ABA Low Molar Mass Triblock Copolymers in Reverse Emulsions: A Rheological Study

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ABSTRACT: The effect of blocks length and molar mass of ABA triblock copolymers on the rheological behavior of water in oil (w/o) emulsions was investigated. Emulsion parameters such as water droplet concentration (and droplet size) of a series of inverted emulsion systems were evaluated. All copolymer/emulsion systems studied showed a non-Newtonian behavior, and the presence of the copolymer in the emulsion system led to an increase of the low shear viscosity when the size of the midblock of the copolymer was in a specific size range. This suggests the formation of a transient network through the interconnection, by the copolymer, of the smaller water droplets present in the emulsion. Consequently, the systems behave as w/o emulsions containing reversibly cross-linked oil-soluble polymers in the continuous phase, resulting in a pronounced shear thinning behavior. For the different emulsions studied, the relative viscosity increased, with few exceptions, with increasing droplet concentration. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 3282–3289, 2012

Key words: rheology; structure–property relation; surfactants; colloids

INTRODUCTION

Emulsion systems are widely used in many areas such as of food, cosmetic, pharmaceutical, and the oil industry.[1–4] The flow behavior of these systems, which may combine liquids with very different viscosities and responses to shear, can vary from Newtonian to shear thinning, depending on factors such as the droplet size and the relative proportion of the two liquids. Some important industrial applications of these systems, such as in oil wells drilling fluids, require that they present a shear thinning behavior. In the case of oil based drilling fluids, which consist of inverted emulsions (water-in-oil), this rheological behavior is usually obtained with the use of organophilic clays.[5,6] So far, the rheological effect of adding associative polymers to this type of system has not been reported. Despite the lack of rheology studies on associative polymers in inverted emulsions, a few studies have been carried out using a microemulsion as a model system.[7–10]

Several authors have pointed out the advantages of using microemulsions as model systems for studying the interaction with associative polymers. In these systems, different parameters can be varied separately, such as the size of the droplets, by adjusting the composition of the microemulsion, the average distance between droplets, which depends on their volume fraction, the number of associative polymer segments inserted per droplet, and the length of the middle block. Thus, the association process can be tailored by adjusting the size and concentration of the droplets and the number and length of the associating groups.[7–10]

Although microemulsions are thermodynamically stabilized systems while emulsions are not, both could be considered as "complex solvents" for ABA triblock copolymers containing hydrophilic end blocks and a lypophilic midblock or vice-versa, depending on the emulsion or microemulsion type. Particularly, such copolymers can form dimeric complexes in reverse microemulsions by inserting their hydrophilic end blocks (A) into the aqueous cores of the droplets and by linking the water domains via their oil-soluble midblocks (B). Above a certain polymer concentration, a three-dimensional reversible structure presenting the typical physical properties of transient networks would be formed.[7–17]

Water-in-oil microemulsion systems interact in a specific manner with ABA triblock copolymers depending on the chemical nature of the emulsifier, i.e., ionic or nonionic. In previous studies[12–18] using microemulsion systems, it was found that droplets covered by ionic surfactants required relatively large

amounts of polymer to form three-dimensional transient networks. Nonionic surfactant microemulsions, in contrast, did show the same properties at much lower polymer concentrations.[11] Previous reports[19,20] show that a further effect is expected for ABA triblock copolymers in w/o microemulsions since the bridging (middle) block of the polymer may act as a spacer between the droplets, hampering droplet cluster formation.

In a previous work on poly(ethylene oxide)–polystyrene–poly(ethylene oxide) triblock copolymers (PEO–PS–PEO), in microemulsion systems, Lynch et al.[10] have concluded that, for systems with PEO blocks of shorter length, an increase in these blocks length would affect the structure of the network formed, since when PEO blocks were too short, a significant fraction of ends stayed unconnected. On the other side, above a certain block length the structure would not be affected by the PEO blocks size.

Dukhin et al.[21–23] studied the evolution of a water-in-oil (kerosene) emulsion controlled by droplet-bulk ion exchange, using sorbitan mono-oleate (SPAN 80) as emulsifier. They found that the emulsion droplet did break up into much smaller (mini- and possibly microemulsion) droplets with time. Although they do not claim that this should be the only possible mechanism, they attribute their results to the occurrence of an ion exchange between the interior of the water droplets and the bulk of the kerosene media. This ion exchange leads to a gradual collapse of the exterior diffuse layer. The surface charge associated with the adsorbed SPAN molecules becomes screened with an interior diffuse layer. This process leads to the reduction of the surface tension and eventual break up of the emulsion droplet into much smaller droplets.

