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Organogels from *ABA* triblock copolymers

Received: 12 March 2001
Accepted: 5 April 2001

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Abstract *ABA* triblock copolymers with two polystyrene endblocks connected by a poly(ethylene/butylene) midblock form highly elastic gels in a solvent which is incompatible for the endblocks but a good solvent for the midblock, for example, paraffin oil. In this situation the polystyrene endblocks aggregate into micelles. The midblocks can either form loops or build up bridges between different micelles; thus, domains and networks of interconnected micelles are produced. We have studied organogels of this kind consisting of a polymer with a molar mass of 90,000 and a

styrene content of 31% per weight (Kraton G 1650) in paraffin oil. Rheological, calorimetric (differential scanning calorimetry) and small-angle X-ray scattering experiments were performed on these systems. An interesting result of our work which was not described previously is that the size ($r \sim 6.8$ nm) and the separation ($d \sim 36$ nm) of the micellar aggregates does not seem to be influenced by the block copolymer content in the concentration range investigated.

Key words Organogel · Block copolymers · Micelles · Rheology

Introduction

It is a well-known fact that *AB* diblock and *ABA* triblock copolymers with hydrophilic blocks and hydrophobic blocks behave similarly to surfactants. Many investigations have been performed with block copolymers of the Poloxamer type, i.e. compounds with hydrophilic poly(ethylene oxide) (PEO) and hydrophobic poly(propylene oxide) (PPO) blocks. These systems form micelles in aqueous solution with a compact core containing PPO blocks and a highly swollen shell of PEO blocks [1, 2, 3, 4, 5, 6]. In analogy to classical low-molecular-weight surfactants Poloxamers are known to form liquid-crystalline phases, for example, cubic [7, 8, 9], lamellar [5, 9, 10] or hexagonal [9, 11, 12] phases.

Similar behaviour is known to occur in systems with *ABA* triblock copolymers for which the *A* blocks are insoluble in a solvent while one midblock is compatible with the solvent [13, 14]. In this situation, the *A* blocks will aggregate into micelles. Depending on whether the

A blocks of one copolymer molecule are located in the same or in different micelles, the midblocks can form either loops or bridges; therefore, it is conceivable that intermicellar bridging could result in the formation of domains with interconnected micelles even at low polymer content. At a sufficiently high copolymer concentration these domains could fill the whole sample volume and such systems show gel-like behaviour. They can have high elasticity and deformability. Their properties are similar to those of thermoplastic elastomers. Gels of this type are formed, for example, by block copolymers with two polystyrene (PS) end blocks and a poly(ethylene/butylene) (PEB) midblock in paraffin oil or aliphatic or alicyclic hydrocarbons. These solvents can dissolve the rubbery midblock, whereas the glassy PS endblocks are insoluble. Morphological investigations on such styrene–ethylene/butylene–styrene gels using electron microscopy have revealed a network of PS micelles physically cross-linked via midblock bridging [15]. This picture is in agreement

with results of small-angle X-ray scattering (SAXS) and small-angle neutron scattering measurements [16, 17]. SAXS measurements also revealed the existence of a cubic morphology at elevated temperatures which is established after annealing the gels for several hours [18, 19]. The morphology is metastable at ambient temperatures and heating the sample above a certain temperature results in an order–disorder transition. Other gels have shown the transition to a cubic morphology almost instantaneously during heating and the morphology could be maintained at room temperature [20]. Application of small-amplitude shear to a gel resulted in the formation of a highly ordered body-centered cubic morphology with a broad stability range [21].

In this article we present results of investigations on systems with a styrene–ethylene/butylene–styrene block copolymer (Kraton G 1650) in paraffin oil. We performed rheological measurements at different temperatures and different copolymer content, calorimetry and SAXS measurements. The results indicate that the size of the micelles formed by PS endblocks and the intermicellar separation within domains are nearly independent of the copolymer concentration in a concentration range between 0.02 and 0.10 g/ml. To our knowledge, such behaviour was not described previously in the literature.

Experimental

The block copolymer used in the present study is poly(styrene-*block*-ethylene/butylene-*block*-styrene) with a molar mass of 90,000 and a styrene content of 31% by weight (Kraton G 1650, Shell). The midblock-selective solvent was a low-molecular-weight paraffin oil (Merck, Darmstadt, Germany). The components were mixed at temperatures around 100–120 °C for 3–4 h until homogenous solutions were obtained. In this way, samples with concentrations between 0.003 and 0.100 g/ml were produced.

