Solution behaviour of α,ω-(dimethylamino) polymers quaternized with alkyl iodides

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Quaternization of the amino end-groups of telechelic polymers with n-alkyl iodides has been found to modify profoundly the solution behaviour of these materials. In toluene, the relative viscosity increases rapidly with concentration, in a manner dependent on the length of the alkyl substituent of the quaternizing agent. It has been observed that the increase in viscosity can be mitigated by lengthening the alkyl substituent shape. This lessening of viscosity levels off as soon as the alkyl substituent contains more than three carbon atoms. For the longest substituents, the viscosity slightly increases again. The sharpness of the increase in viscosity upon increasing polymer concentration can be significantly reduced in polar solvents. A lower medium polarity appears to promote higher differences in viscosity between quaternized and unquaternized polymers. Empirical equations have also been derived to fit the experimental hydrodynamic behaviour.

(Keywords: ionomers; telechelic polymers; quaternary ammonium; solution behaviour; aggregation number)

INTRODUCTION

Ionomers

In a medium of low dielectric constant (hydrophobic matrix), the ionic groups randomly distributed on an ionomer backbone are not dissociated, forming dipoles which can interact electrostatically. This phenomenon leads to thermally reversible crosslinking which greatly affects the ultimate properties of the materials[1–4]. The ionomers have been studied extensively in terms of their morphology and bulk properties. However, less information is available about their solution behaviour, owing to a limited solubility in most of the usual solvents. The ion content (~15 mol%) is indeed too low to allow ionomers to be dissolved in polar solvents, such as water, whereas the ionic groups prevent dissolution in apolar media. Gels are very often observed at concentrations as low as a few weight per cent. Nevertheless, investigations have been undertaken using low ion content ionomers or high dielectric constant organic solvents (dimethylsulphoxide, dimethylformamide) and mixtures of non-polar solvents with solvating agents (alcohols, etc.)[5–19].

Lundberg and Makowski[5] observed that the solubility of metal-sulphonate-containing polymers (polystyrene, EPDM rubber) in apolar solvents could be enhanced by decreasing the ion content and by adding alcohols to the solvent. The ion pair solvation obviously depends on the nature of the alcohol, and especially on its steric hindrance: the more significant it is, the lower the solvation. Temperature is another parameter which has to be taken into account as influencing in particular the solvation equilibrium[5]. At very low concentrations, the ionic groups tend to associate in an intramolecular manner decreasing the hydrodynamic volume of the macromolecules and accordingly, the solution viscosity. On the other hand, at higher concentrations the ion pairs of a macromolecule are capable of interacting with those attached to other polymer chains. This extends the apparent molecular weight of the polymer, the viscosity increasing with the ion content[6]. Theoretical models were described to account for the variation of the reduced viscosity as a function of polymer concentration, macromolecular features and ion content[11].

The viscosimetric behaviour of ionomers is completely different when studied in non-aqueous polar solvents. The reduced viscosity suddenly rises while decreasing the concentration to the lowest limits[6]. This polyelectrolyte effect is ascribed to repulsive interactions between ions of the same charge attached to the backbone, therefore leading to chain extension[6,9,10,13–17]. Although the existence of the polyelectrolyte effect has been known for a long time, its interpretation is still debated. According to some authors[8], it is rather intermolecular interactions, occurring between ions of the same charge via their counterions, that leads to aggregation of macromolecules. The polyelectrolyte effect should therefore be more intermolecular than intramolecular in nature.

It is well known that the dielectric constant (ε) of solvent is a crucial parameter governing the associative behaviour of ionomers in solution. The solvation of the ion pairs is, however, another parameter that should not be disregarded[5–7,13]. The viscosity of polystyrene bearing alkaline metal carboxylate groups varies with the cation size according to the trend $Cs^+ < K^+ < Na^+ < Li^+$. The sequence is reversed if sulphonate functions are substituted for carboxylate ones; this is ascribed to the better ability of the former to be solvated[7].

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Complexation phenomena involving ionomers also have to be taken into account. They are very well illustrated and explained in refs 18 and 19. As the present work does not deal with this matter, they will not be discussed herein.

