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Polymer Vol. 36 No. 19, pp. 3705–3710, 1995
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0032-3861/95/$10.00 + 0.00

Solution behaviour of sodium maleate/1-alkene copolymers

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(Received 11 October 1994; revised 13 December 1994)

In this study the rheological behaviour, air–liquid surface and liquid–liquid interfacial activities of solutions of water-soluble associative copolymers of sodium maleate/1-dodecene and sodium maleate/1-hexadecene are investigated with respect to the polymer concentration, temperature, salinity, shear rate and time. The copolymers have been found to exhibit good air–liquid surface and liquid–liquid interfacial activities. The viscosity of the copolymer solutions is characteristically low and invariant with shear rate. Adding salt to the solution results in an increase in the liquid–liquid interfacial activity and viscosity of the polymer solution. The magnitude of the viscosity and the behaviour of the air–liquid surface tension *versus* concentration indicate that the copolymers form small micelles, each containing a few polymer molecules. The factors that lead to an increase in viscosity also lead to an increase in air–liquid surface and liquid–liquid interfacial activities of these polymer solutions.

(Keywords: solution behaviour; viscosity; copolymers)

INTRODUCTION

Interest in water-soluble associative polymers which are characterized with hydrophobic moieties has increased over the years owing to their extensive technical applications in such areas as enhanced oil recovery, detergents, cosmetics, paints, metal working/hydraulic fluids, mineral/ceramic/material processing systems and in biology and medicine. A particularly interesting class of water-soluble polymers is the 'micellar polymers' or 'polysoaps'[1–3]. These polymers have been known since the early 1950s and a substantial body of literature dealing with surface activity of these polymers has been developed. Recently, Anton *et al.*[1] reviewed micellar polymers and presented some useful rules for the relationship between the molecular structure of the polymers and their surface activity and solubilization capacity.

Although the air–liquid surface tension and the solution viscosity of polysoaps have been studied, very little work is available on the liquid–liquid interfacial tension of polymers in general, and polysoaps in particular. In addition, no work has been done on optimizing the polymer structure to simultaneously provide high viscosity and high surface activity. In this work, the viscosity and surface and interfacial activities of alternating copolymers are studied at different conditions as part of a continuing research programme to study the relationship between polymer structures and their solution viscosity, and surface and interfacial activities, with the objective of designing polymers with optimized structure for high solution viscosity and, simultaneously, high surface activity for applications in areas such as enhanced oil recovery.

The polymers under investigation were prepared by alternating copolymerization. This copolymerization technique was first discovered in copolymers of propylene with butadiene or isoprene, and it has been extended to reactions involving substituted olefins, substituted dienes and substituted acetylenes[4–8]. A number of olefins, ethylene, *cis*-butene-2, *trans*-stilbene and allylacetate, undergo alternating copolymerization with maleic anhydride. The reaction with ethylene under pressure and in the presence of benzoyl peroxide has been described in detail[4], and this procedure was also applied to propylene, 1-dodecene, vinylacetate, methylether and styrene[4,5]. Alternating copolymers involving substituted maleic anhydrides and alkenes have also been reported[6–8].

The micellization of a series of alternating comb-shaped copolymers, poly(1-alkene-*co*-maleic anhydride), in the diacid state in water with 1-alkenes ranging from 1-octane to 1-octadecane and weight-average molecular weights of 6000–20 000, has been studied using small-angle neutron scattering[9,10]. It was found that the copolymer derived from 1-octadecene forms cylindrical micelles, while the copolymers derived from lower 1-alkenes form ellipsoidal micelles, with the transition occurring at 1-hexadecene copolymer. The formation of micelles by copolymers of maleic anhydride/1-alkenes with hydrophilic ester and ether groups (CH_2–CH_2O), and hydrophobic alkyl side-chains, ($CH_3(CH_2)_9$), and ionic carboxyl groups has also been studied. A microscopic model for the formation of micelles by the polymers has been developed[11,12]. As a result of the amphiphilic structure of these polymers, which can be

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linked to the structure of surfactants, the polymers are expected to show good surface and interfacial activities. In view of the behaviour expected of these polymers, we became interested in synthesizing and consequently investigating the aqueous solution properties of the polymers.