The objective of this work was to study the potential of triblock copolymers as additives for producing a pronounced shear thinning behavior in reverse emulsions, using the concept and theory of three-dimensional reversible transient networks, as described in the literature for microemulsions systems. In view of the above remarks, it is suggested that the studied systems would present a wide water droplet size distribution, enabling the formation of the transient network by the triblock copolymers studied.

EXPERIMENTAL

Materials

A mineral oil (*n*-paraffin : isoparaffin, 2 : 1), was used as the oil phase. SPAN80 (Sorbitan Mono-oleate) and TWEEN80 (POE$_{(20)}$ Sorbitan Mono-oleate) were obtained from Sigma–Aldrich (Brazil) and Isofar (Brazil) and used as the surfactant and cosurfac-

TABLE I
Characteristics of the Triblock Copolymers Used in This Study

Polymer	PEG block length (EG units)	PPG block length (PG units)	PEG–PPG–PEG	Polymer (M_n)
1	3	15	3–15–3	1.100
2	11	16	11–16–11	1.900
3	3	30	3–30–3	2.000
4	15	53	15–53–15	4.400
5	20	70	20–70–20	5.800
6	76	30	76–30–76	8.400
7	17	76	17–76–17	5.700

tant, respectively. A series of poly(ethylene glycol)–block-poly(propylene glycol)–block-poly(ethylene glycol) (PEG–PPG–PEG) from Sigma-Aldrich (Brazil) were used as the low molar mass ABA triblock copolymers additives. Their characteristics are summarized in Table I. All components were used as received without further purification.

Synthesis of MPEG–PB–MPEG triblock copolymer

A triblock copolymer poly(ethylene glycol) methyl ether-*block*-polybutadiene-*block*-poly(ethylene glycol) methyl ether—MPEG–PB–MPEG (Fig. 1) was synthesized to evaluate the effect of the nature of the copolymers middle block on the rheology of the emulsions. The procedure was adapted from Li et al.,[24,25] who described the synthesis of poly(ethylene oxide)–poly[(R)-3-hydroxybutyrate]–poly(ethylene oxide)—PEO–PHB–PEO. The general procedure used in this work is described as follows: polybutadiene, dicarboxy terminated (PBCT, 3.7 g, 8.8×10^{-4} mol, $M_n \sim 4200$, Aldrich), poly(ethylene glycol) methyl ether (MPEG, 2.0 g, 2.67×10^{-3} mol, $M_n \sim 750$, Alfa Aesar), and 4-(dimethylamino)pyridine (DMAP, 0.10 g, 8.8×10^{-4} mol, Merk) were introduced into a two-neck flask and the system was dried under vacuum at 60°C for 16 h (oil bath). Anhydrous methylene chloride (around 125 mL) was added to the flask and then distilled, to remove from the system any remaining water. *N,N'*-dicyclohexylcarbodiimide (DCC, 0.71 g, 3.4×10^{-3} mol, Aldrich) was dissolved in 30 mL of methylene chloride and then added to the system which was stirred at room temperature for 16 h under nitrogen atmosphere. The precipitated coproduct dicyclohexylurea (DCU) was removed by filtration and the product (MPEG–PB–MPEG) was precipitated from methanol (twice). The product was characterized by infrared (IR) spectroscopy and gel permeation chromatography (GPC). IR (KBr): 3074 (=C—H), 2916 and 2845 (—CH$_2$—), 1349 (—CH$_3$), 1738 (C=O, ester), 1147 (C—O, ester), 1639 (C=C), 1111 (C—O, ether), 1448, 725, 1242, and 1189 (—CH$_2$—), 1419, 966, and 684
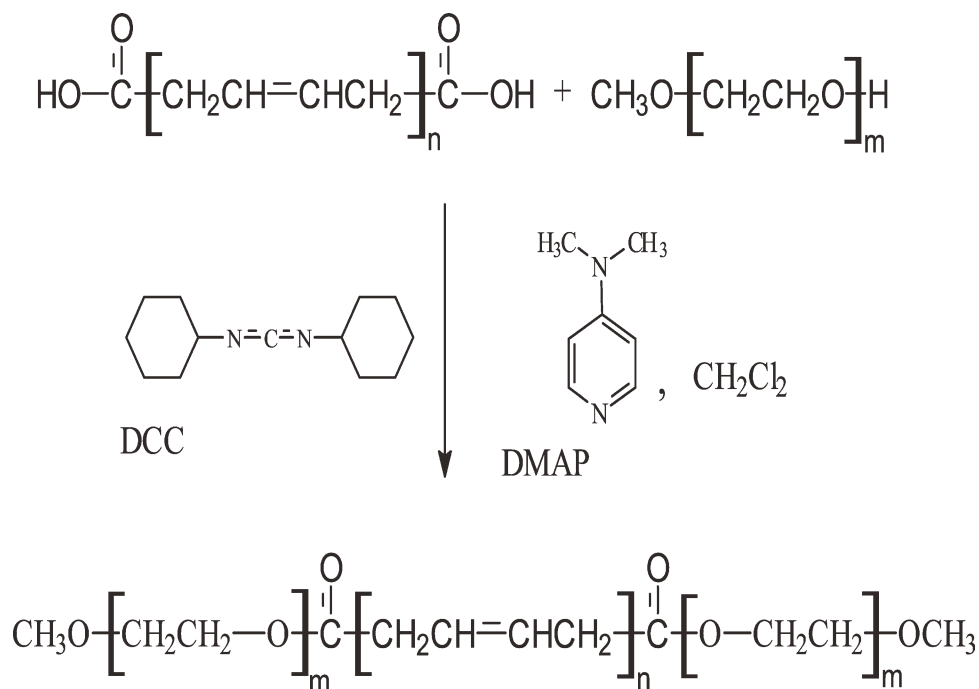
Figure 1 General scheme of the synthesis of MPEG–PB–MPEG triblock copolymer.

