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Dilute solution behaviour of carboxylatobetaine end-capped polyisoprenes

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The synthesis and characterization of polyisoprene bearing carboxylatobetaines of various intercharge lengths, either at one or at both ends of the polymer chain, are described. Peculiar properties such as associative behaviour may be expected due to their original functionalization. These materials are prepared by anionic polymerization of isoprene and deactivation with dimethylaminopropyl chloride, followed by reaction with bromoalkyl ethyl carboxylic esters and subsequent hydrolysis. Highly viscous solutions are obtained when the polymers are dissolved in solvents of low polarity. Average aggregation numbers are calculated from the viscosity results, which depend on the molecular weight of the aminated precursor polymer as well as the intercharge length of the zwitterionic groups. The effects of temperature and polar additives are also considered.

(Keywords: polyisoprenes; solution behaviour; carboxylatobetaines)

INTRODUCTION

The solution properties of hydrophobic polymers are dramatically modified when the macromolecules contain a small molar percentage of ionic side groups (ionomers). In non-polar solvents, aggregation processes occur due to mutual electrostatic interactions of the ion pairs which protect themselves from the unfavourable environment and produce clusters, which may persist well below the coil overlap concentration c^*. Lightly sulfonated polystyrenes and styrene–methacrylic acid copolymers are well known examples of such ionomers. Strong associations cause high viscosities and sometimes gelation in the bulk or in low-polarity solvents. The behaviour of ionomer solutions has been described in some recent reviews[1,2]. These associations are strongly temperature dependent and may lead to physically reversible networks.

End-capped ionomers with well defined architecture and several intercharge lengths have been synthesized as models in an attempt to understand the fundamental structure–property relationships. For example, Teyssié and coworkers have synthesized halato-telechelic polymers consisting of carboxylato or sulfonato polydienes or polystyrenes neutralized with metal salts[3,4]. The solution viscosity rises very rapidly when concentration increases, which leads to gelation. The critical concentration of gelation C_{gel} depends on the polymer molecular weight according to the relationship $C_{gel} = KM^{-0.5}$, where K depends on the polymer–solvent–temperature system. Hara and coworkers introduced the notion of degree of aggregation by comparing the viscosities of α–ω-alkali metal carboxylate polybutadienes with that of the acid form[5]. Kennedy and coworkers investigated the properties of sulfonated polyisobutene telechelic ionomers[6].

The behaviour of telechelic amino polymers quaternized with alkyl halides has been studied by Teyssié and coworkers[7,8]. In contrast to metal carboxylate and sulfonate telechelic polymers, gelation never occurs, even in apolar solvents, although a rapid initial growth of viscosity with concentration is noticed. The viscosity decreases as the alkyl chain length increases from methyl to propyl, and then tends to level off.

Zwitterionic (also known as betaine) polymers are potentially interesting associating structures because the anion and the cation 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 classes of ionomers. The sulfonatobetaines are the well known representatives of this class of ionomers and have been extensively studied by many authors[9–12]. They are quite chemically accessible, although restricted to only one intercharge length ($n = 3$) because propanesultone is the only available reactant. Polymers with only one zwitterion group form large aggregates and those containing two or more functional units per chain give rise to gels in cyclohexane. It was noticed that gelation never occur in aromatic solvents, owing to the greater polarizability of the aromatic ring[12].

Carboxylato-, phosphonato- or phosphinatobetaines grafted on polymer backbones have also been proposed[13]. The synthesis and characterization of polymers with carboxylatobetaines randomly scattered

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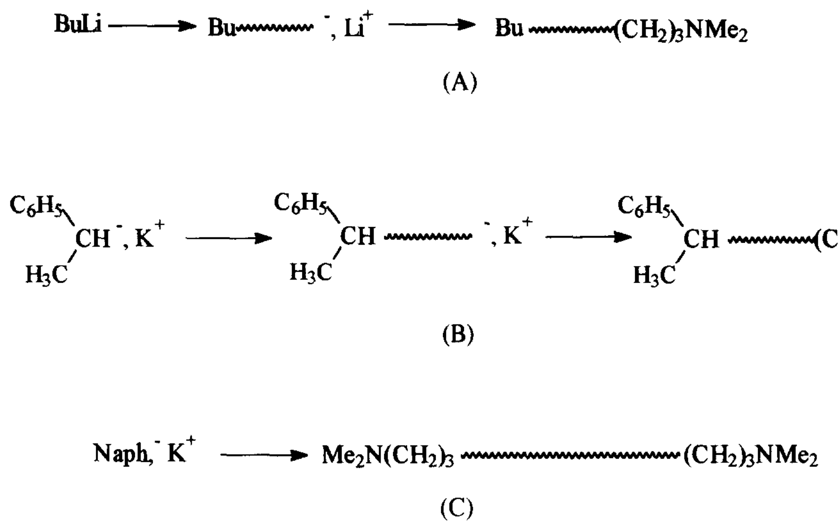


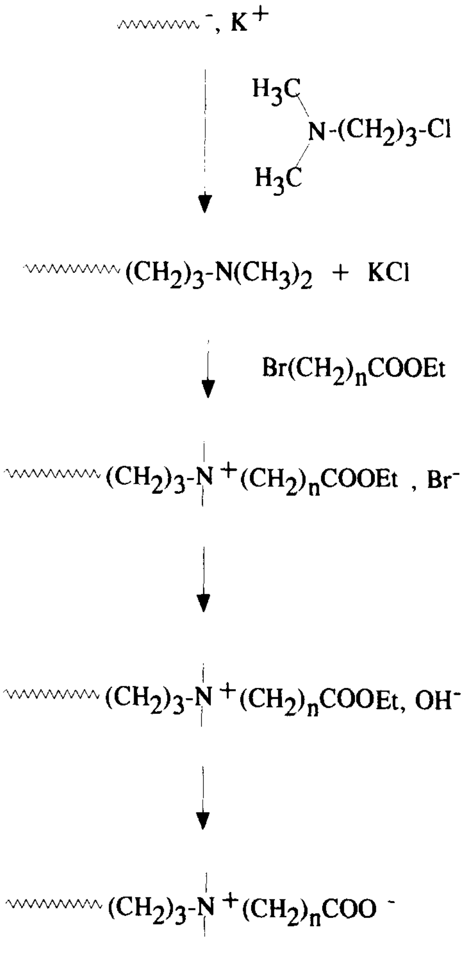
Scheme 1

along the polystyrene chains have been reported and the association processes in solution studied by viscosity and static light scattering experiments[14]. In order to extend this study, telechelic polystyrenes bearing such carboxylatobetaines have been prepared and the average aggregation numbers were compared with those of randomly grafted carboxylatobetaines[15]. It was found that the aggregation number of randomly grafted polystyrene increases more rapidly with concentration than that of the telechelic polymers, reflecting stronger intermolecular interactions per polymer chain.

