End-to-End Fusion of Polymer-like Micelles in the Lecithin Organogel under the Action of an Electric Field

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The effects of an external electric field on the lecithin organogels consisting of polymer-like micelles have been studied by means of oscillatory rheology. It was shown that the applied voltage changed the rheological behavior. Frequency dependencies of complex viscosity and storage modulus had intermediate plateaus that were evidence of an appearance of a new additional relaxation process. An examination of the results in the framework of an approach used in the rheology of polymer blends led to a conclusion that the electric field induced a fusion of a fraction of the polymer-like micelles. The organogel under the applied voltage is made up of uniform micellar aggregates of various lengths. A possible mechanism is considered.

Introduction

The formation of lecithin organogels (jelly-like phases) is caused by the addition of small amounts of water[1,2] or such polar organic solvents as glycerol, ethylene glycol, and formamide[3,4] into a nonaqueous solution of lecithin. The polar additives induce a transition of the initial spherical reverse micelles into extended tubular aggregates.[5−7] The latter are often called polymer-like micelles because of their entanglement into a three-dimensional network, much like the polymer molecules. Furthermore, their rheological properties bear similarities to those of semi-dilute or concentrated solutions of polymers.[8,9]

The lecithin organogels demonstrate a high sensitivity to external influences. When an electric field is applied to nonaqueous systems with the polymer-like micelles, one can observe a sharp increase of the viscosity and dynamic moduli. The effects, which may be assigned to the electrorheological phenomena, were established and examined rather thoroughly in our recent publications.[10−12] We also found a new rheological regime for frequency dependencies of the dynamic moduli.[12] It was previously observed only for the polymers. The reasons for the change of the rheological regime in the micellar system under the action of an electric field have not been so far revealed.

The nature of the electrorheological phenomena in the lecithin organogels has become rather obvious for us after a detailed study on the main features of the effects of an electric field. In this Letter we present the essential result that provides an insight into a mechanism of the phenomena. It was first established that the electric field induces a micelle fusion. The micellar aggregates join together end-to-end, which results in their further extension. A possible mechanism for the micellar merger under the electric field is suggested.

Experimental Section

Soybean lecithin (*Epikuron 200*) was obtained from Lucas Meyer. *n*-Decane (*puriss quality*) was the product of Fluka, and glycerol (*puriss quality*) was from Merck.

The mixtures were prepared by dissolving weighed amounts of lecithin and glycerol in *n*-decane. The samples were stirred at about 50 °C for 1 h and then left under stirring at ambient temperature for several days. Before the measurements, the mixtures stayed without stirring for at least 1 day in order to bring them into the equilibrium state.

For the rheological and electrorheological measurements, a Bohlin CS 10 stress-controlled rheometer was used. It was equipped with an in-house built cell which allowed application of a voltage to examine organogel samples placed in the gap. The cell was of parallel plate geometry. The upper plate had a diameter of 40 mm and the gap was 1 mm. An electric contact to the upper plate was provided via a thin metal wire touching the shaft. The voltage was supplied by a Heinzinger NEL-6000-30neg dc power source. The temperature was 25.0 °C.

Experimental Results and Discussion

The study was performed on glycerol-containing organo-gels. They were preferred over the water-containing systems owing to a more extended region for a reproducible, stable electrorheological response. This is character-ized, as suggested in ref 12 with two critical field strength values. A schematic phase diagram in Figure 1 demon-strates their dependence on the molar ratio n of glycerol to lecithin. The lower straight line refers to a minimal field strength, E_{min}, that is necessary to induce a measur-able change in the rheological parameters. The upper curve presents the second critical field strength, denoted as E_{max}, at which a transfer to the unstable electrorheological

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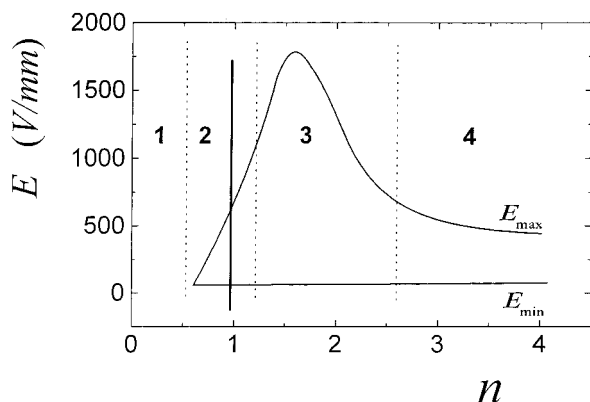
Figure 1. Minimal E_{min} (lower straight line) and maximal E_{max} (upper curve) electric field strengths vs molar ratio of glycerol to lecithin. The lecithin concentration in an organogel is 35 mg/mL. Vertical dotted lines indicate boundaries between four different phase regions: (1) a low viscous solution with spherical or short tubular reverse micelles, (2) a homogeneous organogel consisting of entangled polymer-like micelles, (3) a two-phase system with precipitated compact organogel, and (4) a two-phase system with solid precipitate and low-viscous nonaqueous solution. A solid vertical line shows an organogel that was studied in this work.

