

Size, Concentration, and Solvency Effects on the Viscosifying Behavior of PEO–PS–PEO Triblock Copolymers in AOT Oil-Continuous Microemulsions

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The effect of changing the block lengths of triblock copolymers of poly(ethylene oxide)–polystyrene–poly(ethylene oxide) on the relative viscosity of AOT oil-continuous microemulsions, with cyclohexane as the oil, was investigated. Five different microemulsion compositions were used to have (a) a series of increasing droplet concentration at constant droplet size and (b) a series with increasing droplet size at constant droplet weight fraction. All polymer and microemulsion mixtures showed Newtonian viscosity, and in all cases the presence of a polymer in the microemulsion led to an increase in the viscosity. Results were presented at 40 °C, which is above the theta temperature of polystyrene in cyclohexane. With all polymers, the relative viscosity decreased with increasing droplet concentration (at constant droplet size) and, in general, increased with increasing droplet size (at constant droplet weight fraction), although there were some exceptions. Comparing the viscosifying behavior of the different triblock copolymers on the molar scale (moles of polymer/dm³) resulted in the emergence of trends that are significantly different from those of previous investigations of triblock copolymers in microemulsions. In particular, we show evidence that increasing the PS block length leads to increased viscosity enhancement. However, at high droplet concentration this increased viscosity enhancement with long PS blocks is lost as the system comes closer to the segregative phase-separation boundary.

Introduction

Hydrophobically modified water soluble polymers are well known to aggregate in aqueous solutions by the spontaneous self-assembly of their hydrophobic groups, which results in a significant enhancement of the low shear viscosity of the solution with increasing polymer concentration. The structures formed in solutions of associating polymers depend on the polymer concentration, the number of associating groups, and the strength of the physical bonds.¹ The simplest aqueous associating systems are linear chains with terminal stickers.^{2–6} The typical viscosity profile of associating systems consists of three regimes: (1) Newtonian at low shear rates, (2) shear thickening at moderate shear rates, and (3) shear thinning at high shear rates. The Newtonian plateau at low shear rates indicates the lack of a yield stress, which implies that the associations are constantly breaking and forming.

Interactions between water-soluble associative polymers and surfactants have also been studied.^{7–13} The typical starting point has been to examine the perturbations to the polymer solution upon addition of surfactant.⁷ More recently, the alternative starting point has been adopted where the effect of addition of hydrophobically modified polymers to micellar solutions has been investigated.¹² When the surfactant and the polymer have similar hydrophobic and hydrophilic parts, it was shown that up to a certain proportion of associative polymer the hydrophobic cores of the micelles remained identical to those of the pure micelles, with substitution of the surfactant by the polymer. The hydrophilic chains preferentially linked the micelles, leading to an effective attraction and eventually to associative phase separation.

The effective interactions introduced by adsorbed associative polymers have also been investigated in other model systems, such as microemulsions with hydrophobically modified water-soluble polymers or hydrophilically modified oil-soluble polymers.^{14–20} The advantage of microemulsions as model systems for studying the interaction with associative polymers is that several different parameters can be varied separately, such as (1) the radius of the droplets by adjusting the composition of the microemulsion, (2) the average distance between the droplets, which is dependent on their volume fractions, (3) the number of associative polymer molecules added per droplet, and (4) the length of the sticker block. Thus, the associations can be tailored by adjusting the size and concentration of the droplets and the number and length of the associating groups. To date, however, the effect of changing the microemulsion parameters (e.g., droplet size or droplet concentration) on the interactions between polymers and droplets have only been investigated for mixtures involving amphiphilic graft copolymers,^{20–22} not for linear polymers as studied here.

A microemulsion–triblock copolymer (A–B–A) system is characterized by an equilibrium between droplets with no copolymer and those which have formed polymer–droplet complexes. Two types of polymer–droplet complexes are known to form, which are described in terms of the polymer conformation; in the loop-type complex both A-blocks are solubilized in a single droplet with the middle B-block forming a loop around the droplet, whereas in a bridging-type complex two droplets are interconnected via the oil-soluble B-block with one A-block in each droplet.¹⁴ Further interlinking of such droplet–copolymer complexes may transform a transparent microemulsion into a transparent gel with the dynamics of a frozen microemulsion. Considerable work has been done to determine the effect of the relative block lengths on the type of

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structure formed, and thus the viscosity enhancement.^{14–16} Eicke et al. concluded that large B-block lengths form loop-type complexes, where the A-blocks could be shielded by the B-block, resulting in no gel formation. In contrast to this, the shielding by short B-blocks was less effective, since the bending energy and steric constraints hamper the shielding, making A-block solubilization in two different droplets more favorable, and resulting in network formation even at low polymer concentrations.¹⁴ Struis et al. studied the effect of the relative amount of hydrophilic A blocks and hydrophobic B blocks on the type of complex formed by A–B–A triblock copolymers using diffusion NMR. Two different copolymers were compared, and again the polymer with the longer B block formed spherically shaped loop complexes with an effective hydrodynamic radius of 1.5 times the droplet radius. The polymer with shorter B blocks formed bridging-type complexes, composed of one polymer molecule and two nanodroplets. The formation of the different types of complexes was reflected in very different viscosity curves; the semilog plots of viscosity versus concentration of polymer (g/dm³ polymer) show either two linear slopes with a well-defined crossover or single lines with constant slopes. The former pattern is also observed in binary polymer solutions and is generally attributed to the dilute–semidilute transition, where the polymer chains start to overlap. From this analogy, it was concluded that polymers which form bridging complexes lead to interconnected networks at higher polymer concentrations.¹⁴

Thus, a significant amount is understood about the effect of triblock copolymers in microemulsions and in particular about the effect of the ratio of the block lengths and the importance of the middle block length. Nevertheless, no previous studies have addressed the effects of changing the microemulsion parameters. Here, the effect of four different PEO–PS–PEO copolymers on the viscosity of five different AOT/water/cyclohexane oil-continuous microemulsions has been determined, and the results are compared systematically. Some very interesting, previously unobserved trends emerge, especially when the relative viscosities are compared at the same molar concentration of polymer or of PEO blocks. These trends, including an increase of the relative viscosity with increasing PS block length, are contrary to the findings of other researchers and to a current model of network formation which suggests that only polymers with short middle blocks can form bridging-type polymer–droplet complexes. The fact that cyclohexane is a poor to marginal solvent for PS (the theta temperature is 34 °C)²³ has significant consequences for the observed properties.