Rheological measurements were performed with a Bohlin CS-10 stress-controlled rheometer with a cone–plate geometry (cone angle: 4°, diameter: 40 mm). The temperature was controlled by a thermostat.

For differential scanning calorimetry (DSC) measurements we used a Setaram Micro DSC III at a rate of 0.2 K/min and with paraffin oil as a reference substance.

SAXS investigations were carried out using a Bruker-AXS Nanostar at a wavelength of 0.15 nm and at wave vectors, q , between 0.1 and 3/nm. The sample cell was built in-house. It consists of two Teflon plates with holes in the middle to place the sample. To prevent solvent evaporation, two thin mica sheets are used as windows.

Results and discussion

Rheological measurements

Three examples of frequency-sweep rheological measurements for a sample containing 0.10 g/ml Kraton G

1650 in paraffin oil at different temperatures are shown in Figs. 1–3. These figures very clearly reveal a transition from an elastic gel with a yield stress value at 20 °C to a viscoelastic liquid without yield stress at 60 °C. An elastic gel with yield stress is characterized by storage and loss moduli which are nearly frequency independent, whereas the complex viscosity decreases linearly with increasing frequency. Usually the storage modulus is about 1 order of magnitude larger than the loss modulus for such systems. In contrast, the dynamic moduli for a viscoelastic liquid are not frequency-independent but increase with increasing frequency with different slopes. The intersection point of the two moduli defines a characteristic relaxation time, τ :

$$\tau = (2\pi f_{\text{int}})^{-1}, \quad (1)$$

where f_{int} is the frequency at the intersection point.

It is also important to note that the complex viscosity of a viscoelastic liquid has a constant value at low frequencies. This value is identical with the zero-shear viscosity of the liquid. The existence of a finite value for the zero-shear viscosity proves that this system has no