cm^{-1} (=C—H); GPC (THF): M_n = 13.380; M_w = 21,184; M_w/M_n = 1.58.

Sample preparation

Oil continuous emulsions of water/S80 : T80/oil were prepared at room temperature first by dissolving the emulsifiers in the oil and then slowly adding water to the system, keeping the emulsions under magnetic stirring during 24 h. The emulsifier (S80) and coemulsifier (T80) ratio was kept constant to obtain a hydrophilic–lypophilic balance (HLB) value of 6.[26] A specific amount of triblock copolymer was added to the emulsion, which was then stirred for 24 h more, at room temperature, to assure a complete copolymer dissolution, although sometimes the emulsions had to be slightly heated beforehand to accelerate the solvency process. A 1.75M NaCl water solution was used as the aqueous phase. The dilution method was used to characterize the type of emulsion formed, W/O or O/W.[27]

Rheological measurements

A Haake RS150 shear rheometer with a double-wall sensor DG41-Ti was used to measure shear viscosity as a function of shear rate under controlled shear stress conditions. The samples were gently transferred to the rheometer cylinder sensor and kept at rest for 5 min before starting the measurements, which were all performed at 25°C.

RESULTS AND DISCUSSION

Considerations on the prepared emulsions

The dilution tests performed did show that all the emulsions prepared were of the water-in-oil type. In addition, all the samples, with w/o ratios from 10/90 to 50/50 (% v/v) were relatively stable to coalescence, but did show phase separation after some hours, releasing a clear oil.

Despite the milky appearance of the samples, it is considered that the droplet size range of the prepared emulsions include micro and/or mini-droplets along with the large droplets that are responsible for the turbidity of the system. According to Dukhin et al.,[21] a transition from emulsion to mini-emulsion or even to microemulsion could happen when an emulsifier double layer is formed in the water oil interface. This transition would be due to the migration of the ions from the water drop to the bulk phase. In our case, more than the emulsifier itself, the triblock copolymers used could be promoting this migration due to the nature of their mid blocks, poly(propylene gycol) (PPG). The oxygen atoms present in the PPG, immersed in the oil phase and close to the water–oil interface, could be also promoting the migration of Na^+ ions to the bulk phase and then screening the charges in the double layer. This screening could be responsible for the drop break up into smaller ones and lead the transition from emulsion to mini or micro emulsion.

