

# Effect of Hydrophilically Modified Graft Polystyrene on AOT Oil-Continuous Microemulsions: Viscosifying Effects of P(S-*g*-PEO) as a Function of Graft Chain Length and Graft Density

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The effect of hydrophilically modified polystyrene, poly(styrene-*g*-poly(ethylene oxide)), P(S-*g*-PEO), on the viscosity of AOT oil-continuous microemulsions has been investigated as a function of PS and PEO chain lengths and PEO chain density. A series of polymers, P(S-*g*-PEO) with PEO chain lengths of 23 or 9, and different graft densities were synthesized by living radical polymerization. Thus, a range of polymers with different PS and PEO chain lengths were prepared. Five different microemulsion compositions were studied in an attempt to determine the effect of the microemulsion droplet concentration and droplet size on the viscosity enhancement by the different copolymers. Viscosities were determined at temperatures in the range 25–40 °C. The presence of polymer in the microemulsions always led to increased viscosity relative to the polymer-free microemulsion, the extent of which depended mainly on the polymer composition. Comparisons between the polymers were made in terms of the molar concentration of PEO to take into account differences in the polymer molecular weights and graft densities. A clear correlation was found between the length of the PS chain between grafts and the relative viscosity, with longer PS chains leading to higher viscosities. Increasing the microemulsion droplet concentration resulted in increasing relative viscosity with each of the graft copolymers, because of the shorter interdroplet distances facilitating the formation of active chains. Increasing temperature resulted in a decrease in relative viscosity. Finally, direct comparisons are made between the viscosifying behavior of the graft copolymers and the compositionally similar PEO–PS–PEO triblock copolymers studied previously.

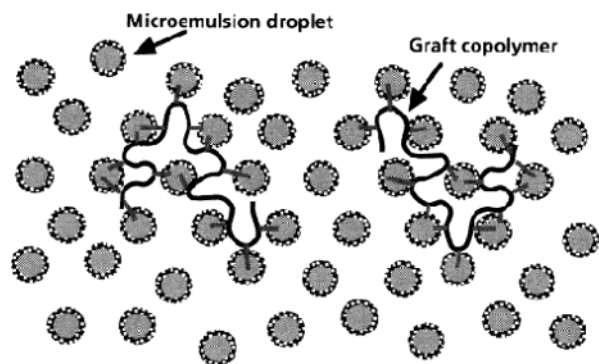
## Introduction

Upon addition of hydrophilically modified oil-soluble polymers to oil-continuous microemulsions, the hydrophilic side chains dissolve into the water droplets and the hydrophobic polymeric backbone dissolves in the oil phase. Work on this type of mixture has to date been mainly concerned with block copolymers or telechelic copolymers, which generate reversible networks in the oil-continuous microemulsions because of association of the hydrophilic end groups with the droplets and the formation of bridges between the droplets.<sup>1–3</sup> Very recently, we conducted a systematic study of PEO–PS–PEO triblock copolymers, with special emphasis on the effects of changing the various block lengths on the viscosifying behavior.<sup>4</sup> When the copolymers were compared in terms of the moles of PEO chains/dm<sup>3</sup>, trends emerged which were contrary to those found by other authors for other triblock copolymers.<sup>1,5,6</sup> In particular, the important parameters for enhanced viscosity were the absolute lengths of the PEO and (especially) the PS blocks and not the ratio of the PEO to PS blocks. Much higher viscosities resulted when the PS block was longer, but only when the solvency conditions were good for the PS block.<sup>4</sup> Additionally, changing the microemulsion composition was found to affect the overall viscosity increase mainly through changes in the droplet concentration,  $C_{\text{droplet}}$ , and through this the number of PEO chains per droplet,  $C_{\text{PEO}}/C_{\text{droplet}}$ .

Recently, Holmberg et al. investigated the effect of comb-type oil-soluble polymers on AOT oil-continuous microemulsions.<sup>7–9</sup> They added hydrophobic poly(dodecyl methacrylate) (PDMA) modified with hydrophilic poly(ethylene glycol) monomethyl ether (PEO) side chains to oil-continuous water/AOT/cyclohexane microemulsions and found marked (100–1000-fold) increases in the viscosity even at low copolymer concentrations (10–30 g/dm<sup>3</sup>). They concluded that in the microemulsion/copolymer system the polymer side chains are dissolved into the water droplets while the backbone polymers are dissolved in the cyclohexane phase and that this results in an interconnecting network and enhanced viscosity. The microemulsion/copolymer interconnecting droplet structure suggested is shown schematically in Figure 1. Similar conclusions were drawn by Wesslén et al. regarding the structures formed when similar graft copolymers dissolved in xylene or ethyl acetate were brought into contact with water.<sup>10,11</sup>

In the present work, we aim to investigate the effect of a different hydrophilically modified oil-soluble graft copolymer on the viscosity of AOT oil-continuous microemulsions. As in our recent work on triblock copolymers,<sup>4</sup> the backbone polymer chosen for this work was polystyrene, which has a theta temperature of 34 °C in cyclohexane,<sup>12</sup> as we are interested in the possible effects of the backbone solvency in the continuous medium on the polymer–droplet complex formation. Using polystyrene as the polymeric backbone for hydrophilically modified graft copolymers will enable the investigation of the effect of the backbone polymer extension on the viscosity of

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**Figure 1.** A sketch of graft copolymers dissolved in a microemulsion, at a polymer concentration below the overlap concentration.