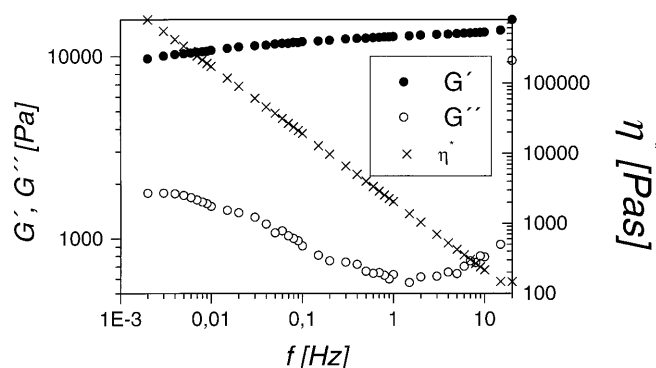


Fig. 1 Rheogram of Kraton G 1650 in paraffin oil ($c = 0.10$ g/ml) at 20 °C

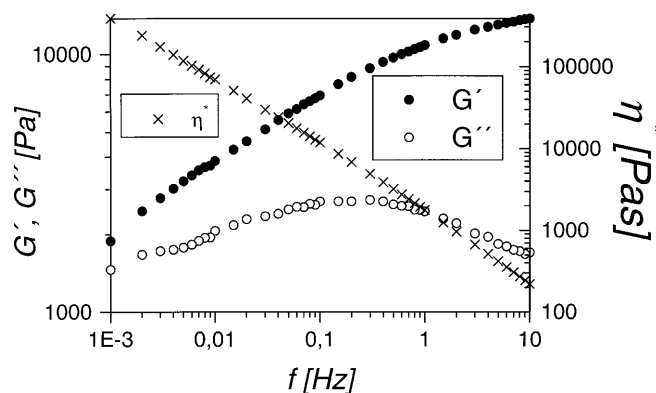


Fig. 2 Rheogram of Kraton G 1650 in paraffin oil ($c = 0.10$ g/ml) at 46 °C

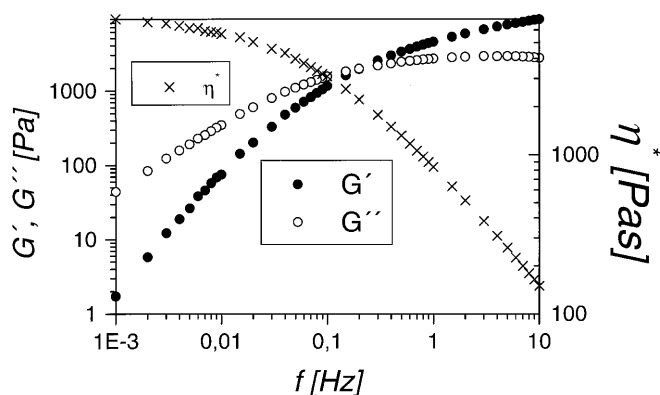


Fig. 3 Rheogram of Kraton G 1650 in paraffin oil ($c = 0.10$ g/ml) at 60 °C

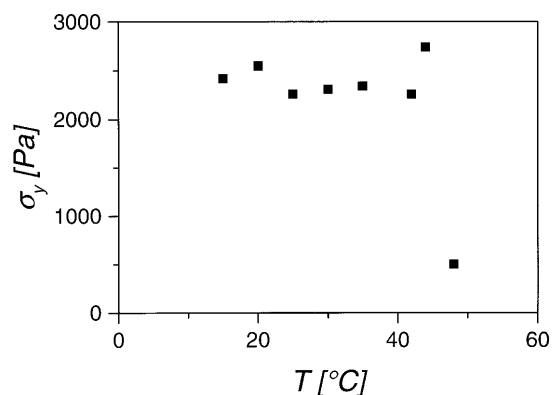


Fig. 6 Yield stress versus temperature for a system with 0.10 g/ml Kraton G 1650 in paraffin oil

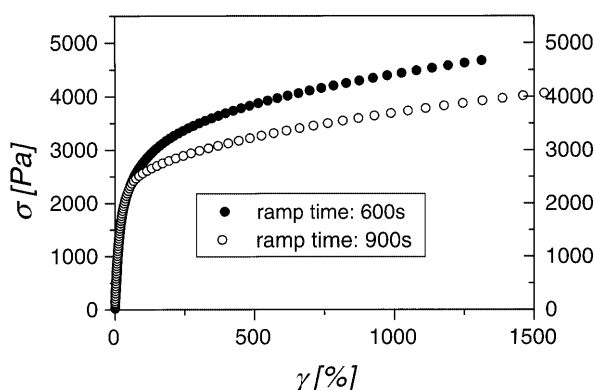


Fig. 4 Yield stress determination of a sample with 0.10 g/ml Kraton G 1650 in paraffin oil at 15 °C. The shear stress, σ , is plotted versus deformation, γ , for two different ramp times. The yield stress is the point where the two curves deviate from each other

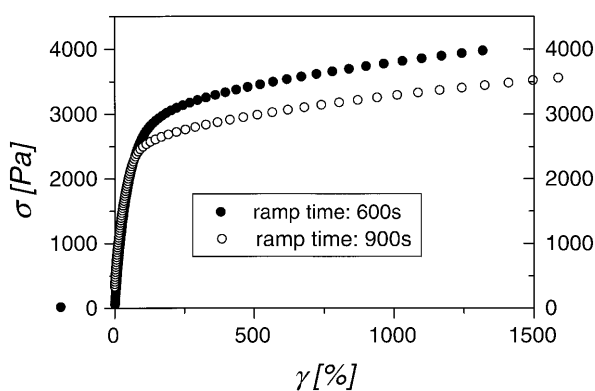


Fig. 5 Yield stress determination of a sample with 0.10 g/ml Kraton G 1650 in paraffin oil at 35 °C. σ is plotted versus γ for two different ramp times. The yield stress is the point where the two curves deviate from each other

yield stress as a yield stress would require the complex viscosity to diverge with decreasing frequency as is the case in Fig. 1.

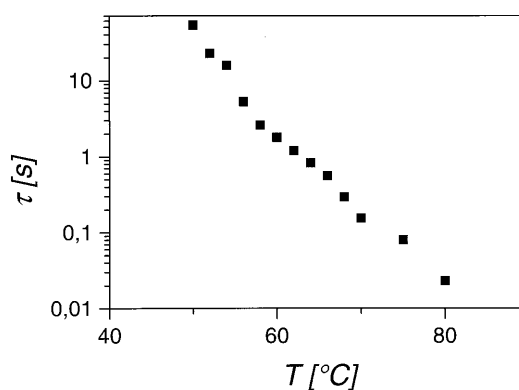


Fig. 7 Relaxation time versus temperature for a system with 0.10 g/ml Kraton G 1650 in paraffin oil

The yield stress was determined in the following manner (Figs. 4, 5). The shear stress, σ , was increased within a certain time and the deformation, γ , was measured. Then, the same experiment was repeated with another ramp time. The yield stress is the point below which both curves are identical. At shear stresses higher than the yield stress the curves deviate from each other as the viscous deformation of a fluid depends on how long the stress is applied, whereas the elastic deformation below the yield stress is time-independent.