This paper deals with the preparation and study of solution properties of polyisoprenes bearing such carboxylatobetaines at either one end (semitelechelic) or at both ends (telechelic) of the polymer chain. Monofunctional polymer chains display an increasing interest since gelation processes can theoretically be avoided[16]. Polyisoprenes were prepared anionically in order to have a narrow molecular-weight distribution. Different initiators were used, according to the desired functionality. Furthermore, the deactivation of the macroanions by a convenient agent allows us to obtain easily quantitatively functionalized polymers.

In any case, the reaction pathway involves the quaternarization of a dimethylamino end-group, which obviously needs to get tertiary amine groups grafted on the polymer chains. In the case of telechelic polymers, the polymerizations were carried out in tetrahydrofuran (THF) with naphthalene–potassium as initiator, leading to macrodianions, which were reacted by an aminated molecule, namely the dimethylaminopropyl chloride (DMAPC) first proposed by the Belgian team[4], resulting in two terminal amine groups on each polymer chain.

In the case of semitelechelic polymers, this group could be produced either by using an initiator carrying an amino group or deactivating the macroanion by an aminated molecule. The first procedure was chosen by Fetters and coworkers[12] and Stewart *et al.*[17], using 3-dimethylaminopropyl lithium as initiator, synthesized by reaching DMAPC with lithium. We chose a second way, namely deactivating the macroanions with DMAPC. The polymerizations were carried out either in cyclohexane or THF with s-BuLi as initiator and in THF with phenyl-1-ethyl potassium[18] as initiator (*Scheme 1*).



Scheme 2

The dimethylamine end-groups were reacted with the appropriate ω-bromoalkyl ethylcarboxylic ester, $Br(CH_2)_nCOOEt$, in excess. Ammonium bromide end-groups were generated accordingly and treated with aqueous NaOH until the ammonium hydroxide functions were formed. By heating, these end-groups were converted into the zwitterionic forms by elimination of an ethanol molecule. This reaction pathway is shown schematically in *Scheme 2*.

Table 1 Average molecular weights of amine-capped polyisoprenes: the molecular weights of samples collected before deactivation by DMAPC are reported in the three first columns

Sample	M_n[a]	M_w[a]	Sample	M_n[a]	M_w[a]	M_w[b]	$[\eta]$[c] ($dl\,g^{-1}$)
PI_1	15100	21160	PI_1–N	15000	21000	24800	–
PI_4	44000	53700	PI_4–N	44000	55000	–	–
PI_6	23100	25900	PI_6–N	23200	26000	28200	0.382
PI_7	18000	21000	PI_7–N	20000	25000	24600	0.339
			PI_8–N	14000	15900	15000	0.265
			PI_9–N	10000	11300	–	0.204

[a] From s.e.c. in THF with 1,4-polyisoprenes as standards
[b] From light scattering in THF
[c] From intrinsic viscosity measurements

EXPERIMENTAL

Synthesis of polymers

THF was dried by refluxing over benzophenone–sodium and distilled under a nitrogen atmosphere. Isoprene was mixed with a n-BuLi and distilled before polymerization. DMAPC was obtained from the corresponding commercially available hydrochloride, neutralized by NaOH in water, extracted with ether and dried over CaH_2 under argon for 3 days. Phenyl-1-ethyl potassium was prepared by reaction of bis(phenyl-1-ethyl) oxide with potassium as described by Beinert and Zilliox[18], while s-BuLi was prepared from 2-chlorobutane and lithium in suspension in cyclohexane. The naphthalene–potassium reagent was obtained by mixing naphthalene and potassium in THF.

Polymerizations were carried out under argon in previously flamed and argon-purged flasks over 24 h at room temperature. The molecular weights were controlled by the monomer/initiator ratio. After reaction, the macroanions were reacted with an excess of DMAPC. Polymers were recovered and purified by repeated precipitation into methanol containing a small amount of Irganox 1010 (Ciba-Geigy) as antioxidant.

The dimethylamine end-groups were reacted with the appropriate ω-bromoalkyl ethylcarboxylic ester $Br(CH_2)_nCOOEt$ in excess at 60°C for three days in THF. After concentration of the solution, the quaternized polymer was recovered by precipitation in methanol and dried. The polymer is then dissolved in THF and a 1 N NaOH solution in water was slowly added until the solution became cloudy. This mixture was heated at 60°C for 1 h at ambient pressure, and then at reduced pressure in order to remove the residual ethanol and THF. The polymer precipitated slowly during this evaporation. It was washed with methanol and then dried under vacuum.

In the following, the symbols PI_m–N and N–PI_m–N refer to the semitelechelic and telechelic amine-capped precursor polyisoprenes, respectively; PI_m–Z_n and Z_n–PI_m–Z_n refer to the derived zwitterionic polymers where n specifies the intercharge length.

Characterizations

All the reaction products were examined by ^1H nuclear magnetic resonance (n.m.r.) and Fourier transform infra-red spectroscopy[13]. The characteristic bands of the dimethylamine end-groups at 2813 and 2771 cm^{-1} (ν_aC–N and ν_sC–N) disappeared after quaternarization in favour of the ν_aC=O of the carbonyl group. The latter is shifted down to 1580 cm^{-1} after conversion into the betaine form.

Potentiometric titration of the dimethylamine end-groups was performed with perchloric acid in a toluene/methanol (90/10) mixture, which allows determination of the yield of the deactivation by DMAPC.

Polymers were examined by size exclusion chromatography (elution with THF at room temperature on crosslinked polystyrenes; calibration with 1,4-polyisoprene standards). Polyisoprene microstructures were determined by ^1H n.m.r. spectroscopy[19].

Solution viscosities were performed by using a Ubbelohde viscometer with a temperature-controlled bath. Solutions were prepared in dried solvents and were centrifuged just before measurements were made. Measurements were repeated until good reproducibility was obtained. When the viscosity plots followed a Huggins-type behaviour, the intrinsic viscosity $[\eta]$ was deduced from the concentration dependence, as follows:

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

Light scattering measurements were performed on a Sofica-type photometer using polarized light of wavelength 632.8 nm from a He–Ne laser. The refractive index increments dn/dc were obtained by using a Brice-Phoenix differential refractometer. The dn/dc values are in the 0.122–0.144 range, of the same order (0.123) as that reported by Hadjichristidis *et al.*[20].

RESULTS AND DISCUSSION

Characterization of the semitelechelic amine-capped polyisoprenes

The average molecular weights were measured by size exclusion chromatography (s.e.c.) and static light scattering and are reported in *Table 1*. Before deactivation of the macroanions with DMAPC, some samples were collected and recovered by precipitation with methanol and characterized by s.e.c. No change in the molecular weights was noticed after functionalization.

The microstructure of the polyisoprenes has been determined by ^1H n.m.r. spectroscopy and depends on both the solvent of polymerization and the counterion[21,22]. A polar solvent such as THF decreases the content of 1,4 units. Using potassium instead of lithium as counterion also decreases the amount of these units, as seen in *Table 2*.