Experimental Details

Materials. AOT (sodium bis(2-ethylhexyl)sulfosuccinate) from Sigma (>99%) was stored in a desiccator and used as supplied. Cyclohexane (Merck) was used as supplied. Water was of Milli-Q quality. A series of poly(ethylene oxide) (PEO) end-capped polystyrene (PS) triblock copolymers, which will be denoted PEO–PS–PEO, with different PEO and PS block lengths were prepared by sequential anionic polymerization at the laboratory of Constantinos Tsitsilianis, Department of Chemical Engineering, University of Patras.²⁴ For comparison, an unmodified polystyrene homopolymer was prepared at our laboratory by radical polymerization in xylene,²⁵ according to the method of Wang and Huang.²⁶

The polymer characteristics are summarized in Table 1.

Sample Preparation. Oil-continuous microemulsions of water/AOT/cyclohexane were prepared and stirred for 1 day at room temperature. The desired amount of triblock copolymer

TABLE 1: Characteristics of the Triblock Copolymers Used in This Study

polymer	PEO block length	PS block length	PEO–PS–PEO	polymer MW
0	0	432	0–432–0	43 000
1	6	206	6–206–6	21 904
2	54	206	54–206–54	25 744
3	31	390	31–390–31	43 040
4	29	663	29–663–29	71 272

TABLE 2: Calculated Values of R_g (using the equation of Sun et al.²⁷) and $\langle r^2 \rangle^{1/2}$ of the Triblock Copolymers at 40 °C

	polymer 1	polymer 2	polymer 3	polymer 4
R_g at 40 °C (nm) ^a	4.2	4.2	5.7	7.5
$\langle r^2 \rangle^{1/2}$ (nm)	10	10	14	18

^a This was calculated from the MW of the PS block only and does not consider any effect from the hydrophilic PEO chains.

was added to the microemulsions, which were then stirred at room temperature until transparent. All samples used for viscosity measurements were transparent and homogeneous, except for polymers 1, 3, and 4 in microemulsion C, and polymer 4 had a tendency to precipitate from all of the microemulsions (except microemulsion E) if left standing without stirring. For this reason, all samples were stirred at 25 °C until used.

Viscosity Measurements. The viscosities of microemulsion and microemulsion/triblock copolymer samples were measured on a Carri-Med CSL controlled stress rheometer with a cone and plate geometry (4 mm, 1 degree acrylic cone). A solvent trap filled with microemulsion was used to avoid solvent evaporation, and the temperature was controlled with a Peltier element. Measurements were carried out in the shear stress sweep mode at 25, 35, and 40 °C. For each microemulsion and microemulsion/copolymer sample, the stress at 30 rads was determined (below the breaking point of the sample), and this value was used as the maximum stress in the flow experiments. All samples showed Newtonian viscosity.

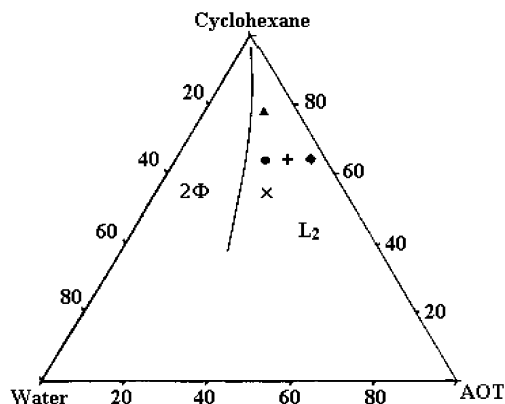
Results and Discussion

Characterization of the System Components. One aim of this work was to elucidate the effects of changing the block lengths (see Table 1) on the viscosity enhancing abilities of triblock copolymers in oil-continuous microemulsions. Comparing polymers 1 and 2 will show the effect of changing the PEO block length at constant PS block length; comparing polymers 3 and 4 will show the effect of changing the PS block length at (essentially) constant PEO block length. Thus, the relative importance and effect of the various block lengths on the viscosity can be established systematically.

Since PS is a temperature-responsive polymer in cyclohexane, the coil dimensions of the polymer are expected to vary with temperature. The extent of this variation in the complex systems studied here is not known nor is the affect of the presence of the PEO end-blocks. However, radii of gyration (R_g) were calculated for the different copolymers at 40 °C (using only the PS backbone molecular weight (MW) and ignoring any effect due to the presence of the PEO side chains), using the formula developed by Sun et al.²⁷ to describe the temperature dependence of the R_g of PS in cyclohexane. The details of this calculation have been given previously.²⁸ The calculated R_g values are shown in Table 2. The root-mean-square end-to-end distance of the polymers, $\langle r^2 \rangle^{1/2}$ can be calculated from $\langle R_g^2 \rangle = 1/6 \langle r^2 \rangle^{1/2}$. The values for $\langle r^2 \rangle^{1/2}$ are also shown in Table 2.

TABLE 3: Compositions of the Microemulsions, Radii, and Concentrations of Water Droplets and Average Interdroplet Distances

micro-emulsion	AOT (wt %)	water (wt %)	w_0	droplet radius (nm)	weight fraction of droplets	C_{droplet} (M)	interdroplet distance (nm)
A	10	7.7	19	3.3	0.177	8.8×10^{-4}	5.7
B	20	15.0	19	3.3	0.35	1.7×10^{-3}	3.2
C	30	23.1	19	3.3	0.531	2.6×10^{-3}	2.0
D	24.2	10.8	11	2.1	0.35	4.7×10^{-3}	2.9
E	30	5.0	4	0.9	0.35	2.4×10^{-2}	2.3

**Figure 1.** Ternary phase diagram water/cyclohexane/AOT at 25 °C.^{30,31} L₂, fluid transparent microemulsion, 2Φ, two-phase system. ▲, composition of microemulsion A; ●, composition of microemulsion B; ×, composition of microemulsion C; +, composition of microemulsion D; and ◆, composition of microemulsion E.