The temperature dependence of the rheological parameters for a system containing 0.10 g/ml Kraton G 1650 in paraffin oil is shown in Figs. 6, 7, 8 and 9. As can be seen from Fig. 6, the yield stress, σ_y , is approximately constant up to 45 °C and then drops and disappears at temperatures above 50 °C. Finite relaxation times, τ , can be determined for systems without yield stress, i.e. at temperatures exceeding 50 °C for the present system (Fig. 7). The relaxation time decreases from about 50 s at 50 °C to 0.02 s at 80 °C. This drop in relaxation time has to be expected as the movement of polymer molecules is facilitated with

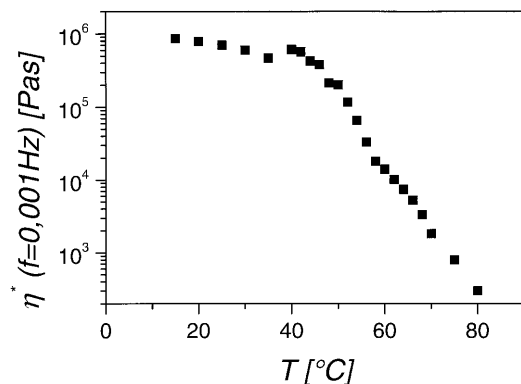


Fig. 8 Complex viscosity at a frequency of 0.001 Hz versus temperature for a system with 0.10 g/ml Kraton G 1650 in paraffin oil

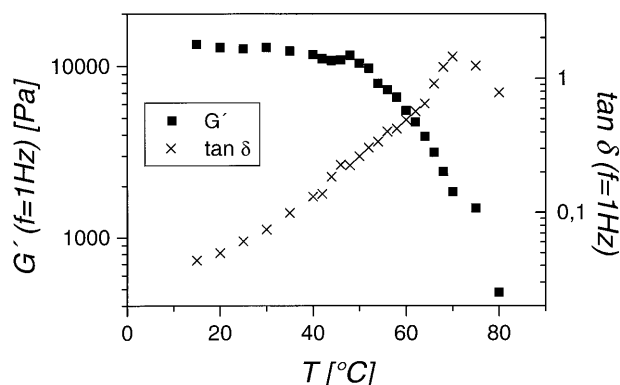


Fig. 9 Storage modulus and loss tangent at a frequency of 1 Hz versus temperature for a system with 0.10 g/ml Kraton G 1650 in paraffin oil

increasing temperature making relaxation processes faster. The behaviour of the complex viscosity shown in Fig. 8 can be understood as follows: as long as the system displays gel-like character, i.e. up to about 50 °C, the decrease in the complex viscosity with temperature is rather small. The temperature dependence of the complex viscosity is more pronounced at $T > 50$ °C: a decrease over several orders of magnitude in the range between 50 and 80 °C is shown in Fig. 8. At these temperatures the system behaves like a viscoelastic liquid and the viscosity of liquids is known to be strongly temperature-dependent [22]. The storage modulus, G' , as well as the loss tangent, $\tan \delta$, both measured at a frequency of 1 Hz, are plotted versus temperature in Fig. 9. G' is nearly constant for temperatures up to 50 °C and then decreases with temperature. Raspaud et al. [23] also report a storage modulus which is temperature-independent at low temperatures up to 30 °C for systems with poly(styrene-*block*-isoprene-*block*-styrene) (SIS) in *n*-heptane. The loss tangent passes a maximum which is located around 75 °C.

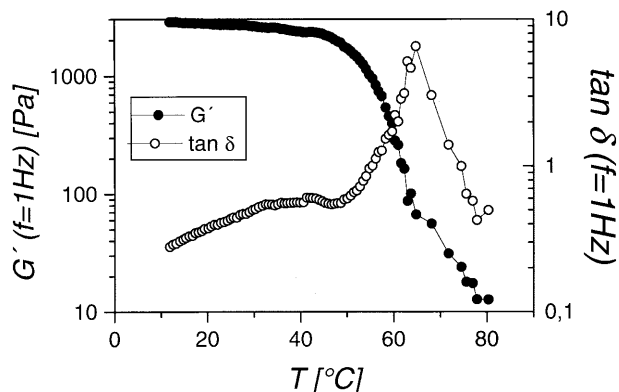


Fig. 10 Storage modulus and loss tangent at a frequency of 1 Hz versus temperature for a system with 0.06 g/ml Kraton G 1650 in paraffin oil