AOT oil-continuous microemulsions. Five different P(S-*g*-PEO) copolymers (with PEO chains of length 23 or 9) were prepared and their effect on AOT oil-continuous microemulsions of different droplet size and concentration was investigated, as a function of temperature. In general, addition of graft copolymers resulted in increased viscosity relative to the bare microemulsions, because of the copolymers acting to cross-link some of the microemulsion droplets into clusters, by inserting their PEO chains into the droplets, in accordance with the schematic representation shown in Figure 1. The effects of changing the copolymer composition (length of the PS chain between the grafts, and graft chain length) were much more significant than the effects of changing the microemulsion composition (droplet concentration or droplet size) on the observed viscosities. The results of the graft copolymer investigation are compared with those obtained for the compositionally similar triblock copolymers<sup>4</sup> and the PDMA-*g*-PEO copolymers of Holmberg et al.<sup>7–9</sup>

### Experimental Details

**Materials.** Styrene (S) (99%), 4-hydroxy-TEMPO (98+%), and xylene (mixed, 96%) from Lancaster were used as supplied. Poly(ethylene glycol) monomethyl ether monomethacrylate macromonomers (with MW = 1000 or 400) (PEO) from Polysciences Inc. were used as supplied. AIBN (2,2'-Azobisisobutyronitrile) was recrystallized twice from methanol. AOT (sodium bis(2-ethylhexyl)sulfosuccinate) from Sigma (>99%) was stored in a desiccator and used as supplied. Cyclohexane (Merck) and Petroleum ether (BDH) were used as supplied. Water was of Milli-Q quality.

**Synthesis of P(S-*g*-PEO).** The synthesis was carried out by controlled radical copolymerization of styrene and the PEO macromonomer according to the method of Wang and Huang.<sup>13</sup> During the reaction, the following equilibrium is established:  $P\bullet + HTEMPO\bullet \rightleftharpoons P-HTEMPO$ , where  $P\bullet$  is the propagating macromolecule,  $HTEMPO\bullet$  is the free radical, and  $P-HTEMPO$  is the dormant compound. Using this procedure, the copolymerization of styrene and a PEO macromonomer is controllable, and the molecular weight of the copolymer and the conversion of the monomer increase with the polymerization time, and the molecular weight distribution is rather narrow.<sup>13</sup> A typical polymerization was as follows: To a 100-mL flask were added 10 mL styrene (87.1 mmol), 3.18 g of PEO (MW 1000 or 400), 26 mg HTEMPO (0.151 mmol), 13.8 mg AIBN (0.084 mmol), and 10 mL xylene. After three freeze–thaw under-vacuum cycles, the flask was sealed and placed into an oil bath at 90 °C for 3 h, and then the temperature was quickly raised to 125 °C for the remaining reaction time (24 or 48 h). At the end of the reaction, the system was frozen in liquid N<sub>2</sub>, and the resulting product was precipitated into petroleum ether. Copolymers were

**TABLE 1: Characteristics of the Graft Copolymers**

polymer	PEO chain length	no. of PEO chains on <i>g</i> -copolymer	no. of S units between grafts	$M_n$ of <i>g</i> -copolymer	$M_w/M_n$
1	23	3.8	108	46 300	1.4
2	23	9.9	27	38 000	1.7
3	23	19.6	5	29 400	1.4
4	9	18.7	13.5	33 700	2.4
5	9	46.6	3	33 800	1.7
PS	0	0	432	43 200	1.8

washed with cold water followed by cyclohexane to remove any unreacted species. An unmodified PS was also prepared for comparison.

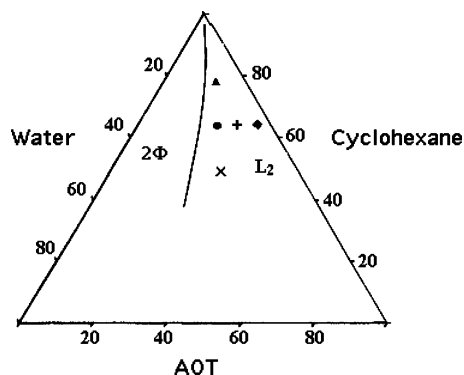
**Characterization of Copolymers.** The PEO content in the copolymers was calculated from the <sup>1</sup>H NMR spectra run in CDCl<sub>3</sub> at ambient temperature by integrating and comparing resonance signals from the hydrophilic methylene protons of the PEO graft chains and the signals from the hydrophobic methenyl protons in the benzene rings of the polymer backbone. <sup>1</sup>H NMR spectra were recorded on a Bruker 200 spectrometer with TMS as internal standard and CDCl<sub>3</sub> as solvent. The peaks of interest were ( $\delta$ , ppm) 6.3–7.3 (benzene ring), 3.3–4.3 (–CH<sub>2</sub>CH<sub>2</sub>O–). The number and weight-average molecular weights of the copolymers were determined by gel permeation chromatograph (GPC) using Waters  $\mu$ -gel columns (10<sup>5</sup>, 10<sup>4</sup>, 10<sup>3</sup>, and 500 Å) coupled in series and a refractive index detector. The injection volume was 1 mL (concentration 10–20 g/mL) and the solvent and eluent was tetrahydrofuran. Monodisperse PS was used as the standard for calibration. Thus, the MWs given for the graft copolymers are approximate, as they do not take into account the nonlinear comblike structure of the polymers.

**Sample Preparation.** Oil-continuous microemulsions of water/AOT/cyclohexane were prepared and stirred for 1 day at room temperature. The desired amount of graft copolymer was added to the microemulsions, which were then stirred at room temperature until the dispersions became transparent (a couple of hours for microemulsion E, overnight for microemulsions A, B, C, and D). All samples used for viscosity measurements were transparent and homogeneous, or for those that were slightly unstable (see Results section) the samples were stirred rapidly at 25 °C immediately before use.