Table 2 Microstructure of amine-capped semitelechelic polyisoprenes[a]

Solvent	Sample	Units (%) 1,4-	3,4-	1,2-
THF	PI_1	17	43	40
THF	PI_2	17	48	35
THF	PI_3	16	47	37
Cyclohexane	PI_4	89	6	5
Cyclohexane	PI_6	90	10	–
Cyclohexane	PI_7	92	8	–
Cyclohexane	PI_8	89	11	–

[a] s-BuLi used as initiator in all cases

Table 3 Calculated[a] and experimental radii of gyration values of semitelechelic amine-capped polyisoprenes

Sample	M_n	M_w	$R_G(M_n)$ (nm)	$R_G(M_w)$ (nm)	R_G(exp) (nm)
PI_1–N	–	24 800	–	6.5	7.3
PI_6–N	23 200	26 000	6.4	6.7	7.8
PI_7–N	20 000	25 000	5.9	6.5	6.8
PI_8–N	14 000	15 900	4.8	5.0	5.5
PI_9–N	10 000	11 300	3.9	4.2	–

[a] From M_n and M_w values

Elemental analysis for nitrogen showed that the deactivation of the macroanions with DMAPC was total. Too high molecular weights made the potentiometric titrations unsuccessful.

In order to obtain reference values for further comparisons, viscosity measurements on dilute solutions were performed in toluene. The $[\eta]$ values are slightly higher than those proposed by Davidson *et al.*[12] for polyisoprene with amine end-groups ($[\eta] = 1.72 \times 10^{-4} M^{0.74}$). Both intrinsic viscosity–molecular weight relationships ($[\eta]-M_n$) and ($[\eta]-M_w$) were derived, although the accuracy was low owing to the very restricted molecular weight range.

$$\begin{aligned} [\eta] &= 2.3 \times 10^{-4} M_n^{0.73} \quad (\mathrm{dl\,g^{-1}}) \\ [\eta] &= 3.2 \times 10^{-4} M_w^{0.69} \quad (\mathrm{dl\,g^{-1}}) \end{aligned} \tag{2}$$

The intrinsic viscosity allows us to deduce the radius of gyration of the polymer chain. For a linear chain, it is well known that the following relationship applies:

$$[\eta] = KM^a = \frac{\Phi_0}{M}(6\langle R_G^2\rangle)^{3/2} \tag{3}$$

which gives:

$$\langle R_G\rangle = \left(\frac{1}{6}\right)^{1/2}\left(\frac{KM^{1+a}}{\Phi_0}\right)^{1/3} \tag{4}$$

where $\Phi_0 = 2.1 \times 10^{23}\,\mathrm{mol^{-1}}$ (K expressed in ml g^{-1} and $\langle R_G\rangle$ in cm) in the case of narrow-molecular-weight distributions. As shown in *Table 3*, experimental and calculated values are in a good agreement and can be used as references. The question of the accuracy of the R_G value for PI_1–N which displays only 17% 1,4-units will be discussed in the next section.

Telechelic polyisoprenes

The polymerizations were performed in THF with naphthalene–potassium as initiator. The n.m.r. spectroscopic analysis yields microstructure values of ~ 12% 1,4-, 55% 3,4-, and 33% 1,2-units.

Molecular weights and functionalization results are reported in *Table 4*. Weight-average molecular weights determined from s.e.c. and light scattering results are in a good agreement, although 1,4-polyisoprenes were used as standard for s.e.c. measurements. This feature was already pointed out with semitelechelic polyisoprenes prepared in THF (PI_1–N in *Table 1*). Values for K and a have been deduced from viscosity measurements, namely 6.59×10^{-4} and 0.61, respectively but their accuracy may be questionable since they are obtained in a restricted molecular-weight range. In fact, calculations show that the intrinsic viscosity values related to any molecular weight located in this range are almost the same, whatever the set of K and a values.

Finally, both elemental analysis and potentiometric titration of nitrogen showed that the deactivation of the macroanions with DMAPC was almost total, so the functionality of these polymers is close to 2.

Solution behaviour of the zwitterionic polymers at room temperature

As previously observed with all ionomers, functionalization of polyisoprenes leads to highly viscous solutions when dissolved in low polar solvents, the behaviour of which cannot be described by the Huggins equation (*Figure 1*). This non-linear decrease of η_{red} with decrease in concentration has been interpreted in terms of a dynamic aggregation process[15].

Table 4 Characterization of the aminated telechelic polyisoprenes in THF

Sample	M_n[a]	M_w[a]	d*n*/d*c*	M_w[b]	$[\eta]$ (dl g^{-1})	%N[c]	%N[d]
N–PI_2–N	4650	5600	–	–	–	96	92
N–PI_3–N	5600	5650	0.142	5550	0.130	100	100
N–PI_4–N	10 250	13 200	0.131	15 400	0.198	94	92
N–PI_5–N	10 950	12 200	0.122	13 100	0.210	100	100
N–PI_6–N	14 300	18 300	0.124	15 500	0.233	100	96
N–PI_7–N	18 450	20 300	–	–	0.294	95	94
N–PI_8–N	25 200	30 250	0.144	27 400	0.365	94	92

[a] Average molecular weights from s.e.c.
[b] Average molecular weights from static light scattering measurements
[c] Functionalization results from elemental analysis
[d] Functionalization results from potentiometry

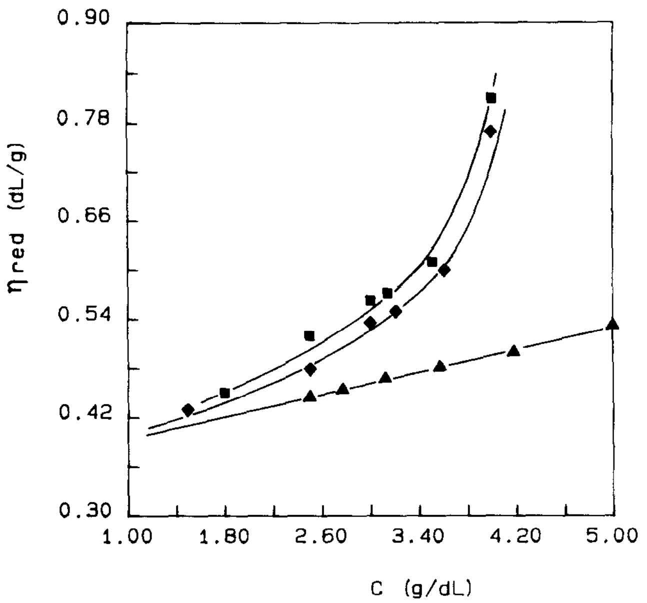


Figure 1 Reduced viscosity vs. polymer concentration for zwitterionic telechelic polyisoprenes in toluene at room temperature, where the molecular weight of the precursor aminated polyisoprene is the same (M_n = 25 200) in all cases: (▲) N–PI$_8$–N; (◆) Z$_1$–PI$_8$–Z$_1$; (■) Z$_4$–PI$_8$–Z$_4$

Determination of the aggregation number from the viscosity data

As previously discussed by Bodycomb and Hara[5] and Jérome and coworkers[8], we assume that we are faced with dynamical aggregates, the size of which increases with the concentration of individual zwitterionic polymers. The molecular weight is thus an apparent molecular weight M_{AG} which can be defined as follows:

$$M_{AG} = N_{AG} M_0 \qquad (5)$$

where M_0 is the molecular weight of the individual zwitterionic chain and N_{AG} is the aggregation number.

