$$P(L_B^{out} > l) = p_B^0\{1 - (1 - p_A^0 P(L_B^{out} > l - 1))^{f-1}\} \quad \text{(V-6)}$$

The probability that $L_B^{out} > 0$ length is just

$$P(L_B^{out} > 0) = p_B^0\{1 - (1 - p_A^0)^{f-1}\} \quad \text{(V-7)}$$

where the term in braces is the probability that at least one of the $f - 1$ arms of the A_f group attached to the B_2 group has reacted.

We can now solve (V-6) and (V-7) recursively, starting with $l = 0$. The expected length looking out of a B_2 unit is

$$E(L_B^{out}) = \sum_{l=0}^{\infty} lP(L_B^{out} = l) = \sum_{l=0}^{\infty} lP(L_B^{out} > l - 1) - \sum_{l=0}^{\infty} lP(L_B^{out} > l) = \sum_{l=0}^{\infty} P(L_B^{out} > l) \quad \text{(V-8)}$$

The number-average molecular weight of the longest chain for monodisperse B_2 is

$$\bar{M}_{n,L,p} = M_{B_2} + E(L_B^{out})M_{B_2} \quad \text{(V-9)}$$

If B_2 is polydisperse, M_{B_2} must be replaced by $\bar{M}_{B_2,n}$.

In order to obtain the weight-average molecular weight, we have to select a portion of a B_2 molecule at random from the pendant material and look for the expected weight in the finite and the infinite directions. As we have already calculated the expectancy in the finite direction, we have to look for the expected weight from the point selected at random up to the root of the pendant chain. This is done with an approach similar to the one we used for $\bar{M}_{w,p}$. Again, all the groups in the infinite direction have reacted, and the expectancy is calculated from the following set of equations:

$$E(W_A{}^{out}{}_{inf}) = E(W_B{}^{in}{}_{inf})$$
$$E(W_B{}^{in}{}_{inf}) = \bar{M}_{B_2,n} + E(W_B{}^{out}{}_{inf})$$
$$E(W_B{}^{out}{}_{inf}) = E(W_A{}^{in}{}_{inf})$$
$$E(W_A{}^{in}{}_{inf}) = CE(W_A{}^{out}{}_{inf}) + (1 - C)0 \quad \text{(V-10)}$$

Solving for $E(W_B{}^{out}{}_{inf})$ yields $\bar{M}_{B_2,n}C/(1 - C)$, and the weight-average molecular weight of the longest chain is given by

$$\bar{M}_{w,L,p} = \bar{M}_{B_2,w} + E(W_B{}^{out}{}_{inf}) + E(L_B^{out})\bar{M}_{B_2,n} \quad \text{(V-11)}$$

which is valid for polydisperse B_2.

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Halato-Telechelic Polymers. 5. A Theoretical Approach to Gel Formation in Nonpolar Solvents

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ABSTRACT: Ion aggregation in halato-telechelic polymers (HTP) is treated from a theoretical point of view. When diluted in media of low dielectric constant, HTP would easily form ionic multiplets up to sextets whereas the energy gained in the formation of higher multiplets would decrease rapidly. This expectation is qualitatively confirmed by the very early gelation of HTP in nonpolar solvents. At high concentration, the ionic multiplets can possibly aggregate and form periodic structures, as evidenced in barium α,ω-carboxylato-polybutadiene. A theoretical relationship is proposed between the critical concentration of gelation (C_{gel}) and the molecular weight of the telechelic prepolymer ($\bar{M}_n$) for a given ion pair, solvent, and temperature: $C_{gel} = k\bar{M}_n^{-1/2}$. This relation is largely confirmed by experience. The proportionality constant k depends on the lability of the ionic bonds and on the conformational state of the polymeric carrier: $[\langle r^2\rangle/M]^{1/2}$. The longer the distance between the ion pairs, the earlier the gelation.

I. Introduction

In previous papers[1,2] we have studied in detail the dilute-solution behavior of halato-telechelic polymers (HTP).

