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Shear thickening of halato-telechelic polymers in apolar solvents

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Short-length polymers selectively end-capped with a metal carboxylato group at both ends, i.e. metal carboxylato-telechelic polymers, exhibit an unusual shear-thickening behaviour in apolar solvents, depending on the main experimental parameters that control the ion-pair association, such as metal cation, concentration and temperature. In contrast to the non-ionic precursors, metal carboxylato-telechelics are indeed responsible for a marked increase in the solution viscosity in a range of shear rates between 0.1 and 1000 s^{-1}. The shear-rate dependence of the solution viscosity has been analysed in a close relationship to metal counterion, polymer concentration, temperature and addition of polar compounds to the apolar solvent. As a rule, the dilatant behaviour depends strongly on the formation of polymer aggregates in relation to the mutual interactions of the ion pairs. A consensus is now emerging on the origin of the shear-thickening effect, which should be found in inter-aggregate associations rather than in a transition from intramolecular to intermolecular associations of the individual chains.

(Keywords: model ionomers; solution viscosity; shear thickening)

INTRODUCTION

Polymeric materials are commonly used in the control of fluid rheology. Indeed, very small amounts of an appropriate polymer can deeply affect the flow properties of a liquid. As a rule, the viscosity of a polymer solution decreases when the shear rate increases. This *shear-thinning* behaviour results from the disentanglement, stretching and orientation of the polymer chains under the effect of the flow field. As an exception to the rule, some polymer solutions exhibit a *shear-thickening* behaviour or dilatancy. Then, the solution viscosity first increases with the shear rate, goes through a maximum and finally decreases when the velocity gradient goes on increasing. Suspensions are an important type of dilatant systems, the rheological behaviour of which has recently been reviewed by Barnes[1]. Dilatancy has also been reported for various types of polymer solutions: solutions of high molecular weight polymers in solvents of high[2] and low viscosity[3]; aqueous solutions of poly(vinyl alcohol)–borate complexes[4,5]; triblock copolymers[6,7] and partially hydrolysed polyacrylamides[8]; and solutions of anti-misting agents[9–12] and ionomers in apolar solvents[13,14]. The unusual solution properties of these systems are usually accounted for by the formation of long-lived polymer associations under the flow.

This paper reports on the solution properties of ion-containing polymers, i.e. ionomers, in apolar solvents. Ionomers are indeed a class of speciality polymers that have a small number of ionic groups (<10–15 mol%) attached along a hydrophobic polymer backbone. Although the random distribution of the ionic moieties along the chain is the usual chain microstructure, the ionic groups can also be selectively located on the chain ends, which is referred to as a telechelic placement. Over the past two decades, a great deal of research has been devoted to ionomers in the bulk, and comparatively less effort has been invested in ionomer solutions[15,16]. Reasons for this include solubility problems in water owing to a low ionic content and in apolar solvents owing to strong ion-pair associations. However, ionomers have great potential owing to their remarkable capability to increase the viscosity of apolar solvents. They can indeed trigger viscosities larger by several orders of magnitude compared with the non-ionic precursors under the same experimental conditions. This unusual shear-induced thickening has been discussed by Witten and Cohen on the basis of chain elongation in the flow direction with formation of interchain associations at the expense of intramolecular associations[17]. The shear-induced rise in viscosity is thus very much dependent on the association lifetime, which must at least be comparable to the hydrodynamic relaxation time. This model has been confirmed by Ballard *et al.*, who have investigated the solution rheology of a fuel anti-misting agent (ICI's FM9, i.e. a copolymer of t-butylstyrene and methacrylic acid)[18]. Small-angle neutron scattering (SANS) has provided, for the first time, an insight into the solution properties of ionomers at the molecular level. Indeed, SANS is a very powerful method that allows the mean radius of gyration of macromolecules within aggregates to be measured by a contrast matching technique[19]. Higgins *et al.* have analysed dilatant solutions of sodium sulfonate poly-

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*To whom correspondence should be addressed styrene in xylene by this technique. They have observed that the single-chain dimensions remain constant, although viscosity increases upon shearing[20]. It has accordingly been proposed that the shear-thickening effect results from aggregate elongation under shear and possibly from inter-aggregate aggregation. The shear thinning that occurs at higher shear rates would be due to alignment of the aggregates and to aggregate dissociation. Very recently, a transient network theory has been developed by Wang for dilatant systems that takes into account all the species expected to be present in the solution[21].