At any concentration, the aggregates are likened to classical polyisoprene macromolecules which would follow the Huggins law with a characteristic intrinsic viscosity $[\eta]_{AG}$, as follows:

$$\eta_{red} = [\eta]_{AG}(1 + k_H[\eta]_{AG}c) \qquad (6)$$

where k_H is the Huggins constant previously determined from the viscosity studies on amine-capped precursor polyisoprenes. It is assumed that k_H keeps the same value over the whole of the molecular weight range being considered.

Knowing η_{red} and c allows us to determine the intrinsic viscosity $[\eta]_{AG}$ of the equivalent amine-capped polyisoprene from the Huggins equation which is second-order in $[\eta]_{AG}$:

$$k_H c([\eta]_{AG})^2 + [\eta]_{AG} - \eta_{red} = 0 \qquad (7)$$

Thus:

$$[\eta]_{AG} = \frac{-1 + \sqrt{1 + 4k_H c\eta_{red}}}{2k_H c} \qquad (8)$$

According to Bodycomb and Hara[5], the apparent molecular weight of the aggregates can be determined by considering the Flory–Fox equation:

$$[\eta]_{AG} = K_\theta \alpha^3 (M_{AG})^{0.5} \qquad (9)$$

provided K_θ and α are the same for both the aggregates and the individual molecules. Indeed, Lantman *et al.*[23] showed that the individual sizes of the ionomer molecules are not perturbed when forming aggregates. The aggregation number will be given by the following:

$$N_{AG} = \frac{M_{AG}}{M_0} = \left(\frac{[\eta]_{AG}}{[\eta]_0}\right)^{\frac{1}{0.5}} \qquad (10)$$

This relationship was first used by Bodycomb and Hara[5] to determine the aggregation numbers of α,ω-metal carboxylato end-capped polybutadienes in THF and more recently by Jérome and coworkers for α,ω-(dimethylamino) polyisoprene coordinated to transition metal salts.

The Mark–Houwink equation gives another relationship between molecular weight and viscosity:

$$[\eta]_{AG} = K(M_{AG})^a \qquad (11)$$

with the same assumptions as made previously, namely that K and a keep the same values for all of the moieties. Equations (10) and (11) become the same in θ solvents ($a = 0.5$). Thus:

$$N_{Ag} = \frac{M_{AG}}{M_0} = \left(\frac{[\eta]_{AG}}{[\eta]_0}\right)^{\frac{1}{a}} \qquad (12)$$

We have already used this relationship when dealing with carboxylatobetaines, either randomly grafted on a polystyrene backbone[14], or located at both ends of polyisoprene or polystyrene[15].

We report below the main features of the dilute solution behaviour of both telechelic and semitelechelic zwitterionic polyisoprenes.

The telechelic polymers

The results of characterization by s.e.c. in THF of the telechelic polymers are reported in *Table 5*. Molecular weights appear to be lower than the amine-capped

Table 5 Characterization of telechelic polymers by s.e.c. in THF

			n^a					
	Amine-capped polymer		1		4		10	
Sample	M_n	M_w	M_n	M_w	M_n	M_w	M_n	M_w
PI$_4$	10 230	13 200	2540	3850	2670	3800	2 530	3 800
PI$_5$	10 900	12 170	2790	4720	7440	10340	2 720	5 410
PI$_6$	14 320	18 280	6050	9060	–	–	6 000	10 020
PI$_8$	25 200	30 240	–	–	–	–	10 200	22 000

^{a} Intercharge length

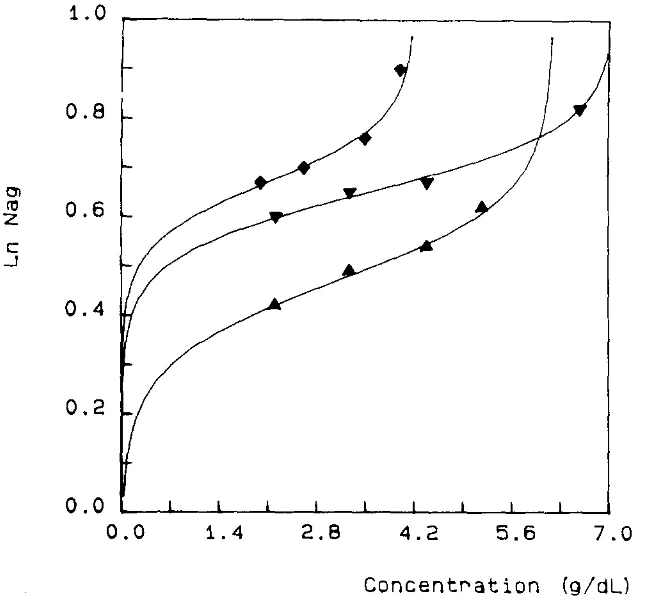


Figure 2 Dependence of the aggregation number on the molecular weight of the aminated precursor polyisoprene: (◆) Z_4–PI_4–Z_4 ($M_n = 10250$); (▼) Z_4–PI_6–Z_4 ($M_n = 14300$); (▲) Z_4–PI_7–Z_4 ($M_n = 18450$). The full line curves are only to visualize the general trends

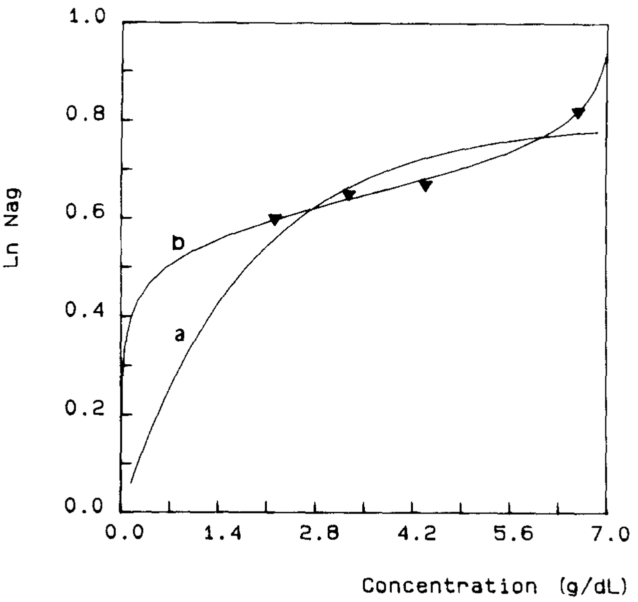


Figure 3 Attempts at fitting for PI_6–Z_4 with both (a) exponential and (b) sigmoidal models; the best parameters for the curves were determined by a non-linear least-squares procedure

polyisoprenes, which is inconsistent with the fact that the solutions are more viscous. This behaviour was already pointed out when studying carboxylatobetaines randomly grafted on polystyrene backbones and has been attributed to retention of microgels either on the column filters or inside the columns themselves[14].