**Viscosity Measurements.** The viscosities of microemulsion and microemulsion/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 an angular velocity of 30 Rad/s was determined (below the breaking point of the sample), and this value was used as the maximum stress in the flow experiments. Thus, the maximum shear rate in the experiments was always <1750 s<sup>–1</sup>.

### Results

**Characterization of the System Components.** The characteristics of the various graft copolymers are summarized in Table 1. The molecular weights, although approximate (see the Experimental section), show that there are no significant differences between the polymers in this respect. The average number of styrene units between the PEO chains was obtained



**Figure 2.** Partial ternary phase diagram for water/cyclohexane/AOT at 25 °C.<sup>15,16</sup> 2Φ, two-phase region; L<sub>2</sub>, fluid transparent microemulsion region. ●, composition of microemulsion A; ●, composition of microemulsion B; X, composition of microemulsion C; +, composition of microemulsion D; and ○, composition of microemulsion E.

**TABLE 2: Compositions of the Microemulsions, Radii, and Concentrations of Water Droplets**

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

from NMR, and using the copolymer molecular weight, the number of graft chains per polymer was calculated.

In a previous paper on triblock copolymers, the factor which most influences network formation was the length of the PS block. Given their comblike structure, the graft copolymers can be considered as a series of short PS chains separated by PEO side chains. Because of the high grafting in some of the polymers, some of the PS chains between grafts are very short (e.g., polymers 3 and 5).

A microemulsion is a thermodynamically stable isotropic solution containing oil, water, and surfactants that can display a range of self-assembly structures (spheres, cylinders, or bicontinuous structures).<sup>14</sup> The compositions of the microemulsions used in this work are given in Table 2 and are the same compositions as used in the investigation with the equivalent triblock copolymers.<sup>4</sup> A partial phase diagram, showing the relative positions of the different microemulsions in the L<sub>2</sub> (microemulsion) phase, is shown in Figure 2. The microemulsions were chosen to illustrate the effects of both droplet concentration and droplet size on the viscosity of the microemulsion/copolymer system. Microemulsions A, B, and C have the same [water]/[AOT] molar ratio,  $w_0$ , (i.e., the same droplet size) but increasing droplet concentrations. Microemulsions E, D, and B have increasing droplet size (increasing  $w_0$ ) at constant cyclohexane weight fraction, which results in a decreasing droplet concentration. Droplet radii and concentrations were calculated as described in the article on triblock copolymers.<sup>4</sup> An important characteristic of the microemulsions is the average interdroplet distance, which obviously depends on both the droplet size and concentration. Approximate values for the average interdroplet distances of the microemulsions were calculated in the triblock copolymer paper and are also shown in Table 2.

**Characterization of the Mixtures.** The nonmodified PS ( $M_n=43\,200$ ) was completely miscible with cyclohexane above 25 °C. The graft copolymers, however, were not soluble in either cyclohexane or water but were in most cases well soluble in

**TABLE 3: Solubility of the P(S-g-PEO) Polymers in the Various Microemulsions**

	microemulsion				
	A	B	C	D	E
polystyrene	soluble	soluble	soluble	soluble	insoluble
Polymer 1	unstable <sup>a</sup>	soluble	soluble	soluble	soluble
Polymer 2	soluble	soluble	soluble	soluble	soluble
Polymer 3	unstable	soluble	soluble	soluble	soluble
Polymer 4	unstable	soluble	soluble	soluble	soluble
Polymer 5	unstable	soluble	soluble	soluble	insoluble

<sup>a</sup> Solutions are described as unstable where the copolymers stick to glass surfaces once stirring is removed and as insoluble when the polymer does not even form a dispersion upon stirring.

**TABLE 4: Number of PEO Chains Per Droplet Calculated from  $C_{\text{PEO}}$  and  $C_{\text{droplet}}$  at Polymer Concentration of 30 g/dm<sup>3</sup><sup>a</sup>**

	Polymer 1	Polymer 2	Polymer 3	Polymer 4	Polymer 5
micro A	2.8	8.9	23	19	47
micro B	1.5	4.6	12	10	24
micro C	1.0	3.0	7.7	6.5	16
micro D	0.5	1.7	4.3	3.6	8.7
micro E	0.10	0.3	0.8	0.7	1.7

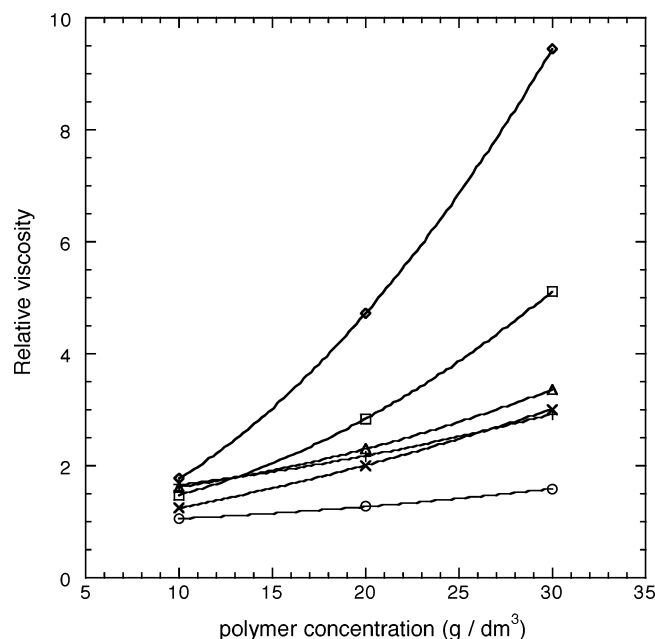
<sup>a</sup> Obviously, the number of PEO chains per droplet is lower at the lower polymer concentrations studied.