Several years ago, a new type of linear polymer[22,23] selectively end-capped with an ionic group at both ends was synthesized and referred to as halato-telechelic polymers (HTPs). They are model compounds for the more complex ionomers that have been thoroughly studied in the solid state[24–27] and in solution[28–30]. HTPs are self-associating compounds in apolar solvents and a sol–gel transition is currently observed at very low polymer concentrations. Preliminary experiments have shown that α,ω-metal carboxylato-polybutadienes can exhibit a dilatant behaviour in decahydronaphthalene[31]. It is the purpose of this paper to investigate further the dialatancy of α,ω-metal carboxylato-polymers in apolar solvents, such as toluene, decahydronaphthalene and a mineral oil, in order to confirm the origin of the shear-thickening effect and to identify the major experimental parameters that control this rheological behaviour.

EXPERIMENTAL

Polymer preparation

Carboxylato-telechelic polymers were prepared by living anionic polymerization in dry tetrahydrofuran as reported by Broze *et al.*[28]. Polydispersity did not exceed 1.2 and the functionality as estimated from the molecular weight and potentiometric titration of the end-groups was better than 1.9. α,ω-Carboxylic acid polymers were neutralized in toluene with the stoichiometric amount of a highly reactive alkaline or alkaline-earth alkoxide, under anhydrous conditions. Neutralization was also carried out with an excess of zirconium alkoxide followed by the hydrolysis of the unreacted alkoxy groups, as detailed elsewhere[32]. Solutions of HTPs in decahydronaphthalene (DHN) and mineral oils were prepared by adding these solvents to the HTP in toluene solution and by distilling off toluene, under reduced pressure, at 80°C. The final solutions were stored for at least 1 day at room temperature before any viscosimetric measurement was carried out.

Viscosimetric measurements

The relative viscosity η_{rel} was measured with a Ubbelohde-type capillary viscometer placed into a temperature-controlled water bath; η_{rel} was defined as t/t_0, where t is the flow time of the solution and t_0 the flow time of the solvent. Steady flow viscosity was measured in relation to shear rate with a Rheotest 2 viscometer. Viscosity measurements were also recorded with a computer-controlled Bohlin VOR rheometer in the increasing shear rate scanning mode, by using several torque bars. A variety of Couette cells were used and the temperature controlled at ± 0.1°C.

RESULTS AND DISCUSSION

General observations

According to previous observations from this laboratory, the solution viscosity of halato-telechelic polymers depends strongly on the polymer concentration in the dilute regime. *Figure 1* is a typical viscosity–concentration curve for α,ω-Mg carboxylato-polyisoprene ($M_n = 21\,000$) in toluene at 25°C. The relative viscosity η_{rel} of the neutralized polyisoprene (PIP) increases asymptotically with concentration, in contrast to the linear dependence for the non-ionic precursor. This experimental observation is convincing evidence for the mutual association of the ionic end-groups of PIP in a medium of low dielectric constant. As soon as they are intermolecular, these dipolar associations can lead to a gelation process, as supported by a sol–gel transition at low polymer concentration. The critical concentration of gelation (C_{gel}) is inversely proportional to the polymer molecular weight and is affected by all the parameters that control the electrostatic interactions of the ionic end-groups (temperature, nature of the ion pairs, solvent polarity)[28]. Bodycomb and Hara have approximated the mean degree of aggregation of HTPs from solution viscosity data[33], whereas the aggregation process has recently been investigated by SANS[34].