The aggregation numbers N_{AG} have been measured in toluene and plotted vs. the concentration (*Figure 2*). The values are of the order 1–10 and depend strongly on a number of parameters, as described in the following.

(*i*) The aggregation numbers increase with the concentration of the polymer in solution, according to a somewhat peculiar behaviour: they begin to increase rapidly in the low-polymer-concentration range, slow down and then tend to increase again. Therefore, this behavior cannot be simply related to the previous ones which have been described so far.

In the low-concentration range, the behaviour could be likened to that observed by Jérôme and coworkers with α,ω-(dimethylamino) polyisoprenes quaternized with alkl iodides[7] or coordinated to transition metal salts[8], which has been described by the following empirical equation:

$$\log N_{AG} = b[1 - \exp(-kc)] \tag{13}$$

The values of b and k can be calculated by a non-linear least-squares method (based on minimization of the first derivatives of the function). In the high-concentration range, it becomes difficult to appreciate the true behaviour, because of the lack of experimental points. It could be described by the exponential dependence observed by Bodycomb and Hara[5] for α,ω-alkali metal carboxylato polybutadienes, for which no gelation process occurs:

$$\log N_{AG} = \beta c \tag{14}$$

In the case of α,ω-alkaline earth metal carboxylato polymers, gelation occurs with a vertical straight line being displayed. It is difficult in our case to check whether or not the $\log \eta_{rel}$–concentration plot displays a vertical asymptote which is characteristic of the gelation process[3]. If assuming that gelation processes take place, sigmoidal curves can be used to depict the general trend, as follows:

$$\log N_{AG} = K\left\{\frac{1}{1 + \exp[-b(c-a)]}\right\} \tag{15}$$

The values of K, b and a can be calculated by a non-linear least-squares method. As an example, *Figure 3* shows the attempts at fittings for one of the zwitterionic polyisoprenes. The same trend is observed for all of the polymers.

In fact, carboxylatobetaine end-capped polyisoprenes can be considered at the same time as quarternized α,ω-(dimethylamino) and ammonium salts of α,ω-carboxylato polyisoprenes, so that it could be thought that both respective behaviours could be observed, namely a slowing down which is due to the quarternized amino groups and a gelation process which is attributed to the carboxylate end groups. Nevertheless, it is difficult to understand why the effects would be separated on the concentration scale.

This behaviour could be explained better by a first formation of pairs of interacting dimers by antiparallel arrangement of the head dipoles, followed by aggregation of these dimers for higher concentrations, in order to give rise to string or tube structures (*Figure 4*). This view is supported by the molecular modeling results of Bredas *et al.* who confirmed that aggregates can be adequately described as pairs of interacting dimers since the chain–chain average distance between the dimers is larger than within the dimers[24].

(*ii*) For the same intercharge length, N_{AG} increases as the molecular weight of the parent polyisoprene decreases. This observation is easily explained when considering that for a given concentration (in $g\,dl^{-1}$) of the polymer chains, a higher molecular weight leads to a

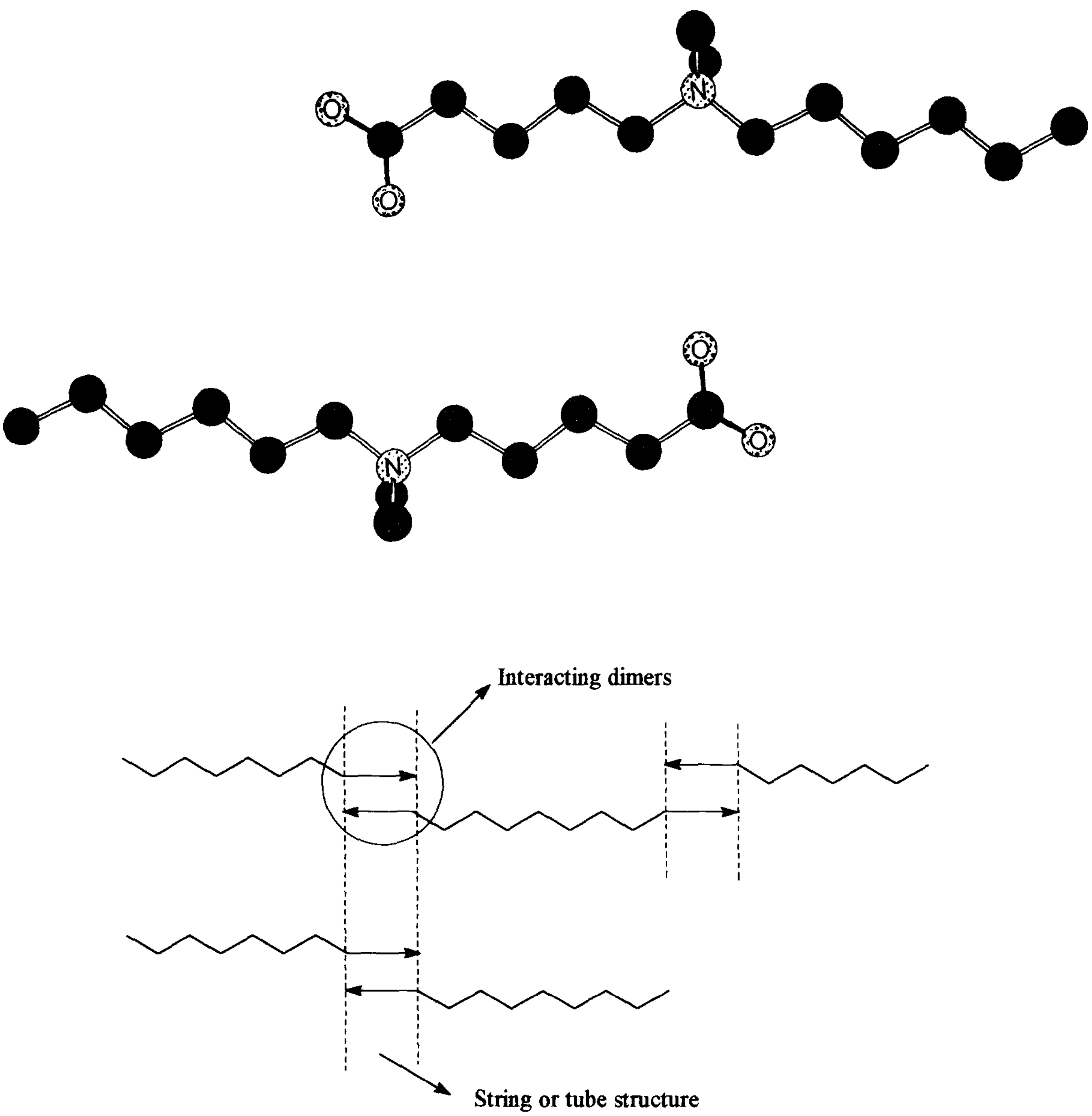


Figure 4 Interacting dimers of dimethylhexylammoniobutyl carboxylates in an all-extended conformation in order to have large interchain interactions. Below this is shown a schematic representation of the interacting dimers and their subsequent organization in to string or tube structures[24] which could be used to visualize the aggregation processes. The dipoles are depicted by arrows

lower number of zwitterionic moieties in the solution and therefore to less dipolar interactions between the ionic groups. These results are in agreement with those of Broze *et al.*[4], who showed that the critical concentration of gelation for α,ω-carboxylato polymers decreases as the polymer molecular weight increases according to a $M^{-0.5}$ dependence, and those of Fetters and coworkers[12] with a M^{-1} dependence for sulfobetaine end-capped polyisoprenes.