Halato-telechelic polymers

Halato-telechelic polymers (HTPs) can be readily dissolved in a large number of common solvents, as well as being proposed as models for ionomers due to a better defined structure[4]. Although exploratory research was undertaken in 1969[20], Broze *et al.*[21–24] were the first to investigate systematically the solution properties of metal carboxylate HTPs. Once dissolved in low polarity solvents (decahydronaphthalene, toluene) the viscosity *versus* concentration rises asymptotically, converting the solution into a gel at concentrations as low as 1–2 g dl^{-1}. The critical concentration of gelation (C_{gel}) depends on polymer molecular weight (M_n) according to the relation $C_{gel} = KM_n^{-0.5}$, where K is a constant for a given polymer–solvent–temperature system. The electrostatic origin of the gelation has been theoretically predicted[23] and experimentally verified[21,22,24]. It results from the above equation that the longer the polymer chain (or the lower the ion content), the lower the C_{gel} value; C_{gel} is supposed to be closely akin to the overlap critical concentration (C^*).

The study of metal sulphate and sulphonate HTPs was undertaken by Misra and co-workers[25,26]. They also observed that an increase in the polymer concentration causes an asymptotic rise of the solution viscosity in non-polar solvents. Similar results were reported for hydrogenated polybutadiene, end-capped with Na^+ or Zn^{2+} sulphonate functions[27]. Metal-sulphonate-terminated linear or three-arm star polyisobutene leads to gelation once dissolved in hexane, even at low concentrations [28,29]. For star polymers, the variation of C_{gel} *versus* molecular weight is closely similar to that observed for the systems studied by Broze *et al.*: $C_{gel} = KM_n^{-0.11}$. The -0.11 exponent indicates that the effect of the molecular weight is mitigated, probably owing to the star-like shape of the macromolecules. It is quite surprising, however, that such a relation does not apply for α,ω-K^+ sulphonate polyisobutene[28] whereas it does for α,ω-Ba^{2+} sulphonate polyisoprene dissolved in chloroform (exponent = -0.5)[30].

The hydrodynamic behaviour of telechelic amino polymers, quaternized with alkyl halides, has also been investigated by Teyssie and co-workers[22,31–33]. It appears that, in contrast to metal carboxylate and sulphonate telechelic polymers, their solutions never lead to gelation, whatever the concentration, even in apolar solvents. Interesting results concerning coordination of α,ω-dimethylamino polyisoprene onto transition metal salts, have recently been published[34]. These results show that viscosity increases depending on the metal cation as $Ni^{2+} < Co^{2+} < Fe^{3+} < Cu^{2+}$, and appears to be maximum at a unitary Cu/amine molar ratio.

Finally, it should be mentioned that the hydrodynamic behaviour of tertiary amino telechelic polymers converted into macrozwitterions has also been reported[32,35,36].

This paper deals with the influence of the alkyl substituent length of the quaternizing agent on the resulting solution properties. The influence of solvent nature is also allowed for.

EXPERIMENTAL

Living anionic polymerizations of styrene and isoprene were performed in tetrahydrofuran (THF), at −78°C, using lithium-naphthalene and sodium-naphthalene, respectively, as difunctional initiators[22]. The living polymers were deactivated by addition of an excess of 1-chloro-3-(dimethylamino) propane, resulting in the expected α,ω-(dimethylamino) polystyrene [$PS(NMe_2)_2$], and polyisoprene [$PIP(NMe_2)_2$], respectively.

Molecular weight, as determined by size exclusion chromatography (THF, 25°C, polystyrene standards) and by vapour pressure osmometry[34], was $M_n = 5700$ g mol^{-1} ($M_w/M_n = 1.4$) and $M_n = 38400$ g mol^{-1} ($M_w/M_n = 1.3$) for $PS(NMe_2)_2$ 6K and $PIP(NMe_2)_2$ 38K, respectively. α,ω-(Dimethylamino) polybutadiene [$PBD(NMe_2)_2$] was obtained as described elsewhere[37]. α,ω-(Carboxylic acid) polybutadiene ($M_n = 4600$, $M_w/M_n = 1.8$) was supplied by B. F. Goodrich (Hycar CTB 2000X156). The carboxylic acid end-groups were converted into dimethylamino groups by esterification with *N,N*-dimethylaminoethanol.

Polymer functionality (f) was determined by potentiometric titration of the amino end-groups by perchloric acid[34]; $f = 1.97$, 1.86 and 1.92 for $PS(NMe_2)_2$ 6K, $PIP(NMe_2)_2$ 38K and $PBD(NMe_2)_2$ 5K, respectively.

The quaternization reactions were carried out by dissolving the polymers in a mixture of THF/methanol (95/5 vol%) and adding a two-fold molar excess of the quaternizing agent. The reaction mixture was refluxed for 4 days; the quaternization was then complete as evidenced by the absence of any amino groups ($HClO_4$ titration). The reaction product was precipitated in an excess of methanol (in order to remove the unreacted alkyl iodide), and dried under vacuum at 60–70°C for 1 week.