These features, i.e. a decrease in the storage modulus and a maximum in the loss tangent, are indicative for a glass transition [24]. The PS endblocks which are incorporated in the micelles because of their insolubility in paraffin oil are in the glassy state. The occurrence of a glass transition explains the change from gel-like to liquidlike behaviour as observed by the drastic decrease in viscosity, relaxation time and storage modulus with temperature. When approaching the glass temperature, the PS endblocks begin to move within the micelles, resulting in a loss of elasticity and, therefore, in a decrease in G' . The glass transition as detected from the maximum in the loss tangent in Fig. 9 would be at approximately 72 °C for the system with a copolymer content of 0.10 g/ml. This value is smaller than that of the glass temperature of bulk polystyrene (90–100 °C). The shift of the glass-transition temperature to lower temperatures is caused by the limited size of the PS micelles in the organogel. Measurements with different concentrations of Kraton G 1650 in paraffin oil (Fig. 10 shows one example with $c = 0.06$ g/ml) revealed an increase in the glass-transition temperature with increasing copolymer concentration from 62 °C ($c = 0.05$ g/ml) to 72 °C ($c = 0.10$ g/ml). We assume that such behaviour originates from a decrease in the solvent content of the PS micelles with increasing Kraton concentration making them more similar to bulk PS.

The dependence of the plateau modulus, G_0 , on the block copolymer concentration is shown in Fig. 11. The measured values at low copolymer concentration are in good agreement with a Rouse modulus in the semidilute regime. In this case the plateau modulus is given by [23]

$$G_0 = CRT/M_w, \quad (2)$$

where C is the concentration of block copolymer (in grams per millilitre), R is the gas constant, T the temperature and M_w the molar weight of the polymer. For the systems investigated, Eq. (2) yields G_0

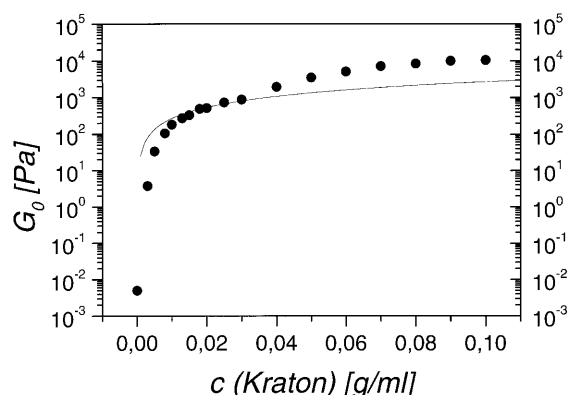


Fig. 11 Plateau modulus versus concentration of Kraton G 1650 in paraffin oil. The solid line represents the function G_0 (Pa) = $2.75 \times 10^4 C$

(Pa) = $2.75 \times 10^4 C$ at 25 °C. A line representing this relationship is included in Fig. 11. This line fits the measured data points rather well at concentrations below 0.04 g/ml; therefore, we can say that in this concentration regime the elasticity is merely due to bridging of aggregates by midblocks. The contribution of entanglement effects to the system's elasticity is negligible in the Rouse semidilute regime. At concentrations exceeding 0.04 g/ml, however, the measured values of G_0 increase more steeply with copolymer content than Eq. (2) predicts. These data can be fitted with a power-law function, i.e. $G_0 \sim C^{1.85}$. The larger exponent in C as compared to Eq. (2) means that in this concentration range not only midblock bridging but also entanglements contribute to the value of the plateau modulus. For semidilute solutions of homopolymers in the reptation regime, G_0 varies as $C^{2.3}$. Semenov et al. [25] have proposed the so-called “flower”-micelle model. In this model, the elasticity of the gels originates from a combination of midblock bridging and entanglements of loop-forming midblocks between adjacent micelles. The “flower”-micelle model predicts that the plateau mod-