effects is observed. Reproducible measurements can be made only in the region confined between E_{min} and E_{max}.

The diagram in Figure 1 shows how both the critical field strengths depend on the molar ratio of glycerol to lecithin in the organogel phase. With successive additions of the polar additive, four phase regions can be found. Their boundaries are marked with vertical dotted lines. Region 1 is a low viscous Newtonian solution consisting of spherical or short tubular reverse micelles. Region 2 is a homogeneous viscoelastic organogel. Region 3 represents a two-phase system in which the polar additive brings about a separation of a ternary mixture into a compact jelly-like phase and a low viscous solution. The fourth region is also a two-phase mixture from a solid precipitate and a low viscous solution. The electrorheological phenomena are observed only with the polymer-like micelles and in the presence of solid precipitate. A system under consideration in this article is marked with a solid vertical line.

Figure 2 demonstrates how an electric field influences the rheological behavior of the lecithin organogels. There are frequency dependencies of the complex viscosity $|\eta^*|$, storage modulus G' and loss modulus G''. The Figure 2A presents data that were measured in the absence of an external electric field. The features of the frequency dependencies are typical of systems made up of entangled flexible polymer molecules or polymer-like micelles that move in a three-dimensional network in accordance with a reptation mechanism.[13,14] Furthermore, the rheological behavior obeys a Maxwell model, as followed from the square and linear dependencies of moduli G' and G'', respectively, on the frequency in the terminal zone.

Under an applied voltage (Figure 2B), the viscosity and the dynamic moduli are increased, but more importantly, the graph takes on a different-looking shape. This shows up as a superposition of two relaxation processes widely separated in relaxation times. The situation closely resembles that in the rheology of polymer blends. As observed for these systems after mixing two monodisperse components of entangled linear polymer molecules, there
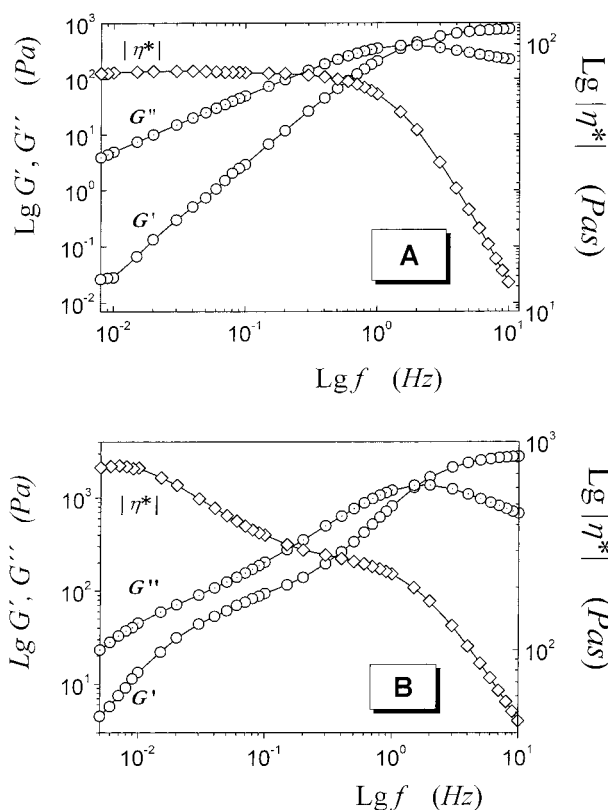
Figure 2. Complex viscosity $|\eta^*|$, storage modulus G', and loss modulus G'' vs oscillation frequency without an applied voltage (A) and under an electric field of 2000 V/m strength (B). An organogel contains 250 mg/mL lecithin and 0.9 mol of glycerol per mole of lecithin in n-decane.

is also an intermediate region in which one can find additional plateaus in viscosity and storage modulus curves.[15,16] The similarity of the behavior for the two different systems suggests that the electric field induces a transition in the organogel after which it consists of micelles of various molecular weights.

