Synthesis, glass transition and solution behaviour of carboxylatobetaine telechelic polymers

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Telechelic polystyrene and polyisoprene bearing carboxylatobetaine end groups of various intercharge lengths were prepared and characterized. Dimethylamino telechelic polyisoprene and polystyrene were anionically synthesized and the dimethylamine end groups were reacted with bromoalkyl ethylcarboxylic esters, comprising a methyl and an n-butyl group. After treatment with aqueous NaOH, the end groups were converted into carboxylatobetaine form of various intercharge lengths. Glass transition temperatures of both functionalized polystyrene and polyisoprene were found to increase with respect to the precursor polymers and to depend on the intercharge length. A smaller intercharge length appears to promote stronger interactions. Solubility of the carboxylatobetaine form depends on both the polymeric nature of the backbone and the intercharge length of the betaine end group. Highly viscous solutions were obtained when dissolving the polymers in a low polarity solvent. The viscosity of the zwitterionic polystyrenes in toluene was affected by the intercharge length of the end group. An average aggregation number was calculated from the viscosity data and the results were compared with those of randomly grafted carboxylatobetaines of the same zwitterionic molar fraction.

(Keywords: carboxylatobetaines; telechelic polymers; glass transition; solution behaviour; aggregation number)

INTRODUCTION

Both solution and solid state properties of hydrophobic polymers are dramatically modified when the macromolecules contain a small fraction of strongly associating groups[1–12]. Until now, the ionomers have been the most extensively studied associating polymers. They consist of non-polar macromolecules, to which are randomly attached a small molar percentage of ionic side groups.

In non-polar solvents, the ion pairs protect themselves from the unfavourable environment by mutual electrostatic interactions. Gelation of the ionomer solutions occurs accordingly. Provided the solvent is a good solvent for the base polymer, it behaves as a swelling solvent for an association-induced network. If the association is too weak gelation is prevented, although extensive aggregation of the chains can persist in solution. Indeed, even in dilute solutions well below c^*, the associating polymers may consist of aggregates[13]. Hence an important feature of the ionic domains is their versatility in forming physical reversible networks either in bulk or in low polarity solvents, in contrast to chemical covalent crosslinks which lead to permanent networks.

Clearly, the behaviour of associating polymers depends in a complex way on a number of parameters, such as the nature and length of the polymer and the nature, content and location of the associating groups. The fundamental structure–property relationships for ionomers are not fully established and model systems are needed in order to understand the evolution of the association in relation to well defined molecular parameters. End-capped ionomers have purposely been synthesized as models since they have a well defined architecture in which the ion pairs are selectively attached at both ends of linear chains with a characteristic separation distance. During the last decade, halato-telechelic polymers consisting of short length polydienes, polyisobutene and polystyrene terminated by metal carboxylate, metal sulphonate or quaternized and complexed amine groups have improved the understanding of the association processes and allowed fine tuning of the structure to obtain desired properties[6,7,10,12,14–20].

'Semi-telechelic' polymers are other good candidates for clarifying the associative behaviour of ionomers. Monofunctional architectures are now attracting increased interest, since gelation can be avoided and the average degree of association determined directly from measurements of the molecular weight of the associating polymer and its precursor devoid of associating groups. Jalal and Duplessix have studied solutions of metal carboxylate polystyrene in toluene by small angle X-ray spectroscopy (SAXS) and small angle neutron scattering (SANS)[21]. They concluded that not spherical but cylindrical aggregates were formed when polystyrene is of low molecular weight (6000). These experimental data are consistent with theoretical calculations by Bredas *et*

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al.[22]. Indeed, associating polymers with only one zwitterionic end-group

$$\text{P-N}^{+}\text{-(CH}_2)_n\text{-SO}_3^{-} \qquad \text{(I)}$$

have been predicted to form reverse micelles that possess either a tubelike or a disk-like structure.

The former structure should be favoured by the excluded volume interaction of the long hydrocarbon tails in the semi-telechelic polymers. For this type of associating group, the driving force toward large aggregation has been predicted to depend on the length of the alkyl moiety between the charge carrying atoms (intercharge length). For instance, the driving force for the ammoniomethylsulphonate zwitterions to associate should be about half that exhibited by the ammoniopropylsulphonatobetaine. Experimental data has been reported on the solution properties and the melt rheology of polyisoprene with an ammoniopropylsulphonate zwitterion on one end of the chain[18,19].

