispersed chain-folded crystals. Filaments of bicopper complex encapsulated this way are therefore of no use. What is needed is a continuous sheath, something which can be achieved by using a thermoreversible gel which display a fibrillar morphology$^{11)}$. Lopez and Guenet$^{1)}$ have reported that encapsulation can effectively be achieved by nucleating the gelation of isotactic polystyrene (iPS) by the bicopper filaments. Isotactic polystyrene gels consist of an array of fibrils with a mesh size of about 0.1-1 μm and fibrils' cross-sections of 2-20 nm$^{12)}$. In these fibrils chains are poorly-organized as they take on a worm-like conformation$^{13,14)}$. This particularly means that chain-folding is absent. Encapsulation is made possible thanks to the following properties:

- the bicopper complex and the iPS gel form in a common solvent, namely *trans*-decahydronaphthalene.
- the bicopper complex and iPS form homogeneous solutions at high temperature in *trans*-decahydronaphthalene.
- bicopper complex threads form at temperatures higher than the gelation threshold, the latter being around 20°C

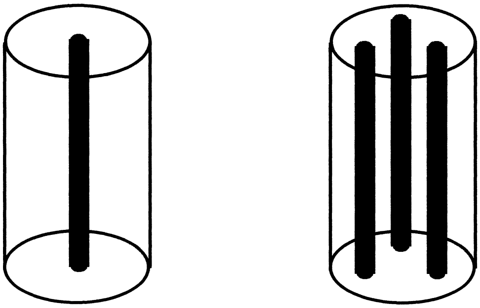
The heterogeneous nucleation process is revealed by the increase of the gelation threshold as a function of the CuS8 fraction. For instance, for a 4%-polymer concentration (w/v) and a CuS8 fraction of 0.2 an increase of the gelation temperature of about 15°C is observed$^{1)}$.

Lopez and Guenet have also shown that the fibrils' cross-section is significantly diminished through the heterogeneous nucleation process. Typical cross-sections derived from the theoretical model are around 4 nm$^{1)}$.

We have studied the morphology of a gel nucleated by addition of CuS8 by using Atomic

Force Microscopy (AFM) operating in the tapping mode. As can be seen in fig. 3 the resulting system is effectively composed of an array of fibrils whose cross-section radius can be estimated to be about 8 nm. This value is about the same derived from neutron scattering experiments. To be sure, the latter value is certainly a better estimate of the actual cross-section as AFM at this resolution range is less acurate. AFM does, however, provide a qualitative support to the conclusions drawn from neutron scattering.

Due to the heterogeneous nucleation process, only one filament is present per fibrils' cross-section, and is located at the centre of the fibril (see fig. 4).

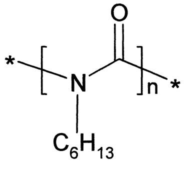


Heterogeneous nucleation Solid solution

Fig. 4: Schematic representation of a section of a polymer fibril containing CuS8 filaments (black cylinders). In the case of heterogeneous nucleation the filament is located in the middle of the fibrils, while several filaments are randomly dispersed in the fibril when a solid solution is formed.

Encapsulation of the bicopper complex filaments by the formation of a solid solution: *poly[n-hexyl isocyanate]/heptane/CuS8*

Poly[*n-hexyl isocyanate*] [PHIC] is a synthetic polymer whose repeat unit is shown in structure 1.



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This polymer is intrinsically rigid and displays therefore a very large persistence length[4,5]. It forms fibrillar thermoreversible gels in organic solvents[5], of which heptane.

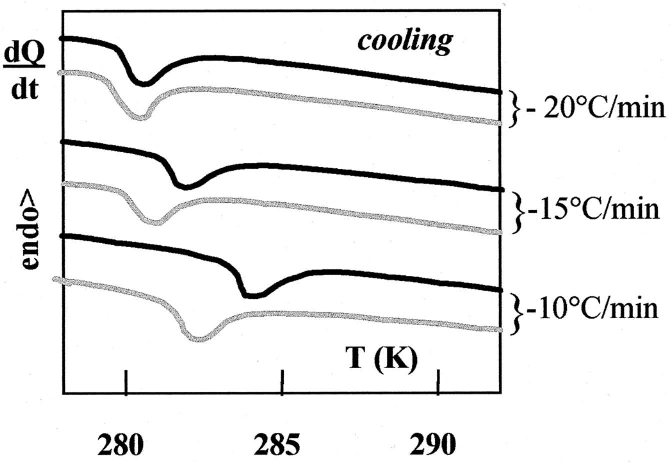

Fig. 5: DSC thermogrammes showing exotherms of gel formation obtained at different cooling rates for PHIC/heptane , C_{PHIC}= 0.1 g/cm^3 (▬) and PHIC/CuS8/heptane, C_{PHIC}= 0.1 g/cm^3 and C_{CuS8}= 0.01 g/cm^3 (▨). The gelation thresholds determined after extrapolation to zero cooling rate are 290 K in the absence of CuS8 and 285 K with CuS8, respectively.

The bicopper complex also forms filaments in these solvents. Mixtures of poly[*n-hexyl isocyanate*] and bicopper complex form also gels. Optical microscopy observations have not detected any rejection of the bicopper complex into the solvent imbedding the fibrils of the gel.

As stated in the introduction, poly[n-hexyl isocyanate] possesses side groups that are chemically very similar to the aliphatic wings of the bicopper complex (see structure 1). Unlike what is seen with *isotactic polystyrene/trans-decalin system*, preliminary results obtained by DSC (see fig. 5) show that the gelation point decreases upon addition of bicopper complex. The absence of incompatibility at the microscopic level therefore suggests that some kind of *solid solution* is formed. This does not come as a surprise as the outer shell of both the polymer and the bicopper filaments are chemically similar.

The formation of a *solid solution* therefore implies that several CuS8 filaments pass through a gel fibril cross-section (see fig. 4). This situation markedly differs from that in *isotactic polystyrene/trans-decalin system* as there can be only one filament per fibril cross-section.

Concluding remarks

The encapsulation of a self-assembled bicopper complex can be achieved in polymer sheath by using the fibrils of thermoreversible gels as encapsulating media. Depending on the nature of the polymer, encapsulation can be achieved either through heterogeneous nucleation or through the formation of a solid solution. Admittedly, the final properties of these materials, especially the magnetic properties, should be significantly dependent upon the molecular structure. Experiments are in progress to find out which type of encapsulation provides the most interesting nanomaterials.

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