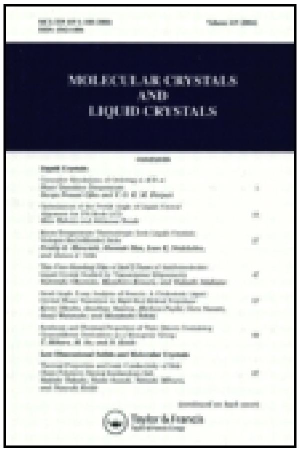

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Bicopper Organic Complexes in a Thermoreversible Gel Matrix

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Bicopper Organic Complexes in a Thermoreversible Gel Matrix

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The preparation conditions and the molecular structure of a composite material which consists of a bicopper complex encapsulated in a cylinder-like, polymer sheath are briefly described.

Keywords: thermoreversible gels, bicopper complex, composite nanothreads

INTRODUCTION

The making of nanoscale materials possessing specific electronic properties, such as high-temperature superconductivity, is a current challenge. The recent synthesis of fullerene nanotubes represents a breakthrough in this domain of material science[1]. Other routes deserve, however, to be explored. Here we report on new type of composite materials consisting of nanowires made up of an organic bicopper complex encapsulated by a polymer sheath as obtained by a heterogeneous nucleation process. The encapsulation of the complex is achieved by nucleating the thermoreversible gelation of isotactic polystyrene (iPS). In the resulting material the bicopper complex takes on a filament structure, which produces a 1-D string of copper atoms. We shall first discuss each system separately (the iPS thermoreversible gel and the bicopper complex), and eventually pre-sent the results obtained on the preparation of the composite material.

ISOTACTIC POLYSTYRENE THERMOREVERSIBLE GELS

Thermoreversible gels are produced by cooling moderately-concentrated polymer solutions (typically 2 to 20% w/w) below a well-defined temperature designated as the gelation threshold[2]. These gels possess a network morphology, as shown in figure 1, made up with interconnected thread-like entities (the fibrils). The mesh size of this network lies typically in the range 0.1-1 μm while the fibril cross-section ranges from 2 to 10 nm. As only van der Waals interactions are involved in the internal cohesion of the fibrils and in establishing the connections between fibrils, these gels are thermally-reversible; they can be melted and reformed at will without altering the system.

The conformation of the chains constituting the fibrils has been determined by small-angle neutron scattering and found to be *worm-like*[2] (see figure 2). This means that chains are globally brownian but locally rigid. The corresponding persistence length is close to $l_p \approx 4\ nm$, namely about 4 times larger than that observed in the usual flexible state of this polymer[3].

Interestingly, the worm-like conformation with about the same persistence length is kept after gel melting. The conclusion was therefore reached that gelation occurs through the bunching of these worm-like chains because chain-folding, as would be required for producing lamellar crystals and eventually spherulites, is precluded[2].

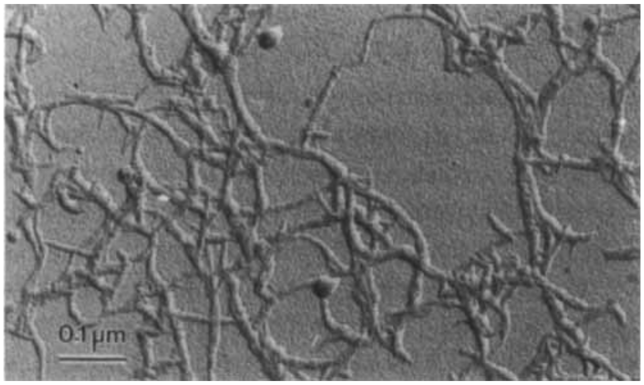

FIGURE 1 Electron micrograph of an isotactic polystyrene xerogel (gel dried prior to observation).

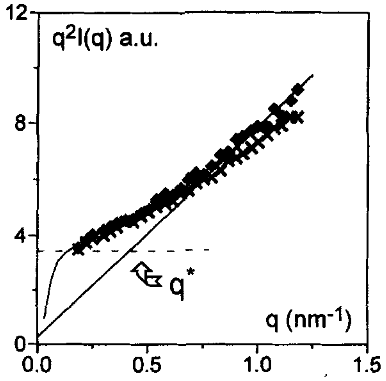

FIGURE 2 Scattering curve for chains in an iPS gel. The fit is achieved with Yoshisaki and Yamakawa 's semi-empirical relation[4] for worm-like chains (solid line). The straight solid line stands for the 1/q behaviour for q>q*.