The synthesis and viscosity, not in solution, of maleic anhydride/1-alkenes terpolymers (liquids and waxes) have been reported in the literature. In a US patent[13], the copolymers of maleic anhydride with long 1-alkene side-chains (<C30 and C18–C20) have been found to be waxy materials, but have high viscosity, while copolymers of maleic anhydride with short alpha olefin chains (i.e. C6–C10) have been found to have low viscosity but without the waxy character. Alternating copolymers of maleic anhydride have also been reported to exhibit low surface tension[14]. Particularly effective are maleic anhydride (acid and/or salt) copolymers with a relatively hydrophobic comonomer such as alky vinyl ether.

In contrast to the large number of studies on the polymerization of alternating copolymers and the formation of micelles by these polymers, few investigations have aimed to establish the general solution properties, such as viscosity and interfacial activity. Although some studies have been made of the solution viscosity behaviour and surface tension of this class of polymers, to our knowledge there have been no investigations of the detailed solution properties, and in particular of interfacial tension behaviour which could be attributed to polymer structures.

In this work, the solution behaviour of copolymers of sodium maleate/1-dodecene and sodium maleate/1-hexadecene were studied. The rheological behaviour, surface and interfacial activities of these polymers have been investigated with respect to the polymer concentration, temperature, salinity, shear rate and time.

EXPERIMENTAL

Materials and sample preparation

The two 1-alkenes—1-dodecene and 1-hexadecene—were supplied by Fluka Chemie AG and used as received. Maleic anhydride, sodium hydroxide (NaOH) and the solvents used in this work, such as methanol and tetrahydrofuran (THF), were also supplied by Fluka Chemie AG and used as received. The initiator, benzoyl peroxide, was supplied by BDH.

The alternating addition copolymers were synthesized via free-radical initiation mechanisms. The copolymerization reactions were performed using procedures described in earlier publications[4–13,15], which gave polymers with weight-average molecular weight in the range of 6000–20 000. The weight-average and number-average molecular weights and other characterization data such as elemental analysis, neutron scattering parameters and glass transition temperatures for these copolymers have been reported in earlier publications[9,10,13]. Typically, an equal number of moles of maleic anhydride and 1-alkene were placed in a flask. Benzoyl peroxide initiator was then added and the whole reaction mixture was maintained at 160°C under N_2 gas while stirring. The polymerization was usually complete after 4 h of reaction.

The copolymers used in this study were purified by removing the trace amount of unreacted 1-alkene. This was performed by dissolving the highly viscous, waxy copolymer obtained in the synthesis in THF and coprecipitating in excess methanol.