water/AOT/cyclohexane oil-continuous microemulsions. Solubility data is presented for the polymers in the various microemulsions in Table 3. Limited solubility was encountered in microemulsion A, and to a lesser extent in microemulsion E; the polymers did not completely dissolve but were present as a dispersion and settled to the bottom when stirring was removed. Heating the samples did not alter their solubility. The lack of solubility of some of the polymers in microemulsions A and E is tentatively ascribed to the low water content in these microemulsions. Such a phase separation in dilute solution was also observed by Batra et al. with triblock copolymers,<sup>17</sup> by Holmberg et al. with graft copolymers,<sup>9</sup> and was predicted theoretically by Semenov et al.<sup>18</sup>

One parameter that describes the potential connectivity of the networks formed by the different graft copolymers and microemulsions is the number of PEO chains per droplet,  $C_{\text{PEO}}/C_{\text{droplet}}$ . This can be calculated from the molar concentration of PEO chains (the molar concentration of polymer  $\times$  the number of graft chains per polymer),  $C_{\text{PEO}}$ , and the molar concentration of droplets,  $C_{\text{droplets}}$ , and the calculated values are listed in Table 4. However, this simple calculation assumes that the extension of the PS chains is sufficient that each PEO chain of a single polymer can be placed into a separate droplet, which is not necessarily the case, as will be seen below. Where the number of chains per droplet is less than 1, this suggests that there are not enough PEO chains to form a network.

**Viscosity: General Considerations.** To systematically study the effects of both the copolymer and the microemulsion composition on network formation, the five different oil-continuous microemulsions were mixed with the five different graft copolymers at three different concentrations (10, 20, and 30 g/dm<sup>3</sup> polymer). The viscosity of the mixtures was investigated as a function of the polymer concentration, polymer composition [graft density (actually the length of PS chain between grafts) and length of the PEO chains], and as a function of the composition of the microemulsion. In all cases, the flow curves were Newtonian, even at the highest concentrations studied (up to 50 g/dm<sup>3</sup> for polymer 1, results not shown). The lack of shear-rate dependence is most likely due to the limited shear-rate regime studied (see Experimental Details). Newtonian



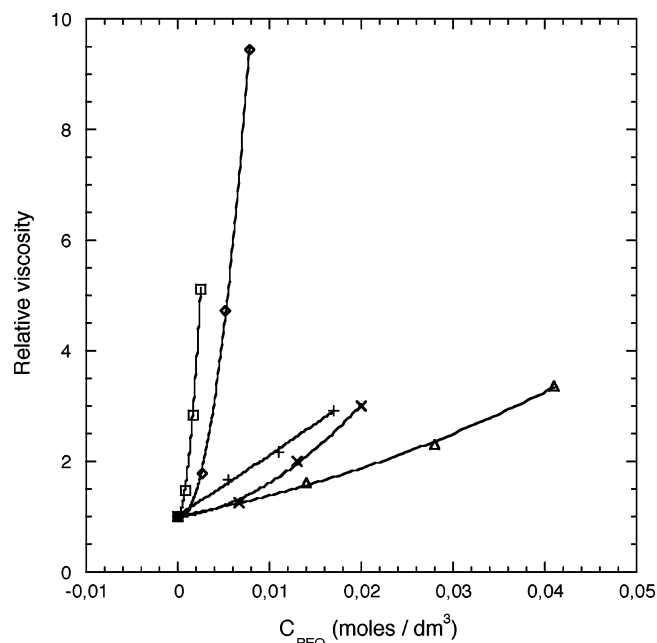


**Figure 3.** Plot of relative viscosity versus polymer concentration ( $\text{g} / \text{dm}^3$ ) in microemulsion B for each of the different polymers. (○) polystyrene, (□) Polymer 1, (◇) Polymer 2, (X) Polymer 3, (+) Polymer 4, and (Δ) Polymer 5. Lines are guides to the eye only.

viscosities have also been observed by Holmberg et al. for PDMA-*g*-PEO with much higher overall polymer MW ( $M_n = 149\,000$ ), higher graft densities (2.7 PEOs per 100 monomers), and longer PEO chains (MW 2000) in a microemulsion of composition E, while they observed shear thinning in microemulsions of composition A and B.<sup>7</sup> Thus, it is also possible that the lack of shear-rate dependence observed here is due to the generally poorer network-forming abilities of the polymers used in this study as compared with those of Holmberg et al. This is also reflected in the much lower relative viscosities observed here compared with the 100–1000-fold viscosity increases observed by Holmberg et al. compared to the polymer free microemulsions.

In the following sections, the effects of changing different parameters in the system (either the copolymer or the microemulsion composition) will be discussed systematically. Microemulsion B is the common link in the two different series of microemulsions investigated (see Table 2); it is of intermediate droplet concentration in the series A, B, and C, and it has the largest droplet size in the series E, D, and B. This is shown also in Figure 2 where the relative compositions are shown in a ternary phase diagram. From Table 1, it is clear that polymers 1– and 3 have the same PEO chain length but different graft densities. Polymers 4 and 5 have a lower PEO chain length and also different graft densities. Unless otherwise stated, all results discussed are at 25 °C, and the effect of increasing temperature is discussed separately. To illustrate the effects of the polymers, the viscosities are given as relative viscosities throughout, taking the corresponding polymer-free microemulsion as the reference.

**Varying the Copolymer Characteristics.** The viscosity of each of the copolymers in microemulsion B is plotted in Figure 3 in terms of the concentration of polymer added ( $\text{g} / \text{dm}^3$ ). All of the graft copolymers result in a higher relative viscosity than the unmodified polystyrene. The differences in the relative viscosity with the different polymers are evident. Polymer 2 results in the highest relative viscosity, followed by polymer 1, with polymers 3–5 having about the same relative viscosity.