Relative viscosity (η_{rel}) was determined at 25 ± 0.1°C in a thermostatically controlled bath using a dilution viscosimeter, equipped with a sintered-glass filter to prevent any dust particles from penetrating into the capillary tube, and capped to prevent evaporation of solvent and exposure to air. The viscosimeter was designed in such a way that the kinetic energy correction did not exceed 0.5% and the end effects could be neglected (capillary length and bore were, respectively, 140 and 0.4 mm). η_{rel} is the ratio of solution (t) to solvent (t_0) flow times, which were measured repeatedly in order to ascertain the reproducibility of the data. η_{red} is the reduced viscosity, i.e. the ratio of specific viscosity ($\eta_{rel} - 1$) over the concentration (C in g dl^{-1}). The errors involved in the determination of η_{red} and $\log \eta_{rel}$ were found to be lower than 10^{-2} dl g^{-1} and 2×10^{-3}, respectively.

RESULTS AND DISCUSSION

The major difference in behaviour between α,ω-(dimethylamino) polymers quaternized with alkyl halides, and metal carboxylate and sulphonate HTPs, is reflected by the fact that no gelation occurs when the former are dissolved in non-polar solvents in spite of a rapid initial growth of viscosity as a function of concentration. For highly dilute solutions, quaternized HTPs display higher relative viscosity compared to the metal carboxylate counterpart (*Figure 1a* and ref. 38). In fact, it seems that, at low concentrations, mutual interactions between ion pairs are less readily achieved for Mg^{2+} carboxylates. The more important steric

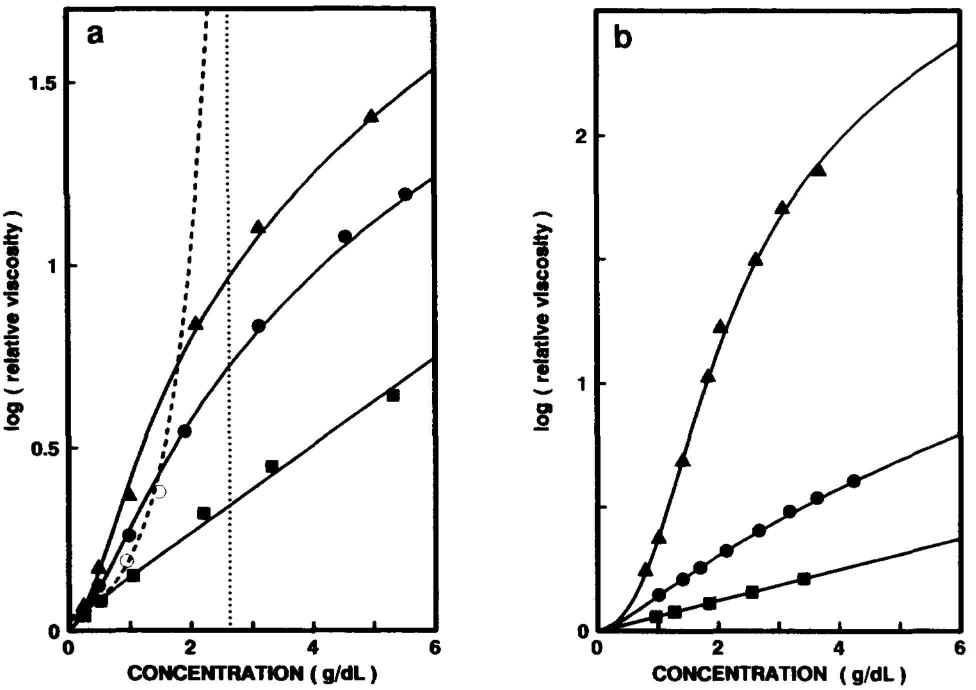

Figure 1 (a) Logarithm of relative viscosity *versus* polymer concentration plots in toluene at 25°C for α,ω-dimethylamino polyisoprene 38K: ■, unquaternized; ▲, quaternized with iodomethane; ●, quaternized with 1-iodooctane. ○, α,ω-Mg^{2+} carboxylato polyisoprene ($M_n = 38000$) in toluene at 25°C (ref. 38). (b) Logarithm of relative viscosity *versus* polymer concentration plots in toluene at 25°C for α,ω-dimethylamino polybutadiene 5K: ■, unquaternized; ▲, quaternized with iodomethane; ●, quaternized with 1-iodooctane