Zwitterions or betaines are potentially interesting associating groups because the anion and the cation of each pair are covalently bonded to each other, which leads to a permanent dipole, the value of which depends on the intercharge length. This intrinsic characteristic makes them distinguishable from the other well known classes of ionomer, such as the lightly sulphonated polystyrenes. The sulphonatobetaines are representative of this class of ionic polymers and have been extensively studied by many authors[23–26].

The nature of the zwitterionic moiety can be modified and carboxylato-, phosphonato- or phosphinatobetaine groups may also be used instead of sulphonatobetaines[27]. Synthesis and characterization of ionomers with carboxylatobetaine groups randomly grafted along a polystyrene backbone have been reported[28–30] and the association process has been studied in solution by viscosity and static light scattering experiments. In low polarity solvents strong associations occur, which are, however, weakened by the addition of small amounts of a dipolar aprotic or protic solvent. In highly polar solvents, such as DMF, polystyrene ionomers of the carboxylatobetaine type do not exhibit the polyelectrolyte behaviour exhibited by sulphonated polystyrenes[31,32].

This paper aims to extend the previous study[30]. It deals with the synthesis and the solution behaviour of telechelic polystyrene end-capped with carboxylatobetaine groups:

$$\text{polystyrene–(N}^{+}\text{–(CH}_2)_n\text{–COO}^{-})_2 \qquad n=1,4 \qquad \text{(II)}$$

To modify the intercharge length of the zwitterion, the α-ω-dimethylamino polystyrene has been quaternized by two bromoalkylcarboxylic esters. Note that the intercharge length of the sulphonatobetaine end groups is restricted to a unique value since only propanesultone could be used to react with the amine end groups and form the expected zwitterion. The quaternization of the amine end groups by various ethylbromocarboxylic esters allows for the controlled modification of the intercharge length. Finally, for comparison, a carboxylatobetaine telechelic polyisoprene has been synthesized and characterized. Preliminary results are reported and discussed below.

EXPERIMENTAL

Synthesis of telechelic polymers

α,ω-Dimethylamino polystyrene (PS) and polyisoprene (PIP) were anionically prepared in THF at −78°C, in previously flamed and nitrogen-purged flasks. Styrene and isoprene polymerization was initiated by naphthalene–lithium and naphthalene–sodium, respectively. After reaction, the activated macrodianions were deactivated by an excess of 3-dimethylaminopropyl chloride (DMAPC), with the formation of α,ω-dimethylamino derivatives.

THF was dried by refluxing over benzophenone–sodium and distilled under a nitrogen atmosphere. Monomers were dried over calcium hydride at room temperature and distilled under reduced pressure just before use. Isoprene was mixed with n-BuLi and again distilled before polymerization. The DMAPC was obtained from the corresponding commercially available hydrochloride (Aldrich). The hydrochloride was dissolved in water and neutralized by NaOH. The DMAPC was then extracted with ether and the solution dried over CaH_2 under nitrogen for 3 days.

Polymers were recovered and purified by repeated precipitation into methanol. Polyisoprene was stabilized by an antioxidant (Irganox 1010, Ciba-Geigy).

The dimethylamine end groups were reacted with the appropriate 1-bromoalkyl ethylcarboxylic ester $\text{Br–(CH}_2)_n\text{–COOEt}$, ($n=1,4$). Ammonium bromide end groups were accordingly generated and treated with aqueous NaOH until the ammonium hydroxide functions were formed. These end groups were converted into the zwitterionic forms by elimination of a molecule of ethanol on heating. This reaction pathway is summarized in *Scheme 1.*

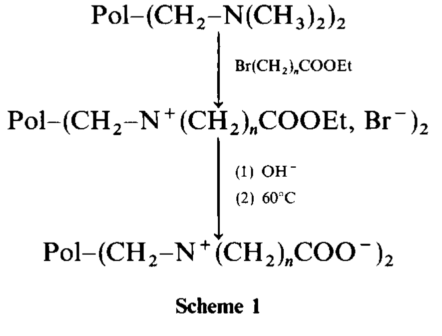
In the following, symbols P-N and P-Zw$_n$ refer to the polymer selectively end-capped with the dimethylamine group and the ammonioalkylcarboxylate zwitterion, respectively. The suffix n specifies the length of the methylene sequence between the two ionic groups.