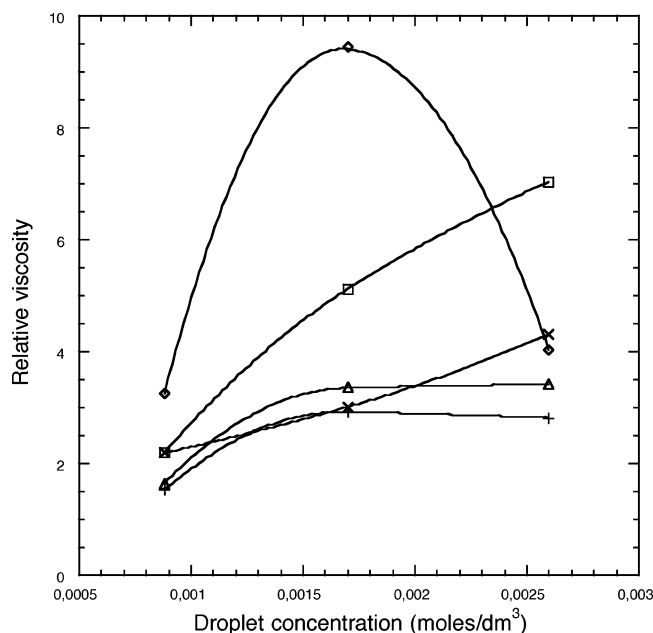


**Figure 4.** Plot of relative viscosity versus  $C_{\text{PEO}}$  in microemulsion B for each of the different polymers. (□) Polymer 1, (◇) Polymer 2, (X) Polymer 3, (+) Polymer 4, and (Δ) Polymer 5. Lines are guides to the eye only.

These trends were observed in all the microemulsions and at each of the temperatures studied. No distinct trends could be observed in terms of graft chain density, while the polymers with the longer graft chain length (23 EO units) generally gave higher relative viscosities than the polymers with the shorter PEO chains.

The concentration scale used in Figure 3 ( $\text{g} / \text{dm}^3$ ) does not take into account differences in the graft density or molecular weight (MW) of the copolymers, which result in differences in the number of active chains that each polymer can theoretically form (see Table 4 for numbers of PEO chains per droplet). Therefore, the results from Figure 3 are replotted in terms of the molar concentration of PEO chains,  $C_{\text{PEO}}$  ( $\text{moles} / \text{dm}^3$ ), in Figure 4. Very different trends emerge in this plot. Polymers 1 and 2 show a very rapid increase in relative viscosity even at low  $C_{\text{PEO}}$ , polymers 3 and 4 have a more gradual increase of relative viscosity with increasing  $C_{\text{PEO}}$ , and polymer 5 showed only a very gradual increase in relative viscosity with  $C_{\text{PEO}}$ . In the detailed description of the effect of polymer composition below, all comparisons will be made in terms of  $C_{\text{PEO}}$  (Figure 4), since we will thus be comparing the polymers directly in terms of “active chain-forming possibilities” or moles of PEO chains.

**Constant PEO Chain Length and Varying Length of PS Chain between Grafts.** Taking the series of polymers 1–3, which have constant PEO chain length of 23 units (MW 1000), we can compare the effect of decreasing the length of the PS chain between grafts (i.e., increasing the graft chain density) on the behavior of the polymers. The viscosity enhancing effects of these three polymers in microemulsion B are shown in Figure 4. Polymer 1 causes the fastest rise in relative viscosity at the lowest  $C_{\text{PEO}}$ , followed by polymer 2, while polymer 3 shows a gradual increase in relative viscosity with increasing  $C_{\text{PEO}}$ . A comparison of these polymers shows that the length of the PS chains between grafts increases in the order polymer 3 < polymer 2 < polymer 1. Thus, it appears that the relative viscosity increase correlates with the PS length between grafts and is highest when the PS chain between the grafts is long. A



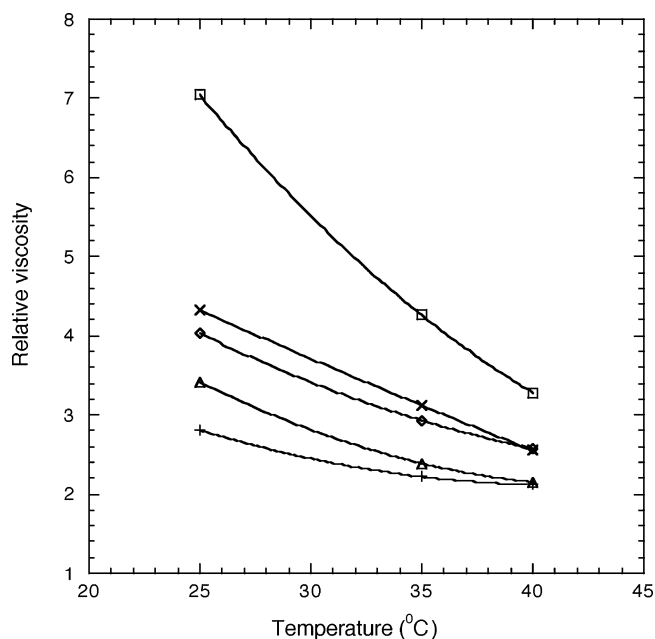
**Figure 5.** Plot of relative viscosity versus droplet concentration (at constant droplet radius of 3.3 nm) at 30 g/dm<sup>3</sup> polymer and 25 °C for (□) Polymer 1, (◇) Polymer 2, (X) Polymer 3, (+) Polymer 4, and (Δ) Polymer 5. Lines are guides to the eye only.

comparison of these copolymers in microemulsions A, C, D, and E reveals similar behavior, so the trend of increasing relative viscosity with increasing PS chain length between grafts holds at all microemulsion compositions.