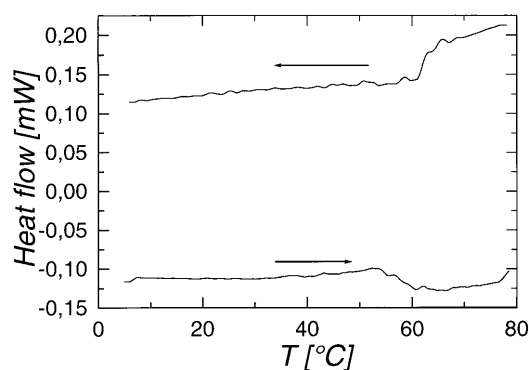


Fig. 12 Differential scanning calorimetry curve for a sample containing 0.04 g/ml Kraton G 1650 in paraffin oil

ulus should vary with block copolymer concentration with an exponent larger than 1. The nonlinear relationship between the plateau modulus and the concentration, as observed at $C > 0.04$ g/ml in Fig. 11, seems to be in agreement with this model. A similar rheological behaviour has been reported recently by Spontak et al. [26]. They investigated mixtures of (SIS) as well as of poly[styrene-*block*-(ethylene-*alt*-propylene)-*block*-styrene] (SEPS) with an aliphatic mineral oil. In their study, they found Rouse behaviour for concentrations below 0.08 g/ml for SEPS and below 0.16 g/ml for SIS. At higher concentrations, G_0 increases with C^β , where $\beta = 2.68$ for SEPS and 1.77 for SIS.

Differential scanning calorimetry

One example of a DSC measurement for a sample containing 0.040 g/ml Kraton G 1650 in paraffin oil is shown in Fig. 12. The experiment was performed at a heating rate of 0.2 K/min between 5 and 80 °C. In both the up curve and the down curve a glass transition appears at around 60 °C. This transition is reproducible and it is also found in samples with other block copolymer concentrations, however shifted to other temperatures. For the concentration range investigated we found glass transitions between 56 and 84 °C, increasing with increasing copolymer content. These results are in good agreement with the data obtained by rheological measurements (Figs. 9, 10). It was already pointed out that the shift of the glass-transition temperature could be due to a decrease in the solvent content of the PS micelles with increasing concentration of block copolymer in the organogel.

DSC experiments were also used to determine the order-disorder transition in styrene-ethylene/butylene-styrene organogels [19]. Weak, but reproducible, endotherms were found in systems with 15 and 20 wt% Kraton G 1650 in an oil containing aliphatic and alicyclic compounds around 105 and 120 °C, respectively, after preannealing the samples at 85 and 90 °C for 24 h. An increase in the copolymer content caused a shift of the peak position to higher temperatures. Without preannealing no transition could be detected as the formation of a long-range ordered structure is a very slow process which takes place on a finite time scale only in a small temperature range above the glass transition of PS blocks.

Small-angle X-ray scattering

SAXS curves for two samples with different Kraton concentrations are presented in Figs. 13 and 14. Characteristic features of these scattering curves are a maximum at 0.17/nm and a minimum at approximately

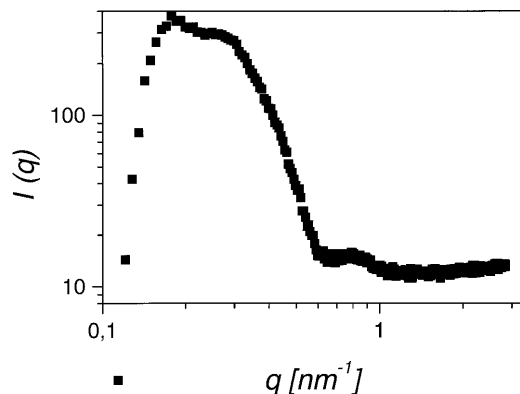


Fig. 13 Result of a small-angle X-ray scattering (SAXS) experiment for a system with 0.025 g/ml Kraton G 1650 in paraffin oil at 25 °C; the scattering intensity, $I(q)$ (arbitrary units), is plotted versus the wave vector, q ($q = 4\pi\lambda^{-1}\sin\theta$)

0.66/nm. Similar results were reported by Mischenko and coworkers [17, 18, 19, 21, 27], who did extensive work on organogels containing styrene–ethylene/butylene–styrene triblock copolymers. They found that the morphology of styrene–ethylene/butylene–styrene organogels strongly depends on the thermal history. Samples which were not annealed showed the same scattering pattern as in Figs. 13 and 14: one structure factor maximum and one side maximum that is characteristic for the form factor. At elevated temperatures, above the glass transition of the PS micelles, the intensity of the maxima decreased, whereas their width increased continuously with increasing temperature. This was interpreted in terms of a dissolution of the micellar network [19]. If the organogels were annealed at temperatures above the glass transition of the PS cores for several hours, additional maxima appeared in the SAXS pattern, indicating a rearrangement of the micellar network into a highly ordered cubic lattice [18, 19, 21, 27].