HTP are obtained by the complete ionization of both ends of telechelic polymers and behave as model ion-containing polymers.[1,2] In nonpolar solvents, a sharp gel formation is noted at concentrations as low as 1–1.5 g·dL^{-1}. The electrostatic origin of this phenomenon is assessed by a large amount experimental evidence as the effect of temperature and nature of solvent or ion pairs.[1,2] For a given HTP, the molecular weight ($\bar{M}_n$) of the prepolymer, i.e., the distance between ion pairs, has a determining effect on the ion aggregation responsible for gelation. In toluene at 25 °C, magnesium α,ω-carboxylato-polyisoprene (PIP), -polybutadiene (PBD), -polystyrene (PS), -poly(*tert*-butylstyrene) (PTBS), and -poly(α-methylstyrene) (PMS) gel at concentrations (C_{gel}) that vary inversely with $\bar{M}_n$, and the apparent general relationship

$$C_{gel} = k\bar{M}_n^{-0.5} \quad (1)$$

is experimentally observed, where k is a function of the solvent, temperature, and nature of the prepolymer. This

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means that gelation, i.e., ionic multiplet formation, becomes more difficult as ion content increases or distance between ion pairs decreases. Since the gelation of ionomers is expected to vary inversely with the fraction of ionic groups,[3] a disagreement between the experimental behavior of HTP and the theoretical predictions for ionomers exists. The aim of this paper is to explore the gelation process of HTP from a theoretical point of view and to explain accordingly the experimental observations and especially eq 1.

II. Preliminary Remarks

In the case of tetraalkylammonium salts in solvents of dielectric constant ranging from 2.27 to 7.38, Pettit and Bruckenstein have concluded that ionic aggregates (ion pairs, triplets, quartets, and sextets) may form.[4] These associated species are referred to as multiplets.

Eisenberg has explored the effects of chain extension and spatial prerequisites on multiplet formation in ionomers.[5,6] In this type of material, the ion pairs are more or less randomly attached to the polymeric backbone as pendant groups. Once involved in separate quartets or higher multiplets, the ion pairs carried by a given chain are responsible for its stretching and use therefore some of the electrostatic energy released in the multiplet formation. The random distribution of the ion pairs is furthermore responsible for some internal cyclization due to the association of neighbor ion pairs of the same chain.[6] When the multiplet is represented as a spherical drop consisting of ions only, Eisenberg assumes that a maximum value of eight pairs may be involved in a multiplet; the electrostatic energies are indeed very much larger than the energies of chain extension, so that only spatial constraints need to be considered in this model of ion aggregation.

Our previous experimental studies[1,2,7,8] have considered HTP in which the ion pairs are attached at both ends of a prepolymeric backbone. The situation is basically different in ionomers and HTP. In ionomers, two chain segments emerge from each ion pair, whereas in HTP only one does. On the other hand, the chain segments separating two successive ion pairs are linked covalently in ionomers but ionically and reversibly in HTP. In the latter case, moreover, the ion pairs fixed at both ends of sufficiently long chains are practically independent of each other.

In this paper we consider in section III the energy released upon multiplet formation in relation to the multiplet size. Afterward we will develop a general relation between multiplet size in HTP and parameters such as concentration, conformation, and molecular weight of the telechelic polymer, i.e., of the polymeric carrier. Finally, we discuss the physical reasonableness of eq 1. The discussion will refer to metal α,ω-carboxylato polymers for which experimental information is largely available;[1,2,7,8] their molecular structure may be described by

$$-[^{-}OOC-P_x-COO^{-}M^{v+}{}_{2/v}]_n-$$

where v is mainly fixed to 1 and 2; however, examples of higher values can also be considered.

III. Energy Released upon Multiplet Formation in Relation to Their Size

Let us consider the energy released upon multiplet formation independently of any spatial constraint.