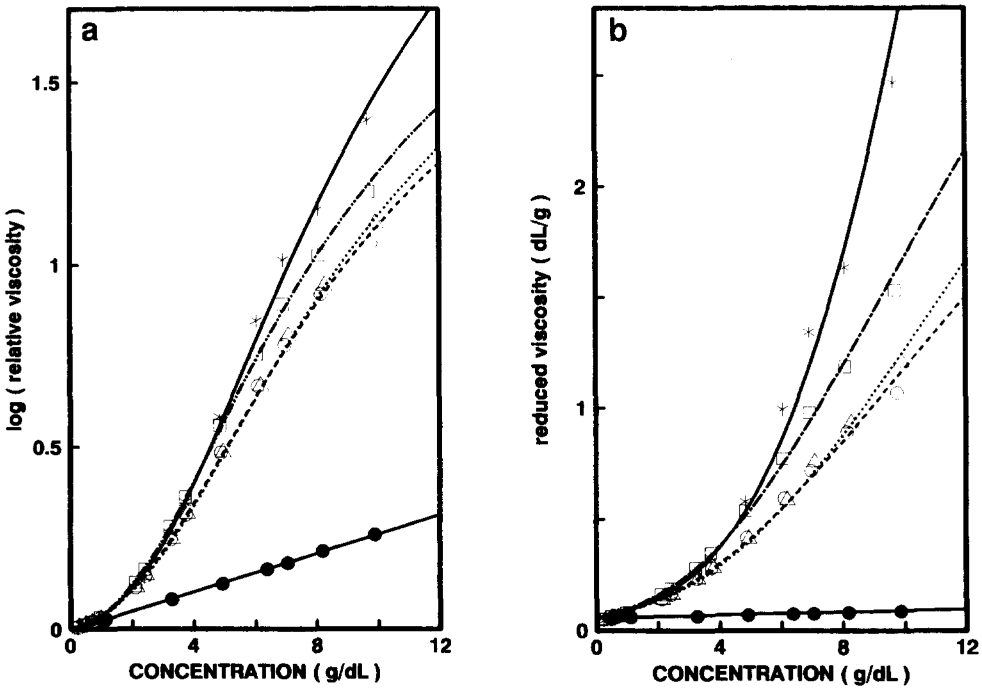

Figure 2 (a) Logarithm of relative visocisty *versus* polymer concentration plots in toluene at 25°C for α,ω-dimethylamino polystyrene 6K: ●, unquaternized; quaternized with *, iodomethane; □, iodoethane; ○, 1-iodopropane; △, 1-iodohexadecane. (b) Reduced viscosity *versus* polymer concentration plots in toluene at 25°C for α,ω-dimethylamino polystyrene 6K: ●, unquaternized; quaternized with *, iodomethane; □, iodoethane; ○, 1-iodopropane; △, 1-iodohexadecane

hindrance of quaternary ammonium ion pairs would, however, prevent three-dimensional chain network from being set up.

Let us now review factors which are likely to affect the solution behaviour of quaternized HTPs.

Alkyl substituent size of quaternizing agent

Figures 1 and *2a* clearly show that quaternization of dimethylamino-terminated polymers greatly modifies the solution viscosity. The less hindered the alkyl substituent, the higher the viscosity. *Figure 2a* displays more clearly the effect of the alkyl substituent length; the relative viscosity steadily decreases as the length increases from methyl to ethyl and, eventually, to propyl substituent. For longer n-alkyl substituents, the viscosity curves match the latter so that they have been omitted