From the position of the first interference maximum, the Bragg spacing, d , of interconnected micelles can be calculated according to the following equation:

$$d = 2\pi/q_{\max}. \quad (3)$$

Interestingly, the position of the maximum is nearly constant in the concentration range investigated (between 0.025 and 0.08 g/ml). This means, according to Eq. (3), that the intermicellar separation is the same for all concentrations, i.e. approximately 36 nm.

Similarly, the radius, r , of the micelles can be calculated from the minimum of the form factor by using the relationship

$$r = 4.49/q_{\min}. \quad (4)$$

As the position of the form factor minimum stays constant for different block copolymer concentrations,

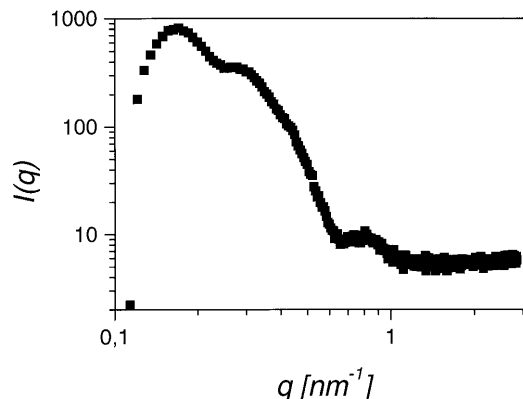


Fig. 14 Result of a SAXS experiment for a system with 0.08 g/ml Kraton G 1650 in paraffin oil at 25 °C; $I(q)$ (arbitrary units) is plotted versus q

the micellar radius is independent of the content of Kraton G 1650. Equation (4) yields a value of approximately 6.8 nm for all the concentrations investigated.

The results of our SAXS measurements thus indicate that both the size and the separation of the micellar aggregates in Kraton organogels do not change in a concentration range between 0.025 and 0.08 g/ml. To our knowledge, such behaviour was not described in the literature before.

Model for the organogel

On the basis of our results we suggest the following model for the organogels composed of Kraton G 1650 in paraffin oil:

The PS endblocks which are insoluble in paraffin oil aggregate into micelles. Bridging of these micelles via the PEB midblocks gives rise to the formation of domains (Fig. 15). According to the results of our SAXS experiments the intermicellar separation within these domains is nearly independent of copolymer content ($d \sim 36$ nm). The same is true for the size of the PS cores of the micelles. Their radius is constant at about 6.8 nm in a concentration range between 0.025 and 0.08 g/ml; therefore it is conceivable that increasing the block copolymer content results just in an enhancement of the number of domains, whereas the size of the aggregates and the intermicellar separation within these domains are not affected. At a certain copolymer concentration the domains extend over the whole sample volume, building up a homogenous network. This is consistent with our observation that samples containing less than 0.05 g/ml Kraton are turbid and separate into two phases, whereas samples with concentrations of 0.05 g/ml or higher are transparent, homogenous gels. The existence of a two-phase system consisting of a low-viscosity transparent phase and a gel-like turbid phase at

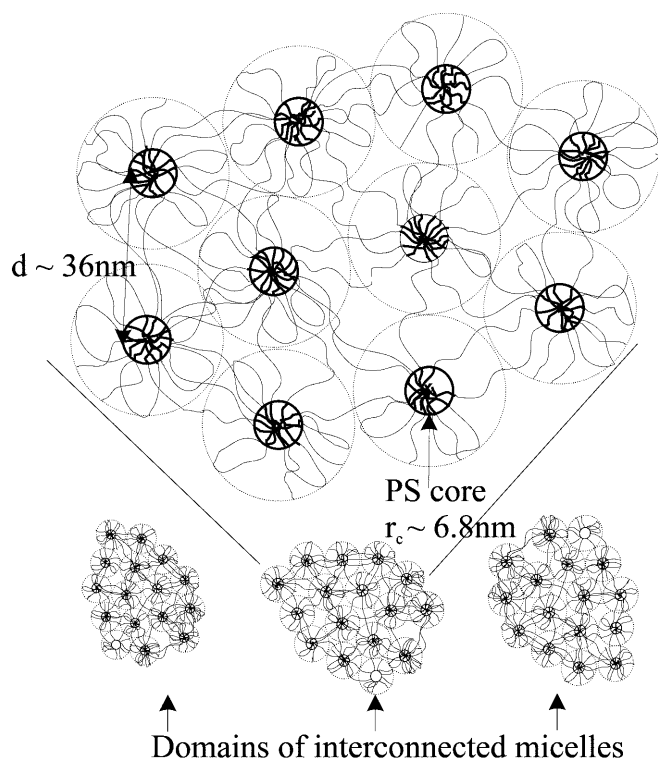


Fig. 15 Model for the organogels consisting of Kraton G 1650 in paraffin oil: polystyrene (PS) endblocks aggregate into micelles bridged by poly(ethylene/butylene) midblocks. Domains with interconnected micelles are formed. The radius of the micellar core containing PS endblocks is 6.8 nm, independent of copolymer concentration. The intermicellar separation within one domain is constant ($d \sim 36$ nm)