Characterization

All the reactions were monitored by Fourier transform infrared (*FT*i.r.) spectroscopy[27]. Characteristic absorption bands of the dimethylamine end groups were observed at 2813 and 2771 cm^{-1}, and have been assigned to the ν_a(C–N) and ν_s(C–N) modes of the $N(CH_3)_2$ group. When quaternized, these bands disappeared in favour of the characteristic ν_a(C=O) absorption band of the carbonyl group. Formation of the carboxylatobetaine was highlighted by a shift of the carbonyl absorption down to $\approx 1580\ cm^{-1}$. This new absorption and that of polystyrene at $1600\ cm^{-1}$ might, however, overlap.

Potentiometric titration of the dimethylamine end groups with perchloric acid in a 9/1 toluene/methanol mixture was done to ascertain that the functionality is better than 1.9.

All polymers were examined by size exclusion



$$\text{Pol–(CH}_2\text{–N(CH}_3)_2)_2 \xrightarrow{\text{Br(CH}_2)_n\text{COOEt}} \text{Pol–(CH}_2\text{–N}^{+}\text{(CH}_2)_n\text{COOEt, Br}^{-})_2 \xrightarrow[(2)\ 60^{\circ}\text{C}]{(1)\ \text{OH}^{-}} \text{Pol–(CH}_2\text{–N}^{+}\text{(CH}_2)_n\text{COO}^{-})_2$$

Scheme 1

chromatography (SEC). μ-Styragel columns were calibrated with polystyrene standards. Elution was carried out with THF at room temperature.

The microstructure of the polyisoprene was determined by ^{1}H nuclear magnetic resonance (n.m.r.) and found to consist of [1,4]–[3,4]–[1,2] units in the ratios 15:43:42. No change in the microstructure was noticed after functionalization.

Differential scanning calorimetry (d.s.c.) was performed on samples weighing $\approx$20 mg with a Setaram analyser model DSC 101. The heating rate was 10°C min^{-1}.

Solution viscosities were measured by using an Ubbelohde viscometer within a temperature-controlled bath. Solutions were prepared in dried solvent. Measurements were repeated until good reproducibility was obtained. Reduced and inherent viscosities were plotted against the concentration of the polymer solution.

RESULTS AND DISCUSSION

Solubility and molecular weight

The solubility of the telechelic polymers is limited to a small range of solvents and depends on the intercharge length: a large intercharge length is favourable to polymer solubility. PIP-Zw_1 only swells in THF, while PIP-Zw_4 is soluble in the same solvent. PS with both intercharge lengths can be dissolved either in THF or in toluene, but not in cyclohexane. The same effect had already been noticed for polystyrene randomly grafted with carboxylatobetaine groups[30].

Molecular weights have been determined by SEC and are reported in *Table 1*. It is obvious that the polystyrene molecular weight remains unchanged during the functionalization process.

A marked decrease is, however, observed in the molecular weight of PIP-Zw_4. There is no reason for the carboxylatobetaine groups to favour the retention of PIP on the chromatographic support and not that of PS. The same argument holds for the possible occurrence of intramolecular rather than intermolecular interactions of the carboxylatobetaine end groups. Intramolecular interactions of the end groups could reduce the hydrodynamic volume but not to such an extent that PIP molecular weight could be reduced by half while that of PS remains unchanged. Furthermore, previous light scattering experiments have shown that intermolecular interactions still prevail in PS randomly grafted with carboxylatobetaines even at concentrations lower than those used in SEC[30]. The reason for the abnormally low molecular weight of PIP-Zw_4 compared with the PIP-N precursor is thus not yet clear.

Glass transition temperature

It is clear that the ionization of the telechelic polyisoprene results in a marked change in the bulk properties since the zwitterionic polymer is recovered as a powder at room temperature, whatever the intercharge length, although the PIP-N precursor is a viscous and sticky material. *Figures 1* and *2* report the d.s.c. traces of α,ω-dimethylamine PS and PIP and of their zwitterionic counterparts. The glass transition temperature of PIP is increased, but the most striking feature is the large broadening of the glass transition zone, which suggests that a crosslinking process has been induced by the zwitterionic moieties. The same groups attached at both ends of polystyrene ($T_g = 88$°C) cause only a slight shift of T_g toward higher temperatures: $T_g = 90$°C for PS-Zw_4