Looking now at the polymers with the shorter PEO chain length of nine units (MW 400), polymers 4 and 5, the viscosity enhancing effects of these two polymers can also be seen in Figure 4. The trend observed here is that polymer 4 shows a steeper increase in relative viscosity with increasing  $C_{\text{PEO}}$  than polymer 5. A comparison of the composition of these two copolymers shows that the length of the PS chains between the grafts increases in the order polymer 5  $\ll$  polymer 4. This again is evidence that the length of the PS chain between the grafts is the important parameter in determining the viscosifying effects of the polymers, with the viscosifying effects being hampered if the PS chain length between the grafts is short, caused by high graft density, as this forces several graft chains to be accommodated in the same droplet and thus limits the number of active chains formed. The behavior of the polymers in microemulsion B is representative of the behavior in all of the microemulsions.

**Comparing PEO Chain Length versus Graft Density.** Figure 4 also shows the effect of PEO chain length on the relative viscosity of microemulsion B. In general, longer PEO chains lead to higher viscosity, because of the longer residence time of long PEO chains in the droplets. However, as can be seen in Figure 4, the polymer with very high graft density of the long PEO chain (polymer 3) has lower relative viscosity than the polymer with low graft density of the shorter PEO chain (polymer 4). This again points to the importance of the length of the PS chain between the grafts as a major controller of viscosity.

**Varying the Microemulsion Characteristics. Increasing the Droplet Concentration at Constant Droplet Size.** Comparing the composition data for microemulsions A, B, and C given in Table 2, it is clear that the droplet concentration,  $C_{\text{droplet}}$  (moles/dm<sup>3</sup>), increases significantly from microemulsion A to microemulsion C. Figure 5 shows the relative viscosity of each of the copolymers in this series of microemulsions at 30 g/dm<sup>3</sup> polymer



**Figure 6.** Relative viscosity versus temperature at 3% polymer (wt/v) of each of the polymers in microemulsion C. (□) Polymer 1, (◇) Polymer 2, (X) Polymer 3, (+) Polymer 4, (Δ) Polymer 5. Lines are guides to the eye only.

at 25 °C, where clearly the general trend is an increase in viscosity with increasing droplet concentration, with a maximum in the viscosity in some cases. The same pattern of trends was observed at each of the three polymer concentrations used (10, 20, and 30 g/dm<sup>3</sup>) at 25 °C, and at each of the temperatures studied, although the viscosity maxima became more apparent at 35 and 40 °C. The observed trend of increasing viscosity with increasing droplet concentration is counter to what one would expect on the basis of the decrease in the number of PEO chains per droplet with increasing droplet concentration, which was calculated and shown in Table 4. Additionally, it is counter to what was observed for the compositionally similar triblock copolymers, which showed a distinct decrease in viscosity with increasing droplet concentration.<sup>4</sup> Also, the maxima observed are reasonable, as the droplet concentration must eventually result in their being less than one PEO chain per droplet with a loss of connectivity of the droplets and a decrease in the viscosity.

**Increasing Droplet Size at Constant Droplet Weight Fraction.** Comparing the composition data for microemulsions E, D, and B given in Table 3, it is clear that the droplet size increases from microemulsion E to microemulsion B, although the molar droplet concentration decreases significantly in the same order. The relative viscosity for each of the polymers in this series of microemulsions at each of the temperatures was also studied. Because of the lack of any one significant trend, it was not possible to draw any conclusions about the effect of droplet size on the relative viscosity. Additionally, because of the large change in droplet concentration with changing droplet size, it is not possible to separate the effect of these two.

**Increasing Temperature.** Figure 6 shows the effect of increasing the temperature on the relative viscosity of each polymer in microemulsion C at 30 g/dm<sup>3</sup> polymer. Similar trends are observed at lower polymer concentrations also. In all cases, a decrease in the relative viscosity with increasing temperature is observed. Decreasing relative viscosity with increasing temperature is typical behavior for polymer–microemulsions systems<sup>8,19</sup> because of an increased rate of exchange between

droplets with increasing temperature.<sup>20</sup> The trends shown in Figure 6 are representative of all of the polymers in all of the microemulsions, with the exception of polymer 1 in microemulsion B where the effect of temperature was nonmonotonic with the relative viscosity at 35 °C being larger than that at 25 °C. Thus, it appears that there is no significant effect of the fact that cyclohexane is a theta solvent for PS on the viscosity behavior of the graft copolymers in the microemulsions studied.

## Discussion

The systems considered here may be considered as transient networks, where the viscosity  $\eta = G\infty\tau$ . Here,  $G\infty$  is proportional to the number of active chains (i.e., chains which connect two droplets), and  $\tau$  is the lifetime of an active chain. Thus, the measured viscosity reflects both the number of active chains and their lifetime (or in polymers in a microemulsion, the residence time of a side chain in a droplet), as was discussed previously for the compositionally similar PEO-PS-PEO triblock copolymers.<sup>4</sup> Thus, we examine the effect of changing the length of the hydrophilic graft chains (which form the cross-links) and the length of the hydrophobic PS backbone between grafts on the relative viscosity of microemulsions of different composition.

In the triblock copolymers in microemulsions, two types of droplet-polymer complex can be formed: a loop-type complex where the two end blocks are placed into the same droplet with the center blocks looped around the droplet or a bridging-type complex where the two end blocks are placed into different droplets with the center block forming a bridge between the two droplets. Only a bridging chain is an active chain in the polymer-droplet network. Extending this to the graft copolymer case, it is clear that if there is a high number of graft chains on the graft copolymer it is unlikely that they will all be contained in a single droplet, but equally it is not necessary that each one be contained in a separate droplet. Indeed, at high graft densities the latter situation will be impossible for steric reasons—the droplets are simply too big to fit around the copolymer chain.