As proposed by Pettit and Bruckenstein,[4] in media of low dielectric constant, the free energy of ion association ΔF can be expressed by means of the thermodynamic cycle defined in Scheme I. Obviously, in Scheme I

$$\Delta F = \Delta F_1 + \Delta F_2 + \Delta F_3 \qquad (2)$$

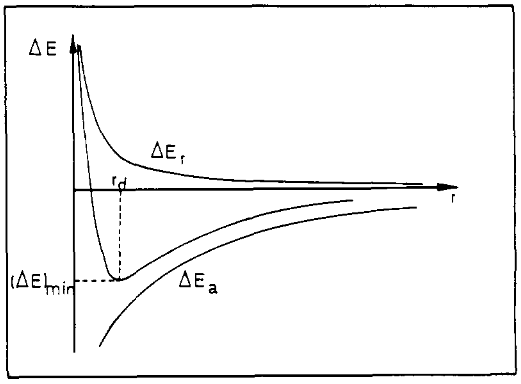

Figure 1. Potential energy curve of contact ion pair.

Scheme I

$$\begin{tikzcd}
\boxed{\text{solvated free ions}} \arrow[r, "\Delta F"] \arrow[d, "\Delta F_1"] & \boxed{\text{solvated associated ions}} \\
\boxed{\text{nonsolvated free ions}} \arrow[r, "\Delta F_2"] & \boxed{\text{nonsolvated associated ions}} \arrow[u, "\Delta F_3"']
\end{tikzcd}$$

In nonpolar media, the changes of free energy upon solvation of free ions ($-\Delta F_1$) and multiplets (ΔF_3) are expected to be small and to have practically the same absolute value. To a reasonable approximation, ΔF can be assumed to be equal to ΔF_2.

$$\Delta F \simeq \Delta F_2 = \Delta H_2 - T\Delta S_2 \qquad (3)$$

ΔH_2 is mainly of electrostatic origin, especially for the alkali metal and alkaline earth cations considered herein.

The entropy variation ΔS_2 is difficult to estimate, but, in a first approximation, it may refer to the average values calculated by Pettit and Bruckenstein[4] and reduce to one M^{v+} ion-gram, i.e., -17 cal·mol^{-1}·K^{-1} for the ion pair and -32 cal·mol^{-1}·K^{-1} for higher multiplets. This assumption maintains the physical meaning of the discussion, as the entropic contribution to ΔF will be shown hereafter to represent less than 10% of the enthalpic contribution at room temperature. Furthermore, the SAXS measurements reported and discussed in section V establish that the prepolymer coil is very weakly modified by neutralization and subsequent ion aggregation. It results that coil expansion or contraction contributions to ΔS are unimportant. In conclusion, the free energy of ion association in nonpolar media is predominantly determined by the electrostatic interaction energy ΔE.

Two oppositely charged particles encounter simultaneous attractive (ΔE_a) and repulsive (ΔE_r) energies so that they are stabilized at the minimum $(\Delta E)_{min}$ of their potential energy curve (Figure 1); r_d is the equilibrium internuclear separation of the ion pair. The calculation of $(\Delta E)_{min}$ is now briefly described for carboxylates of the alkali metals and alkaline earths. The most probable ionic multiplets (ion pair, triplet, quadruplet, and sextet) will be considered.

The potential energy ΔE for an alkali metal carboxylate ion pair includes (i) interactions between ions ($-e^2/\epsilon r$) as well as their induced dipoles (the latter contribution is minor and accordingly neglected; ΔE_a is therefore equal to $-e^2/\epsilon r$, where e is the electronic charge, ϵ the dielectric constant, and r the distance between the centers of positive and negative charges in the contact ion pair) and (ii) various other forces, the effect of which is expressed as a general term B/r^n as proposed by Pettit and Bruckenstein.[4] The same authors have adjusted empirically the value of