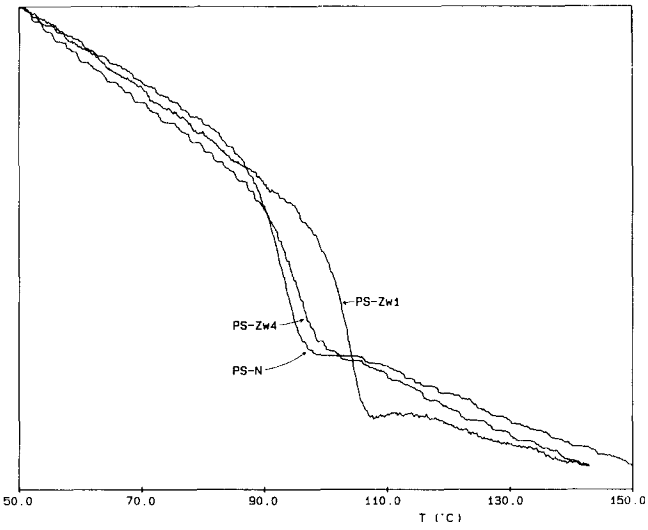


Figure 1 D.s.c. heating curves recorded at 10°C min^{-1} for the telechelic polystyrene PS-N and the related zwitterionic polymers PS-Zw_1 and PS-Zw_4

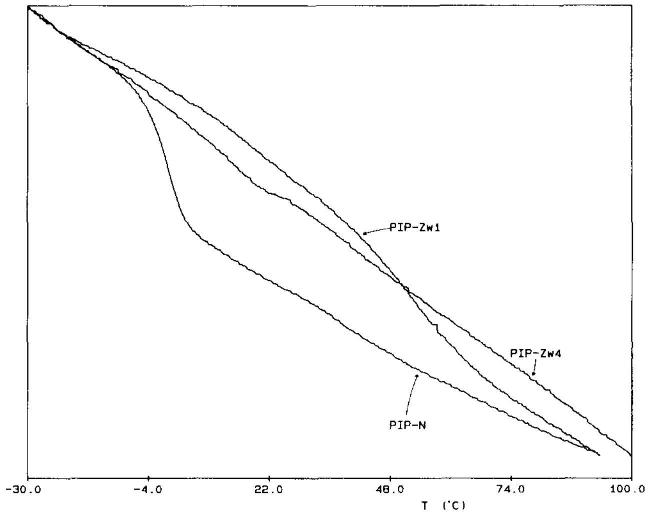


Figure 2 D.s.c. heating curves for the telechelic polyisoprene PIP-N and the related zwitterionic polymers PIP-Zw_1 and PIP-Zw_4

Table 1 SEC characterization of the aminated telechelic polymers and their related functionalized materials

	PS-N	PS-Q_4	PS-Zw_4	PS-Zw_1	PIP-N	PIP-Zw_4
M_n	7800	7600	7400	8100	10000	4600
M_w	8750	7900	8100	9400	13700	7800
I	1.12	1.04	1.09	1.16	1.37	1.69

Three μ-styragel columns with porosities of 10^3, 50 and 10 nm. PS-Q refers to the intermediate ammonium bromide form and 99°C for PS-Zw$_1$. In contrast to the PIP samples, there is no broadening of the glass transition domain of the zwitterionic PS. It might be concluded that the efficiency of a possible crosslinking process is then very poor. This could be accounted for by the temperature range in which the glass transition occurs, i.e. a much higher temperature range for PS than for PIP. It has been observed that the mutual interactions of carboxylatobetaines grafted onto PS decrease drastically with temperature[30]. Indeed, when the intercharge length corresponds to four methylene groups, the solution viscosity either in THF or in toluene shows that only a very partial aggregation persists around 100°C. Although the increase in T_g promoted by the carboxylatobetaine end groups depends on the nature of the polymer, the shorter the intercharge length of the carboxylatobetaine the more pronounced is its effect on T_g. This is consistent with the solubility behaviour and it probably means that the association strength of smaller size carboxylatobetaines is greater.