Since the microemulsion characteristics, such as the molar droplet concentration, C_{droplet} , and the droplet size, are also expected to influence the behavior of the mixed microemulsion-copolymer systems, a series of microemulsions of different droplet concentration, C_{droplet} , and droplet size were prepared. An oil-continuous microemulsion consists of nanometer-sized water droplets surrounded by surfactant and dispersed in an oil-continuous phase. The size of the water droplets is controlled by the molar water/AOT ratio, w_0 , and the droplet concentration is controlled by the cyclohexane weight fraction. The microemulsions used here were chosen to illustrate the effects of both droplet size and C_{droplet} on the viscosity of the microemulsion/copolymer system. Microemulsions A–C have the same w_0 but different cyclohexane weight fractions and thus different C_{droplet} . Microemulsions E, D, and B have the same weight fraction of droplets but increasing w_0 , which results in decreasing numbers of larger droplets. The droplet size (water core radius) was calculated according to

$$3\nu_w w_0 / \{N_A f(\text{AOT})\}$$

where ν_w is the water molecular volume (18 cm³/mol), N_A is Avogadro's number, and $f(\text{AOT})$ is the mean area of the water/oil interface covered by one AOT molecule,²⁹ which can be calculated from $f(\text{AOT}) = 59.6 - 46.8 \exp(-0.401(w_0)^{1/2})$.¹⁸ From the radius, the mean surface area of a droplet can be determined, and dividing this by $f(\text{AOT})$ gives the number of AOT molecules per droplet. Dividing the molar concentration of AOT by the number of AOT molecules per droplet finally gives the molar droplet concentration, C_{droplet} . Droplets were assumed to be monodisperse and spherical in the calculations. The characteristics of the microemulsions are given in Table 3 and their positions in the AOT/water/cyclohexane phase diagram are shown in Figure 1. More detailed phase diagrams can be found in the literature.^{30,31}

An important characteristic of the microemulsions is the average interdroplet distance, which will obviously depend on

both the droplet size and concentration. The average separation between droplets in the various microemulsions was calculated from the cube root of the inverse droplet number concentration minus the droplet diameter (the water core diameter plus two AOT tail lengths). The calculated values are also shown in Table 3, showing that the average interdroplet distance decreases as C_{droplet} increases (at constant droplet size) as expected and also increases with increasing droplet size (at constant droplet weight fraction), as a result of there being a much larger number of the smaller droplets. Comparing Tables 2 and 3, all relevant length scales of the systems are in the range 1–20 nm, the droplets are slightly smaller than the coiled polymers, and the root-mean-square end–end distances of the PS blocks are longer than the average separation between the droplets.

Characterization of the Mixtures. To make meaningful comparisons between the networks formed by the different triblock copolymers, it is necessary to have some way to characterize the connectivity of the networks. The simplest way to achieve this is to get an indication of the number of polymer molecules per droplet in the microemulsions, which is possible assuming that the size of the droplets does not change upon addition of the copolymers. This is a reasonable assumption since small-angle neutron scattering (SANS) experiments on triblock copolymers in oil-in-water microemulsion showed no change in the size of the hydrophobic droplets upon addition of either diblock or triblock polymers, and there was no evidence of the existence of aggregates of the associative polymers alone either.³² Holmberg et al. reported a limited increase in droplet size upon addition of graft copolymer, but their graft chains were much longer than the PEO blocks used here.²⁰ The number of polymer molecules per droplet is calculated from the molar concentration of polymer, C_{polymer} , and the molar concentration of droplets, C_{droplets} , and the calculated values are listed in Table 4.

The nonmodified polystyrene (PS, polymer 0), was completely miscible in cyclohexane above its critical temperature, which was estimated to be 19.9 °C for a MW of 43 000 using Flory's equation.³³ The triblock copolymers, however, were not soluble in either cyclohexane (with the exception of polymer 1) or water but were in most cases well soluble in water/AOT/cyclohexane oil-continuous microemulsions. The exceptions to this were as follows. Polymer 4 had a tendency to precipitate from all of the microemulsions at 25 °C whereas its solubility was good above 35 °C in most cases except for microemulsion C. Presumably, the poor solubility of polymer 4 was due to the poor or marginal solvent quality of cyclohexane for the long PS backbone. Polymer 1 did not mix well with microemulsions C and E, both of which had a high concentration of droplets. It is probable that the very short PEO blocks of polymer 1 are actually not inserted into the water droplets to a large extent, since this polymer was soluble in pure cyclohexane (see also below). We therefore ascribe the lack of miscibility of polymer 1 with the most concentrated microemulsions to an effective droplet–polymer repulsion, resulting in a segregative phase separation, as was recently shown to occur for PS homopolymers

TABLE 4: Number of Polymer Molecules Per Droplet Calculated from C_{polymer} and C_{droplet} at Different Polymer Concentrations

	polymer 1	polymer 2	polymer 3	polymer 4
		micro A		
10 g/dm ³	0.52	0.44	0.27	0.16
20	1.04	0.88	0.53	0.32
30	1.55	1.33	0.79	0.48
		micro B		
10 g/dm ³	0.27	0.23	0.14	0.09
20	0.54	0.46	0.28	0.17
30	0.81	0.69	0.41	0.25
		micro C		
10 g/dm ³	0.18	0.15	0.09	0.06
20	0.35	0.30	0.18	0.11
30	0.53	0.45	0.27	0.16
		micro D		
10 g/dm ³	0.10	0.09	0.05	0.03
20	0.20	0.17	0.10	0.06
30	0.29	0.25	0.15	0.09
		micro E		
10 g/dm ³	0.02	0.02	0.01	0.005
20	0.04	0.03	0.02	0.01
30	0.06	0.05	0.03	0.02

in oil-continuous AOT microemulsions.²⁸ Finally, polymer 3 was not fully miscible with microemulsion C.