The coexistence of various micelles in the lecithin organogel becomes more obvious if the imaginary part of the complex viscosity is considered against the oscillation frequency. A corresponding graph for a sample with 250 mg/mL lecithin in n-decane and 0.9 molecule of glycerol per mole of lecithin is presented in Figure 3. The approach for the examination of polymer blends was developed by Montfort and Marin.[17-19] In the case of a monodisperse polymer, one has a singled-peaked curve. This is observed for an organogel that is not exposed to the action of an external electric field (curve 1, Figure 3). When a voltage is applied, the peak, as seen also in Figure 3 (curve 2), is decreased in its height while a second peak appears in the low-frequency region. A curve with two well-defined maxima was obtained in the case of binary blends of monodisperse polymers differing significantly in their molecular weight.[17-19]

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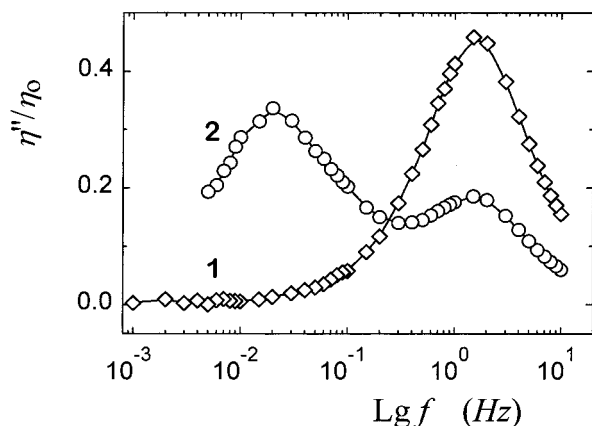(16) Struglinski, M. J.; Graessley, W. W. *Macromolecules* **1985**, *18*, 2630−2643.
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Figure 3. The imaginary part of a complex viscosity, normalized by the zero shear viscosity, vs oscillation frequency without an applied electric field (1) and at 2000 V/mm strength (2). An organogel contains 250 mg/mL lecithin and 0.9 mol of glycerol per mole of lecithin in *n*-decane.

The finding of the transformation of the singled-peaked curve into the doubled-peaked one under the action of an external electric field is suggestive evidence for a change of micellar length distribution. The appearance of the peak (curve 2, Figure 3) in the low-frequency region indicates that the modified polymer-like micelles have a larger molecular weight in comparison with that of the initial aggregates. This result means that the external electric field is responsible for merging some of the micelles. The observed increase in the viscosity (Figure 2) signifies a growth of the micellar length. From the separated peaks (Figure 3) it can be inferred that the growth proceeds in a discrete manner, which is possible if micellar aggregates merge by their ends.

Thus, the results considered above lead to the following preliminary conclusions. (i) The glycerol-containing lecithin organogel consists of polymer-like micelles that are rather uniform in their length. (ii) An external electric field induces a micellar fusion by an end-to-end mechanism. (iii) The organogel under the applied voltage is also made up of uniform polymer-like micelles, but they have various lengths.

A mechanism for the action of the electric field on the polymer-like micelles could be the following. An applied voltage, as shown previously from birefringent measurements,[10-12] causes micellar alignment along the field lines. The polarization can proceed along linear hydrogen bonding networks, that are formed by lecithin phosphate groups and molecules of the polar additives.[3,20] As a consequence, unlike charges can be induced in the opposite ends. The polarized micelles or their parts behave like large dipoles that can interact electrostatically. When oppositely charged ends interact, they will attract each other, which can lead to their coalescence and the formation of significantly larger cylindrical micelles than those in equilibrium in the absence of the applied voltage. In the terms of a mechanism of the micellar growth that has been suggested for the cylindrical aggregates,[21,22] the electric field induces a change in the end cap energy, but there is a principal difference. The growth of micelles proceeds through their fusion not through the addition of individual molecules.

We do not rule out also that the temporal dipoles induced by the electric field can be distributed along a micellar chain owing to its huge dimension (up to several micrometers in length[23,24]) and curvature. Therefore, the attractive interactions can take place not only between the micellar ends but also between the chains. Sticky contacts because of their certain lifetime will have an impact on the relaxation processes, the time of which could be also increased.

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