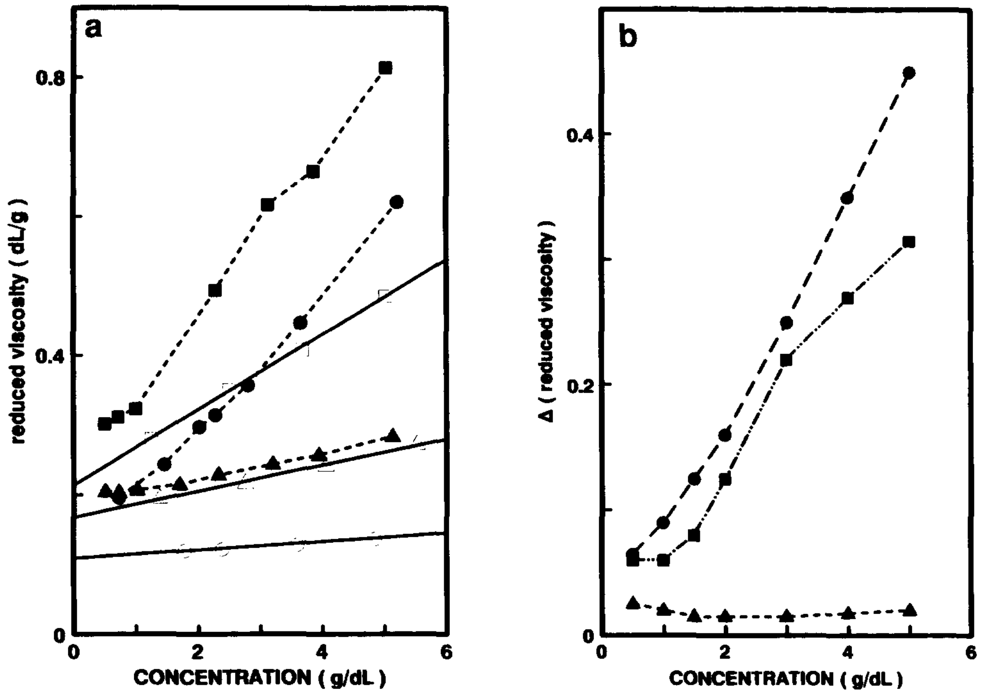

Figure 3 (a) Reduced viscosity *versus* polymer concentration plots at 25°C for unquaternized (open symbols) and quaternized (solid symbols) (CH_3I) α,ω-dimethylamino polystyrene 13K in: ○, ●, toluene; □, ■, THF, △, ▲, DMF. (b) Difference of the reduced viscosity between quaternized and unquaternized α,ω-dimethylamino polystyrene 13K in: ●, toluene; ■, THF; ▲, DMF

in *Figure 2* for the sake of clarity. This behaviour has, however, been borne out using an extra series of n-alkyl iodides[33]. Comparing the 16-carbon substituent sample with the n-propyl one, the solution viscosity is a little higher for the former. This might be due to a slight increase of the polymer chain hydrodynamic volume once the substituent becomes long enough. Similar behaviours were reported for $PS(NMe_2)_2$ 13K and amino-terminated PBD neutralized with extra series of n-alkyl carboxylic acids[32,39]. The relative viscosity of the polymer solution in toluene decreases with increasing the alkyl substituent length, then levels off and eventually increases again. However, the effect is less pronounced compared to quaternized HTPs. This must be due to weaker interactions between ammonium carboxylate ion pairs.

Quaternization of telechelic amino polymers obviously modifies their solution properties depending on the concentration range. *Figure 2b* shows the intrinsic viscosity value of each sample (toluene, 25°C) does not, however, seem to be affected by quaternization. These results are supported by the work of Hara *et al.*[8]. They observed that the neutralization of a sulphonic acid end-capped polymer with molecular weight below 9000 g mol^{-1}, does not affect its intrinsic viscosity in a non-polar solvent[8]. This behaviour also applies for α,ω-carboxylic acid polybutadiene ($M_n = 4200$) in THF[40].

It is noteworthy that, unlike viscosity measurements, a study based on fluorescence techniques (excimer formation) allowed determination of the concentration at which intramolecular ion pair associations become intermolecular. This critical concentration was assessed as 0.17 g dl^{-1} in toluene at 25°C, for $PS(NMe_2)_2$ 12K quaternized with ethyl bromide[41].

Effect of the solvent

It is well established that the ionic groups structure (free ions, solvated ions, dipoles, etc.) is highly dependent on the solvent nature, and especially on its dielectric constant (ε). The formation of dipoles, interacting via electrostatic attraction, occurs only in media of low dielectric constant. In order to assess the effect of that parameter on quaternized HTP properties, we have studied the hydrodynamic behaviour of $PS(NMe_2)_2$ 13K, before and after quaternization with methyl iodide, in toluene ($\varepsilon = 2.4$), THF ($\varepsilon = 7.4$) and dimethylformamide (DMF) ($\varepsilon = 37$), at 25°C. The corresponding plots are displayed in *Figure 3a*.

The solution viscosity of unquaternized polystyrene is essentially governed by polymer–solvent interactions. In order to eliminate that variable and focus only on the effect of the end-group interactions, *Figure 3b* compares the difference between the reduced viscosity of quaternized and unquaternized polymers ($\Delta\eta_{red}$) as a function of concentration. It is obvious from that figure that the aggregation of the ion pairs becomes less and less important when solvent polarity is increasing. This emphasizes the crucial role of dipolar interactions between chain extremities in low dielectric constant media.