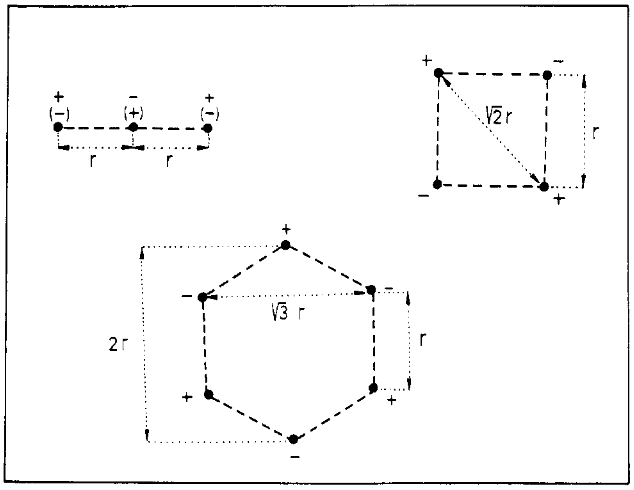

Figure 2. Schematic structure of triplet, quartet, and sextet formed by alkali metal carboxylates.

n to 6.9 from the characteristics of alkali metal halide ion pairs, and they have extended this value to the ion triplet, quartet, and sextet. It results that

$$\Delta E = -e^2/\epsilon r + B/r^{6.9} \tag{4}$$

When the first derivative of ΔE is canceled, B is easily deduced (eq 6) and introduced into eq 4 to express $(\Delta E)_{\min}$ (eq 7).

$$\left[\frac{\partial \Delta E}{\partial r}\right]_{r=r_d} = \frac{e^2}{\epsilon r_d^{2}} - \frac{6.9B}{r_d^{7.9}} = 0 \tag{5}$$

$$B = r_d^{5.9}e^2/6.9\epsilon \tag{6}$$

$$(\Delta E)_{\min} = -0.855e^2/\epsilon r_d \tag{7}$$

For the sake of simplicity in the forthcoming calculations, symmetrical arrangements of ions are assumed in the triplet, quadruplet, and sextet (Figure 2). These geometries are the most probable from an electrostatic point of view. However, they can be disturbed by coordination effects in metal carboxylates. Nevertheless the meaning of the conclusions is thought to be significant.

Alkali metal carboxylate triplets result from the association of either two carboxylates and one alkali metal ion or one carboxylate and two alkali metal ions (Figure 2). In solution, both types of triplets, which are assumed to be linear, must exist in equal amounts to ensure electroneutrality. The attractive interaction between anion and cation $[2(-e^2/\epsilon r) + 2(B/r^{6.9})]$ and repulsive interaction between ions of the same charge $[e^2/\epsilon 2r + B/(2r)^{6.9}]$ are to be considered in the calculation of ΔE

$$\Delta E = -1.5(e^2/\epsilon r) + 2B/r^{6.9}$$

$B/(2r)^{6.9}$, being ca. 120-fold smaller than $B/r^{6.9}$, is neglected. By cancellation of the first derivative $[\partial \Delta E/\partial r]_{r=r_t}$, the equilibrium distance r_t in the triplet is deduced:

$$r_t^{5.9} = 6.9(2B)\epsilon/1.5e^2 \tag{8}$$

and $(\Delta E)_{\min}$ is given by

$$(\Delta E)_{\min} = -1.5(e^2/\epsilon r_t) + 2B/r_t^{6.9} \tag{9}$$

The value of B calculated for the ion pair (eq 6) is introduced in eq 8 and 9, respectively. It results from eq 8 that

$$(r_t/r_d)^{5.9} = 4/3 \tag{10}$$

and from eq 9 that

$$(\Delta E)_{\min} = -1.5(e^2/\epsilon r_t) + (2/6.9)(r_d/r_t)^{5.9}(e^2/\epsilon r_t) \tag{11}$$

Table I
Potential Energy of Alkali Metal Carboxylate Multiplets

multiplet	$(\Delta E)_{\min}$ / $e^2/\epsilon r_d$	$\bar{n}$ [a]	$(\Delta E)_{\min}$ / $(e^2/\epsilon r_d)\bar{n}$
doublet	−0.855	1	−0.855
triplet	−1.221	1.5	−0.814
quartet	−2.053	2	−1.026
sextet	−3.227	3	−1.076

[a] Mean number of cations per multiplet.