(iii) For a given parent polyisoprene of determined molecular weight, the higher N_{AG} is obtained with $n = 4$ as the intercharge length. This point can be interpreted in terms of conformations of the zwitterionic group. The dipole moment does not increase linearly with the intercharge length because the zwitterionic group can adopt a curled structure which reduces the distance between both charges and this decreases the dipole moment. Following the previous studies of Bredas *et al.*[24], we have used the CSC Chem3D program[25] for analysing the chemical structures of dimethylhexylammoniopropyl carboxylate as a model for carboxylatobetaine end-capped polymers. Both extended and curled conformations are depicted in *Figure 5*. In both structures, the two oxygen atoms of the carboxylate group are not at the same distance from the nitrogen atom (a difference of ~ 1 Å can be found for some structures) and only the average intercharge distance is reported in *Table 6*, from which the dipole moment could be calculated.

By using molecular modelling, Bredas *et al.*[24] found that the more stable conformation of (dimethylhexylammoniopropyl) sulfonate zwitterion is the curled one because of strong intramolecular electrostatic interactions. When the intercharge length is equal to 1, the monomer is found to be more stable in the all-*trans* extended conformation. The extended conformation is adopted by dimers and tetramers because of it allowing larger interchain interactions.

The average intercharge distance was experimentally estimated by Chevalier *et al.*[26] by using a method based on the ^{13}C n.m.r. chemical shift. This method allows

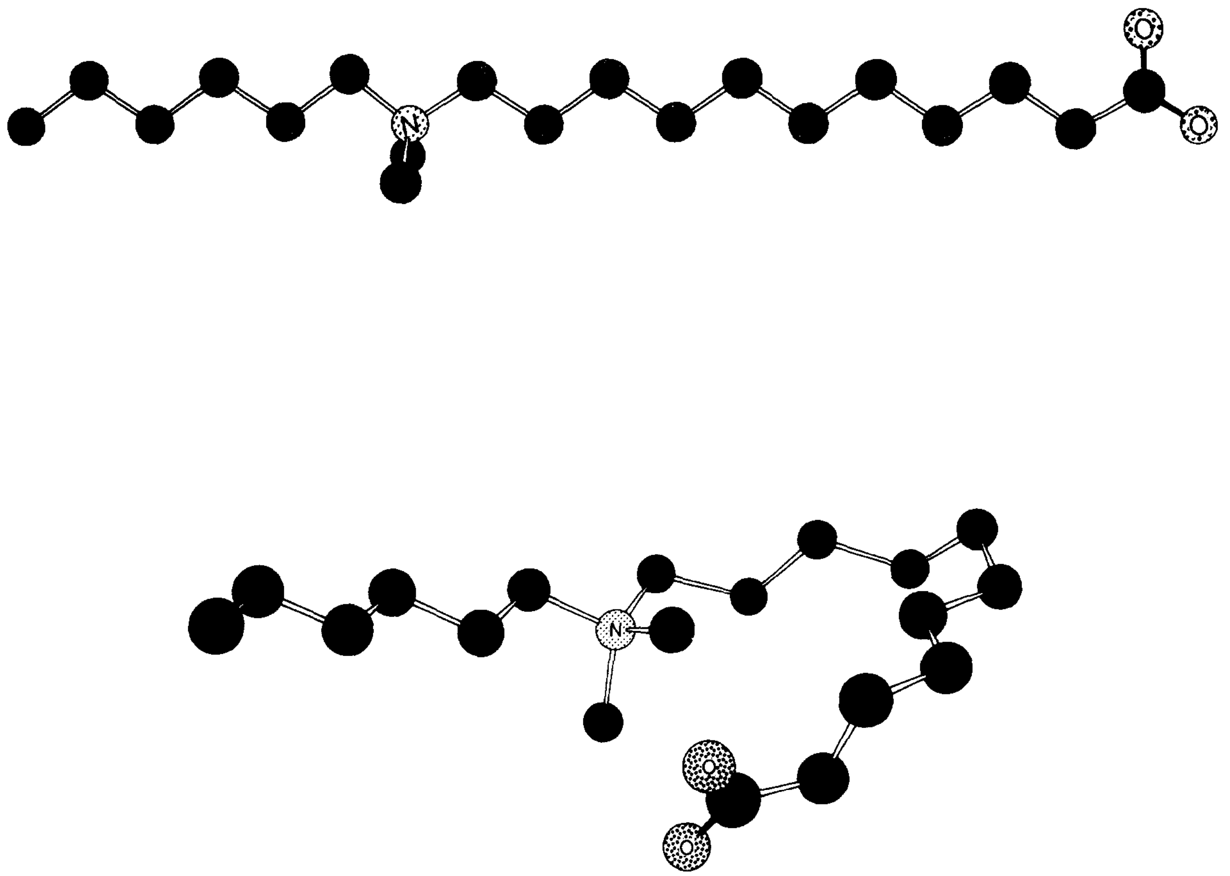


Figure 5 Extended and curled conformations of dimethylhexylammoniodecyl carboxylates as molecular models of zwitterionic end-capped polymers; hydrogen atoms are hidden from view for sake of clarity. The distances between the nitrogen and oxygen atoms are 14.18 and 15.10 Å, respectively, for the extended conformation, and 4.67 and 5.48 Å, respectively, for the curled conformation

Table 6 Dependence of the intercharge distances (in Å) and dipole moment on the intercharge methylene group

n	2	3	4	5	6	7	8	9	10
$d(N^+-O^-)$ extended	4.62	5.76	7.09	8.28	9.60	10.75	12.12	13.26	14.64
$d(N^+-O^-)$ curled	4.02	4.35	5.33	4.80	5.38	4.85	5.13	5.03	5.07
$d(N^+-C)$ extended	3.99	5.17	6.48	7.70	9.01	10.22	11.55	12.74	14.07
$d(N^+-C)$ curled	3.46	3.90	5.08	4.70	5.28	4.89	5.13	5.39	4.96
$d\,^{13}C^a$	3.81	4.64	5.74	6.59	–	8.35	–	–	9.35
μ (D)	21.0	25.0	30.3	34.4	–	42.7	–	–	47.7

[a] $d\,^{13}C$ is the N^+–Coo$^-$ distance as experimentally determined by ^{13}C n.m.r. spectroscopy[26]

determination of the distance between the nitrogen and carbon atoms of the carboxylate group. The intercharge N^+-O^- distance was calculated by adding 0.58 Å to this N^+-C distance (*Table 6*). In the same table are reported the values deduced for the dipole moment $\mu = qd(N^+-O^-)$. Measurements were made on dimethyldodecylammonioalkyl carboxylate zwitterions in methanol in order to prevent any self-association and the molecule can be considered as being isolated. It was also found that increasing the length of the alkyl chain grafted on the nitrogen causes a very small extension of the intercharge distance (< 0.1 Å) which was attributed to steric hindrance. It may be pointed out that the estimated N^+-C distance lies between the distances obtained from the extended and curled modelled structures. An explanation for this could be a screening effect by the methanol, which would reduce the electrostatic interactions between both the ammonium and carboxylate groups. Consequently, this distance would be increased.