The purified copolymers were hydrolysed in NaOH

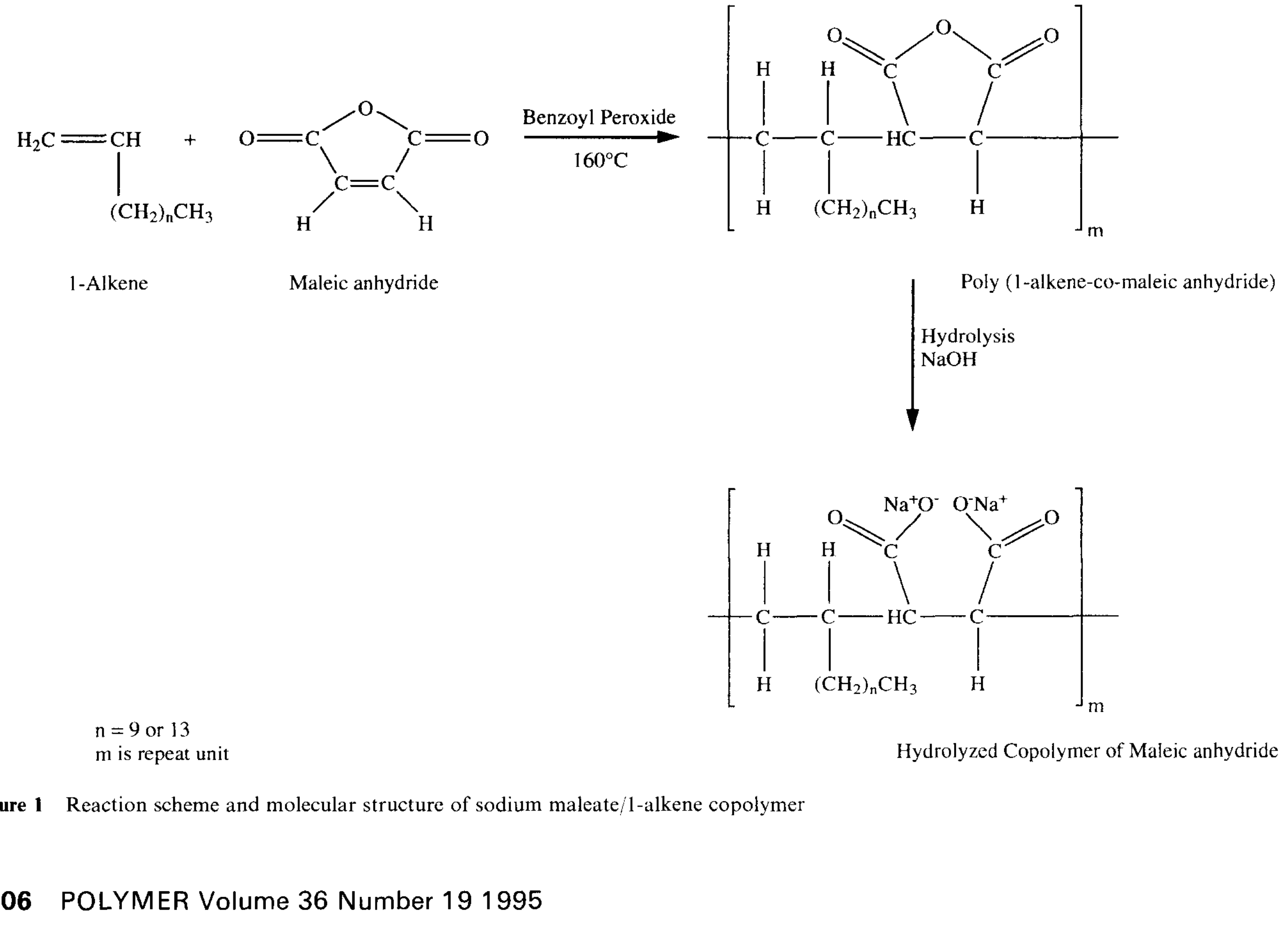

Figure 1 Reaction scheme and molecular structure of sodium maleate/1-alkene copolymer

solution by using the procedure described in an earlier publication[5]. The reaction scheme and molecular structure of the alternating copolymers are given in *Figure 1*.

It should be noted, however, that no analysis was done to determine the composition of the copolymers, because it is known from previous studies[4–13,15] that the two monomers (maleic anhydride and 1-alkene) form an alternating copolymer, i.e. equimolar.

Measurements and instrumentation

The solution properties of the copolymers, such as viscosity behaviour and surface and interfacial tensions, were investigated with respect to temperature, polymer concentration, salinity, shear rate and time. In this work, concentrated stock solutions were prepared at least 24 h before use. Final solutions of desired composition were obtained by dilution of the appropriate stock solutions with water or NaOH solution and, if needed, addition of solid NaCl.

Solution viscosities of the two copolymers were determined by using a digital Brookfield rotational viscometer with Brookfield UL adapter accessories at shear rates ranging from 0.4 to 73.4 s^{-1}. All viscosities for copolymer concentrations of 2.7, 6.7, 3.2 and 8.1 wt% were measured at temperatures in the range of 25–90°C. The surface tensions of the copolymers were determined by using the plate method of the processor tensiometer K12 (Kruss). All measurements at different polymer concentrations were performed at 30°C.

The oil–aqueous solution interfacial tensions of the copolymers were determined using the ring method of the processor tensiometer K12 (Kruss). n-Decane was used in this study as the oil phase. The interfacial tensions of the n-decane–aqueous polymer solution interface were measured for two polymer concentrations, i.e. 2.5 and 5.0 wt%, and for both polymers at different NaCl concentrations ranging from 0 to 1.0 wt%. All the measurements were performed at 40°C. Prior to the measurement, mixtures of the n-decane and aqueous polymer solution were left to equilibrate for a period of $2\frac{1}{2}$ months and maintained at 40°C.