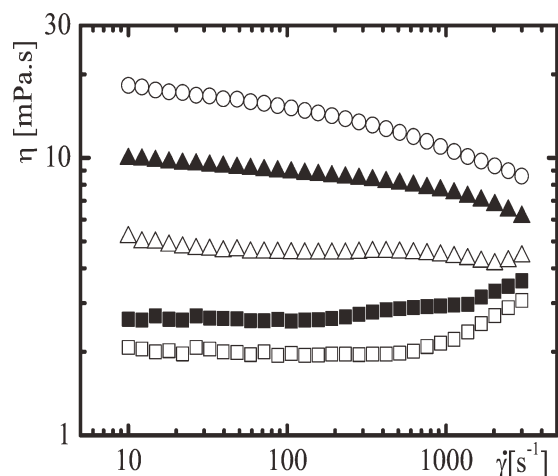In this case, it is proposed that the emulsion droplets would break primarily to form mini-emulsion

Figure 2 Rheological behavior of reverse emulsions with different water/oil ratios. (□: 10/90, ■: 20/80, △: 30/70, ▲: 40/60, and ○: 50/50). Emulsifier concentration was kept constant (10% wt/v_{water}).

droplets size, since they still show sedimentation with time. However, stirring them up would promote the aggregate breakage to form once again the mini-emulsion system.

Simple shear rheology of the reverse emulsions

Figure 2 shows the rheological behavior of a series of reverse emulsions with different water/oil ratios. It is clearly observed that the emulsions with lower amounts of water (i.e., 10/70 to 30/90) show a Newtonian behavior, i.e., the viscosity does not show any dependence on the shear rate. The upward turn exhibited by the curves at higher shear rates could indicate the onset of inertial effects. However, for systems with higher amounts of water (i.e., 50/50 and 40/60), the emulsions behaved as a shear thinning fluid, where the viscosity decreases with increasing the shear rate. Shear thinning behavior has been previously observed in rheology studies of surfactant or polymer stabilized w/o and o/w emulsions and also in particle stabilized emulsions.[28–36]

Pal[30] has shown that a sharp leap in the viscosity of reverse emulsion systems occurs at a water volume fraction equivalent to that of the percolation threshold, which is at the same water volume fraction at which the shear thinning behavior sets in. The viscosity increment with increasing water content was attributed to droplets aggregates.

Effect of the addition of triblock copolymers on the simple shear rheology of the reverse emulsions

Effect of the emulsion parameters

Emulsion droplet size. To evaluate the effect of the presence of the triblock copolymer on the viscosity and rheological behavior of the systems, when the

amount of emulsifier is increased, the relative viscosity (η_{sol}/η_{ste}) was calculated and the values plotted against shear rate, η_{sol} and η_{ste} being the viscosities of the emulsions with and without the copolymer, respectively.

Figure 3 shows the relative viscosity (η_r) of a series of 40/60 water/oil ratio emulsions with different emulsifier concentrations and the effect of the addition of the Copolymer 4 (see Table I) at a concentration of 10,000 ppm. It is clear that for higher concentrations of emulsifier (40%, wt/v_{water}), the shear thinning behavior was not pronounced. However, when lower concentrations of emulsifier were used (30, 20, 10% wt/v_{water}) a remarkable shear thinning effect was observed, which becomes more pronounced as the emulsifier concentration decreases. At first, we attributed this viscosity enhancement to the formation of an entangled network of interconnected droplets. According to the transient network theory, the entanglement points of the network would be the droplets that contain more than two PEG-blocks. The distance between the entanglement points should be controlled by the length of the PPG-blocks[13] and the concentration of the dispersed phase.[10]