THE BICOPPER COMPLEX

The basic structure of the bicopper complex is drawn in figure 3. It consists of a near-cubic core onto which are attached 4 aliphatic wings. These wings hinder sideways aggregation so that it forms monomolecular thread-like structures are obtained in organic solvents, at least in the early stage [5,6].

The existence of monomolecular thread-like structure is ascertained by small-angle neutron scattering experiments.

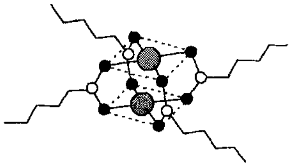

FIGURE 3 Sketch of the bicopper complex molecule. Grey= copper, black= oxygen, white= carbon. The aliphatic wings are schematized by means of broken lines. The stability of the complex is achieved through an antiferromagnetic bond via the carboxylate bridges.

The scattering curve shown in figure 4 can be accounted for through:

$$q^2 I(q) \propto C_H \mu_L \times 4J_1^2(qr_H)/q^2 r_H^2 \times \left[\pi q - 2/<L>\right] \qquad (1)$$

where C_H is the bicopper concentration, $<L>$ the filament mean-length, μ_L its mass per unit length and r_H its cross-sectional radius.

The mean length $<L>$ of these filaments is expressed as a function of volume fraction φ and temperature:

$$<L> \propto \varphi^{1/2} \times \exp(E_{scis}/2kT) \qquad (2)$$

where E_{scis} is the energy required for breaking a bond between two molecules.

The bicopper complex filaments possess, however, a *finite* time of life as E_{scis} is of the order of kT. The dynamic properties of these systems is well described by Cates' theory on « living » polymers[7]. In particular, two relaxation times are needed to account for stress relaxation: the reptation time, τ_r and the scission time τ_b. In other words, if one could label all the molecules pertaining to one given filament at time t, then at time $t+\tau_b$ most of them would be scattered into newly-created filaments. Typical values for τ_b are around *0.1 to 1s* so that the preparation of materials for application purposes by classical spinning cannot be achieved from solutions in organic solvents. This is where encapsulation by heterogeneous nucleation proves to be of invaluable help.

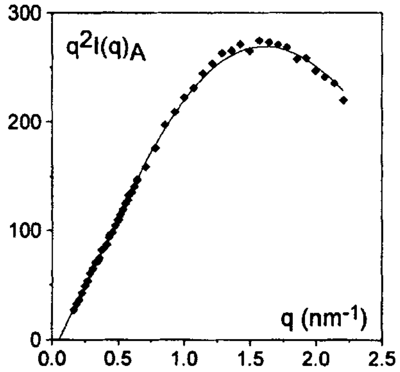

FIGURE 4 Scattering curve for bicopper complex threads. The solid line represents the best fit obtained through relation (1).

THE COMPOSITE MATERIAL: PREPARATION AND STRUCTURE

The first requirement is to find a common solvent of isotactic polystyrene and bicopper complex. Homogeneous solution of the ternary system *polymer/complex/solvent* can be then prepared easily at temperature where the bicopper complex has still not formed threads (usually 90°C). This is a prerequisite for dispersing molecularly the complex within the polymer matrix. As bicopper complex threads grow well-above the gelation threshold of iPS ($T_{gel} \approx 20°C$), they should in principle nucleate the gelation of this polymer. Indeed, as gelation occurs through a bunching process of the worm-like chains this should be enhanced by the presence of rod-like structure (provided there is no incompatibility which turns out to be the case).