Some dependence of properties on the intercharge length, such as certain tensioactive properties, were already evidenced with phosphobetaine-[27] and carboxylatobetaine-based molecules[26], the general structure of which is $C_{12}H_{25}N^+Me_2(CH_2)_nCOO^-$. Both surface tension and critical micellar concentration (c.m.c.) exhibit maximum values for an intercharge distance $n \sim 4$. This behaviour has been interpreted in terms of a competition between the hydrophobicity of the molecule and the dipole moments: increasing the intercharge length n increases the total hydrophobicity of the molecule, but decreases the c.m.c. However, at the

Table 7 Results obtained from static light scattering experiments in THF for telechelic polymers

Sample	M_w	R_G (nm)	$A_2\,10^3$ ($cm^3\,mol\,g^{-2}$)	N_{AG}
Z_1–PI_5–Z_1	83 000	125	<0	6.8
Z_1–PI_6–Z_1	70 000	282	5	3.8
Z_1–PI_7–Z_1	49 400	–	1	2.4
Z_4–PI_5–Z_4	289 000	236	0,5	23.7
Z_4–PI_6–Z_4	448 000	439	0,9	24.5
Z_{10}–PI_5–Z_{10}	70 000	71,9	<0	5.7
Z_{10}–PI_6–Z_{10}	96 850	87,8	1,19	5.3
Z_{10}–PI_8–Z_{10}	4 960	51,3	<0	1.6

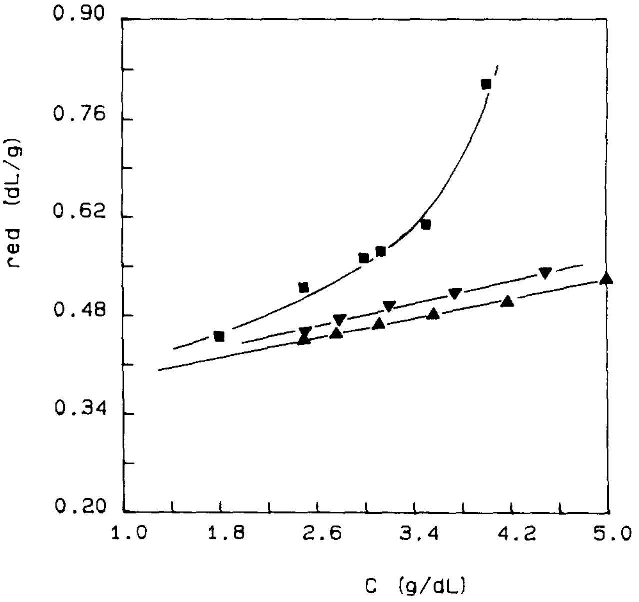


Figure 6 Effect of the addition of a very small amount of methanol on the reduced viscosity of Z_4–PI_8–Z_4 in toluene: (■) 0% MeOH; (▼) 1% MeOH; (▲) N–PI_8–N in toluene

same time, the charge separation of the zwitterionic end-group increases and strengthens the repulsive dipole–dipole interaction between the end-groups at the interface (owing to the parallel alignment of the dipole at the interface) so that the c.m.c. must increase. Therefore, the c.m.c. changes according to the predominance of one effect or the other and depends on the flexibility of the alkyl chain between charges, which controls both the dipole moment and the charge separation.

This interpretation does not hold in our case since there is no liquid interface, but the viscosity results can nevertheless be seen in terms of an alignment of dipoles. As underlined by Bredas *et al.*[24], the zwitterionic end-groups tend to adopt an antiparallel alignment in order to achieve interchain interactions as large as possible, which leads to extended conformations for the intercharge alkyl chain. The largest interaction will be obtained when both dipoles are fully antiparallel. This parallelism and the all-extended conformation for the intercharge methylene groups seem to be more and more difficult to achieve for longer intercharge distances because of the increase in the number of possible conformations.

Finally, *Table 7* reports some light scattering measurements which are worth discussing. The weight-average molecular weights are higher than those obtained with s.e.c. and confirm the aggregation process. This is particularly true when looking at the radius of gyration. Another set of aggregation numbers can be deduced from these values by using the ratio $(M_w)_{ZW}/(M_w)_{PI}$, with both values determined by light scattering. These aggregation numbers are higher than those obtained from the viscosity method, but cannot be really compared because of the different concentration domains which were explored. An hypothesis of a polyelectrolyte effect could explain the enhancement of molecular weights at the very low concentrations required for light scattering experiments. Furthermore, the R_G values depend on the intercharge length and are always higher for $n = 4$, as found for the aggregation numbers.

The viscosity of the solution is strongly decreased when adding a protic solvent, such as methanol, even at a very low level (1%). The reduced viscosity becomes quite similar to that of the parent amine-capped polyisoprene and can be fitted by using the Huggins equation (*Figure 6*). This behaviour is generally observed whatever the nature of the ionomer involved.

It must be pointed out that actual zwitterionic polymers have branched structures due to these aggregation processes. This can involve differences in polymer size for a given molecular weight. We also checked that variation in the intrinsic viscosity, which could be due to this fact, does not make a decisive difference[15].

In fact, branched polymers would imply interactions between more than two zwitterionics heads and only an increase of the chain length could be expected with such telechelic or semitelechelic polymers. This view is supported by the fact that only low aggregation numbers have been calculated, even with telechelic polymers.

The semitelechelic polymers

In contrast to the previous case, values for the weight-average molecular weight M_w deduced from s.e.c. are in good agreement with those obtained from light scattering in THF and aggregation numbers can be derived (*Table 8*). These values are lower than those found for telechelic polymers, indicating very small degrees of association. Moreover, the aggregation numbers tend to remain roughly constant whatever the molecular weight. Nevertheless, values for the radii of gyration are too high and inconsistent with the molecular-weight results.

The reduced viscosity displays the same behaviour as that observed for the telechelic polymers, which allows us to deduce another set of aggregation numbers. These range between 2 and 4, slightly higher than those obtained previously from s.e.c. or light scattering experiments, and tend to decrease when increasing the molecular weight of the parent polyisoprene.

As previously discussed for telechelic polymers, these results seem to reflect the preferential association of the zwitterionic end-groups in pairs of interacting dipoles. Because of the monofunctionality, these polymers cannot give rise to gelation, but only to an increase of the apparent molecular weight.