Having in mind the previous statement based on Dukhin et al. mechanism,[21] it is considered that the triblock copolymer here used is acting within the mini-emulsion and/or microemulsion droplets domains. Thus, the mechanism here proposed for transient network formation, involves drop-polymer-drop dimeric complexes formed over these domains, and the structure could be like a beads necklace, which in a microscopic view, would be similar to a "long polymer chain" able to act in the continuous oil phase. Also, this "long polymer chain" could be highly branched to allow the formation of the
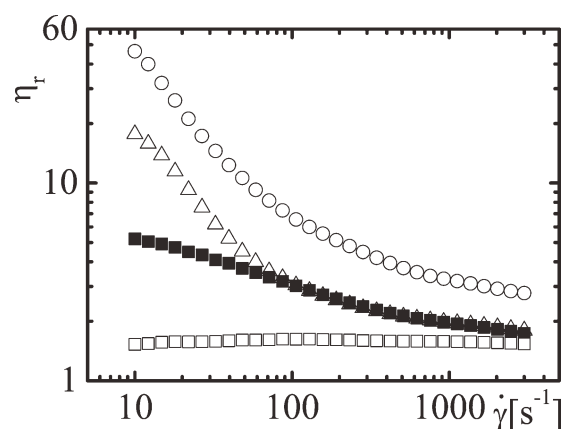

Figure 3 Relative viscosity for 40/60 (v/v) water/oil emulsions with different emulsifier concentrations, (○: 10%, △: 20%, ■: 30%, and □: 40% wt/v_{water}). The triblock copolymer PEG–PPG–PEG added was Copolymer 4 and its concentration was kept constant at 10,000 ppm.
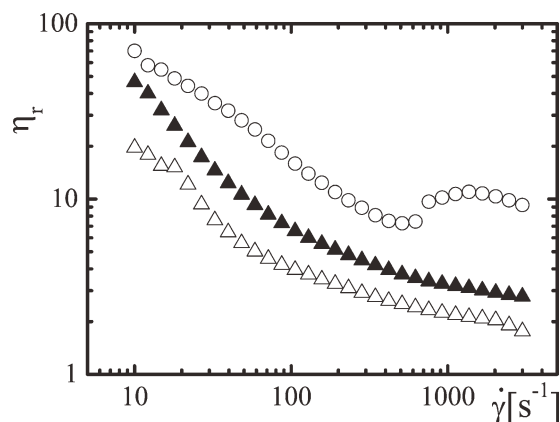
Figure 4 Dependence of relative viscosity on the shear rate of three different water/oil ratios (○: 50/50, ▲: 40/60, and △: 30/70) emulsions. The triblock copolymer PEG-PPG-PEG added was Copolymer 4 and its concentration was kept constant at 10,000 ppm and the emulsifier concentration at 10% wt/v_{water}.

transient network that would then cause the high viscosity at low shear rates.

It could be suggested that the number of PEG-end-blocks per droplet would decrease as the emulsifier concentration increases, since smaller droplets would be obtained, which would induce a decrease in the relative viscosity as previously reported by Lynch et al.[10] On the other hand, it could be also suggested that in a high droplet concentration, the probability of a single droplet to be connected by more than two copolymers is low, resulting in a less efficient network and consequently in a low viscosity, as observed.

Emulsion droplet concentration. To evaluate the real effect of the triblock copolymer addition on the viscosity increment and on the rheological behavior when the water content is increased, the dependence of the relative viscosity (η_r) of the systems on the shear rate was examined. Figure 4 shows the relative viscosity of emulsions for systems with three different water/oil ratios (50/50, 40/60, and 30/70) and containing the triblock copolymer (Copolymer 4) at the concentration of 10,000 ppm. A pronounced shear thinning effect is observed for all of the three copolymer-emulsion systems. Nevertheless, when the amount of water in the system is high (50/50), the shear thinning behavior disappears at a relatively high shear rate, a shear thickening behavior sets in, the viscosity reaches a maximum value and starts to decrease again. It is suggested that in the shear rate range in which the thickening occurs, the reduction of the water droplets size that is associated with the increasing shear rate, is so significant that the ability of the copolymer to link these small droplets is higher than the shear effect that would result in the expected shear thinning behavior.

The droplet concentration could be expected to increase when the water/oil ratio increases, therefore decreasing the number of PEG end blocks segments per droplet and then the relative viscosity. However, the opposite trend was observed (Fig. 4), with the viscosity increasing as the water/oil ratio was increased. The observed trend for the three copolymer–emulsion systems studied could be attributed to the fact that increasing the number of droplets would decrease the interdroplets distance, promoting the formation of a dense aggregate, where the connected droplets are closer. This would lead to higher viscosity (η) values and to systems that perhaps would be more difficult to break.