From Table 4, it can be seen that within each microemulsion, the number of polymer molecules per droplet increases in the order polymer 4 < polymer 3 < polymer 2 < polymer 1, since the polymer molecular weights decrease in this order. The higher the polymer MW the lower the number of polymer molecules at a constant mass concentration of polymer. For each polymer at a given C_{polymer} , increasing the molar concentration of droplets, C_{droplet} , results in a decrease in the number of polymer molecules per droplet, as shown in Table 4. Increasing the droplet size (at constant droplet volume fraction) also increases the number of polymer molecules per droplet, since there are less of the larger droplets. The number of polymer molecules per droplet gives an indication of the maximum number of junctions in the system. Thus, on the basis of only the information in Table 4, it would appear that polymer 1 results in the highest number of junctions and polymer 4 in the least, and from this we would expect polymer 1 to result in the highest viscosities. However, this calculation does not take into account that the residence time of a PEO chain in a droplet is dependent on the PEO chain length or whether bridging between droplets occurs. Also, because of their very low number of EO units, it is not clear whether the PEO blocks of polymer 1 are actually solubilized into water droplets at all.

The interactions between the different polymers and the microemulsions were probed by determining the viscosity of different mixtures. The viscosity experiments were conducted at different temperatures (25, 35, and 40 °C). In all cases, the viscosities determined were Newtonian. In the sections below, the data presented and discussed is always for the samples at 40 °C, since this is well above the theta temperature of the PS blocks, and thus there should be no complications due to insolubility of the PS blocks. Differences due to temperature are discussed as relevant. All graphs show the relative viscosity, which is the measured viscosity divided by the pure microemulsion viscosity. This normalizes the results and enables direct comparisons of the different microemulsions.

Effect of Changing the Microemulsion Characteristics.

Increasing the Microemulsion Droplet Concentration. Figure 2 shows the effect of increasing the microemulsion droplet

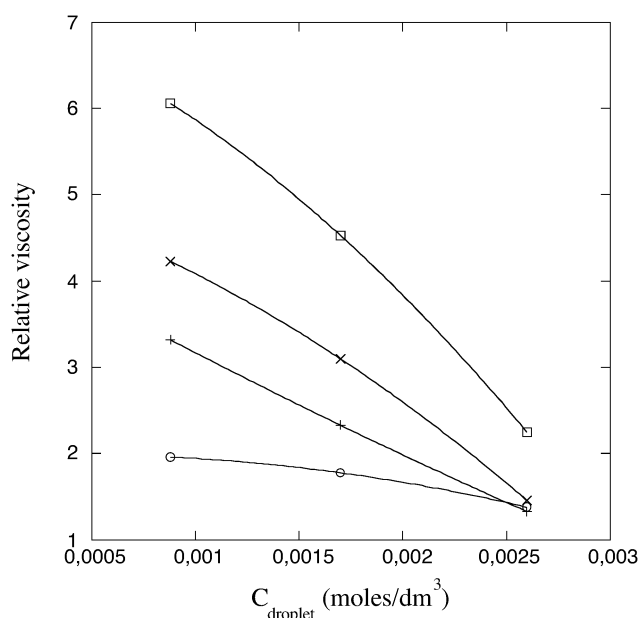


Figure 2. Plot of relative viscosity versus C_{droplet} at 40 °C and 30 g/dm³ of (○) polymer 1, (□) polymer 2, (X) polymer 3, and (+) polymer 4 with increasing droplet concentration (i.e., comparing microemulsions A, B, and C). Lines are guides to the eye only.

concentration, C_{droplet} , at constant droplet size (comparing microemulsions A, B, and C) on the relative viscosities of the various copolymers. In all cases, increasing C_{droplet} results in a reduction of the viscosifying effect, with the effect being most pronounced with the longest PEO side chain (polymer 2), followed by the polymer with intermediate PEO and PS chain length (polymer 3), as shown in Figure 2. With polymer 1, there is not much change in the relative viscosity with increasing C_{droplet} , while for polymers 2, 3, and 4 there is a clear decrease in the relative viscosity with increasing C_{droplet} , presumably as a result of the higher C_{droplet} resulting in lower numbers of PEO chains per droplet, as shown in Table 4. Polymer 1 had limited solubility in microemulsion C, and it was suggested previously that the PEO chains of polymer 1 may not be inserted into droplets at all, accounting for the small change in relative viscosity. Similar trends were observed at lower polymer concentrations, and at lower temperatures, although with decreasing temperature the solubility of polymer 4 decreased, and at 25 °C it had relative viscosities similar to those of polymer 1. Looking at the data in Table 4, it is clear that as the concentration of droplets increases, the number of PEO chains per droplet decreases, resulting in decreased connectivity and thus reduced relative viscosity.

Increasing the Microemulsion Droplet Size. Figure 3 shows the effect of increasing the droplet size at a constant droplet weight fraction (comparing microemulsions E, D, and B) on the relative viscosities of the copolymers. There is a general trend of increasing relative viscosity with increasing droplet size, however, distinct differences in the behavior of the polymers of different block lengths can be observed. For polymer 1, there was essentially no effect of droplet size, presumably as a result of the PEO blocks not being solubilized into droplets, as discussed above and illustrated below. For polymer 2, there was a significant increase of the relative viscosity with increasing droplet size. We attribute this increase in viscosity with increasing droplet size (at constant droplet weight fraction) to the increased number of polymer molecules per droplet in the microemulsions with large droplets, which is a consequence of the decreased number of droplets. The behavior of polymer 3

