Solution behaviour of carboxylatobetaine-based ionomers

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A new class of carboxylatobetaine-based ionomers was prepared from some styrene–chloromethylstyrene precursor copolymers, which have been previously elaborated in order to have better control of their average molecular weights and functionalities. The functionalization steps allowed us to obtain easily various intercharge lengths. The solution behaviour was examined in various apolar, dipolar aprotic and protic solvent systems by viscosity and static light scattering experiments in order to investigate the intermolecular associations. Numbers of aggregations were estimated by comparing the actual viscosities of the ionomers with those of precursor copolymers. Finally, the temperature dependence of the solution viscosity was examined and described by an Arrhenius-type behaviour.

(Keywords: ionomers; carboxylatobetaines; solution behaviour; intermolecular associations; temperature dependence)

INTRODUCTION

The physical properties of hydrophobic polymers, either in solution or in the bulk, are drastically changed when they contain some ionic moieties, even at a low content[1]. Such polymers form a new class of ionic polymers, called ionomers. They display generally enhanced mechanical properties, high glass temperature and highly increased viscosities in low-polarity solvents. Such behaviour is attributed to aggregations between the ionic groups, which reduce the unfavourable environment of the non-polar solvent. The first theoretical model was proposed by Eisenberg[2], who developed the concept of clusters by showing that ion-pair aggregation is a thermodynamically favourable process. This approach was followed by some others. Joanny presented a theoretical study on the phase diagram of ionomers in solution in water, which showed a demixing and a gelation transition[3]. In that case, gelation was expected to vary inversely with the fraction of ionic groups along the polymer backbone. Forsman used thermodynamics to predict the mean-square end-to-end distance between the ionic units and reported the effect of ion-pair clustering on the chain extension[4,5]. As an important consequence, such interactions may lead to physically reversible networks in bulk or in a low-polarity solvent, in contrast to chemical covalent crosslinks, which cause the formation of permanent networks.

The ionic structures are generally obtained by neutralization of organic acids, such as carboxylic or sulphonic acids, with a metal cation, attached by covalent bonds and randomly distributed all along the hydrophobic polymer backbone. In that case, the anionic group and its counterion are more or less tightened by attractive coulombic associations while the ionic groups grafted on the polymer backbone are submitted to repulsive forces. The strength of these interactions depends on the solvent environment: in the bulk or in a non-polar solvent, the ion pairs may be considered as dipoles because of the very low degree of ionization and then may be involved in dipole–dipole interactions.

The solution behaviour of such types of ionomers was extensively studied in different solvent systems by Lundberg[6–8]. As an example, a lightly sulphonated polystyrene in a low-polarity solvent (dioxane, toluene or tetrahydrofuran (THF)) exhibits a higher viscosity than the polystyrene precursor, due to intermolecular associations of the ion pairs, provided that the polymer concentration is higher than the coil overlap concentration c^*. Below this concentration, the intramolecular interactions prevail and the viscosity becomes smaller than that of its precursor. In highly polar solvents, such as dimethylsulphoxide (DMSO) or dimethylformamide (DMF), these ionomers display a polyelectrolyte-type behaviour[6,7]. Adding a small amount of an alcohol to the ionomer solution causes a marked reduction of the viscosity; in addition, its temperature dependence is quite different from that of conventional polymer solutions. These results were explained on the basis of an equilibrium between the sulphonate groups and the molecules of alcohol.

In order to have a better understanding of these properties, some model ionomers have been synthesized by Jérôme, namely the halato-telechelic polymers, such as carboxylato- or sulphonato-telechelic polyisoprene or polystyrene, neutralized with a metal salt. Viscosity and viscoelastic properties were fully investigated[9,10]. An interesting feature was that homogeneous gels could be formed from semi-dilute solutions of these polymers in non-polar solvents. For the Mg carboxylato telechelic polymers, the critical concentration for gelation was found to depend inversely on the square root of the molecular weight.

Another class of ionic polymers was reported by Salamone[11], who carried out the copolymerization of some 'ion-pair' comonomers. These syntheses lead to polymers containing no inorganic ions. In addition, the hydrophobic–hydrophilic balance of these new copolymers may be modified by using a third comonomer

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such as styrene[12] or acrylamide[13]. Nevertheless, the distribution of the ionic charges along the polymer backbone depends on the reactivity ratios of these comonomers and some heterogeneity in the material can occur: even if the polymer is neutral, a given chain might contain an excess of cationic groups while another chain would present more anionic units. Their solution behaviour was also investigated and the measurements have confirmed that strong intermolecular ionic interactions are occurring between the ionic monomer units.

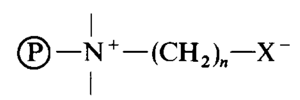
A third class of ionic polymers may be obtained by using the zwitterions, also called betaines, where the anionic and cationic groups are in the same molecular unit. One of the main features of these moieties is the presence of a permanent dipole, which is due to the covalent chemical bonds between both ionic functions. These dipoles have to be regarded as an intrinsic characteristic of these zwitterions, which makes them distinguishable from the above classes of ionomers. Nevertheless, both oppositely charged ions of the dipoles lead to ion pairs, which may be free, solvated or associated, according to the solute–solvent interactions.

Typical materials of this class are the sulphonatobetaines, which are prepared by reaction of the propanesultone on a tertiary amine, such as the vinylpyridine, as first reported by Hart and Timmerman[14] and extensively studied by Galin[15–17], the imidazole or the urethane group, as described by Salamone[18] and Cooper[19] respectively. Very recently, Fetters *et al.* have reported the synthesis and properties of semitelechelic polyisoprenes capped with one sulphonatobetaine[20,21]. These polymers were found to be highly aggregated in cyclohexane and to behave like star polymers. Strong associations were also present in the melt. Bredas studied these zwitterionic interactions from the theoretical point of view and proposed the formation of extended conformations with the dipoles all aligning in an antiparallel arrangement[22].

Monomeric and polymeric glycerophosphorylcholine types have been already reported as models for biological membranes[23–25], but they all present the major drawback of being easily hydrolysable, owing to a C–O–P phosphate linkage between the ionic centres.