RESULTS AND DISCUSSION

Surface tension behaviour of the copolymers

The effects of polymer concentration and time on the surface tension of the two copolymers were studied. As depicted in *Figure 2* for the copolymer of sodium maleate/1-dodecene, a sharp decrease in surface tension is observed with increasing polymer concentration. The surface tension decreases up to a certain concentration, above which it remains nearly constant. The break point, which resembles a critical micelle concentration in surfactant, is observed to occur at a polymer concentration of 0.29 wt% and the corresponding surface tension of 45 mN m^{-1} for the copolymer of sodium maleate/1-dodecene. The behaviour of the copolymer of sodium maleate/1-hexadecene is similar to that shown in *Figure 2* except that the break point concentration is 0.491 wt% and the corresponding surface tension is 42.7 mN m^{-1} for the copolymer of sodium maleate/1-hexadecene. This break point indicates that polymer micelles exist in the bulk solution and an equilibrium is established between the polymer molecules at the air–liquid interface and the molecules in these micelles. As the polymer concentration increases, the surface tension decreases because of the increased adsorption of polymer molecules at the air–aqueous solution, interface[16,17]. The higher surface activity of the hexadecene copolymer compared to the dodecene copolymer is due mainly to the longer hydrophobic ($C_{14}H_{29}$ compared to $C_{10}H_{21}$) side-chains which have more preference to the air–liquid interface.

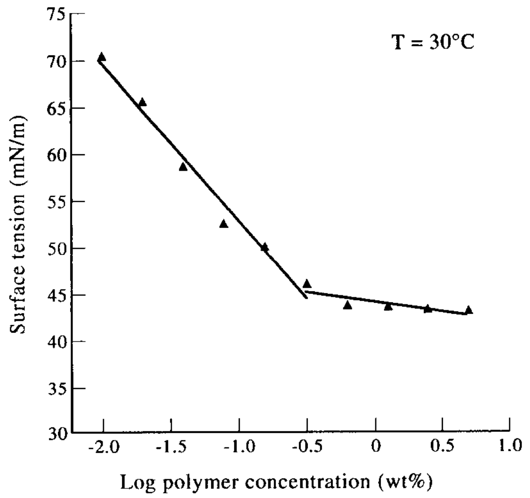

Figure 2 Surface tension *versus* log polymer concentration (wt%) for the copolymer of sodium maleate/1-dodecene

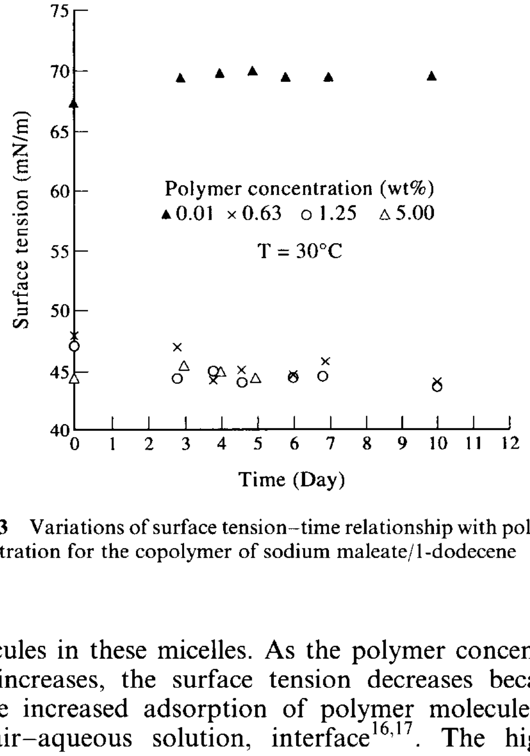

Figure 3 Variations of surface tension–time relationship with polymer concentration for the copolymer of sodium maleate/1-dodecene

The time dependence on surface tension of the copolymers is displayed in *Figure 3* for the copolymer of sodium maleate/1-dodecene. Similar dependence was observed for the copolymer of sodium maleate/1-hexadecene. The surface tension of the copolymer decreases with time for polymer concentrations between 0.63–5.0 wt%. Below a polymer concentration of 0.64 wt%, a weak time dependence is observed. The time dependence is attributed to the surface reorientation process of hydrophobic moieties with additional adsorption from the bulk phase to the air–aqueous solution interface. Extensive equilibration times are also required owing to slow diffusion and conformational changes of the polymer molecules. Similar trends