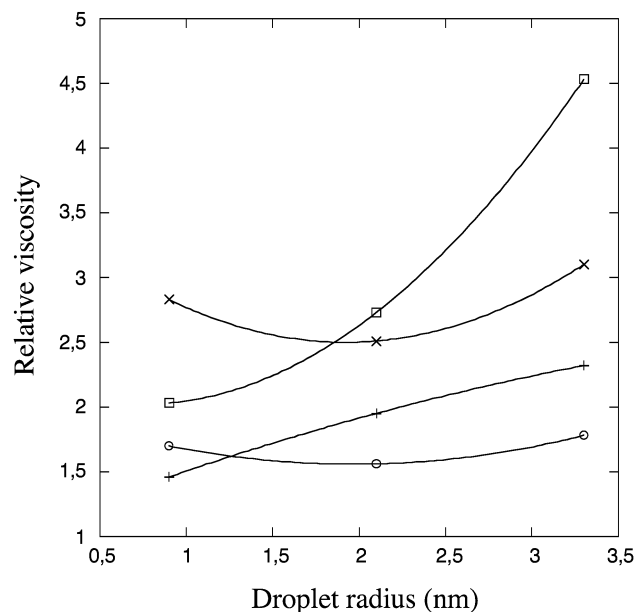


Figure 3. Plot of relative viscosity versus droplet size at 40 °C and 30 g/dm³ of (○) polymer 1, (□) polymer 2, (×) polymer 3, and (+) polymer 4 in microemulsions of increasing droplet size (i.e., comparing microemulsions E, D, and B). Lines are guides to the eye only.

with increasing microemulsion droplet size was unusual; the viscosity was similar for microemulsions B and E (the largest and smallest droplets) but was significantly less for the intermediate droplet size, as shown in Figure 3. No convincing explanation for the increased viscosity at the smallest droplet size can be provided, but the trend was confirmed by several repeat measurements at each temperature. The high viscosity in microemulsion B is expected from the increased number of PEO chains per droplet with the larger droplet size, as explained above. With polymer 4, the behavior followed the more straightforward pattern of increasing viscosity with increasing droplet size, as shown in Figure 3, although the effect of droplet size was much less pronounced than for polymer 2. Similar trends were observed at the lower polymer concentrations and at lower temperatures (although the solubility of polymer 4 decreased with decreasing temperature). Examining the data in Table 4, it can be seen that increasing the droplet size at constant droplet weight fraction results in a decrease in the droplet concentration, which is reflected as an increase in the number of PEO chains per droplet. Thus, the change in relative viscosity with increasing droplet size is more likely to be a consequence of the change in droplet concentration than to be related to the change in droplet size directly.

Effect of Changing the Polymer Characteristics. Up to now, the polymers have been compared at the same mass concentration of polymer (g/dm³) added to the microemulsions. However, this does not take into account differences in MW of the polymers and thus differences in the number concentration of polymer molecules present. Thus, direct comparisons on the effect of changing the polymer characteristics will be made in terms of the molar concentration of polymer, C_{polymer} (moles/dm³).

Effect of Increasing the PEO Block Length at Constant PS Block Length. Figure 4 shows the viscosifying effects of increasing concentrations of polymers 1 and 2 in microemulsion B at 40 °C. Increasing the PEO block length at constant PS block length clearly results in a dramatic increase of the relative viscosity of the microemulsion. The relatively low increase of viscosity with increasing C_{polymer} of polymer 1 supports the

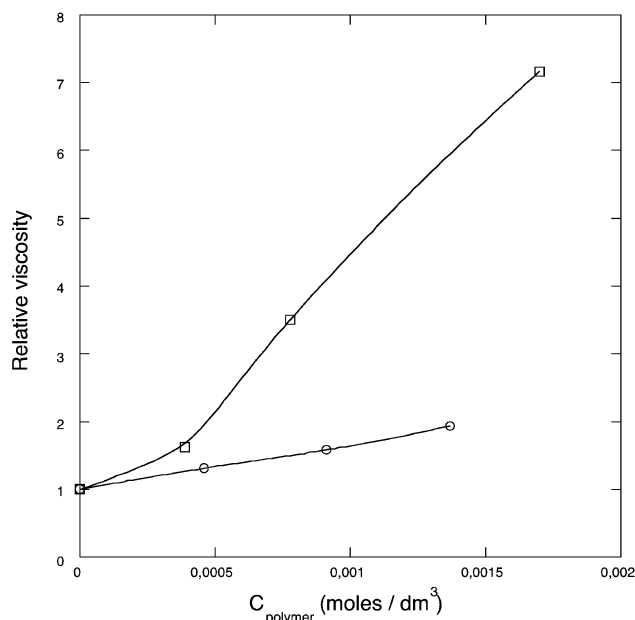


Figure 4. Plot of relative viscosity versus C_{polymer} of polymer 1 (○) and polymer 2 (□) in microemulsion B at 40 °C. Lines are guides to the eye only.

notion that the PEO blocks of this polymer are not inserted into the droplets to any large extent. On the other hand, the steep increase of viscosity with increasing C_{polymer} of polymer 2 suggests the formation of bridging complexes, where the two PEO blocks are inserted into different droplets, with the PS block bridging the droplets, by comparison to the results of Eicke et al.¹⁴ and Struis et al.¹⁸ Similar trends were observed at lower temperatures (with the relative viscosity of polymer 2 increasing even more steeply at lower temperatures) and in each of the five microemulsions studied.