low copolymer content can be explained as follows. The gel phase is built up in part of isolated domains of interconnected micelles like the ones shown in Fig. 15. These isolated aggregates are responsible for the turbidity of the gel phase. Some of the domains, however, are already linked together to build up a network that is responsible for the elastic properties of the gel. The gel undergoes a slow syneresis process: restructuring of the network causes the gel to shrink and some of the solvent molecules are excluded from the gel, giving rise to the formation of a two-phase system. When the Kraton concentration is sufficiently high the network is dense enough that no syneresis occurs. In this situation, most of the domains are integrated into the network and, therefore, the systems appear transparent. The transition from a two-phase, turbid system to a one-phase, transparent gel takes place at a copolymer concentration of approximately 0.05 g/ml. Although the network is fully established at 0.05 g/ml, the results of our SAXS experiments indicate that the size and the separation of the micellar aggregates stay constant up to a block copolymer concentration of 0.08 g/ml. We assume that

although the gel looks homogenous on a macroscopic scale there may be some defects in the network structure. These defect points could be occupied by domains or micelles when the concentration of Kraton is increased. Moreover, we suppose that in the concentration range between 0.05 and 0.08 g/ml the packing of PS endblocks in the core of the micelles changes with increasing copolymer content, thus allowing more PS endblocks to be incorporated into one micelle without significant change in the size of the aggregate. Some solvent which is included in the micelles could be replaced by PS blocks; hence, the core of micelles would become more similar to bulk PS. This explains why the glass transition is shifted towards higher temperatures when the copolymer concentration is increased, as observed by rheological as well as by the calorimetric measurements.

Conclusions

We have investigated organogels composed of the styrene–ethylene/butylene–styrene triblock copolymer Kraton G 1650 and paraffin oil by means of rheology, calorimetry and SAXS.

Rheological measurements clearly show a transition from gel-like behaviour at room temperature to a viscoelastic liquid without a yield stress at around 50 °C. From the values of the plateau modulus measured we can say that the elasticity at low copolymer content (below 0.04 g/ml) is solely due to midblock bridging of micellar aggregates. At higher concentrations of block copolymer, however, not only midblock bridging but also entanglements between loop-forming midblocks of adjacent micelles contribute to the elasticity of the organogel.

The glass transition of PS endblocks can be detected by temperature-dependent rheological measurements. It turns out that the glass temperature increases with increasing copolymer content from 62 °C ($c = 0.05$ g/ml) to 72 °C ($c = 0.10$ g/ml), i.e. it shifts towards the glass temperature of bulk polystyrene (90–100 °C). This result is confirmed by DSC experiments.

SAXS investigations revealed a maximum at 0.17/nm and a form factor minimum at around 0.66/nm. Both the maximum and the minimum are nearly independent of the concentration of the block copolymer. This means that the separation and the size of the aggregates should not change with increasing copolymer content.

From the results of our investigations we suggest the following model for the organogel. As the paraffin oil solvent is incompatible for PS, the PS endblocks aggregate into micelles. These micelles are connected by the PEB midblocks, thus giving rise to the formation of domains of interconnected micelles. Increasing the content of block copolymer results in an increase in the number of domains, while the size ($r_{\text{core}} = 6.8$ nm) and

the separation ($d=36$ nm) of the micelles within the domains does not change. At a Kraton concentration of approximately 0.05 g/ml a network of interconnected micelles is formed which extends over the whole sample volume. We assume that some defect points are left within the structure of the network which can be occupied with increasing copolymer content. Additionally, the packing of PS endblocks in the micelles could change, allowing more endblocks to be incorporated into the aggregates, while their size stays constant. It is

also possible that some solvent molecules which were included in the micelles are replaced by PS endblocks. The aggregates would therefore become more similar to bulk PS and this would explain the shift of the measured glass transitions towards higher temperatures when the content of the block copolymer is increased.

Acknowledgements We are grateful to Shell for providing Kraton G 1650 for this work. We thank Volker Abetz (Macromolecular Chemistry II, Bayreuth University) for performing SAXS measurements.

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