Finally, up to now, polymeric carboxylatobetaines have been scarcely described. Ladenheim and Morawetz reported the synthesis of a betaine with only one methylene group between the ionic functions[26]. Some applications as pharmaceutics were claimed by a patent[27].

In a previous paper[28], we have reported the preparation and characterization of copolymers with some non-hydrolysable zwitterionic units as pendant groups, such as carboxylato-, phosphinato- or phosphonatobetaines. These polymers were synthesized by a two-step sequence that allows one to obtain easily various inter-charge lengths, whereas using the propanesultone restricts this length to a single value. Their general structure is:



$$\text{Ⓟ}-\underset{|}{\overset{|}{N^+}}-(CH_2)_n-X^-$$

with $n = 1$ to 5; $X^- = COO^-$, $\underset{\substack{| \\ R}}{P(O)}-O^-$ and $R = Ph, OEt$

Some preliminary data from solution and dynamic melt viscosity measurements of polymers with such grafted carboxylatobetaines at a low content have shown that important intermolecular interactions took place[29,30].

This paper deals with a more in-depth investigation of the solution behaviour of such ionomers in various solvent systems and their temperature dependence. Size exclusion chromatography (s.e.c.), viscosity and static light scattering experiments were carried out, in an attempt to understand this behaviour.

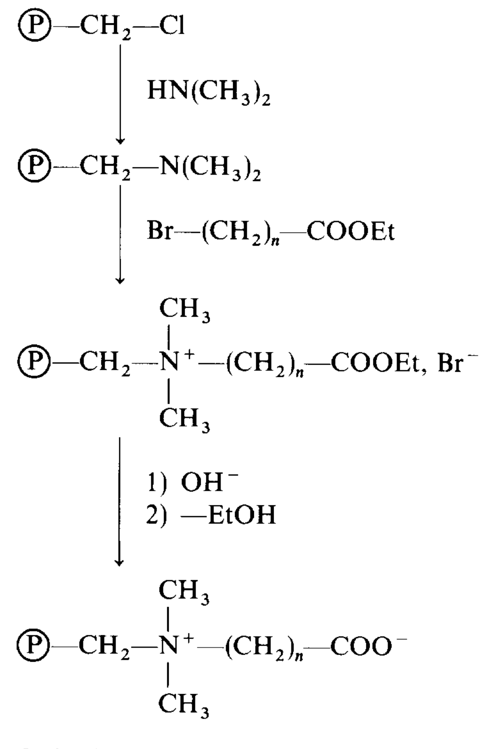
EXPERIMENTAL

Synthesis and characterization

The synthesis of the carboxylatobetaine-based ionomers was achieved from aminated supports such as poly(styrene-*co*-dimethylaminomethylstyrene) according to *Scheme 1*, as reported previously[28].

These supports were first elaborated by copolymerization of styrene and vinylbenzyl chloride in an aqueous suspension. The chloromethylated copolymer was reacted with dimethylamine to give the aminated product and quaternization was carried out with the appropriate ethylbromocarboxylic ester. The subsequent ammonium bromide solution in THF was treated with aqueous NaOH. After stripping the solvent, the copolymer was recovered as the ammonium hydroxide, from which the zwitterionic form was obtained by elimination of a molecule of ethanol upon heating. In the following, the symbols P–Cl, P–N, P–Q and P–Zw refer to the chloromethylated, aminated, quaternized and zwitterionic polymer respectively. The various ionomers used in this study are denoted P(*m*)–Zw(*n*) where (*m*) is related to the precursor copolymer (see *Table 2* in the 'Results' section) and (*n*) specifies the inter-charge length, that is the number of methylene groups between the two charged atoms.

The amination step, the quaternization and the



Scheme 1 Synthesis of the carboxylatobetaine-based ionomers

subsequent formation of the zwitterionic structure are monitored by *FT*i.r. spectroscopy on films cast from polymer solutions onto KBr pellets and by elemental analysis. *Table 1* reports the assignments of the major i.r. absorption bands which are used in the characterization of these polymers.

S.e.c. was used to determine the molecular weights (μ-Styragel columns and THF as eluent at room temperature). The injection concentrations are about 1% and the calibration curve is obtained from polystyrene standards. S.e.c. measurements of the ionomers always fail, giving non-reproducible results, except for the less functionalized ionomer P1–Zw4. The deduced molecular weights are generally very much lower than those of the precursor copolymers. As discussed below, the retention of microgels either on the column filters or inside the columns themselves is supposed to be responsible for these results, rather than a decrease of the hydrodynamic volume due to intramolecular interactions.

Viscosity measurements

The solution viscosities of the precursor polymers and the related ionomers were measured on an Ubbelohde viscometer placed into a temperature-controlled water bath. The solutions were prepared by dissolution of the copolymer in a previously distilled and dried solvent. They were then centrifuged just before the viscosity measurements. Repeated measurements were made until good reproducibility was obtained. The reduced and inherent viscosities η_{red} and η_{inh} were calculated and plotted against the concentration of the polymer solution. When the viscosity plots followed a Huggins-type behaviour, the intrinsic viscosity and the Huggins constant k_{H} were deduced from this concentration dependence:

$$\eta_{\text{red}} = [\eta](1 + k_{\text{H}}[\eta]c) \qquad (1)$$

Table 1 Assignment of the representative i.r. absorption bands of the polymers during the different functionalization steps

Polymer	Vibration modes		Wavenumber (cm^{-1})
P–Cl	δ (CH_2)	in CH_2Cl	1265
P–N	ν_a (C—H)	in -NMe_2	2813
	ν_s (C—H)	in -NMe_2	2771
P–Q	ν_a (C=O)	in COOEt	1734
	ν_a (C—O—C)	in COOEt	1180
P–Zw	ν_a (COO^-)		1575

Light scattering measurements

Light scattering (LS) measurements were performed on a Sofica-type photometer using polarized light of wavelength 632 nm from a He–Ne laser. The refractive index increments d*n*/d*c* were obtained with a Brice–Phoenix differential refractometer. The solvents were distilled and filtered through a Millipore filter. The solutions were centrifuged before the measurements. The data were plotted as $Kc/\Delta R_\theta$ vs. concentration *c* according to the equation:

$$Kc/\Delta R_\theta = (1/M_{\text{w}})[1 + K' \sin^2(\theta/2)] + 2A_2c \qquad (2)$$

where ΔR_θ is the excess Rayleigh ratio at concentration *c* and scattering angle θ, *K* is an optical constant and $K' = (4\pi n R_{\text{g}})^2/3\lambda^2$. The Zimm data treatment was used for the calculation of the weight-average molecular weight M_{w}, the second virial coefficient A_2 and the radius of gyration R_{g}.