Heterogeneous nucleation can be readily observed by measuring the evolution of the gelation temperature as a function of the fraction of bicopper complex. As is seen in figure 5, an increase of the gelation temperature of about $\Delta T \approx 15\ °C$ occurs (see caption for details). Above a given mole fraction of bicopper complex, f_c^*, ΔT no longer increases. This effect is due to the occurrence of a phase separation: the bicopper complex and the polymer are no longer compatible. Additional amounts of bicopper complex are simply rejected into a polymer-poor phase, and are therefore useless for nucleation purposes. Note that the gel melting point does not vary which does indicate true heterogeneous nucleation.

The nucleation effect has also consequences on the size of the gel fibrils: as expected the larger the number of nuclei (i.e. the higher the bicopper concentration), the thinner the fibrils (see figure 6). The curve obtained for $f_c > f_c^*$ can be fitted with an equation similar to (1)[8,9] indicating that a large fraction of the fibrils is constituted by *1 bicopper complex thread surrounded by 4 iPS chains*.

In figure 7 are shown the intensities scattered by the bicopper complex for $f_c = f_c^*$ and for $f_c > f_c^*$. For $f_c = f_c^*$ the same scattering pattern as that recorded for the pure complex is found which ascertains the molecular dispersion of the threads within the gel matrix. For $f_c > f_c^*$ a significant upturn is seen at low-angle which is consistent with phase separation suggested from the thermodynamic study (see figure 5). The rejected material does not remain under the form of thread-like structures but eventually forms microcrystals that scatter as $1/q^4$. The scattered intensity can then be qualitatively written:

$$q^2 I(q) \propto A / q^2 + q f(qr_H) \tag{3}$$

where the first term corresponds to those microcrystals, while the second term stands for those threads molecularly-encapsulated in the polymer sheaths. At low-angle the first term of relation (4) dominates, hence the upturn, while at large angle the second term takes over.

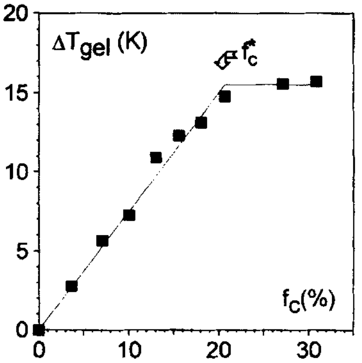

FIGURE 5 $\Delta T = T_{gel}(f_c) - T_{gel}$ where T_{gel} is the gelation temperature of the pure polymer and $T_{gel}(f_c)$ its gelation temperature in the presence of bicopper complex).

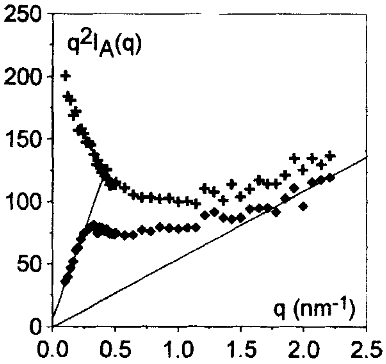

FIGURE 6 Scattering curve for a pure polymer gel (⊇) and a ternary system with $f_c > f_c^*$ (⌋). Here only the iPS gel structure is seen by using an adequate mixture of deuterated and hydrogenous solvents. The decrease of

the intensity at low-angle indicates thinner fibrils. For further details on the gel structure see reference[2].

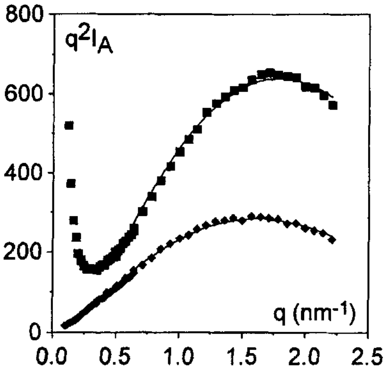

FIGURE 7 Scattering curve of the bicopper complex ($f_c = f_c^*$.(⌟), $f_c > f_c^*$.(ϒ). Only the complex structure is seen by using an adequate mixture of deuterated and hydrogenous solvents. Solid lines from a fit with relation 1.

CONCLUDING REMARKS

The heterogeneous nucleation of fibrils from iPS gels is a convenient tool for encapsulating threads of a bicopper complex. These threads are most certainly spin scales so that the resulting material is likely to possess specific electronic and magnetic properties. Future studies will be directed towards this aim.

Acknowledgments

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