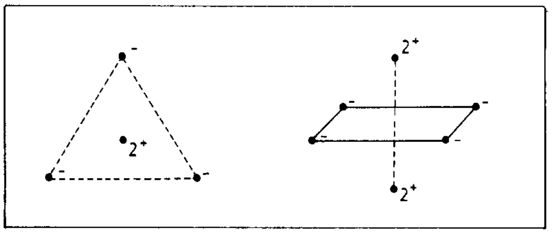

Figure 3. Schematic structure of quartet and sextet formed by alkaline earth carboxylates

Accounting for eq 10, one can express $(\Delta E)_{\min}$ in terms of $(e^2/\epsilon r_d)$; i.e.

$$(\Delta E)_{\min} = -1.221(e^2/\epsilon r_d) \tag{12}$$

Alkali metal carboxylate quartets are assumed to have a square-planar structure in which opposite corners are occupied by ions with the same charge (Figure 2). Attractive interactions between anion and cation amount to $4(-e^2/\epsilon r) + 4B/r^{6.9}$ and repulsive interactions between ions of the same charge to $2(e^2/\epsilon(2^{1/2}r)) + 2B/(2^{1/2}r)^{6.9}$. As $2B/(2^{1/2}r)^{6.9}$ is small compared to $4B/r^{6.9}$, ΔE is given by

$$\Delta E = -4(e^2/\epsilon r) + 2(e^2/\epsilon(2^{1/2}r)) + 4B/r^{6.9}$$

By the same calculation scheme, $(\Delta E)_{\min}$ is derived:

$$(\Delta E)_{\min} = -2.053(e^2/\epsilon r_d) \tag{13}$$

The structure of the sextet is pictured as a regular hexagon, the vertices of which are alternately occupied by each ion type (Figure 2). The attractive interactions between the nearest-neighbor anion and cation $[6(-e^2/\epsilon r) + 6B/r^{6.9}]$ but also between opposite anion and cation $[3(-e^2/\epsilon 2r) + 3B/(2r)^{6.9}]$ are to be considered, as well as the repulsive interaction between ions of the same charge $[6(e^2/\epsilon(3^{1/2}r)) + 6B/(3^{1/2}r)^{6.9}]$. When the terms $B/(2r)^{6.9}$ and $B/(3^{1/2}r)^{6.9}$ are neglected, it can be calculated that

$$(\Delta E)_{\min} = -3.227(e^2/\epsilon r_d) \tag{14}$$

Table I summarizes the $(\Delta E)_{\min}$ value of each multiplet and the values reduced to one cation.

The same calculations have been applied to alkaline earth carboxylates. The doublet is positively charged (+1), the quartet is negatively charged (−1), and the triplet and sextet are uncharged. Figure 3 represents the assumed structure of the quadruplet and sextet. The quartet cannot exist without the presence of a positively charged species (+1), i.e., the doublet, whereas the doublet could also exist in the presence of a free anion. Table II summarizes the $(\Delta E)_{\min}$ values of these various species.

From Tables I and II it appears that the potential energy (reduced to one cation) of both alkali metal and alkaline earth carboxylates decreases as the number of cations in a multiplet (n) increases. Upon doublet formation, a very important potential energy is indeed released, but the energy gained through formation of higher multiplets rapidly decreases as shown by the series doublet $(-0.855e^2/\epsilon r_d)$ > quadruplet $(-1.026e^2/\epsilon r_d)$ > sextet

Table II
Potential Energy of Alkaline Earth Metal Carboxylate Multiplets

multiplet	$\frac{(\Delta E)_{\min}}{e^2/\epsilon r_d}$	$\bar{n}$ [a]	$\frac{(\Delta E)_{\min}}{(e^2/\epsilon r_d)\bar{n}}$
doublet + free anion	−1.710	1	−1.710
doublet + quartet	−5.156	1 + 1	−2.578
triplet	−2.925	1	−2.925
sextet	−6.336	2	−3.168

[a] Mean number of cations per multiplet.