RESULTS AND DISCUSSION

Characterization of the precursor copolymers

The average molecular weights and the chlorine molar fraction F_{Cl} of the precursor chloromethylated copoylmers are reported in *Table 2*. The high polydispersity is due to the high conversions obtained during the radical copolymerizations. The viscosities of the precursor solutions were studied in apolar or low-polarity solvents such as toluene or THF. Owing to the very low functionalization, the precursor polymers were assumed to have the same hydrodynamic parameters as polystyrene. The data are well fitted by the Huggins plots and the viscosity-average molecular weights were calculated by using the Mark–Houwink coefficients $k = 1.14 \times 10^{-4}\,\text{dl g}^{-1}$, $a = 0.72$ for the solutions in THF[31] and $k = 1.7 \times 10^{-4}\,\text{dl g}^{-1}$, $a = 0.69$ in toluene[32]. The light scattering measurements of the weight-average molecular weight are in a good agreement with the other determinations.

From the mole fraction F_{Cl} of chlorine, it is possible to determine an average number of chloromethylated units $\langle \text{Cl} \rangle = \overline{DP}_{\text{n}} F_{\text{Cl}}$ per polymer chain, $\overline{DP}_{\text{n}}$ being the number-average degree of polymerization of the precursor polymers. In the following, the average number of zwittionic units $\langle \text{Zw} \rangle$ will be assumed to be equal to or a little smaller than $\langle \text{Cl} \rangle$, because of the very good yields of the functionalization steps (always more than 90% as shown by elemental analysis).

Table 2 Characterization of the chloromethylated precursor copolymers

Ref.	M_{n}[a]	M_{w}[a]	$[\eta]$ (dl g^{-1})	M_{v}[b]	M_{w}[c]	F_{Cl}	$\langle \text{Cl} \rangle$
P1–Cl	24 300	48 000	0.25	43 700	–	0.004	0.93
P2–Cl	23 500	67 000	0.31	59 000	–	0.006	1.35
P3–Cl	31 000	71 000	0.33	64 200	–	0.013	3.87
P4–Cl	21 000	45 000	0.29	53 700	58 000	0.033	6.66
P5–Cl	120 000	301 000	1.0	300 000	299 000	0.021	24.23

[a] S.e.c.
[b] Viscosity
[c] LS, $dn/dc = 0.209\,\text{ml g}^{-1}$. The solvent is THF in all these experiments

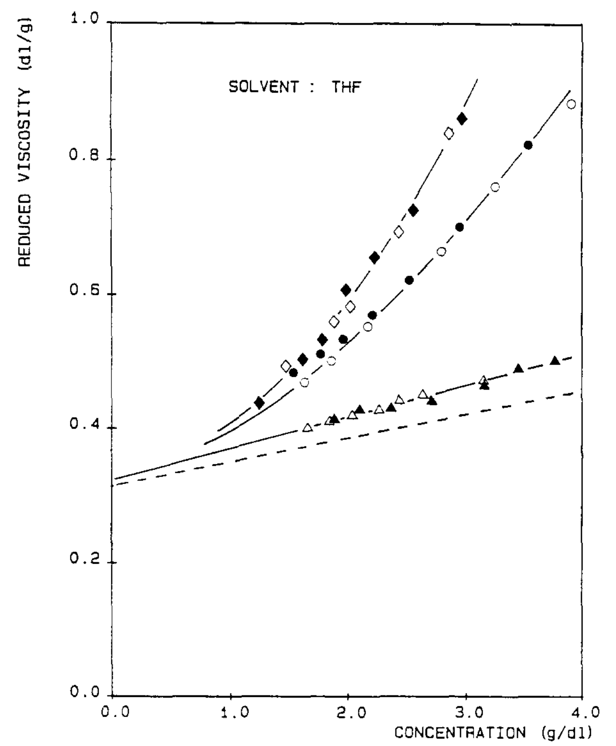


Figure 1 Reduced viscosity of some carboxylato-based ionomer solutions in THF and dependence on the ionic groups ⟨Zw⟩ fraction. Symbols: (△, ▲) P1-Zw4, ⟨Zw⟩ = 0.93; (○, ●) P3-Zw4, ⟨Zw⟩ = 3.87; (◇, ◆) P4-Zw4, ⟨Zw⟩ = 6.66. The open and full points refer to different experiments in order to indicate the reproducibility of the measurements. The broken curve represents the domain of reduced viscosities of the various precursor chloromethylated copolymers

Solubility of the ionic copolymers

The solubility of these ionic polymers is limited to a very small range of solvents and depends also on the inter-change length. When $n = 1$, the polymer only swells in aromatic solvents and in THF to form a gel, and attempts to perform solubilization have been unsuccessful. In the same solvents, solubilization occurs when a larger inter-charge length ($n = 4$) is used. This inter-charge length effect was also noted with telechelic polyisoprenes capped at both ends with the same carboxylatobetaines[33]. Attention must be drawn to this last observation: the functionality of the telechelic polyisoprenes is equal to 2 and formation of gels could not be explained by a simple dipole–dipole interaction between two zwitterionic moieties; in that case, a higher molecular weight would only be observed. It could then be postulated that aggregates or clusters must occur.

When using a shorter inter-charge length, stronger interactions take place, which are inconsistent with only the increase of the dipole moment with this length, even if not increasing linearly with n owing to the polymethylene chain flexibility, as shown by some ^{13}C n.m.r. experiments[34,35]. A more sensitive parameter would then be the distance between the dipoles. As a first conclusion, it appears that gelation can occur in non-polar aromatic solvents provided that the inter-charge length is short enough.