The remarkable dilatant behaviour of some ionomer solutions manifests itself by gel formation when the solution is vigorously shaken, although it flows when gently rocked[35]. The same qualitative observation is reported for the shear-induced (reversible) gelation of HTP solutions of a concentration slightly smaller than C_{gel}. Dependence of the steady flow viscosity upon shear rate provides quantitative information on this rheological behaviour. *Figure 2* shows a typical viscosity–shear rate curve for a 4 wt% solution of α,ω-carboxy-PIP ($M_n = 21\,000$) neutralized with Zr alkoxide in a mineral oil. Although the steady flow viscosity of the unneutralized polymer solution is independent of the shear rate, neutralization of the carboxylic acid end-groups is responsible for an increase in viscosity by about two orders of magnitude at low shear rates. This confirms the intermolecular aggregation of HTPs although the

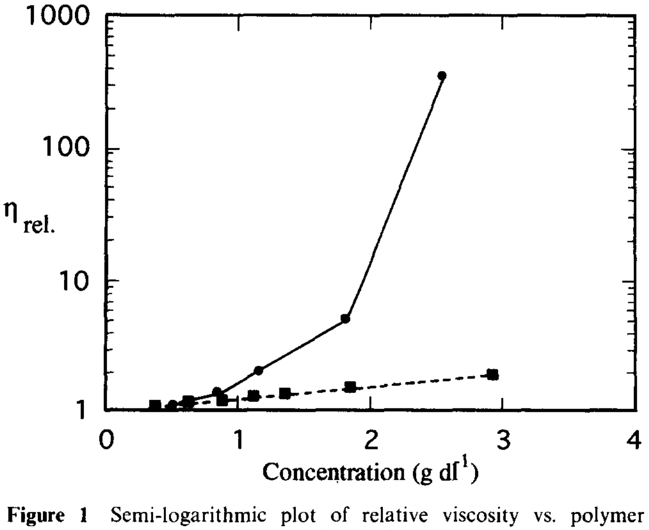

Figure 1 Semi-logarithmic plot of relative viscosity vs. polymer concentration for α,ω-Mg carboxylato-polyisoprene ($M_n = 21\,000$) (●) and the non-ionic precursor (■), in toluene at 25°C

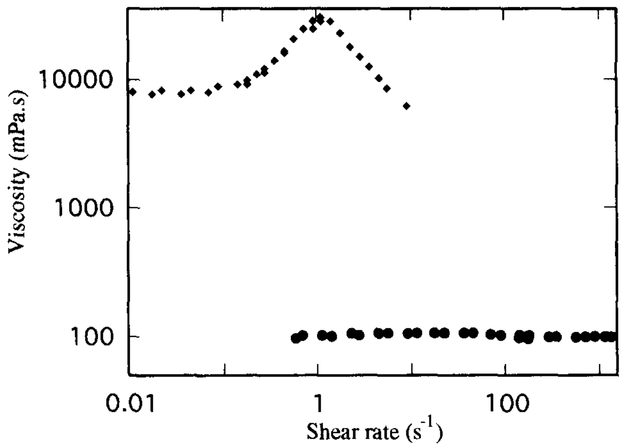

Figure 2 Steady flow viscosity vs. shear rate for α,ω-Zr carboxylato-polyisoprene ($M_n = 21\,000$) in a mineral oil (4 g dl^{-1}) at 25°C: (●) non-ionic precursor; (◆) end-groups neutralized with a 1.5-fold molar excess of Zr alkoxide, followed by hydrolysis of the unreacted alkoxy groups

concentration is below C_{gel}. In contrast to the mineral oil, which is a Newtonian fluid, the viscosity of the neutralized polymer solution increases (shear thickening) above 0.1 s^{-1} and then reaches a maximum value. The shear rate at which the onset of the increase in viscosity is observed depends on several parameters, as will be discussed hereafter. Beyond the maximum, shear thinning is observed upon increasing the shear rate.