($-1.076e^2/\epsilon r_d$) for the alkali metal carboxylates and the series doublet ($-1.710e^2/\epsilon r_d$) > triplet ($-2.925e^2/\epsilon r_d$) > sextet ($-3.168e^2/\epsilon r_d$) for the alkaline earth carboxylates.

In media of low dielectric constant, the ion aggregation lowers significantly the potential energy of the system. For instance, at 300 K, for $\epsilon = 3$ and $r = 2.5$ Å, $e^2/\epsilon r$ is indeed 44 kcal·mol^{-1} whereas RT is only 0.6 kcal·mol^{-1} or $0.014e^2/\epsilon r$. When alkaline earth carboxylates form a sextet, the enthalpy variation is about 44(−3.168) = −140 kcal·mol^{-1} whereas the entropic contribution to the free energy is only −300(−32) = 9.6 kcal·mol^{-1}. As mentioned before, the entropic contribution to ΔF is very limited in comparison to the enthalpic one. Furthermore, when two triplets formed by alkaline earth carboxylates aggregate into one sextet, the gain in energy seems limited ($0.243e^2/\epsilon r$), but it is still high compared to the thermal energy at 300 K ($RT = 0.014e^2/\epsilon r$).

In conclusion, both alkali metal and alkaline earth carboxylates tend spontaneously to form at least limited-size multiplets. The calculations show that the association into larger multiplets releases a decreasing amount of energy, so that their formation must be influenced by the presence and, more especially, by the molecular characteristics of the polymeric carrier. In that respect, it is instructive to compare the situation prevailing in ionomers and HTP. In the case of bulk ionomers, Eisenberg assumes that the "multiplet can be represented as a spherical liquid drop consisting of ions only, and that the hydrocarbon chain segments are confined to the surface of the drop".[6] From geometrical considerations, the author concludes that "a maximum value of eight pairs is indicated for perfect volume occupation. Beyond that point, an additional ion pair could not contact the liquid drop since the surface of the drop is completely coated with nonionic chain material. The multiplets can possibly aggregate to form clusters of a wide range of possible structures, each of which leads to a slightly different electrostatic interaction".[6] Still, according to Eisenberg, at increasing ion content the ionic drops discussed above could act as nuclei for ion pair clustering or they could themselves aggregate to form some sort of clusters, but rod-shaped or sheet-shaped ion aggregates could also be possible.[6]

Barium α,ω-carboxylato-polybutadienes analyzed by SAXS in bulk exhibit a periodic structure with an apparently lamellar character.[8] Recently, we observed that this morphology is maintained even in the presence of 54% solvent but disappears at high dilution. These results could agree with a "bidimensional growth" of the initial multiplets into layered structures as observed for soaps.[9] It is to be noted that the lamellar thickness observed is dependent on the prepolymer chain length but apparently insensitive to the nature of the cation.[8] This would mean that the parameters of the periodic structure are determined mainly by the prepolymer conformation, independently of the electrostatic interactions between dipoles. In other words, at increasing concentrations, the multiplet size increases without stretching the prepolymer chains significantly. Furthermore, the extent of the "bidimensional growth" of initial multiplets seems to depend on cation size and valency. The biggest mono- and divalent cations (K and Ba) appear to be largely favorable whereas no X-ray diffraction is exhibited in the presence of trivalent cation (Al). Consequently, depending on the cation characteristics, layered but more or less limited-size multiplets would be formed and give rise to ordered but localized regions. Such a picture is to be compared with the ordered and localized distribution of macroions in polyelectrolyte solution, as suggested by Ise et al.[10] It appears therefore that in nonpolar media, the ions tend to form aggregates of the largest size possible, corresponding to the highest gain in energy. When possible, this trend can induce the formation of large clusters (ionomers) or layered structures (some HTP), which arise from successive association of limited-size multiplets. Of course, in solution, the presence of a good solvent is responsible for the expansion of polymer coils and interferes with the extent of the ion association process.