Dipolar aprotic solvents such as DMSO, DMF or propylene carbonate lead only to gels and a small amount of methanol is required to obtain a solution. Therefore, hydrogen bonding appears to be more efficient than the interactions between the polymer and the dipolar aprotic solvents. This point will be confirmed later with the viscosity measurements. Then, the characterization of these ionic polymers in terms of hydrodynamic parameters will be difficult to appreciate, owing to the strong ionic interactions that occur even at a low concentration of the polymer solution.

Solution behaviour at ambient temperature

Viscosity. Highly viscous solutions are obtained when dissolving the ionic polymers in a low-polarity solvent. A typical curve of the viscosity vs. concentration of the polymer in THF (dielectric constant $\varepsilon = 7.4$) is shown in *Figure 1*. The same behaviour is observed in toluene (*Figure 2*) with higher viscosities due to the lower dielectric constant ($\varepsilon = 2.4$), and the data cannot be fitted by the Huggins equation, except for the polymer P1-Zw4, which contains the smallest fraction of ionic groups. In this latter case, the Kraemer plots display a conventional negative slope, which does not represent the general tendency. The reduced viscosities of both precursor and related ionomers tend to the same intrinsic viscosity at infinite dilution, contrary to the observation noted by Lundberg with lightly sulphonated polystyrenes[6,8]. Following the author's arguments, the intramolecular interactions seem not to occur with these carboxylato-based ionomers. As a consequence, the s.e.c. results cannot be explained by these interactions, but rather by a retention of microgels inside the columns.

An aggregation number N_{ag} may be defined as $N_{ag} = M_{app}/M_0$ and estimated by comparing the actual viscosity of the ionomer with that of precursor polymers, which would have various molecular weights[30]. M_{app} is the molecular weight of a precursor polymer that would display a viscosity identical to that of the ionomer at a

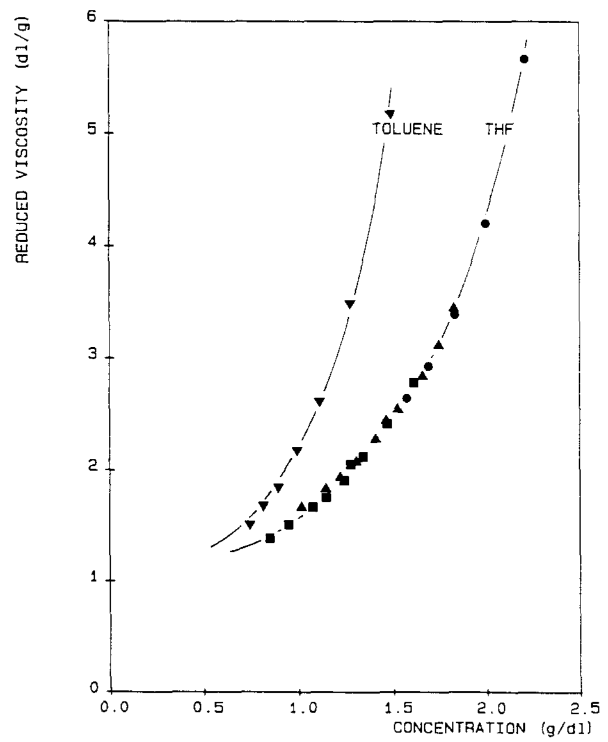


Figure 2 Effect of the polarity of aprotic solvents on the reduced viscosity of P5-Zw4: (▼) toluene; (●, ▲, ■) THF. As in *Figure 1*, the various symbols are related to different experiments, which show the good reproducibility of the measurements

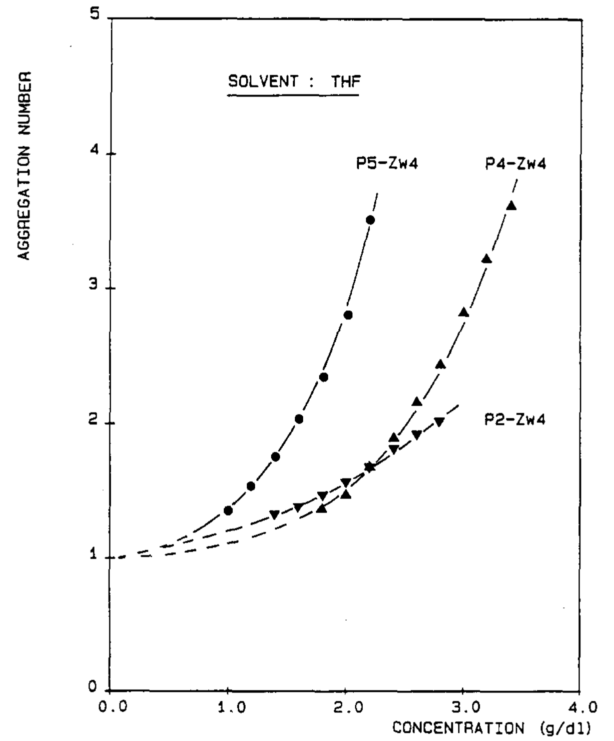


Figure 3 Dependence of the aggregation number in THF on the molecular weight and the zwitterionic fraction for various ionomers: (▼) P2-Zw4; $M_n = 23\,500$, $\langle Zw\rangle = 1.35$; (▲) P4-Zw4, $M_n = 21\,000$, $\langle Zw\rangle = 6.66$; (●) P5-Zw4, $M_n = 12\,000$, $\langle Zw\rangle = 24.23$