A water-in-oil emulsion-triblock copolymer (A–B–A) system would be characterized by an equilibrium between droplets with no copolymer and those which have formed copolymer–droplet complexes. Several authors have proposed that two types of copolymer–droplet complexes can be formed, which are described in terms of the copolymer association. The first one is a loop-type complex (core–shell) where both A-blocks are solubilized in a single droplet, with the middle B-block forming a loop around the droplet [Fig. 5(a)]. The second one is a bridging-type complex (dimeric complex) where two droplets are interconnected via the oil-soluble B-block, with each A-block immersed in different droplets [Fig. 5(b)].[12] Considerable work has been done to determine the effect of the relative block lengths on the type of structure formed, and thus on the observed viscosity enhancement.[12,13,37] Some authors reported that long B-block lengths form loop-type complexes, where the A-blocks could be shielded by the B-block, resulting in no network formation. In contrast to this, the shielding by short B-blocks would be less effective, since the bending energy and steric constraints would hamper the shielding, making A-block solubilization in two different droplets more favorable, and therefore favoring network formation.[12,38]

On the other hand, Lynch et al. also reported that the length of the midblock affects the structure of the network as well. However, they found that for short middleblocks a loop formation would be expected and for the longer ones the bridging-type complex should be present, explaining the observed viscosity enhancement. Moreover, the critical midblock length required to obtain these bridging complexes should also depend on the droplet concentration, as it influences the average interdroplet distance.[10]

It should be pointed out that a transition from a viscous fluid to an elastic system should be expected when the triblock copolymer is added, as shown by the large viscosity increase that was observed at low
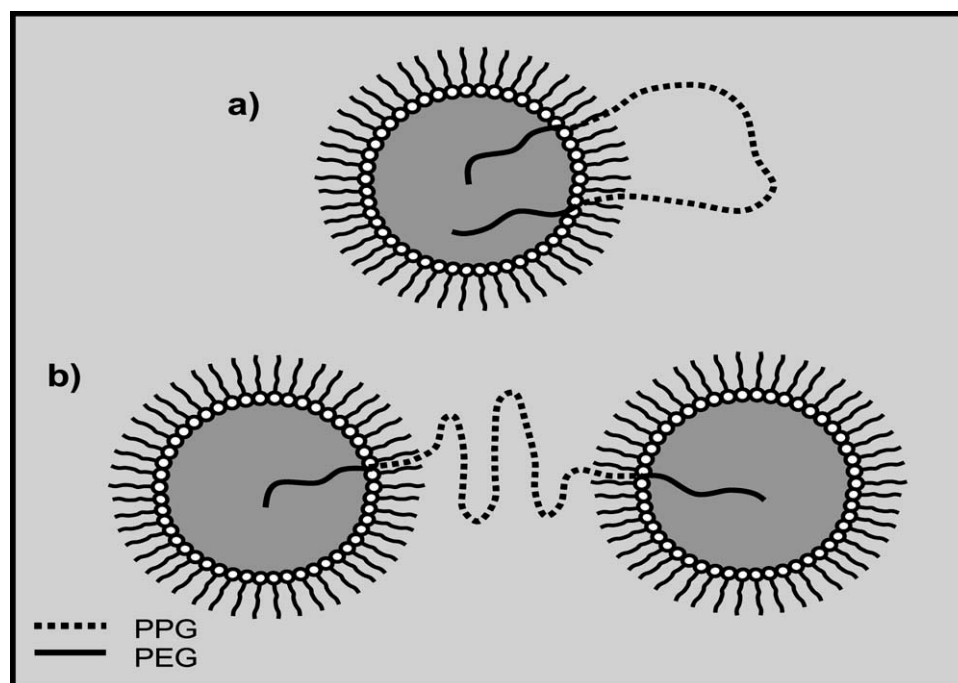
Figure 5 Proposed structures of copolymer–droplet complexes: (a) loop-type (core–shell) and (b) bridging-type (dimeric complex).

shear rates. In emulsions free of triblock copolymer, one should expect the rheological properties of the fluid to be essentially viscous. However, for triblock copolymer/emulsion systems, one could assume that the energy required to deform the system is stored within the oil-copolymer films separating the close-packed droplets, preventing its rupture and hence the coalescence.