Lundberg and Duvdevani have observed the same qualitative dependence for the steady flow viscosity of ionomer solutions on the shear rate[36], which indicates that ionomers and HTPs have the same basic rheological behaviour in solution.

It is worth noting that the whole typical curve shown in *Figure 2* can only be reported if the available viscometer covers the appropriate range of shear rates and torques. In this respect, the choice of the solution concentration is of the utmost importance, as shown later on. As a rule, the viscosity at a constant shear rate does not change with time, whatever the shear gradient. As the shear stress is suppressed, the torque falls to zero within a period of time too small to be measured (1 or 2 s). Peng and Landel have observed the same general behaviour for anti-misting solutions[9,10]. Furthermore, in agreement with a study by Pedley[37], the shear thickening of HTP solutions is completely reversible. The viscosity reported while increasing the shear rate is quite reversible, thus observed again when the shear-rate scanning is reversed. Short-lived effects are thus responsible for the non-Newtonian behaviour of HTP solutions. These solutions remain perfectly homogeneous during and after shearing, when observed by the naked eye. Shear-thickening measurements are reproducible over periods of several days.

Shear-thickening behaviour of HTPs in apolar solvents

It might be anticipated from *Figure 1* that the dilatant behaviour of HTP solutions depends closely on the polymer concentration. *Figure 3* confirms that a very small dilution of a dilatant solution can have a deep effect on the rheological behaviour, since the viscosity rapidly decreases and the shear-thickening signature is shifted towards higher shear rates. Polymer concentration has been reported to have the same influence on the rheological properties of ionomer solutions[36]. A decrease in the average size of the polymer aggregates upon dilution is undoubtedly responsible for the data reported in *Figure 3*. If the aggregation of aggregates is assumed to be responsible for dilatancy, higher shear rates are required in order to bring smaller aggregates into mutual contact and to promote an increase in viscosity. The assumption of an aggregate association, rather than a transition from intramolecular to intermolecular associations of terminal ion pairs as proposed by Witten *et al.*, is in qualitative agreement with the high solution viscosity of low molecular weight HTPs in the low shear rate range. In reference to the calculation method proposed by Bodycomb and Hara[33], the mean degree of polymer association (*DA*), defined as the ratio of the average molecular weight of polymer aggregates over the molecular weight of a single HTP molecule, has been estimated as 300 for a solution of 2.51 g dl^{-1} concentration at 1.16 s^{-1} shear rate (*Figure 3*). It must be clear that *DA* refers to aggregates of polymer chains connected to each other by multiplets. *DA* has nothing to do with the aggregation number of the ion pairs, thus size of the multiplets, as approximated from SAXS data. This high degree of association has been calculated at a concentration close to gel formation and it is in agreement with values reported by Bodycomb and Hara for a different ionomer. A value of 530 has been calculated at the maximum in viscosity. Thus in this dilute solution, large aggregates are expected to exist, as confirmed by preliminary SANS experiments on HTP solutions[38]. Deformation under shearing is a way to trigger the percolation of these large aggregates, i.e. formation of a continuous network. Actually, two different mechanisms can be proposed to explain the shear thickening of ionic polymers in apolar solvents, depending on the molecular structure of these polymers. A transition from intramolecular to intermolecular associations would prevail in solutions of ionomer complexes and polyampholytes[36,39], in agreement with some theoretical predictions. In contrast, interactions between large chain aggregates should be the key parameter in the shear thickening of ionomer[37] and HTP solutions.