The effect of the zwitterionic end groups on T_g of the base polymer deserves additional comment. In a previous paper dealing with the glass transition behaviour of carboxylato-telechelic polymers, it was concluded that in rubbery materials (T_g of the precursor is a few degrees lower) the metal carboxylate end-groups have no effect on T_g (Reference 33). This observation has been reported several times, particularly for PIP of the same microstructure as in this study. According to the data of *Figure 1*, the carboxylatobetaine end groups would behave in a very different way. In contrast, for thermoplastics, annealing above T_g suppresses first an initial plasticization effect[33] and finally leads to an increase in T_g by <10°C for polystyrene and usually >10°C for poly(α-methylstyrene)[34]. This behaviour has been observed for both metal carboxylate and metal sulphonate end groups. The data in *Figure 2* are in a qualitative agreement and do not confirm the contrasting behaviour of carboxylatobetaines and metal carboxylates in telechelic rubbers. The T_gs of zwitterionic telechelic rubbers other than PIP of a mainly 3–4, 1–2 microstructure should be analysed before any definite conclusion can be drawn.

Solution behaviour

As generally observed for any type of ionomer, solutions are highly viscous in a low polarity solvent. Reduced and inherent viscosities have been measured in toluene and plotted against the polymer concentration in a range well below the overlap concentration $c^* \approx [\eta]^{-1}$ of the precursor polymer. The inherent viscosity of the precursor polystyrene was found to be 0.11, in good agreement with the molecular weight determined by SEC and the Mark–Houwink coefficients: $k = 1.7 \times 10^{-4}\,\text{dl}\,\text{g}^{-1}$ and $a = 0.69$. The c^* concentration should accordingly be close to $10\,\text{g}\,\text{dl}^{-1}$. As shown in *Figures 3* and *4*, the experimental data cannot be fitted by the Huggins equation

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

The non-linear decrease of the reduced viscosity with decreasing c reflects the character of the aggregation process. If the aggregation state was steady, the molecular size would be independent of the concentration and the Huggins-type behaviour obeyed. A change in the intercharge length of the carboxylatobetaine attached at both ends of polystyrene does have a great effect on the reduced viscosity in toluene. Going from one to four methylene groups in the zwitterion structure only has an effect on the viscosity at polymer concentrations $\gtrsim 2\,\text{g}\,\text{dl}^{-1}$. Above that concentration, the association of the Zw$_4$ units is more effective in increasing the reduced viscosity than that of the Zw$_1$ units.

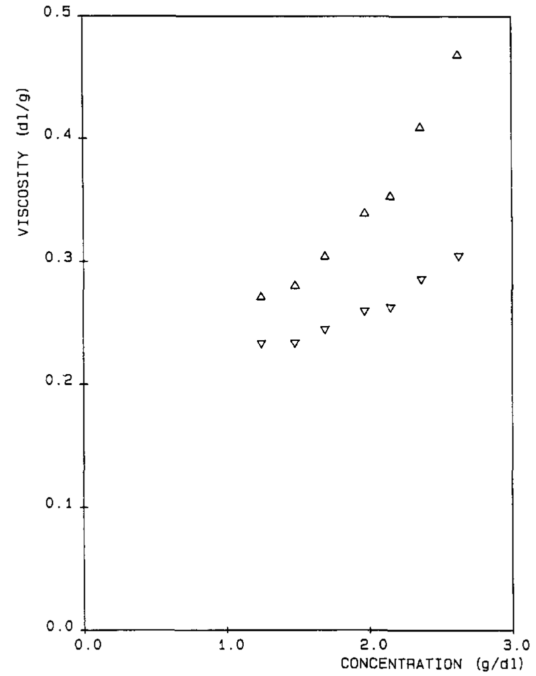


Figure 3 Reduced (Δ) and inherent (∇) viscosities of solutions of telechelic polyisoprene with carboxylatobetaine end groups, PIP-Zw$_4$, in toluene at 20°C