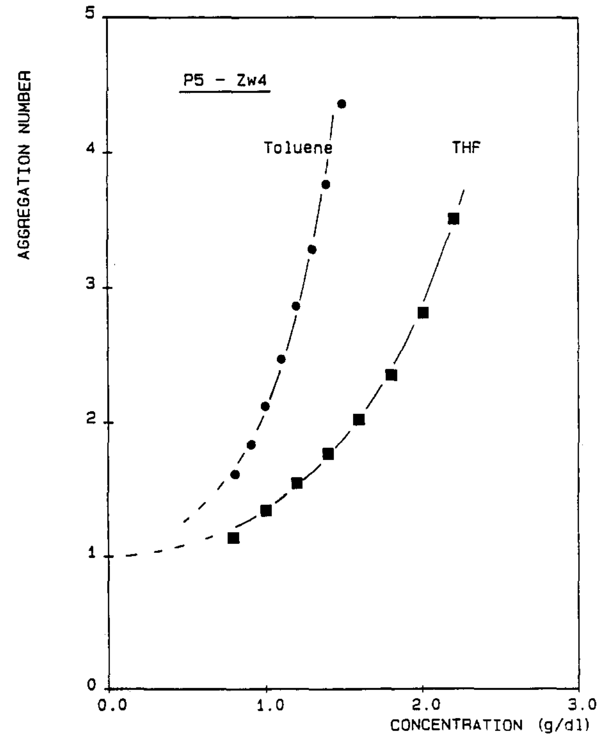


Figure 4 Dependence of the aggregation number of P5-Zw4 on the solvent: (●) toluene; (■) THF

given concentration and M_0 is the actual molecular weight of the precursor copolymer. It is assumed that the precursor polymer follows the Mark–Houwink law and that the limiting number viscosity can be calculated from the Huggins constant k_H, which is supposed to display the same value over the whole range of molecular weights.

Figures 3 and *4* display the aggregation numbers N_{ag} estimated from the viscosity curves for two ionomers. This number depends obviously on the nature of the solvent: the more polar the solvent, the lower the aggregation number (*Figure 4*). Another interesting point is the dependence of N_{ag} on the molecular weight or the average number of zwitterionic units (*Figure 3*): the comparison between both curves related to P2-Zw4 and P4-Zw4, which have roughly the same molecular weight, shows that the average number of zwitterionic units $\langle Zw\rangle$ is the relevant parameter rather than the molecular weight.

Static light scattering. The Zimm plots were found to depend strongly on the investigated ionomer and on the concentration range. For instance, *Figure 5* shows the Zimm plot for a solution of the carboxylatobetaine P4-Zw4 in THF. The apparent molecular weight is much higher than that of the precursor, but decreases when the domain of concentration studied also decreases (*Table 3*). The radius of gyration also varies in the same way.

It is worth noting the unusual negative value of the second virial coefficient (*Figure 6*): although a good solvent for the polystyrene backbone, THF appears to

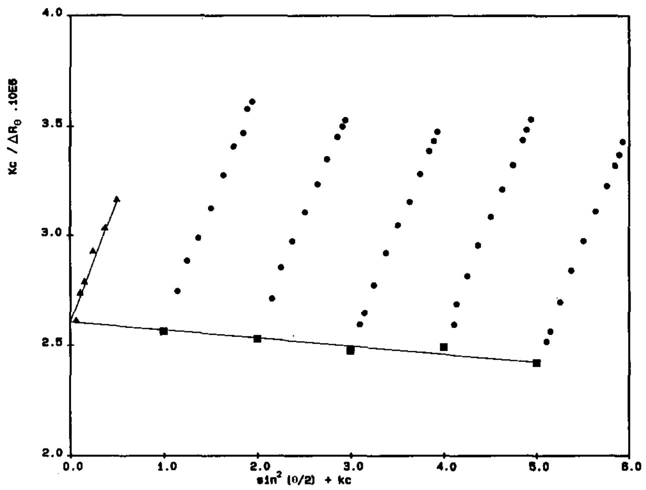


Figure 5 Static light scattering of an ionomer solution: Zimm plot of P4-Zw4 in THF at ambient temperature. $dn/dc = 0.194\,\mathrm{ml\,g^{-1}}$. The squares refer to the extrapolations at infinite dilution and the triangles to the extrapolations at $\theta = 0$

Table 3 Concentration dependence of the average molecular weights and radii of gyration of P4-Zw4 and P5-Zw4 in THF measured by LS and the calculated radii of gyration of polystyrene with the same molecular weight according to relation (3)

Polymer: P4-Zw4			
Concentration range $(\mathrm{mg\,ml^{-1}})$	7.24–1.25	2.26–0.45	1.01–0.20
Apparent molecular weight	395000	319000	293000
Radius of gyration (Å)	418	384	322
Calculated radius of gyration of an equivalent PS (Å)	267	236	225
Polymer: P5-Zw4			
Concentration range $(\mathrm{mg\,ml^{-1}})$	6.07–1.22	4.19–1.68	1.51–0.30
Apparent molecular weight	284000	318000	201000
Radius of gyration (Å)	603	659	254
Calculated R_g (Å)	221	236	181

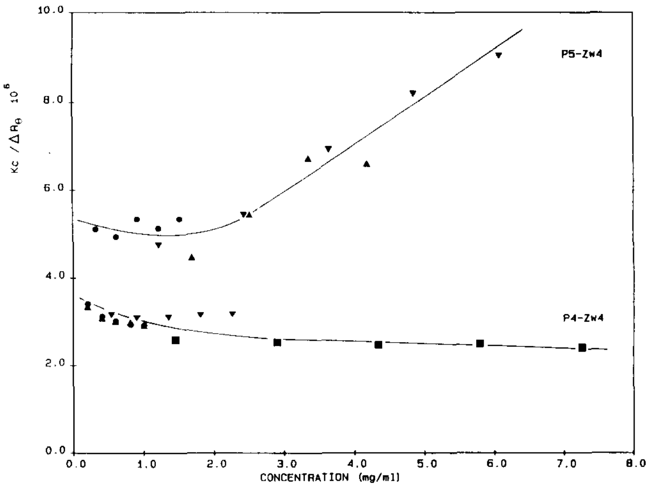


Figure 6 Static light scattering of P4-Zw4 and P5-Zw4 in THF. Extrapolation at $\theta=0$. The slope is a measure of the second virial coefficient A_2. Different symbols refer to different experiments, which have been carried out in various ranges of dilutions

be a very bad solvent for these ionomers and is not polar enough to break the intermolecular associations between the zwitterionic units. The same behaviour was noted with the sulphonate ionomers in the dilute solution range. A_2 was found to decrease on increasing the ion content and may become negative[36,37]. Nevertheless, this aggregation effect is inconsistent with the fact that the concentration is below c^* defined as $[\eta]^{-1}$ (ref. 38). An explanation would be that strong intermolecular interactions occur in bulk and cannot be broken upon dissolution.