Studies of the phase behavior of microemulsions with triblock copolymer have suggested that when the droplets are far apart, the chains are too short to bridge them, meaning that a chain having one of its stickers in one given droplet prefers to loop so that its second sticker adsorbs in the same droplet.<sup>21</sup> When the droplets are close enough to one another (at a distance on the order of  $R_g$ , the radius of gyration of the telechelic polymer chain), loop conformations are still possible, but in addition, bridging conformations are now accessible.<sup>21</sup> Thus, the conformational entropy of the chain is larger when the droplets are at the right distance for bridging. With the graft copolymers, it is the length of the PS chains between the grafts that is the relevant distance, and as can be seen from Table 1, these lengths are very small and thus it is not possible to calculate  $R_g$  values for them. While increasing the number of graft chains should increase the number of droplets that can be bound, decreasing the length of the PS chain between the grafts reduces the ability of the polymer to place the graft chains into separate droplets. The difference in the viscosity enhancing abilities of polymers 1 and 3 clearly illustrates the effect of the length of the PS chain between grafts on the droplet binding and thus the relative viscosity of the system, as these polymers represent the two extremes: polymer 1 has a long PS chain length between the grafts and a low number of graft-chains, whereas polymer 3 has a much shorter PS length between its much higher number of graft chains. On the basis of the idea that the more graft chains a polymer has the higher its potential for forming active

chains, one would expect polymer 3 to cause a much greater increase in viscosity than polymer 1 at the same mass concentration, as it has 5 times as many graft chains. However, the short PS chains between the grafts of polymer 3 forces several PEO chains to occupy the same droplet resulting in a low viscosity. Thus, it is clear that a central parameter for controlling the relative viscosity is the length of the PS chains between grafts, since the polymers with the longest PS lengths between grafts led to the highest relative viscosities.

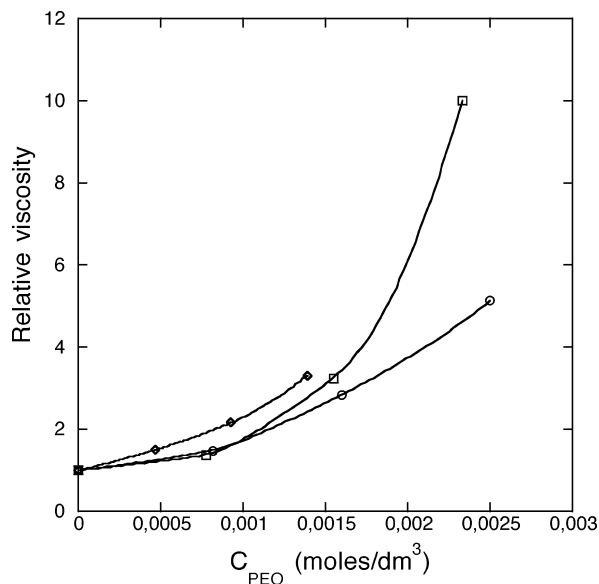
The same argument, where the length of the PS blocks between grafts is the controlling parameter, can be used to explain the general trend of increasing viscosity with increasing microemulsion droplet concentration (Figure 5). As the droplet concentration increases, the average distance between droplets decreases (as shown in Table 2), which should make it easier for the graft copolymers with short PS chains between the grafts to place their PEO chains into different droplets, resulting in an increased number of active chains. Thus, generally, relative viscosity increases with increasing droplet concentration. However, in some cases a viscosity maximum was observed, with further increases in droplet concentration resulting in the viscosity decreasing again because there is a limit to how many droplets can be present and still form a connected network; if the droplet concentration is too high, then there are simply not enough PEO chains to bind them and thus the connectivity decreases.

Such a viscosity maximum was also observed by Holmberg et al. with PEO grafted PDMA polymers upon increasing the  $C_{\text{droplet}}$  at a constant 10 g/dm<sup>3</sup> of polymer.<sup>8</sup> A maximum was found for three different droplet sizes, but the effect was more pronounced with larger droplets (higher  $w_0$  value).<sup>8</sup> Thus, in general, increasing  $C_{\text{droplet}}$  of the microemulsions, at constant droplet size, results in an increase in the relative viscosity, up to a maximum, followed by a decrease as the connectivity decreased. Eicke et al. looked at the effect of dilution by adding microemulsion of the same concentration (decreasing the number of polymers per droplet) on the viscosity of PEO-PI-PEO triblock copolymers and found highly nonlinear but monotonic and reasonably normal decreases in viscosity.<sup>22</sup>

The lack of effect of increasing temperature on the relative viscosities appears strange at first sight, given that cyclohexane is a theta solvent for PS with the theta temperature being at 34 °C.<sup>12</sup> However, the observed transition temperature is dependent on the PS molecular weight, with shorter PS chains being soluble in cyclohexane at lower temperatures.<sup>23</sup> As mentioned in the results section, the graft copolymers can be considered as a series of short PS chains separated by PEO side chains. From Table 1, it can be seen that in most cases the PS chains between the grafts are very short and are thus unlikely to show any temperature dependence of their coil dimension or to suffer from any insolubility in cyclohexane below the theta temperature. This very short PS length between the PEO chains is thus the reason for the lack of a significant temperature effect on the graft-copolymer-microemulsion systems.