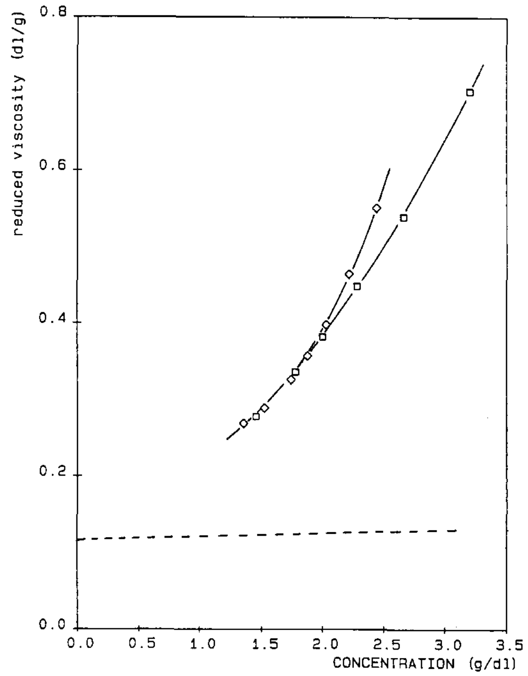


Figure 4 Dependence of reduced viscosity of solutions of carboxylatobetaine telechelic polystyrenes in toluene on intercharge length. □, PS-Zw$_1$; ◇, PS-Zw$_4$. ---, Reduced viscosity of the precursor aminated polystyrene

The average aggregation number N_{ag} at any concentration has been estimated from the molecular weight of the telechelic polymer and that of the base polymer whose molecular weight would have the same reduced viscosity as the associated telechelic chains in the same solvent at the same concentration[29]. Then, $N_{ag} = M_{app}/M_0$. It is assumed that the intrinsic viscosity of the base polymer obeys the Mark–Houwink–Sakurada (MHS) law and can be derived from the Huggins law (1) and the η_{red} and k_H values. The Huggins constant k_H of PS is supposed to be equal to 0.33 over the whole range of molecular weights considered. The dependence of k_H on molecular weight has been estimated elsewhere on the basis of the expansion factor[35] and actually has little effect on the aggregation number.

From the reduced viscosity at a given concentration, the Huggins and MHS laws allow calculation of the intrinsic viscosity $[\eta]_{Zw}$ and the molecular weight of the base polymer which would display the same viscosity at the same concentration. Since two polymers of the same nature but of different molecular weights (M_0 and M_{app}) are compared and since the MHS law is assumed to be valid, N_{ag} may be written as follows:

$$N_{ag} = ([\eta]_{Zw}/[\eta]_0)^{1/a} \qquad (2)$$

where a is the exponent of the MHS law. Recently, Hara has discussed the solution behaviour of some samples of metal carboxylato-telechelic polybutadiene in THF[36] and calculated N_{ag} on the basis of an equation equivalent to equation (2). In this work, Hara has assumed that both the precursor and the ionomer display the same expansion factor (α), independent of the molecular weight, so he has used equation (2) with $a = 0.5$.

The aggregation numbers of the zwitterionic telechelic polystyrenes PS-Zw$_1$ and PS-Zw$_4$ have been calculated according to equation (2) and plotted against concentration in *Figure* 5. The curves have been extrapolated to $N_{ag} = 1$ at zero concentration since aggregates should be completely dissociated in this limit. Similarly to the reduced viscosity, N_{ag} values depend on the intercharge length of the carboxylatobetaine only above ≈ 2 g dl^{-1}. In fact, N_{ag} has been underestimated since the aggregation process leads to branched polymers. Therefore, the intrinsic viscosity must be modified as follows:

$$[\eta]_B = g^x[\eta]_L \qquad (3)$$

where the subscripts B and L refer, respectively, to branched and linear polymers having the same molecular weights. The coefficient g is <1 and depends on the number of branching points (P) and on their functionality (f). The exponent x depends on the solvent and varies from 0.5 (good solvent) to 1.5 (θ solvent)[37,38]. Toluene is a good solvent for polystyrene and the zwitterionic moieties behave as branching points, so x might be equal to 0.5. M_{app} must accordingly be modified by a factor $g^{-1/2a}$ with respect to the previous values. As an example, let P and f be equal to 5 and 3, respectively. Then $g = 0.698$ (Reference 37) and both M_{app} and N_{ag} have to be multiplied by 1.3, which does not make a decisive difference.

When an ionomer and its telechelic counterpart are available, something can be learnt about the effect of the distribution mode of the ionic groups along the polymeric backbone on the association process. *Figure 5* compares the aggregation numbers of PS-Zw$_4$ and PS-Zw$_1$ with those calculated for a polystyrene sample randomly grafted with carboxylatobetaine groups of intercharge length 4. The number average molecular weight of that sample is 120 000 and the average number of zwitterionic units per chain is 25. Thus [Zw]/[styrene] $\approx$ 1/50 in the telechelic polymer and the related ionomers. Undoubtedly, N_{ag} of the ionomer varies more rapidly (by about a factor of two) with concentration than that of the telechelic polystyrene. This probably reflects the larger number of intermolecular interactions per polymer chain for ionomers. Any telechelic polymer chain has two interaction sites compared with 25 potential sites in the ionomer. Of course, these figures are only indicative since steric hindrance can prevent some interactions from occurring. If the intrinsic viscosity was modified for the branching effect, values would be obtained which should enhance the difference in the aggregation to the advantage of the ionomer (i.e. the more branched polymer).