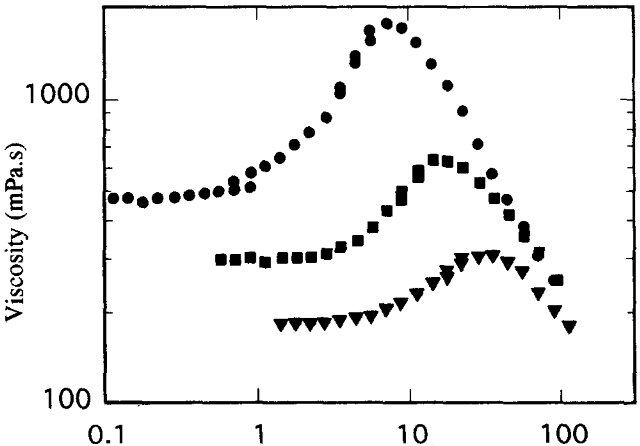

Figure 3 Dependence of the steady flow viscosity on shear rate for solutions of α,ω-Mg carboxylato-polyisoprene ($M_n = 21\,000$) in decahydronaphthalene at 25°C: (●) 2.56 g dl^{-1}; (■) 2.54 g dl^{-1}; (▼) 2.51 g dl^{-1}

The shear-thinning behaviour that occurs at high shear rates may be attributed to the orientation, deformation and possibly dissociation of the polymer aggregates above a critical shear rate. SANS analysis of ionomer solutions has shown that alignment of the aggregates certainly contributes to shear thinning[37].

It also appears from *Figure 3* that the critical shear rate γ_c beyond which shear thickening occurs is highly dependent on concentration. In this particular example, γ_c is shifted by one order of magnitude when the polymer concentration is decreased from 2.56 to 2.51 wt%. Actually, the effect that the polymer concentration has on γ_c is directly dictated by the change that occurs in the solution viscosity η in the Newtonian regime, according to the following power law:

$$\eta = a\gamma_c^{-b} \qquad (1)$$

where a and b are constants characteristic of the system under consideration. According to equation (1), dilute solutions might be dilatant at high shear rates ($\gamma_c > 1.000\,\mathrm{s}^{-1}$). In this respect, Lundberg *et al.* have postulated[36] that dilute ionomer solutions that are Newtonian under the current experimental conditions might be dilatant at shear rates that are too high to be accessible to common viscometers. Data in *Figure 3*, however, show that the behaviour of the α,ω-Mg carboxylato-polyisoprene in decahydronaphthalene is complex, since the shear stress τ in the dilatant region ($\gamma_c < \gamma < \gamma_{max}$) obeys the power law:

$$\tau = K\gamma^n \qquad (2)$$

where K is a constant and the exponent n decreases from 1.54 down to 1.34 when the polymer concentration is decreased from 2.56 down to 2.51 g dl^{-1}. The 'severity' of the shear thickening[1] is thus also dependent on the polymer concentration. Furthermore, there is a parallel decrease from 3.7 to 1.7 in the amplitude of the shear thickening, defined as the ratio of the maximum in viscosity to the average value in the Newtonian plateau. As a result, both the amplitude and the severity of the shear-thickening effect decrease so rapidly that the potential dilatancy of dilute HTP solutions at high shear gradients might go undetected even though these shear gradients could be made available.

Lundberg *et al.* have also reported on a power-law dependence between the maximum in viscosity and the shear rate at which this maximum is observed (γ_{max}) for a series of ionomer solutions[36]. Qualitatively, the same type of dependence is observed for HTP solutions. The problem is, however, that the dilatancy of these solutions can be accompanied by the onset of normal forces. This phenomenon has been visually recorded as a strong Weissenbeg effect (rod climbing) at shear rates higher than γ_c. This additional effect prevents the maximum in viscosity being observed and the experimental power law being set up accurately enough. The reversible Weissenberg phenomenon might be due to the deformation of large aggregates under shearing.