It is worth noting that, in DMF, the reduced viscosity of quaternized polystyrene shows an upward trend at low concentrations (*Figure 3*); this is typical of polyelectrolyte behaviour. It is indeed likely to occur insofar as, using a viscosimeter suitable for investigations at very low concentrations, Hara *et al.*[42] observed such an increase of η_{red} for dilute DMF solutions of $PS(NMe_2)_2$ 12K quaternized with ethyl bromide. The same 'polyelectrolyte effect' was also reported for telechelic hydrogenated PBD ($M_n = 2000$ g mol^{-1}) end-capped

Table 1 Intrinsic viscosities and Huggins constants of the (unquaternized) α,ω-dimethylamino polymers in various solvents at 25°C

Polymer	Solvent	k'	$[\eta]_0$ (dl g^{-1})
$PIP(NMe_2)_2$ 38K	Toluene	0.38	0.37
$PBD(NMe_2)_2$ 5K	Toluene	0.83	0.13
$PS(NMe_2)_2$ 6K	Toluene	1.02	0.06
$PS(NMe_2)_2$ 13K	Toluene	0.51	0.11
$PS(NMe_2)_2$ 13K	THF	1.19	0.21
$PS(NMe_2)_2$ 13K	DMF	0.66	0.17

with zinc or sodium sulphonate functions, in butanol and butanol–water mixtures[27], as well as for ionomers containing a low percentage (<2 mol%) of ionic groups[8].

Treatment of viscosimetric data

Bodycomb and Hara[40] have recently proposed a method to evaluate the mean degree of association of the end-groups as long as gelation does not take place. It is assumed that the partial association of the end-groups results in aggregates of macromolecules which behave as a single macromolecule of higher macromolecular weight and which mutually interact as traditional macromolecules do. Furthermore, the average size of the molecular aggregates changes with polymer concentration. In agreement with the well known Huggins equation, equation (1), the procedure assumes that the size of the aggregate persists to infinite dilution and is therefore characterized by an intrinsic viscosity, $[\eta]_{ag}$, which, of course, changes with the concentration, equation (2) (for detailed explanation, see refs 34 and 40):

$$\eta_{red} = [\eta] + [\eta]^2 k'C \qquad (1)$$

$$[\eta]_{ag} = \frac{-1 + (1 + 4k'C\eta_{red})^{1/2}}{2k'C} \qquad (2)$$

where k' is the Huggins constant characteristic of a polymer– solvent–temperature system. C and η_{red} are, respectively, the polymer concentration and the reduced viscosity of the solution.

The degree of aggregation (DA) defined in ref. 40, can be determined for each concentration:

$$DA = ([\eta]_{ag}/[\eta]_0)^2 \qquad (3)$$

where $[\eta]_0$ is the intrinsic viscosity of the unquaternized polymer. By least-squares fits, k' and $[\eta]_0$ have been determined; the corresponding values are given in *Table 1*.

By comparison with *Figure 2*, *Figure 4* shows much more convincingly that the ion pairs tend to associate easily at low concentrations (up to 5 g dl^{-1}), then with more difficulty, finally reaching a degree of association that levels off (saturation). At low concentrations, the plot slopes are nearly constant, attesting that the aggregation grows exponentially with the concentration. Bodycomb and Hara[40] also noticed an exponential growth of DA as a function of concentration ($C < 2$ g dl^{-1}) for α,ω-sodium carboxylate polybutadiene ($M_n = 4200$ g mol^{-1}) in THF (*Figure 4*). For quaternary-ammonium-terminated polymers, the flattening of the DA *versus* C curves can account for the absence of gelation. DA is also sensitive to the length of the alkyl substituent. It levels off at concentrations higher than 10 g dl^{-1} as soon as the alkyl substituent contains more than three carbon atoms. For substituents containing from 3 to 16 carbon atoms, the curves intermingle so that only two of them are reported in *Figure 4*.

The DA *versus* concentration plots for quaternized polybutadiene and polyisoprene samples are displayed in *Figure 5a*. Again DA is higher for the amino polymers modified with iodomethane rather than with longer alkyl substituent iodide. It is clear that the steric hindrance of the ammonium ion pairs is a parameter of the utmost importance in determining their aggregations.

The changes of DA *versus* concentration are illustrated in *Figure 5b* for quaternized polystyrene in toluene, THF and DMF. This graphic representation readily shows how the effect of the solvent polarity is a consequence of the tendency of the end-groups to associate. The beginning of the polyelectrolyte effect at low concentrations is revealed much better in this figure compared with the plots of the reduced viscosity *versus* concentration (*Figure* 3). It must be pointed out, however, that the aim of drawing curves of DA *versus* concentration is to show how the association of end-groups is changing depending on the system considered.