When plotted on a semilog arithmetic scale, the N_{ag} data exhibit a linear dependence on concentration for the ionomer and the telechelic PS carrying the Zw-4 groups. Note, however, that these straight lines do not pass through the origin as they should do. In the concentration range where log(N_{ag}) *versus* c is linear, the rate of aggregation for the ionomer is about twice that for the telechelic PS. As a tentative comparison, we mention that Hara has reported a slope of 0.94 for the sodium salt of a carboxyl terminated polybutadiene (Hycar CTB; $M_n = 4200$) in THF[36], compared with 0.35 for PS-Zw$_4$ and 0.68 for the randomly grafted ionomer. Finally, log(N_{ag}) of PS-Zw$_1$ is no longer linear against concentration at concentrations >2 g dl^{-1}. The aggregation seems to level off progressively at increasing concentrations. Similar behaviour has been observed for telechelic polyisoprene end-capped by both quaternary ammonium salts and complexed amines by transition metal salts. It has been attributed to a steric hindrance in the association of bulky end-groups[20].

It is worth noting that according to the theoretical predictions made by Bredas *et al.* ammonioalkyl-

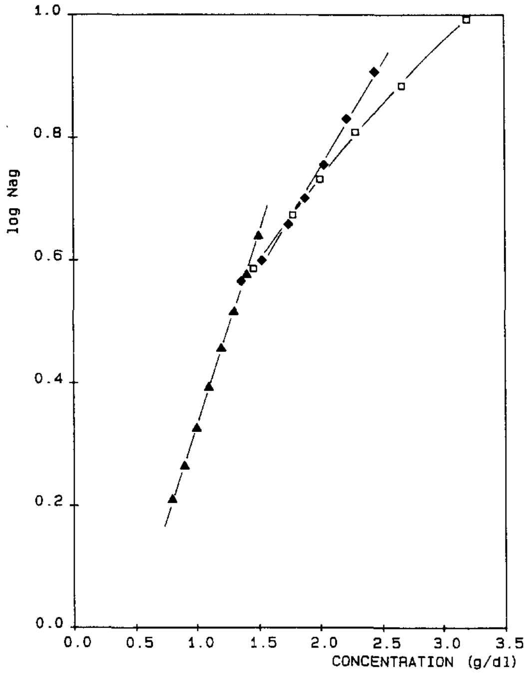


Figure 5 Dependence of aggregation number on both intercharge length and distribution of carboxylatobetaine moieties on the polystyrene backbone for telechelic polystyrenes with carboxylatobetaine end-groups, PS-Zw$_1$ (□) and PS-Zw$_4$ (◆), and randomly grafted polystyrene with carboxylatobetaine groups (intercharge length is four methylene groups) (▲). [Zw]/[styrene] $\approx$ 1/50 in all the cases

sulphonate zwitterions should adopt an extended structure when associated instead of the curled structure of the free zwitterions[22]. When ammonioalkylcarboxylatobetaines are concerned, *Figure 5* shows that formation of large aggregates is restricted when the alkyl group is methyl instead of n-butyl. It might be rationalized that the bulkiness of the ions pairs increases when the interchange length decreases. Accordingly, the repulsive forces would be enhanced and the size of the aggregates reduced. In the low concentration range (<2 g dl^{-1}), i.e. when the degree of association increases linearly with c, both PS-Zw$_1$ and PS-Zw$_4$ appear to be associated to the same extent. This means that the strengths of the dipolar interactions do not depend significantly on the intercharge length (methyl or n-butyl). This observation in solution is in contrast to that in bulk where the interactions of the Zw$_1$ zwitterionic groups appear to be higher than those of Zw$_4$. The latter observation conflicts with the higher dipolar moments of Zw$_4$ compared with Zw$_1$ and with the predictions by Bredas *et al.*[22]. A systematic study of a series of ammonioalkylcarboxylatobetaines is thus required to obtain a reliable picture of both strength and size of the aggregates.

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