Effect of the midblock length

It is important to mention that, according to the systems studied and the type of structure proposed, in the emulsion–copolymer systems it should exist an equilibrium between copolymer molecules that are in the core–shell form and those that are in a dimeric complex association. As the middle block (B) length is increased, it becomes easier for the macromolecule to adopt the dimeric complex association. Moreover, this configuration is also affected by the interdroplets distance.

A great deal of effort has being spent to understand the effect of triblock copolymers in microemulsions and in particular the effect of the ratio of the blocks lengths and the importance of the middle block length.[9–12] Other studies have addressed the effect of changing the microemulsion parameters.[10] In this study, the effect of four different low molar mass PEG–PPG–PEG triblock copolymers on the viscosity of a 40/60 w/o emulsions was investigated, with the copolymer concentration remaining con-

stant at 10,000 ppm. The results are compared systematically in Figure 6.

Contradictory trends have been found in the literature for triblock copolymer microemulsion systems. Some authors[12,15,18] have concluded that triblock copolymers with a large middle block formed core–shell complexes, whereas the ones with a shorter middle block formed bridging-type polymer–droplet complexes (dimeric complexes). On the other hand, authors such as Lynch et al.[10] have found the
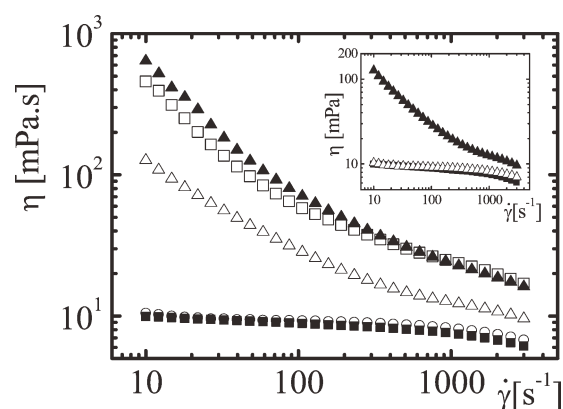

Figure 6 Rheological behavior of systems with different molar mass ABA triblock copolymers, in a 40/60 (v/v) water/oil emulsion. ■: no copolymer, ○: copolymer 1, △: Copolymer 3, □: Copolymer 4, and ▲: Copolymer 5. The inset shows the effect of the PPG length keeping constant the total copolymer molar mass, ■: no copolymer, △: Copolymer 2, and ▲: Copolymer 3. Copolymer concentration was kept constant at 10,000ppm.
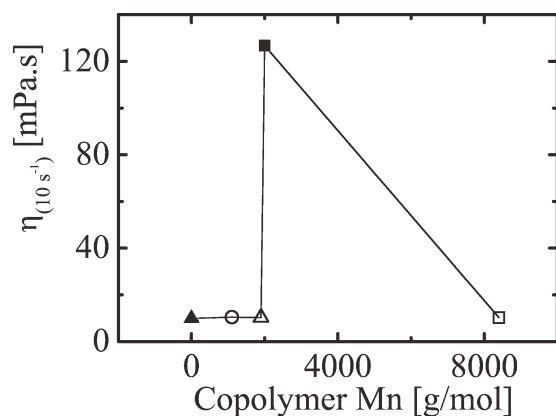
Figure 7 Low shear rate viscosity (η_{10}) as a function of copolymer molar mass (M_n) for 40/60 (v/v) water/oil emulsions. ▲: no copolymer, ○: Copolymer 1, △: Copolymer 2, ■: Copolymer 3, and □: Copolymer 6. Copolymer concentration remains constant at 10,000 ppm.

inverse trend. The results obtained in this work are in agreement with those obtained by Lynch et al.[4] for microemulsion systems, what means that the relative viscosities increase for systems with copolymers with longer middle blocks. As shown in Figure 6, increasing the PPG block length, the viscosity at low shear rates also increased. This could indicate that systems with longer middle block copolymers would present a higher number of triblock copolymer molecules forming the dimeric complexes and therefore able to produce the transient network.

To demonstrate that a minimum size for the middle block would be required to obtain the referred structure, the inset in Figure 6 shows the rheological behavior of systems with copolymers with the same total chain length but different PEG/PPG ratios. The results show that the triblock copolymer with the longer PPG-block (Copolymer 3) was able to form the transient network structure, as suggested by the viscosity enhancement obtained, whereas the triblock copolymer with shorter PPG-block (Copolymer 2) was not able to form the structure.