The viscosities measured here were significantly lower than those determined by other authors working with associating polymers, particularly those of Holmberg et al. for PDMA-PEO graft copolymers.<sup>7</sup> However, the viscosities of the PS-g-PEO polymers were of the same order of magnitude as those of the PEO-PS-PEO triblock copolymers of similar composition.<sup>4</sup> Batra et al. report that the only triblocks that have been successful in creating reversible networks with a high low shear viscosity consist of PEO endblocks with poly(isoprene) midblocks.<sup>17</sup> Some  $\alpha,\omega$ -telechelic ionomers with the same midblock





**Figure 7.** Comparison of the viscosity enhancing behavior of graft and triblock copolymers of similar composition in microemulsion B. (○) Graft copolymer (Polymer 1), (□) triblock copolymer 2,<sup>4</sup> and (x) triblock copolymer 4.<sup>4</sup> Lines are guides to the eye only.

but terminal groups consisting of a sodium salt of sulfonic acid gave much weaker associations and a relative viscosity 3 orders of magnitude lower at the same polymer concentration.<sup>22</sup> Additionally, Batra shows that PEO–PPO–PEO triblock copolymers with short PPO midblocks give relative viscosities 2–3 orders of magnitude lower than PEO–PI–PEO triblocks which have longer PI blocks.<sup>24</sup> Thus, the lower viscosities reported here for both the graft and triblock copolymers of PS with PEO are not that exceptional.

#### Comparison between Graft and Triblock Copolymers.

Finally, a direct comparison between the graft and triblock copolymers can be made. To this end, representative polymers of each type are compared. The polymers chosen for comparison are Polymer 1 from the graft copolymers which has PEO chain lengths of 23 EO units, PS length between grafts of 108 styrene units, and the number of grafts per polymer being 3.8; triblock Polymer 2 which has PEO block lengths of 54 EO units and PS block length of 206 styrene units; and triblock Polymer 3 which has PEO block lengths of 31 EO units and PS block length of 390 styrene units. The details of the triblock copolymers were given previously.<sup>4</sup> Thus, we have a series of polymers of increasing PS length: graft copolymer 2 < triblock copolymer 2 < triblock copolymer 3, since we discovered already that the PS block length or length of PS chain between grafts is the most important parameter for enhancing the viscosity.

The simplest comparison that can be made is the effect of increasing polymer concentration on the microemulsion viscosity, and this is shown in Figure 7 for the graft and triblock copolymers. Since the polymers do not have the same number of PEO chains per polymer, the concentration is expressed as the PEO chain concentration,  $C_{\text{PEO}}$ . Clearly, the relative viscosity increases much faster with both of the triblock copolymers than with the graft copolymer, with the rate of increase following the pattern of the length of the PS blocks, that is, the longer PS blocks lead to higher viscosities. Since the graft copolymer has approximately the same PEO chain length as triblock copolymer 3, the higher viscosity with triblock copolymer 3 is clearly due to the longer PS block length of the triblock copolymer. The difference in the viscosity between the graft copolymer and

triblock copolymer 2, which appears only at higher  $C_{\text{PEO}}$  (where significant connectivity could be expected), is clearly due to the difference in the residence times between the PEO segments of these two polymers, since the triblock copolymers PEO blocks are over twice as long as the graft copolymer PEO chains. Thus, even comparing between the two different geometries, it is the PS length that controls the viscosity enhancement, and increased PS length is of greater benefit than additional PEO chains, as shown by comparing the graft copolymer (which has about twice the number of PEO chains as the triblock copolymers) with triblock copolymer 3.

Increasing  $C_{\text{droplet}}$  resulted in decreased relative viscosities for the triblock copolymer because of the decreased number of PEO blocks per droplet (reduced number of active chains). On the other hand, increasing  $C_{\text{droplet}}$  resulted in increased relative viscosity for the graft copolymers, since the shorter distance between the droplets facilitates the placement of the PEO chains into several different droplets, increasing the number of active chains and thus the relative viscosity. However, there was a limit to the amount the droplet concentration could increase before the number of PEO chains per droplet was below that required for connectivity to occur, at which point the viscosity decreased with increasing droplet concentration.

Decreasing the droplet size, at constant droplet weight fraction, also resulted in a large increase in  $C_{\text{droplet}}$  and thus a significant decrease in the relative viscosity of the triblock copolymer containing microemulsions. No significant trend in the viscosity could be observed for the graft copolymers upon changing the microemulsion droplet size.

#### Conclusions

The viscosity enhancing behavior of a series of PS-*g*-PEO copolymers in AOT oil continuous microemulsions was determined as a function of the microemulsion composition (droplet concentration) and the copolymer composition (graft chain length and graft chain density).

Since the different graft copolymers had different numbers of graft chains, clear trends emerged only when the polymers were compared in terms of the actual number of graft chains (mol/dm<sup>3</sup>). Then, it became immediately clear that a central parameter in determining the degree of viscosity enhancement by the graft copolymers was the length of the PS chain between the grafts. In all cases, polymers with a greater distance between the grafts resulted in higher viscosities than polymers with less distance between the grafts. This is a consequence of the fact that the efficiency with which a polymer could place its PEO chains into different droplets to form active chains depended on the extension of the PS chains. The short PS chain lengths between the graft chains could also explain the lack of a significant effect of temperature on the viscosity of the microemulsion–graft copolymer systems. The PEO chain length affected the viscosity by affecting the residence time of the chains in the droplets.

A comparison with the results obtained previously for PEO–PS–PEO triblock copolymers showed strong similarities in the behavior of the two types of copolymer. In both cases, the length of the PS segments (PS block in the triblock copolymer case and length of PS chains between grafts in the graft copolymer case) was the most important factor in controlling the viscosity, with longer PS segments leading to higher viscosities in both cases.

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