Facing this unusual, but quite explained, behaviour, the ionomer denoted P5-Zw4 displays normal Zimm plots, which appear unusual in the ionomer context. Positive A_2 values are noted (*Figure 6*) and the molecular weights are in the same range of values as the precursor copolymer (*Table 3*), except at very low concentration where the measured molecular weight is rather lower than that of its precursor.

It is also of interest to compare the radii of gyration with those of polystyrene of equivalent molecular weight. The value of R_g can be estimated from the molecular weight by using an equation derived from the Flory and the Mark–Houwink–Sakurada relations[39]:

$$[\eta]=KM^a=\Phi_0(1-2.63\alpha+2.86\alpha^2)(R_g\sqrt{6})^3M^{-1}$$

where $\alpha=(2a-1)/3$ and Φ_0 is the Flory universal constant equal to $2.5\times10^{21}\,\text{mol}^{-1}$ when the polymer is polydisperse and the units of $[\eta]$ are dl g^{-1}. With the above values of K and a for polystyrene in THF, the relation between R_g and the molecular weight may be written as:

$$R_g=0.166M^{0.573}\,\text{Å} \qquad (3)$$

Two features may be underlined:

(a) Whatever the concentration of the ionomers, the measured values of R_g are larger than those of their precursors (73 and 228 Å). This point was also noted by Earnest *et al.*[40], who showed that clustering of ionic groups in ionomers is accompanied by an increase of the mean radius of gyration of the polymer chains.

(b) Measured molecular weight and radius of gyration of the ionomers are not connected by the same relation as above. This is not surprising because the aggregation effects depend strongly on the concentration, as seen by the variation of the aggregation number.

Adding a polar solvent. The viscosity of the THF solutions is strongly decreased when adding a dipolar aprotic solvent such as DMSO ($\varepsilon=48$) or DMF ($\varepsilon=37$), as shown by *Figure 7*. The reduced viscosity is affected in the same way by both solvents. A higher proportion of these solvents make the solution slightly turbid, due to precipitation of the ionomer. These results may be interpreted by assuming a decrease of the number of aggregations because of the formation of new more efficient interactions between the zwitterionic units and the dipolar solvent.

Methanol, although having a dielectric constant ($\varepsilon=32.7$) very close to DMF, causes a more drastic decrease of the viscosity. This underlines the efficiency of hydrogen bonding. In a mixture of THF and MeOH (90/10), normal Huggins plots are obtained again (*Figure 8*), contrary to what was observed with a lightly sulphonated polystyrene that displayed a polyelectrolyte behaviour in polar solvents such as DMF[6,7]. The Huggins constant and the intrinsic viscosity are slightly higher than those of its precursor. These observations agree with the light scattering experiments, which show that the apparent molecular weight decreases (130 000 instead of 395 000 in the same range of polymer concentration), but still remains higher than that of the related aminated precursor copolymer ($M_w=58\,000$). In addition, a positive value of the second virial coefficient is recovered (*Figure 9*). This result may be compared to that of Salamone[12] who observed a normal Zimm plot with solutions of ampholytic ionomers in benzyl alcohol, although the weight-average molecular weight was high.

These results are well connected with the attempts at solubilization in various solvents as reported above.

Temperature dependence of the solution behaviour

The influence of temperature on viscosity measurements of the P5-Zw4 ionomer is illustrated in *Figure 10*. Increasing the temperature results in a marked decrease of the viscosity, whereas the precursor copolymers

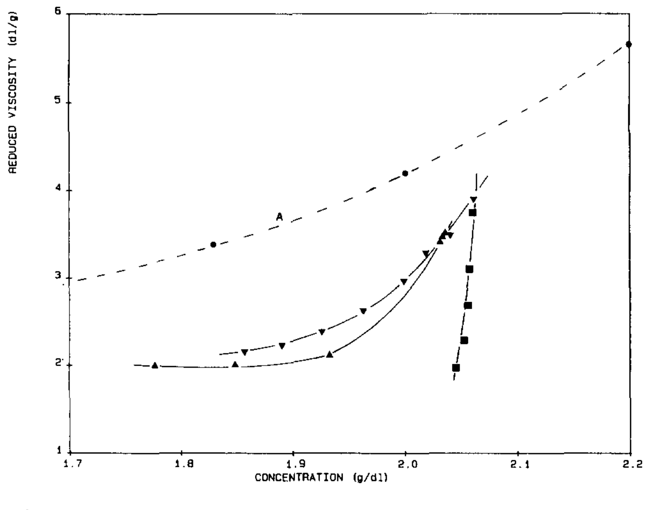


Figure 7 Effect of the addition of small amounts of dipolar aprotic and protic solvents on the reduced viscosity of a solution of P5-Zw4 in THF: (▼) DMF; (▲) DMSO; (■) methanol. The full circles and broken curve A represent the behaviour of this ionomer in THF