On an empirical basis, it has been found that the following equation fits the DA values in toluene very closely:

$$\log DA = b(1 - e^{-kC}) \qquad (4)$$

where b and k are independent constants calculated by least-squares fits, and are listed in *Table 2*. The log DA *versus* C curves, determined using equation (4) and the data of *Table 2*, are plotted in *Figures 4* and *5a*. A very good fit between the experimental data and theoretical

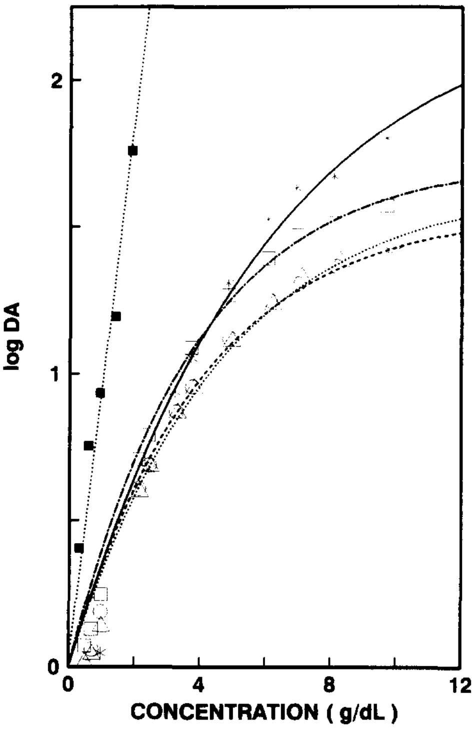

Figure 4 Logarithm of degree of aggregation *versus* polymer concentration plots in toluene at 25°C for α,ω-dimethylamino polystyrene 6K quaternized with: ∗, iodomethane; □, iodoethane; ○, 1-iodopropane; △, 1-iodohexadecane. ■, α,ω-Na^+ carboxylato polybutadiene ($M_n = 4200$) in THF at 25°C (ref. 40)

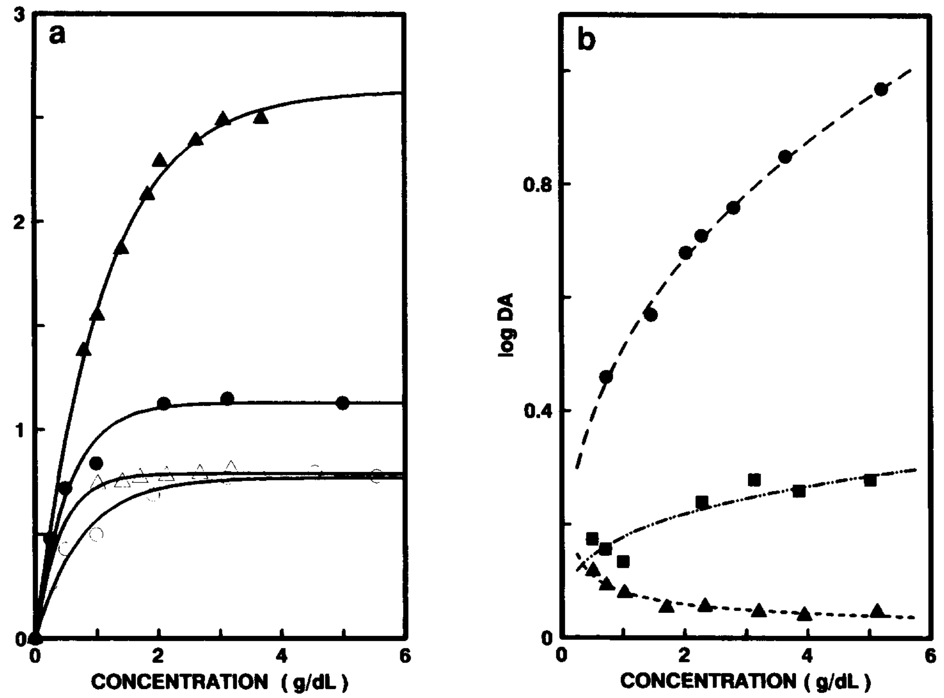

Figure 5 (a) Logarithm of degree of aggregation *versus* polymer concentration plots in toluene at 25°C for α,ω-dimethylamino polybutadiene 5K (▲, △) and α,ω-dimethylamino polyisoprene 38K (●, ○), quaternized with iodomethane (solid symbols) and 1-iodooctane (open symbols). (b) Logarithm of degree of aggregation *versus* polymer concentration plots for α,ω-dimethylamino polystyrene 13K quaternized with CH_3I in: ●, toluene; ■, THF; ▲, DMF