Effect of Increasing the PS Block Length at Constant PEO Block Length. Here, we compare results for polymers 3 and 4. The effect of increasing PS block length was a little more complicated than expected in the context of the Struis and Eicke model, where the relative block lengths determine whether loop or bridging polymer-droplet complexes form.¹⁸ According to their idea, a long PS block would shield short PEO blocks, causing the latter to be placed into a single droplet. A shorter PS block would, on the other hand, give less effective shielding of the PEO blocks causing them to be inserted into separate droplets, resulting in bridging complexes. In fact, no single trend could be found in our measurements, and the relative positions of polymers 3 and 4 with respect to each other actually change from microemulsion to microemulsion. For this reason, the viscosifying effects of the two polymers are compared in all microemulsions except microemulsion C, where miscibility problems occurred for both polymers, in Figure 5a–d at 40 °C. In microemulsion A, the relative viscosity of polymer 4 exceeds that of polymer 3; in microemulsions B and D, the two polymers have essentially the same relative viscosity; and in microemulsion E, finally, the relative viscosity of polymer 3 exceeds that of polymer 4. The changeover in the relative viscosity occurs with increasing droplet concentration, implying that the droplet concentration in some way influences the polymers, with high droplet concentrations having a negative impact on the ability of polymer 4, with its longer PS blocks, to form effective bridging polymer-droplet complexes. Similar trends were also observed at lower temperatures, with the changeover of the relative viscosities occurring at even lower droplet concentrations at lower temperatures; at 25 °C, the changeover occurs in

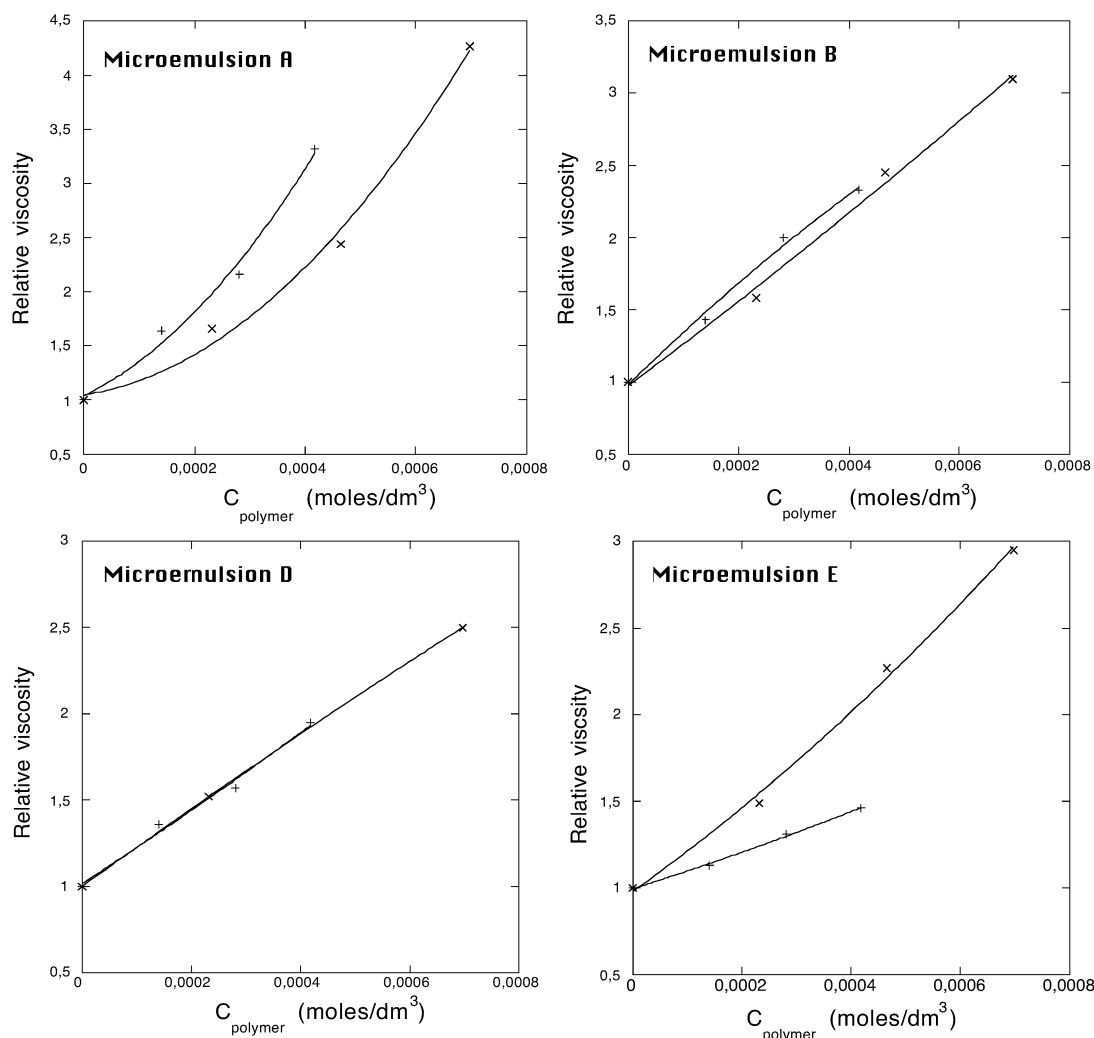


Figure 5. Plot of relative viscosity versus C_{polymer} of polymer 3 (x) and polymer 4 (+) in microemulsions A, B, C, and E at 40 °C. Lines are guides to the eye only. Droplet concentration increases dramatically on going from microemulsion A to microemulsion E, as shown in Table 3.

microemulsion B. Thus, there is also some solvency effect, since the experiments are performed around the theta point of PS in cyclohexane, with the longer PS block of polymer 4 being more affected than the shorter PS block of polymer 3, as would be expected.

The behavior of the PEO–PS–PEO triblock copolymers of increasing PS block length at low (or relatively low) droplet concentrations is clearly contrary to the results of Struis et al.¹⁸ and Eicke et al.¹⁴ on PEO–PI–PEO triblock copolymers in oil-continuous microemulsions, where increasing the PI block length at constant PEO block length resulted in a large decrease in the viscosity. However, the relative viscosity of polymer 4 only exceeds that of polymer 3 when the data are plotted in terms of the moles of polymer and not when the data are plotted as g/dm^3 polymer (as shown in Figures 2 and 3 above).