Table 1 Interfacial tension (IFT), polymer concentration and NaCl concentration for the sodium maleate/1-dodecene copolymer, measured at 40°C

NaCl concentration (wt%)	IFT ($mN\,m^{-1}$) at polymer conc. of 2.5 wt%	IFT ($mN\,m^{-1}$) at polymer conc. of 5.0 wt%
0.0	13.77	8.68
0.5	11.04	7.563
1.0	1.750	1.050

Table 2 Interfacial tension (IFT), polymer concentration and NaCl concentration for the sodium maleate/1-hexadecene copolymer, measured at 40°C

NaCl concentration (wt%)	IFT ($mN\,m^{-1}$) at polymer conc. of 2.5 wt%	IFT ($mN\,m^{-1}$) at polymer conc. of 5.0 wt%
0.0	14.26	11.66
0.5	14.19	10.73
1.0	5.34	1.76

have been observed by Okubo[18] and Ishimuro and Ueberreiter[19,20].

Interfacial tension behaviour of the copolymers

Interfacial tension behaviour of the two copolymers with respect to the polymer concentration and NaCl concentration are depicted in *Tables 1* and *2*. As expected, the interfacial tension (IFT) decreases as the polymer concentration increases from 2.5 to 5.0 wt% for the two copolymers. Another feature observed for the two polymers is the decrease in IFT with increasing NaCl concentration. The explanation for the decrease in surface tension with increasing polymer concentration observed in the previous section also holds here for the decrease in IFT as the polymer concentration increases from 2.5 to 5.0 wt%. The adsorption of polymer molecules at the aqueous solution–oil interface is enhanced by the amphiphilic structure of the copolymers. This consequently causes the reduction in IFT between the polymer aqueous solution and oil (n-decane). This trend is observed for the two polymers under investigation and for all polymer/NaCl solutions considered. This behaviour is similar to that found in surfactant systems[21–23].

Adding NaCl to the polymer solution decreases the IFT up to 1.0 wt% of salt. Beyond this concentration, the polymer precipitates. The decrease in the IFT is attributed to the decrease in repulsion between the ionic (hydrophilic) groups such as COO^-, present in the polymer structure, which allows a closer packing in the interfacial layer as the ionic strength is increased. The reduction in repulsive forces enhances the adsorption of polymer molecules at the interface as the attractive forces between these molecules become predominant. By depressing the dissociation of the charged groups and hence reducing their hydrophilicity, the added salt enhances the interfacial activity of polyelectrolyte polymers, such as the one under investigation. At high salt concentration, salting-out typically takes place. This undesirable behaviour can be avoided by using non-ionic hydrophilic groups.

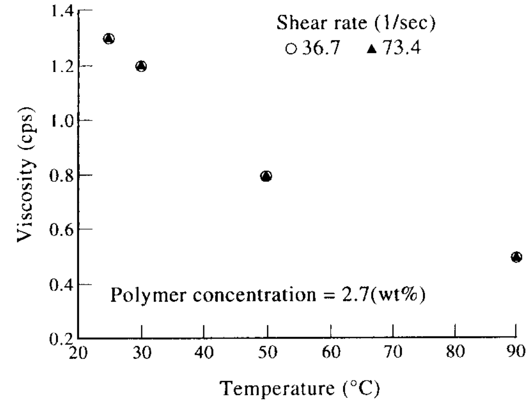

Figure 4 Viscosity *versus* temperature for the copolymer of sodium maleate/1-dodecene for polymer concentration of 2.7 wt%

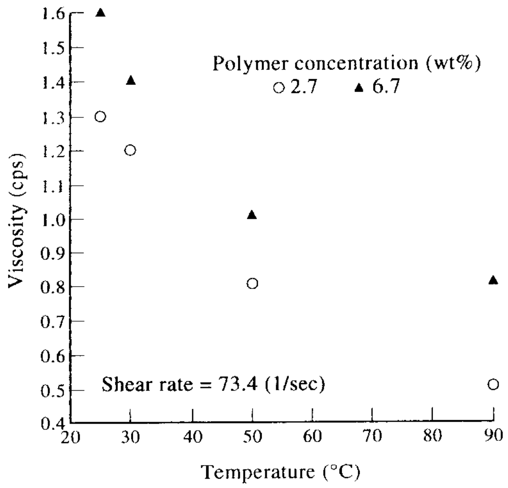

Figure 5 Viscosity *versus* temperature for the copolymer of sodium maleate/1-dodecene at a shear rate of $73.4\,s^{-1}$