Temperature also has a major role on the rheology of HTP solutions, as is illustrated by *Figures 4* and *5* in the particular case of solutions of α,ω-Mg carboxylato-poly(t-butylstyrene) (PtBS) ($M_n = 10\,000$) and α,ω-Mg carboxylato-polyisoprene ($M_n = 21\,000$), respectively, in decahydronaphthalene. Any increase in temperature is observed to decrease the solution viscosity in the whole investigated shear-rate range and to shift the shear-thickening signature towards higher shear gradients. Since the strength of the dipolar interactions, and thus the size of the aggregates, are known to decrease as the temperature increases[28], it is not surprising that dilution at a constant temperature and increase in temperature at a constant concentration have qualitatively the same effect on solution dilatancy. *Figure 6* shows that 3 wt% solution of α,ω-Zr carboxylato-poly(t-butylstyrene) ($M_n = 90\,000$) in a mineral oil is dilatant at 60°C, although it forms a gel at 25°C. Dilatancy still persists at 100°C, which is the upper measurement temperature for the equipment used. Although temperature has a pronounced effect on the amplitude, severity and temperature at which the shear thickening occurs, the underlying dipolar associations are still strong enough to trigger dilatancy at relatively high temperatures.

The cation associated with the carboxylate end-groups affects the properties of HTP solutions. In the series of alkaline and alkaline-earth metals, C_{gel} decreases with

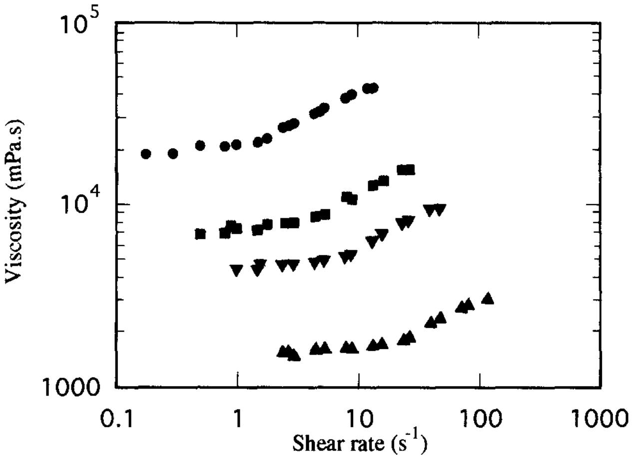

Figure 4 Dependence of the steady flow viscosity on shear rate for a solution of α,ω-Mg carboxylato-poly(t-butylstyrene) ($M_n = 10\,000$) in decahydronaphthalene (6.7 g dl^{-1}) at various temperatures: (●) 20°C; (■) 25°C; (▼) 30°C; (▲) 40°C

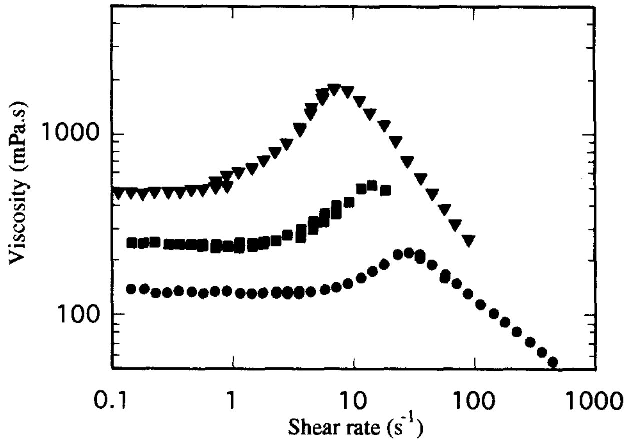

Figure 5 Dependence of the steady flow viscosity on shear rate for a solution of α,ω-Mg carboxylato-polyisoprene ($M_n = 21\,000$) in decahydronaphthalene (2.56 g dl^{-1}) at various temperatures: (▼) 25°C; (■) 30°C; (●) 35°C