IV. Dependence of the Multiplet Size on the Concentration and the Molecular Characteristics of the Prepolymer

As explained in the Introduction, the ion pairs fixed at both ends of sufficiently long prepolymers are expected to be largely independent. The distribution of the multiplets in the bulk of the HTP solutions must accordingly be largely controlled by the distance between the end groups of the prepolymer. For the sake of simplicity, we assume that the prepolymer chains have a unique and constant end-to-end distance (r, Å) and that the multiplets occupy certain positions within a space lattice. Under these conditions, we seek the relationship between the mean number of cations per multiplet ($\bar{n}$) and both the concentration and molecular characteristics of the prepolymer. This relationship will be developed on the basis of alkaline earth cations, but the same procedure could obviously be applied to cations with different charges.

Since four chains emerge from multiplets containing two cations, a spatial structure with tetrahedral coordination will be considered, with special reference to the diamond structure. Similarly, lattices with coordination numbers 6, 8, and 12 are suitable for describing the spatial distribution of multiplets containing three (cubic), four (body-centered cubic), and six (face-centered cubic) cations, respectively. For each of these lattices, the volume V containing one multiplet can be related to the nearest-neighbor distance between multiplets r (or periodicity of the assembly). From elementary considerations, the general relationship $V = ar^3$ can be established, with $a = 0.707$, 0.769, 1, and 1.561 for lattices with coordination numbers 12, 8, 6, and 4, respectively. If C is the prepolymer concentration in g·dL^{-1}, M its molecular weight (for monodisperse prepolymers), and N_0 Avogadro's number, the mean number of divalent cations per unit volume is CN_0/M, and $\bar{n}$ is accordingly given by eq 15, where r is in angstroms.

$$\bar{n} = ar^3\frac{CN_0}{M} = \frac{ar^3}{166}\frac{C}{M} \qquad (15)$$

However, in reality, polymeric species display a considerable range of end-to-end distances, and it is usual to use the root-mean-square $\langle r^2\rangle^{1/2}$ as an average value of r. To each end-to-end distance r_i corresponds a well-defined $\bar{n}_i$ (eq 15), and the overall multiplet size is accordingly given by the summation over all $\bar{n}_i$ values. Therefore the end-to-end distance appears in eq 15 as a mean cubic value $\langle r^3 \rangle$. The relation between the mean cubic and the mean square values of r is easily established by applying Flory's treatment to calculate both average $\langle r \rangle$ and the average square $\langle r^2 \rangle$ values[11]

$$\langle r^3 \rangle^{1/3} = 1.07 \langle r^2 \rangle^{1/2}$$

Equation 15 is easily extended to a real monodisperse prepolymer

$$\bar{n} = \frac{1.23a}{166} \langle r^2 \rangle^{3/2} \frac{C}{M} \qquad (16)$$

Finally, for a polydisperse prepolymer, averaged values of $\langle r^2 \rangle^{3/2}$ and M are to be considered. In particular, the number average of $\langle r^2 \rangle^{3/2}$ over the molecular weight distribution should be used in conjunction with $\bar{M}_n$.[12] $\langle r^2 \rangle^{1/2}$ can also be separated into its components, i.e., $\langle r_0^2 \rangle^{1/2}$ (the unperturbed root-mean-square end-to-end distance) and α (the intramolecular expansion coefficient). The final expression for $\bar{n}$ is accordingly

$$\bar{n} = 7.4 \times 10^{-3} a_{\bar{n}} \left[\frac{\langle r_0^2 \rangle}{M} \right]^{3/2} \alpha^3 C \bar{M}_n^{1/2} \qquad (17)$$