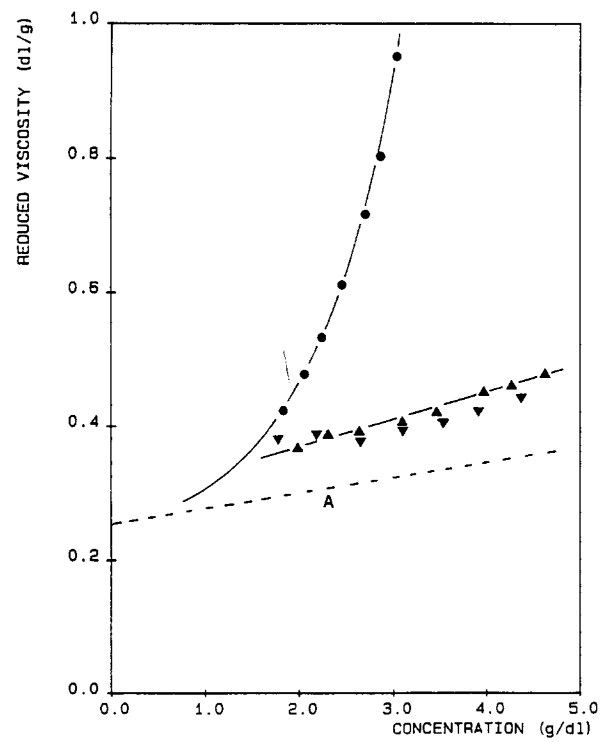


Figure 8 Reduced viscosity of a solution of P4-Zw4 in THF-methanol mixtures (composition by volume): MeOH/THF = 0 (●), 10/90 (▲), 20/80 (▼). The broken curve A represents the viscosity of the precursor copolymer in a 20/80 methanol/THF mixture

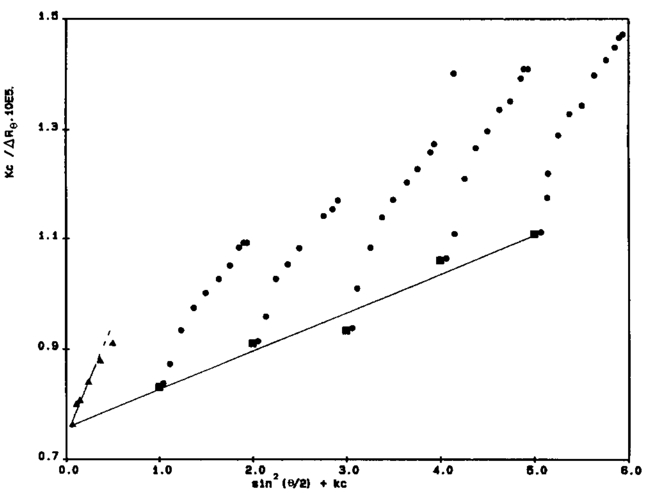


Figure 9 Zimm plot of P4-Zw4 in a THF-methanol mixture (90/10 by volume). d*n*/d*c* = 0.232 ml g^{-1}. The symbols are the same as in *Figure 5*

display a very small decrease in voscisity in the same ranges of temperature and concentration. The experiments carried out with the P4-Zw4 ionomer show the same behaviour. This temperature effect confirms the important role of the dipolar interactions. A similar effect with alkaline-earth carboxylato polybutadienes[9] was seen by Jérôme, who noted a relation between the effects of temperature and the size of the cations. Lundberg[41] pointed out some unusual behaviour of sulpho-EPDM (terpolymer of ethylene/propylene/diene monomer) solutions, which was interpreted in terms of an equilibrium involving solvated ion pairs.

Assuming that dipole–dipole type interactions occur between the zwitterionic units, these associations would be governed by a thermally activated process[42] and can be described by an Arrhenius-type equation:

$$\eta_{\text{red}} = \text{constant} \times \exp(E_a/RT)$$

Figure 11 displays the evolution of the reduced viscosity in Arrhenius plots, which confirms the good

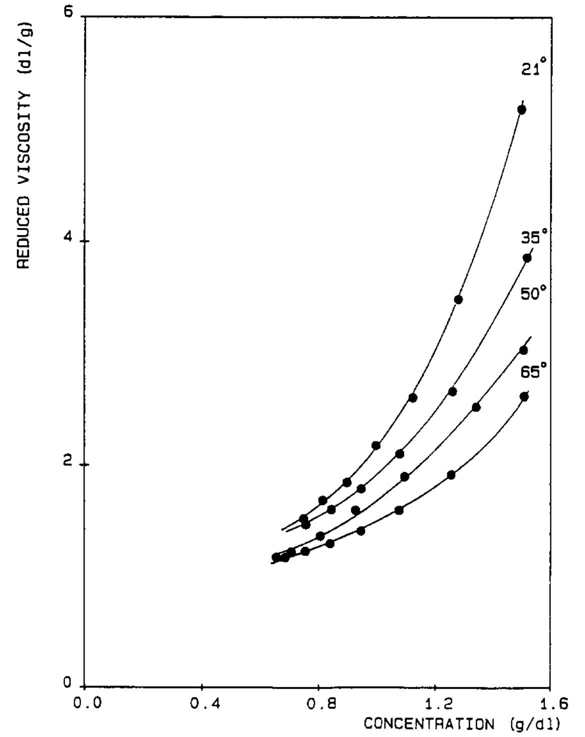


Figure 10 Temperature effect on the reduced viscosity of P5-Zw4 in toluene. The viscosity of the precursor copolymers is very slightly affected by the increase of the temperature in the same range of concentrations. Temperature (°C) is shown to right of each curve

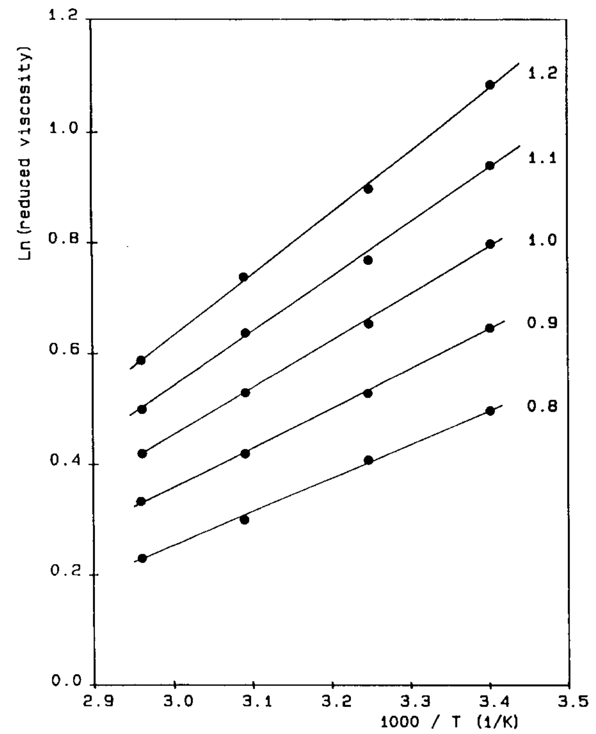


Figure 11 Arrhenius plots of the reduced viscosity for various concentrations (as indicated at the end of every straight line of the graph; units g dl^{-}) of the P5-Zw4 solution in toluene, deduced from the data of *Figure 10*