Table 2 Empirical characteristic constants of the quaternized α,ω-dimethylamino polymers in toluene at 25°C

Sample[a]	b	k	$DA_{\max}$[b]	C_{ip} (g dl^{-1})[c]
PS C1	2.31	0.165	204	2.9
PS C2	1.73	0.262	54	2.4
PS C3	1.56	0.248	36	2.4
PS C16	1.65	0.218	47	2.6
PBD C1	2.63	0.904	429	1.2
PBD C8	0.79	2.48	6.2	0.8
PIP C1	1.13	1.87	13	0.7
PIP C8	0.77	1.33	5.9	0.8

[a] PS = $PS(NMe_2)_2$ 6K; PBD = $PBD(NMe_2)_2$ 5K; PIP = $PIP(NMe_2)_2$ 38K; C1 = methyl; C2 = ethyl; etc.

[b] $DA_{\max} = 10^b$

[c] $C_{ip} = C$ at the inflection point of the log η_{rel} *versus* C plot calculated from equation (6) assuming $d^2 \log \eta_{rel}/dC^2 = 0$ (see ref. 34)

predictions from equation (4) is shown. It is also possible to predict the concentration dependence of η_{red} and log η_{rel}, i.e. the experimental data reported in *Figures 1* and *2* (equations (5) and (6)) (for detailed explanations, see ref. 34).

$$\eta_{red} = [\eta]_0 \exp\{b\,(\ln 10)(1 - e^{-kC})/2\} + [\eta]_0^2 k'C \exp\{b(\ln 10)(1 - e^{-kC})\} \quad (5)$$

$$\log \eta_{rel} = \log(1 + C\eta_{red}) \quad (6)$$

Once again, the fit between the measured values and the theoretical curves is excellent and supports the validity of equation (4). We should not forget, however, that constants b and k are merely empirical. Equation (4), derived from equations (1), (2) and (3), requires the use of the Huggins constant; the interpretation of this parameter is still debated even for simple systems such as non-associated polymers. It would therefore be presumptuous to assign physical significance to b and k. Nevertheless, DA can be interpreted as a measure of the tendency of the ionic macromolecules to associate as a function of concentration. As no gelation occurs, this association should level off above a certain concentration. According to equation (4), the maximum value of DA, $DA_{\max}$, is equal to 10^b upon extrapolation to infinite concentration (*Table 2*). Therefore, b may be correlated to the maximum association of halato-telechelic chains.

Another characteristic feature of interest in equation (4) is that plots of DA *versus* C exhibit an inflection point at $C = k^{-1} \ln(b \ln 10)$ (Appendix 1 of ref. 34). It should be recalled that the log η_{rel} *versus* C curves also have a typical sigmoidal shape, suggesting that an initial intramolecular association of the end-groups disappears rapidly in favour of intermolecular interactions. However, in the concentration range corresponding to the inflection point, the rise in the aggregate size decreases and levels off fairly rapidly. By applying equations (5) and (6) to the data, the concentration at the inflection point of the log η_{rel} *versus* C curves (C_{ip}) was determined for each sample[34]. They are consistent with the experimental curves plotted in *Figures 1* and *2a* (*Table 2*).

Equation (4) is quite universal for halato-telechelic amino polymers in toluene (low dielectric constant medium), as it closely reflects the solution behaviour of both the quaternized polymers investigated in this study, and the transition metal/$PIP(NMe_2)_2$ complex samples for which the hydrodynamic behaviour was discussed in a previous paper[34].

CONCLUSIONS

Like complexation with transition metal salts[34], quaternization of the amino end-groups of a telechelic polymer is responsible for a substantial increase in the solution viscosity in toluene at 25°C. The log η_{rel} *versus* concentration plots exhibit a sigmoidal shape, which has not been observed so far in traditional ionomers and which is consistent with the absence of any gelation process. The length of the alkyl substituent of the quaternizing agent is a key parameter controlling the solution viscosity, i.e. the degree of aggregation of the polymer chains which decreases when the number of carbon atoms of the alkyl substituent increases, and eventually levels off when that number exceeds three. Increasing the polarity of the solvent gives rise to a drop in viscosity. Upon quaternization, the polymer seems to behave as a polyelectrolyte in high dielectric constant solvent. Finally, empirical equations have been proposed which closely correlate both the calculated degree of aggregation and the experimental data of solution viscosity to the polymer concentration.

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