Finally, some experiments involving static light scattering and osmometry were carried out in toluene, showing higher average molecular weights (*Table 9*). As expected, due to the different dielectric constants, the

Table 8 Characterization of semitelechelic polymers in THF and derived aggregation numbers

Sample	$M_n{}^a$	$M_w{}^a$	$M_w{}^b$	$R_G{}^b$ (nm)	$A_2 \times 10^{3b}$ (cm^3 mol g^{-2})	$N_{AG}{}^a$	$N_{AG}{}^b$
PI_8-Z_4	14800	17500	–	–	–	1.10	–
PI_9-Z_4	15000	26000	28000	74	0.88	2.30	–
PI_1-Z_4	18000	24000	24090	100	0.78	1.14	0.97
PI_6-Z_4	23200	31000	35200	82	<0	1.19	1.35
PI_7-Z_4	32700	38900	41010	91	<0	1.55	1.66
PI_4-Z_4	41000	73000	75000	133	<0	1.32	-

[a] Results from s.e.c.

[b] Results from static light scattering measurements

Table 9 Characterization of semitelechelic polymers in toluene and derived aggregation numbers

Sample	$M_w{}^a$	$R_G{}^a$	$A_2 \times 10^{3a}$ (cm^3 mol g^{-2})	$M_n{}^b$	$A_2 \times 10^{3b}$ (cm^3 mol g^{-2})	N_{AG}
PI_1-Z_4	114000	100	1.6	116000	10.5	5.7
PI_4-Z_4	75000	100	<0	76000	<0	1.4
PI_7-Z_4	64000	96	1.01	63000	<0	2.5

[a] Results from static light scattering measurements

[b] Results from osmometry

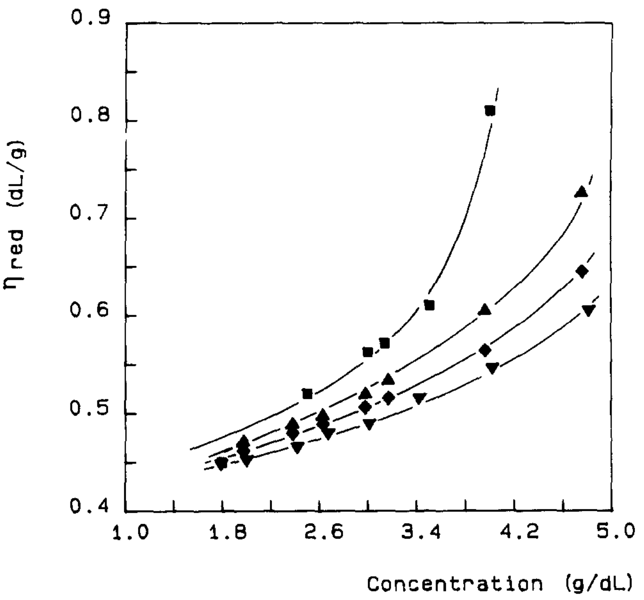


Figure 7 Dependence of the reduced viscosity of Z_4-PI_8-Z_4 in toluene on the temperature: (▼) 25; (◆) 35; (▲) 45; (■) 50°C

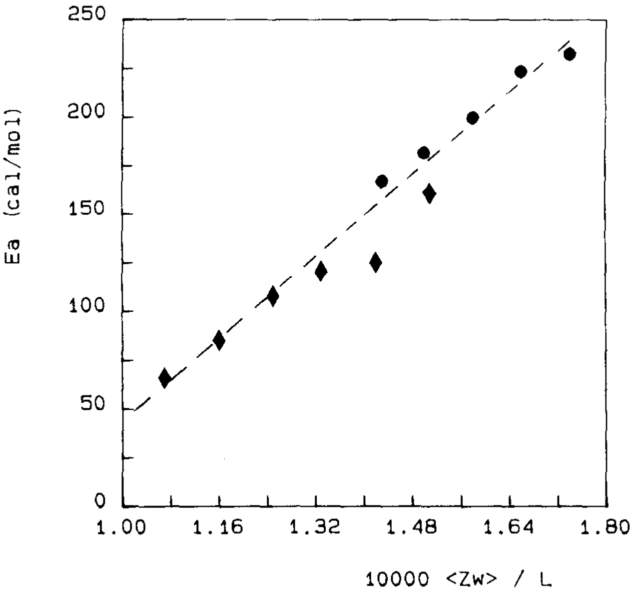


Figure 8 Activation energy as a function of the concentration of the zwitterionic end groups for a semitelechelic polyisoprene (◆; PI_6-Z_4; M_n = 23200) and a telechelic polyisoprene of approximately the same molecular weight (●, Z_4-PI_8-Z_4; M_n = 25200)

aggregation process is more significant in toluene ($\epsilon = 2.4$) than in THF ($\epsilon = 7.4$).

Temperature dependence of the solution behaviour

Increasing the temperature from 25 to 50°C leads to a marked decrease of the viscosity of telechelic polymers, whereas the parent polymers are almost insensible to this parameter in the same range of temperature and concentration (*Figure 7*). This effect can be described by an Arrhenius-type equation, as follows:

$$\eta_{\text{red}} = A \exp(-E_a/RT) \qquad (16)$$

from which activation energies of $\sim 0.2\,\text{kcal mol}^{-1}$ can be deduced. As the temperature increases, all dipole orientations become equally populated so that the energy of the dipole interactions is zero. The same behaviour is observed with semitelechelic polymers and activation energies can be obtained in the same manner.

The activation energy is a linear function of the concentration of the ionomer solution. The activation energies of telechelic polymers appear more important than those of semitelechelic polymers when plotting these values vs. the concentration of the polymer solution, but only one straight line is obtained when taking the concentration of the zwitterionic units into account (*Figure 8*). Since intermolecular associations prevail in the solutions, the pertinent parameter is therefore the concentration of zwitterionic units in the solution. This feature was previously observed with polystyrenes bearing carboxylatobetaine moieties randomly grafted along the backbone[14]. Therefore, end-capped polyisoprenes follow the same activation processes whatever the molecular weight and the functionality of the macromolecular chain.

CONCLUSIONS

Carboxylate end-capped polyisoprenes are easily obtained by reaction of the parent amino end-capped polyisoprenes with the appropriate α,ω-bromoalkyl ethyl carboxylic esters. These polymers give highly viscous solutions in toluene and this behaviour has been interpreted in terms of the aggregation number N_{AG}.

This aggregation number increases with the polymer concentration in solution, but decreases when the molecular weight of the parent aminated polymer increases. A schematic representation based on the attractive dipole–dipole interactions has been tentatively given in order to understand the increasing apparent molecular weight and the gelation process. Finally, N_{AG} displays the highest value when the intercharge length is equal to 4, whatever the molecular weight. This is attributed to a competition between an increase in the dipole moment and the difficulty of a pair of interacting dimers to attain the best antiparallel alignment, because of the increase of the possible conformations of the methylene groups between both ions.

The aggregation is highly temperature-dependent. A single activation energy was determined whatever the molecular weight and the functionality of the polymer, provided that the concentrations are expressed in terms of zwitterionic units per unit volume.

It is worth noting that some potential exists for the use of these zwitterionic oligomers as surfactants for reverse micellization. For investigating these possibilities another series of polyisoprenes have been synthesized, with molecular weights below 5000[28].

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