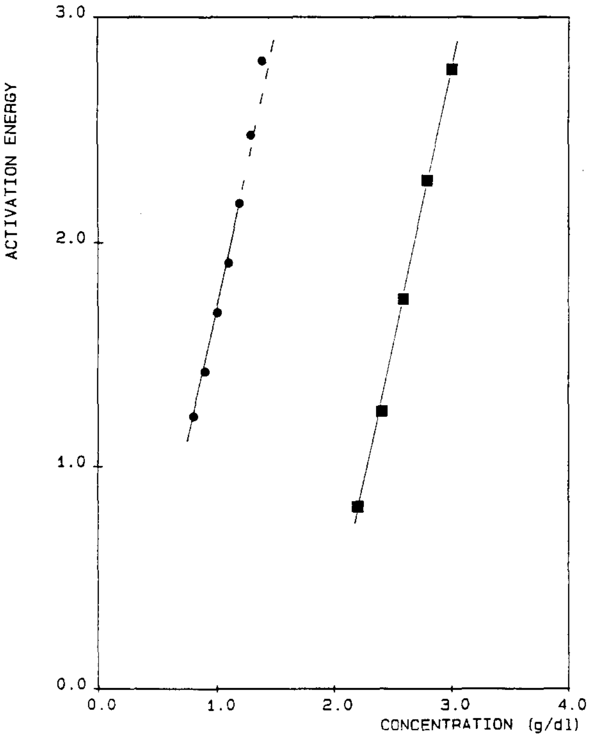


Figure 12 Activation energy E_a (kcal mol^{-1}) *versus* concentration in toluene for two ionomers. E_a is deduced from the Arrhenius plots, which have been drawn for various concentrations as shown in *Figure 11*: (■) P4-Zw4; (●) P5-Zw4

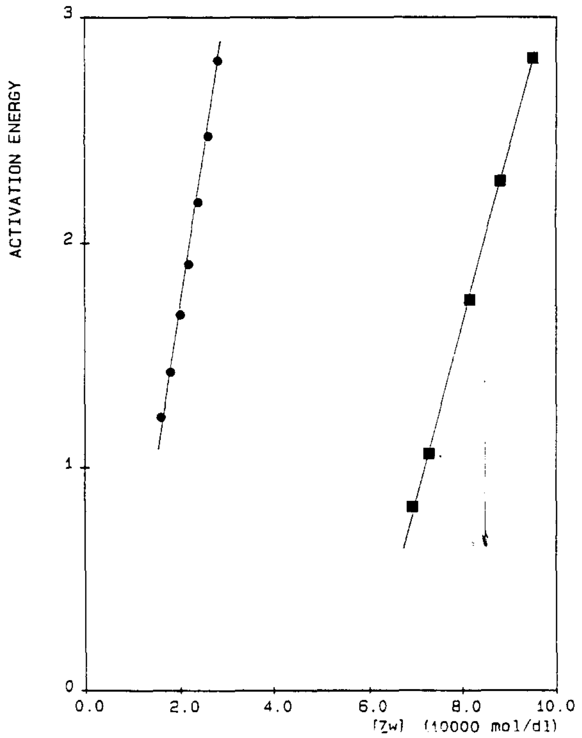


Figure 13 Activation energy (kcal mol^{-1}) *versus* concentration of the zwitterionic groups assuming a homogeneous distribution of the chains in the medium: (■) P4-Zw4; (●) P5-Zw4

accuracy of this hypothesis. In addition, it may be seen that the activation energy E_a is not a constant, but seems to be a linear function of the concentration of the ionomer solution (*Figure 12*). Since the intermolecular associations prevail, an average concentration of zwitterionic units may be used as a parameter instead of the polymer concentration if assuming a homogeneous distribution of the clusters in the solution (*Figure 13*). The average number of zwitterionic units $\langle Zw \rangle$ appears to be the most relevant parameter: the higher the value of $\langle Zw \rangle$, the higher the slope and then the higher the interactions. This result could also be explained in terms of molecular weight: P5-Zw4 has the highest molecular weight and the highest radius of gyration, which allows more extensive intermolecular interactions.

The thermal stability of the zwitterionic units was also investigated by submitting the polymer solutions to prolonged heating. The zwitterionic unit with the shortest inter-charge length ($n = 1$) was found to be stable, whereas the other one ($n = 4$) was not: after heating, the viscosity behaviour was that of its precursor polymer and *FT*i.r. spectra revealed that the carboxylate group had disappeared.

CONCLUSIONS

The carboxylatobetaine-based ionomers are found to display an original behaviour in solutions. In low-polarity solvents, these ionic polymers lead to strong associations through dipolar intermolecular interactions and gels can even be formed. These associations depend also on the inter-charge length. The apparent molecular weights are much higher than those of the precursor aminated copolymer and highly viscous solutions can be obtained. The viscosity data cannot be fitted by the Huggins equation, and an aggregation number may be deduced from these measurements, which depends on the solvent and on the ionomer itself. In addition, the aggregation phenomena are also clearly shown by some static light scattering experiments.

The viscosity of these solutions is greatly reduced by adding small amounts of a dipolar aprotic or protic solvent, which decreases the number of aggregations by formation of new stronger interactions between the zwitterionic unit and the dipolar solvent. Nevertheless, the classical polyelectrolyte behaviour that is obtained with lightly sulphonated polystyrene is not observed with these ionomers.

Increasing the temperature causes a marked decrease in viscosity, which confirms the important role of the dipolar intermolecular interactions, and the interaction energy depends on the concentration of the zwitterionic units. The temperature effect may be described for each concentration in terms of an Arrhenius-tye equation.

Finally, destruction of the betaines may occur when heating is carried out for too long.

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