Effect of the end blocks length and the total chain-length

Figure 7 shows the effect of increasing the end blocks length, either when the copolymer has assumed the core–shell association or the dimeric complex association. Comparing the effect of adding Copolymers 1 and 2 to the emulsion, it is possible to observe that the increase of the end blocks length did not produce a viscosifying effect, even when the total copolymer molar mass was increased.

When comparing the effect of the addition of Copolymer 1 with the effect from Copolymer 3, both with the same end blocks length, it is possible to observe that the Copolymer 3 increases the viscosity,

presumably, due to the longer middle block, as previously discussed. However, when comparing the viscosity at low shear rate (10 s^{-1}) produced by Copolymers 3 and 6, both of them probably adopting the dimeric complex association, since they have the same middle block length, it is possible to observe that Copolymer 6 does not increase the viscosity at low shear rate as much as Copolymer 3 does. Therefore, larger end blocks have negative impact in viscosity when the copolymers adopt the bridging-type configuration. It is assumed that the longer end blocks would produce a crowding effect that would reduce the number of end blocks per droplet, as far as no bridging dominance is found.

Effect of the nature of the copolymer midblock

The effect of the interaction between the middle block of the copolymer and the oil phase (chemical affinity) on the viscosity of the emulsion is shown in Figure 8. As previously mentioned, in the emulsion–copolymer systems, it should exist equilibrium between the molecules that are in the core–shell and those that are in the dimeric complex association. According to the aforementioned, one could expect that a better affinity between the middle block of the copolymer and the oil continuous phase, should increase the number of macromolecules that would be adopting the dimeric complex conformation. When the middle block is polybutadiene (Copolymer 7) a better affinity would be expected, and as a consequence the viscosity achieved would be higher than the one with a middle block of poly(propylene glycol) (Copolymer 5).

On the other hand, according to the mechanism proposed by Dukhin et al.,[21] the formation of mini and also microemulsions, that would occur due to
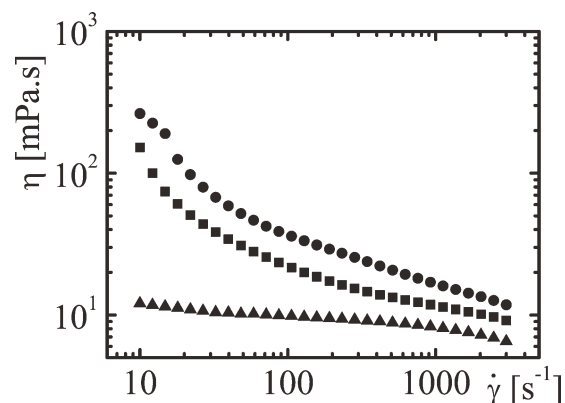

Figure 8 Rheological behavior of systems with two different copolymers with different nature of middle blocks in a 40/60 (v/v) water/oil emulsion. ▲: no copolymer, ■: Copolymer 5 (PEG–PPG–PEG), and ●: Copolymer 7 (PEG–PB–PEG). Copolymer concentration was kept constant at 5000 ppm.

droplets breakage, could be favored by polybutadiene middle blocks since the C=C double bond could promote ions migration when they reach the oil/water interface where the diffuse layer is.

CONCLUSIONS

The results obtained in this work have shown that ABA triblock copolymers can act very effectively as additives to produce strong shear thinning behavior in reverse emulsions. It was found that the concept and theory of three-dimensional reversible transient network formation could be used to explain the obtained results. It was found that the middle blocks length of the ABA copolymer used will determine whether the copolymer will form loop (core–shell) or bridging complexes with the emulsion droplets (although only with those that present mini and microemulsion droplet sizes) and these associations also depend on emulsion characteristics such as water/oil ratio and emulsifier concentration. Furthermore, for a specific droplet size and concentration, the end block dimension should also affect the transient network formation. Above an optimum end block size, a decrease in the viscosity will occur, probably due to a crowding effect in the droplets. Finally, it was also found that the middle block chemical nature and its affinity for the oil phase should affect the triblock copolymer conformation, inducing the macromolecules with better affinity to adopt the dimeric complex associations as the preferred one.

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