Effect of Temperature. The effect of temperature on the viscosities of the various microemulsion–triblock copolymer mixtures was also determined and has been mentioned above where relevant. Figure 6 shows the effect of temperature on microemulsion B with each of the triblock copolymers and unmodified PS (MW 43 000) as a reference. The behavior in microemulsion B is representative of the behavior of the copolymers in all of the microemulsions. The unmodified PS causes the relative viscosity to increase very slightly with increasing temperature, presumably because of the more expanded conformation of the PS at higher temperature. With the

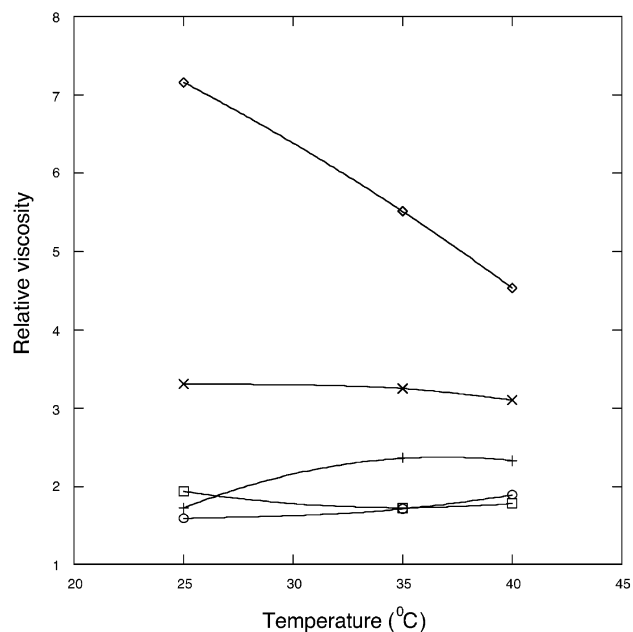


Figure 6. Effect of increasing temperature on the various polymers at 30 g/dm^3 in microemulsion B. (O) polystyrene; (□) polymer 1; (◇) polymer 2; (X) polymer 3; and (+) polymer 4. Lines are guides to the eye only.

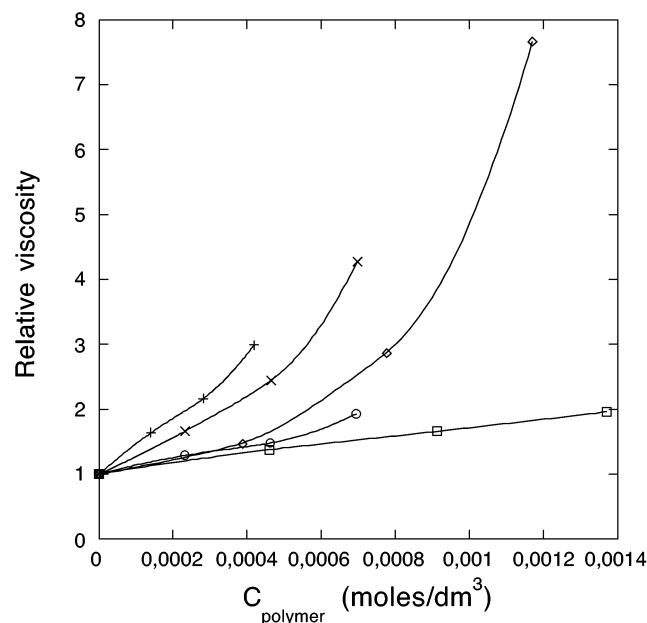


Figure 7. Plot of relative viscosity versus number concentration of polymer in Microemulsion A for each of the different polymers at 40 °C. (○) Polystyrene; (□) polymer 1; (◇) polymer 2; (X) polymer 3; and (+) polymer 4. Lines are guides to the eye only.

exception of polymer 2, the triblock copolymers show only a very weak temperature dependence. Polymer 2, however, shows a clear decrease in the viscosity with increasing temperature. There are two possibilities for this decrease—either a reduction in the number of bridges or a decreased lifetime of the bridges. We see no reason the number of bridges would decrease on increasing the temperature. On the other hand, the PEO blocks of polymer 2 are long, and thus at 25 °C the rate of exchange of these blocks between droplets would be rather slow, accounting for the high viscosity at 25 °C. Thus, it is most likely that the long PEO block of polymer 2 undergoes much more rapid exchange as the temperature increases, resulting in decreased relative viscosity. Polymer 3 also shows a slight decrease in viscosity at the higher temperatures, but because of its considerably shorter PEO block length, the effect is less pronounced than for polymer 2. The slight increase in the relative viscosity with polymer 4, which occurs in the temperature range 25–35 °C (i.e., below the theta temperature of PS in cyclohexane), suggests that it is related to an expansion of the R_g of the PS block with increasing temperature and possibly because of an increased number of bridging-type polymer–droplet complexes with the more expanded conformation. Polymer 4 is the only triblock copolymer that has a sufficiently long PS block to show a significant temperature sensitivity of its radius of gyration.

Discussion

The different viscosifying effects observed with the different polymers in the various microemulsions should be due to differences in the number of the junctions or the lifetimes of the junctions, that is, the length of time the PEO blocks reside in the water/AOT droplets. To get a summary of the different behaviors of the polymers, the relative viscosities of each of the investigated triblock copolymers are compared in a single microemulsion, that is, microemulsion A, at 40 °C in Figure 7. Similar trends were observed at all temperatures studied. The viscosifying efficiencies were compared on a molar basis to draw conclusions as to the molecular parameters that govern

this efficiency. Comparing polymers 1 and 2 immediately shows that the length of the PEO block is important. This is readily understood—the length of the PEO block controls the partition coefficient between free and droplet-bound blocks, which, in turn, controls the lifetime of a PEO block in a droplet. Both the degree of binding and the dynamics of exchange affect the viscosity. The similarity of the results for the unmodified PS and polymer 1 implies that a block length of six EO units gives only a weak, if any, binding of the blocks to the water droplets.