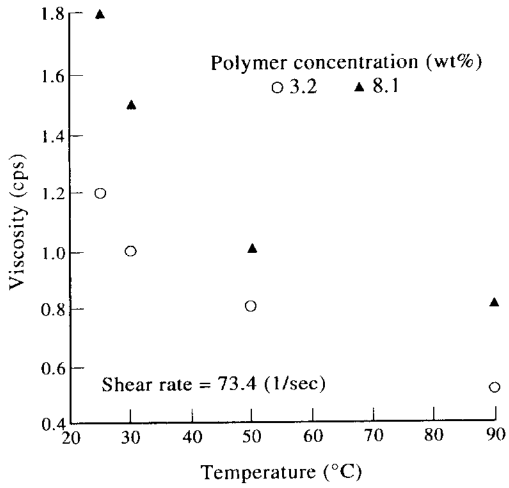

Figure 6 Viscosity *versus* temperature for the copolymer of sodium maleate/1-hexadecene at a shear rate of $73.4\,s^{-1}$

Viscosity behaviour of the copolymers

The effects of shear rate, polymer concentration and temperature on the solution viscosity of the copolymers of sodium maleate/1-dodecene and sodium maleate/1-hexadecene were studied. For both copolymers, a shear-rate-independent viscosity is observed when shear rate is 36.7 and 73.4 s^{-1}, as shown in *Figure 4*. In *Figures 5* and *6* an increase in viscosity is observed as the polymer concentration increases from 2.7 to 6.7 wt% and from 3.2 to 8.1 wt% for the copolymers of sodium maleate/1-dodecene and sodium maleate/1-hexadecene, respectively. This behaviour is observed for the two copolymers at a shear rate of 73.4 s^{-1}, and over the whole temperature range studied, i.e. 25–90°C.

As can be seen from *Figures 4–6*, the viscosity of these polymers is characteristically low up to high polymer concentrations. The unusually low viscosities are attributed to the mainly intramolecular aggregation of the hydrophobic side-chains, with a few polymer molecules per micelle[11,12]. These micelles keep the hydrodynamic radius small. The low molecular weights of these polymers (weight-average molecular weight = 6000–20 000) keep the micelles small. A similar trend was observed for polysoaps[1]. A slight increase in viscosity is observed with increasing polymer concentration of the copolymers.

Figures 4–6 display the effect of temperature on the solution viscosity of the copolymers. As expected, a decrease in viscosity with increasing temperature is observed for the copolymers and for all the ranges of shear rate and polymer concentrations considered.

In order to assess the effect of NaCl on the solution viscosity of the copolymers, the viscosity of 2.7 wt% of the polymer solution with NaCl concentration ranging from 0.1 to 1.0 wt% was measured at 30°C and at a shear rate of 73.45 s^{-1} for both polymers. The copolymer of sodium maleate/1-dodecene is observed to be more salt-tolerant than the copolymer of sodium maleate/1-hexadecene. The former is tolerant up to 1.0 wt% NaCl concentration, while the latter is observed to be tolerant up to 0.5 wt% NaCl concentration. Beyond these concentrations, a precipitate formed. This behaviour is due to the larger hydrophobic groups of the hexadecene copolymer. *Figure 7* displays the effect of NaCl concentration on the solution viscosity of the copolymers. For the copolymer of sodium maleate/1-dodecene, an increase in viscosity is observed up to 0.1 wt% NaCl concentration and then levels off from 0.1 to 0.75 wt% NaCl concentration. From 0.75 wt%, a further increase in viscosity is observed up to the last point. Similar behaviour is observed for the copolymer of sodium maleate/1-hexadecene, except for the second increase.