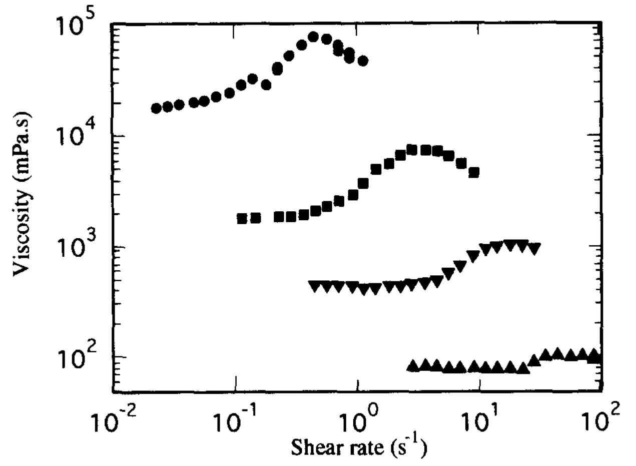

Figure 6 Dependence of the steady flow viscosity on shear rate for a solution of α,ω-Zr carboxylato-poly(t-butylstyrene) (M_n = 90 000) in a mineral oil (3 g dl^{-1}) at various temperatures: (●) 65°C; (■) 85°C; (▼) 92°C; (▲) 100°C. End-groups neutralized with a 1.5-fold molar excess of Zr alkoxide

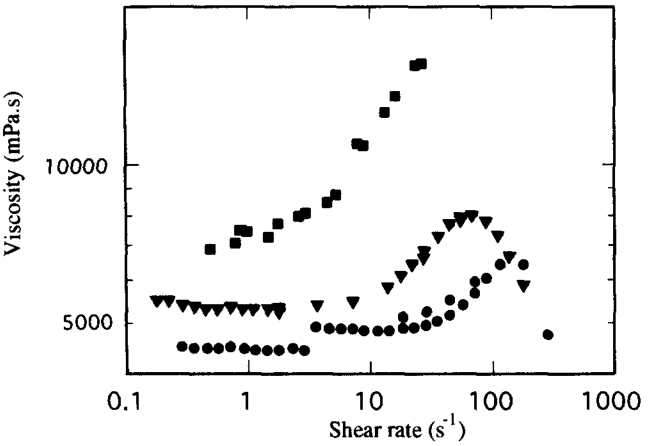

Figure 7 Dependence of the steady flow viscosity on shear rate for solutions of α,ω-carboxylic poly(t-butylstyrene) (M_n = 10 000) in decahydronaphthalene neutralized with various cations: (●) Na, 9 g dl^{-1}; (■) Mg, 6.7 g dl^{-1}; (▼) Ca, 10.6 g dl^{-1}

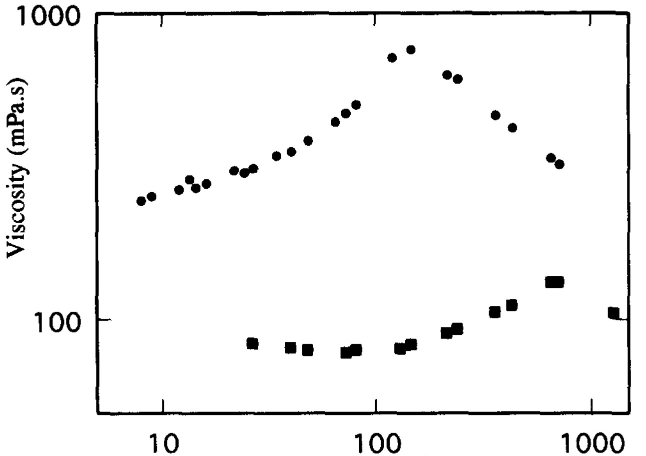

Figure 8 Dependence of the steady flow viscosity on shear rate for solutions of α,ω-Mg carboxylato-polystyrene (M_n = 17 000; 2.9 g dl^{-1}) in toluene (●) and in a toluene/octadecanol mixture (0.25 wt% alcohol) (■), at 25°C