More surprising is the observation that polymers 3 and 4 are, on a molar basis, more efficient viscosifiers than polymer 2, despite their much shorter PEO blocks. We find no reason to suspect that there should be an optimum PEO block length of around 30 units in these mixtures. Crowding could conceivably be a problem for high concentrations of long PEO chains, but the following calculations indicate that the mixtures studied here are far from such conditions. From the intrinsic viscosity data of Kawaguchi et al.³⁴ we obtain an overlap concentration, c^* , of 22.7 g dl⁻¹ for PEO of MW 750 (17 EO units) and 14.36 g dl⁻¹ for PEO of MW 2000 (45 EO units). These PEOs roughly span the MW range of the PEO blocks of the copolymers studied here. Thus, a droplet of radius 3.3 nm could contain up to 28 PEO chains of MW 750, or 6.5 chains of MW 2000, before there is a significant crowding of the PEO chains. From the data in Table 4, it is clear that the average number of PEO blocks in the droplets is far below these numbers, that is, well below the critical overlap concentration even at the highest C_{polymer} . Additionally, other studies suggest a stronger viscosity enhancement for polymers with longer PEO blocks (up to 500 EO units).¹⁴ We are then left with the conclusion that the greater length of the PS block must be the reason behind the greater relative viscosity enhancement with polymers 3 and 4, compared to polymer 2.

According to the results obtained by Struis et al.¹⁸ and their model for network formation in triblock copolymer/microemulsion mixtures, longer PS blocks should increase the probability for loop formation (as opposed to bridge formation) and thus decrease the connectivity of the polymer–droplet network. We show here that this trend does not apply in the case of PEO-PS-PEO triblock copolymers, where increasing the PS block length acts to increase the relative viscosity and thus presumably the amount of bridging-type complexes that form. For each of the polymers, the concentration is well below the overlap concentration, so the increased relative viscosity with increasing PS block length cannot be related to entanglements. We therefore conclude that a longer middle block gives a higher bridging probability. This is also expected from the well-known fact that the probability of loop formation decreases with increasing length of a flexible chain.³⁵

On the other hand, as pointed out in the Results section, the higher relative viscosity with longer PS blocks is only true when the PS block is fully soluble in the oil-phase (for polymer 4 this means at or above its theta temperature in cyclohexane) and at relatively low concentrations of microemulsion droplets. So, why does the concentration of droplets affect the viscosity enhancement ability of polymer 4 more than that of polymer 3? In our recent study of the segregative phase behavior of PS in AOT oil-continuous microemulsions, we found that increasing the PS molecular weight or increasing the droplet concentration resulted in decreased miscibility and earlier onset of phase separation.²⁸ On the basis of these findings, it seems entirely plausible that increasing the droplet concentration and increasing the PS block length in the PEO-PS-PEO droplet mixtures could also bring the system closer to the phase-separation

boundary. This would explain the lower solubility observed with polymer 4 in some of the microemulsions and could also be the reason for a decrease in viscosity prior to phase separation.

The viscosities obtained in this work are consistently lower than those reported by other investigators, such as Quellet et al.¹⁵ and Struis et al.¹⁸ For example, Quellet et al. reported relative viscosities on the order of 15 for polymer concentrations as low as 1.6×10^{-5} moles/dm³ (corresponding to 1 g/dm³ of polymer of MW 61 000) whereas the maximum relative viscosities observed here were about 7 at 1.17×10^{-3} moles/dm³ polymer 2 in microemulsion C (corresponding to 30 g/dm³ of polymer of MW 25 744). One possible explanation for this large difference is the fact that the PEO blocks in our polymers are much shorter than those used by Quellet et al., especially in the cases where they observed high viscosity enhancement. Also, the microemulsion droplets used in our work were significantly smaller than those used by Quellet et al.^{14,15} (who used droplets of $w_0 = 60$ which corresponds to a droplet radius of 9.34 nm, over 3 times larger than the largest droplet used in this study).

Summary of Effects of the Block Lengths in PEO–PS–PEO Triblock Copolymers. *PEO Blocks.* At short lengths, an increase in PEO block length affects the structure of the network (a significant fraction of loose ends should exist for very short blocks). Above a certain block length, the structure is not affected, but only the kinetics (the probability of a block leaving the droplet). For very long PEO blocks—much longer than those studied here—we may have to consider crowding or overlap effects, which may influence the distribution of PEO chains between the droplets (this effect should favor bridges rather than loops).

PS Block. The length of the PS block affects the structure of the network. For short PS blocks, loop formation is expected. The critical PS block length required for “bridge dominance” should depend on the droplet concentration (as this influences the average interdroplet distance). However, an additional affect of droplet concentration was observed, since a higher concentration of droplets seems to effectively worsen the solvency for the PS block, which, in turn, leads to a decreasing bridging probability.

Conclusions

The behavior of PEO–PS–PEO triblock copolymers in AOT oil-continuous microemulsions where the oil is cyclohexane, a poor to marginal solvent for the PS block, was more complex than the behavior observed by previous authors for nontheta triblock copolymers. The conclusions of previous authors, that the most important parameter in determining the degree of viscosity enhancement is whether the B block can shield the A blocks or not, that is, the ratio of the A and B blocks, did not hold for PEO–PS–PEO triblock copolymers. In fact, the evidence here is that the probability for bridging increases with increasing PS block length when the solvency conditions are good. However, there is a strong dependence of the viscosity enhancement on the droplet concentration, especially for polymers with longer PS blocks, since these conditions (high droplet concentrations and long PS chains) correspond to poor solvency conditions for the PS blocks.

The viscosity behavior of the PEO–PS–PEO microemulsion system can then be explained as follows. The length of the PEO block influences the probability that a block is inserted into a droplet and the residence time of the block in a droplet. For one or both of these reasons, the short PEO blocks on polymer 1 contribute no additional viscosity enhancement to a mixture.

The PS block length determines if the copolymer will form loop or bridging complexes with the microemulsion droplets. The microemulsion composition (droplet concentration) influences the solvency for the PS block and thus the probability for formation of bridges. Additionally, the droplet concentration affects the number of PEO chains per droplet, which determines the connectivity of the system. This explains the general trends of decreasing relative viscosity with increasing droplet concentration or decreasing droplet size (at constant droplet weight fraction) observed for polymers 2, 3, and 4.

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