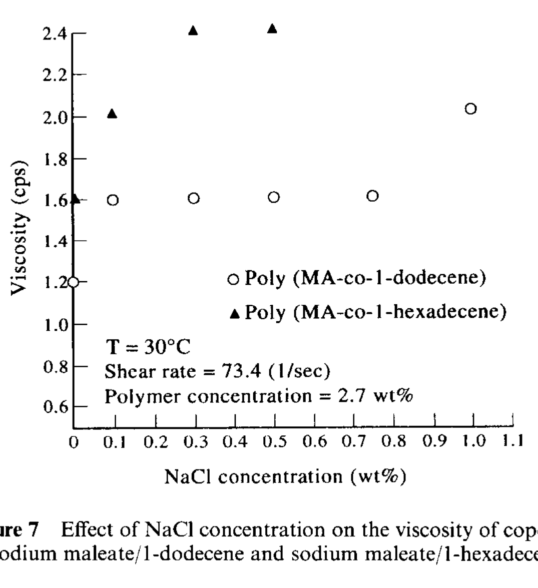

Figure 7 Effect of NaCl concentration on the viscosity of copolymers of sodium maleate/1-dodecene and sodium maleate/1-hexadecene

As expected for polyelectrolytes (charged polymers), addition of inorganic salts brings about important changes in the behaviour of the polymers. The screening of charge repulsion tends to decrease the viscosity of non-hydrophobic polymers such as copolymers of acrylamide. Viscosity enhancement can take place when interchain association prevails over the polyelectrolyte effect. However, when interchain association in pure water is high enough, addition of salt leads to a more compact network which rapidly collapses[24,25]. Taking into account the above considerations, one can interpret the results of *Figure 7* in terms of hydrophobic chain aggregation. The increase in viscosity observed with increasing NaCl concentration could be attributed to the formation of larger micelles. In other words, the effective intermolecular association might have prevailed over the polyelectrolyte effect, thus the addition of NaCl results in an increase in viscosity. The typical viscosity reduction of polyelectrolyte solutions in the presence of salt can be successfully prevented or reduced if the polyelectrolyte chain is grafted by a hydrophobic group, as evident from our observations with these copolymers, and the findings of others[24–27]. The higher viscosities of the hexadecene copolymers are due to the longer hydrophobic side-chains which cause the formation of micelles with larger diameters[11,12].

CONCLUSIONS

Because of the unique structural features of the water-soluble copolymers, which are characterized by hydrophobic moieties (amphiphilic), they exhibit good surface and interfacial activities, including low surface and interfacial tensions. However, the surface and interfacial tensions of the copolymers studied in this work are only moderate compared to conventional surfactants, which exhibit ultimate surface and interfacial tensions in the range of 20–40 $mN\,m^{-1}$ and 10^{-3} $mN\,m^{-1}$, respectively. It is also found that adding NaCl to the polymer solution increases its interfacial activity. However, this is expected, since the polymers under investigation are polyelectrolytes.

The viscosity of the copolymers is found to be low, even at high polymer concentrations, which implies that the hydrophobic interactions are predominantly intramolecular in nature, resulting in micelles with a small number of molecules. The relative invariance or a slight increase in solution viscosity with NaCl concentration is another attractive feature of associative polymers, especially for applications where salts are present. It also shows that the typical viscosity reduction of polyelectrolyte solutions in the presence of salt can be successfully prevented or even reversed if the polyelectrolyte chain is grafted by hydrophobic groups. In this case, hydrophobic groups aggregate all the more as ionic strength increases, leading to some interchain association which consequently causes viscosity enhancement. The polymer solutions considered in this work exhibit a constant viscosity (Newtonian) behaviour. Furthermore, increasing polymer concentration leads to an increase in the polymer solution viscosity and a decrease in surface and interfacial tensions. Smaller solution viscosities are found at high temperatures. In addition, the polymers exhibit a decrease in surface tension with time at high polymer concentration, and a weak time dependence is exhibited at low polymer concentration.

The overall behaviour of the solutions indicates that the viscosity and surface activity for the hexadecene copolymer are higher than those for dodecene polymer owing to the longer hydrophobic groups. This conclusion lends support to the possibility of designing polymers with both high viscosity and high surface activity. The solution viscosity and surface activities are enhanced by the same structural modification and state variables.

ACKNOWLEDGEMENTS

The financial and material support of this study by King Fahd University of Petroleum and Minerals, Dhahran, Saudi Arabia, is gratefully acknowledged. Discussions and suggestions from Asrof Ali, Shafkat Beg and Mohammed Al-Naafa are also acknowledged.

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