the cation radius, in agreement with elementary electrostatic considerations[28]. It is therefore not straightforward to compare the dilatant behaviour of solutions of α,ω-carboxylic acid polymers neutralized with different cations under the same experimental conditions. *Figure 7* compares the viscosity–shear rate curve for solutions of α,ω-carboxylic acid poly(t-butylstyrene) (M_n = 10 000) neutralized with three different cations. DHN is the solvent and concentrations are different and such that the viscosity at very low shear rates is of the same order of magnitude. When Mg and Ca are compared, it is clear that Mg is much more efficient since dilatancy occurs at a lower shear rate and the amplitude and severity of the shear-thickening effect are much larger compared with Ca, although the polymer concentration is substantially smaller (6.7 wt% compared with 9 wt%). This difference in efficiency is in line with a smaller critical concentration for gelation when a telechelic polymer is end-capped with a Mg carboxylate rather than with a Ca carboxylate, all the other conditions being the same[28]. The definitely smaller efficiency of Na with respect to Ca and Mg in promoting shear thickening might basically be related to the lower thermal stability of multiplets consisting of monovalent alkali-metal carboxylate dipoles rather than of divalent alkaline-earth-metal carboxylate ion pairs[40]. This would clearly be a valency effect of the metal cation. Ketz *et al.* have shown that the steady shear viscosity of polyampholyte solutions depends on the counterion at a constant concentration and that the onset of the shear-thickening effect occurs over a rather small critical stress region[41].

It is very well known that the strength of the dipolar interactions is very sensitive to any polar additives[28,42]. This deleterious effect has been illustrated by a less sharp sol–gel transition occurring at a higher polymer concentration when a small amount of, for example, tetrahydrofuran or methanol is added to the apolar solvent. Polar additives are thus expected to affect markedly the dilatant behaviour as is assessed by *Figure 8*. Indeed, 0.25 wt% octadecanol has a remarkably large depressive effect on the shear-thickening ability of a solution of α,ω-Mg carboxylato-polystyrene (M_n = 17 000) in toluene (2.0 g dl^{-1}) at 25°C. If small amounts of this alcohol do not completely prevent the solution from shear thickening, large amounts (2 wt%) decrease the solution viscosity to the point where no reliable measurement can be reported anymore. It is thus clear that the rheological properties of HTP solutions are directly related to the propensity of the terminal dipoles to associate and that strong enough mutual interactions are required to promote dilatancy. Influence of strength of the associations is usually disregarded when a model is proposed for dilatancy, although it is very clear from this study that this effect is of critical importance.

CONCLUSIONS

Rheology of semi-dilute solutions of α,ω-metal carboxylato-polymers in solvents of low polarity has shown that dilatancy is a rather common behaviour provided that the terminal dipoles are strong enough self-associating species and that the polymer concentration lies in the appropriate range, i.e. close to the sol–gel transition on the low-concentration side. This particular behaviour has been observed for various polymer chains (polybutadiene, polyisoprene, poly(t-butylstyrene), polystyrene, ...), end-capped with different metal carboxylate groups (magnesium, calcium, barium, zirconium, ...) in a large range of molecular weight (e.g. up to 90 000). Solvent of a very low dielectric constant is required and polymer concentration should be close enough to the sol–gel transition for the shearing forces to favour the formation of large-sized aggregates responsible for a rapidly increasing viscosity. Any external effect (such as increase in temperature, dilution or increase in solvent polarity) that shifts the polymer solution further away from the sol–gel transition toward the sol is unfavourable to the occurrence of dilatancy with high severity and amplitude at low shear rates. A possible transition from intramolecular to intermolecular associations does not seem to have a major role in shear thickening. HTPs can thus be designed as vey efficient gelling or thickening agents in apolar solvents and, since most of them are soluble in mineral oils, they might be used as dilatant additives in lubricant oils for motor engines. Preliminary experiments have shown that block copolymers containing ionic blocks can give rise to dilatant solutions in apolar solvents, which indicates that HTPs are the lower-limit case (lower ionic content) of an expectedly large range of shear-thickening 'ionic' polymers.

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