The parameter $a_{\bar{n}}$ is well-defined for all values of $\bar{n}$; otherwise its weight-average value is calculated as follows:

$$a_{2 \leq \bar{n} \leq 3} = 2.683 - 0.561\bar{n}$$

$$a_{3 \leq \bar{n} \leq 4} = 1.693 - 0.231\bar{n}$$

$$a_{4 \leq \bar{n} \leq 6} = (6 - \bar{n})0.385 + (\bar{n} - 4)0.354$$

In conclusion, the multiplet size depends on both the prepolymer concentration and its molecular characteristics, i.e., molecular weight, intrinsic flexibility ($\langle r_0^2 \rangle / M$), and expansion coefficient, for a given solvent and temperature.

V. Theoretical Approach to the Critical Gel Concentration (C_{gel})

In the case of HTP herein studied, the functionality of both the metal and the prepolymer is 2. Accordingly, the critical gelation condition corresponds to only one cation per multiplet ($n_{gel} = 1$), but this condition assumes the formation of stable bonds. As the ionic bonds formed in HTP solutions are thermolabile, they undergo a constant redistribution with a rate depending on temperature, dielectric constant of the medium, and nature of ion pairs. As a consequence, the critical mean number of cations per multiplet ($\bar{n}_{gel}$) must be higher than 1. The higher the exchange rate of the ionic bonds, the higher the $\bar{n}_{gel}$ value.

For a given set of experimental conditions (solvent, temperature, ion pair), $\bar{n}_{gel}$ is a constant, and application of the critical conditions to eq 17 leads to

$$\frac{\bar{n}_{gel}}{7.4 \times 10^{-3} a_{\bar{n}_{gel}}} = \left[\frac{\langle r^2 \rangle}{M} \right]^{3/2} C_{gel} \bar{M}_n^{1/2} = K \qquad (18)$$

K is a constant for a given alkaline earth carboxylate, solvent, and temperature. It appears accordingly that the longer the distance between the ion pairs, the earlier the gelation process. Over a limited molecular weight range (extending to about 50 000), $\langle r^2 \rangle / M$ can be assumed to be independent of M;[13] it results that

$$C_{gel} = k \bar{M}_n^{-1/2} \qquad (19)$$

The theoretically deduced eq 19 has been experimentally tested for a large number of prepolymers, the polydispersity ($\bar{M}_w / \bar{M}_n$) of which is usually less than 1.2.[1] The experimental results of Mg α,ω-carboxylato prepolymers in toluene at 25 °C are gathered in Table III (k values).

Table III
k Values of Mg α,ω-Carboxylato Polymers and $[\langle r^2 \rangle / M]^{1/2}$ of the Corresponding Nonneutralized Prepolymers in Toluene at 25 °C

prepolymer	k, $g^{3/2} \cdot dL^{-1} \cdot mol^{-1/2}$	$\bar{M}_n$	$[\langle r^2 \rangle / M]^{1/2}$
PTBS	800	15 000	0.714
PMS	490	6 000	0.740
PIP (65% 3,4, 35% 1,2)[a]	407	70 000	0.816
PS	370	11 500	0.846
PBD (65% 1,4 trans, 20% 1,4 cis, 15% 1,2)	136	4 600	1.145

[a] If 1,4 units are present, their content is lower than 5%.

From eq 18 and 19, it is evident that k depends on the ratio $[\langle r^2 \rangle / M]^{-3/2}$, i.e., on the nature of the prepolymer

$$k = K[\langle r^2 \rangle / M]^{-3/2}$$

or

$$k^{-1/3} = K^{-1/3} [\langle r^2 \rangle / M]^{1/2} \qquad (20)$$

The value of $[\langle r^2 \rangle / M]^{1/2}$ can be estimated from the Flory relation

$$[\eta] = \phi (\langle r^2 \rangle / M)^{3/2} \qquad (21)$$

where $[\eta]$ is the intrinsic viscosity and ϕ a universal constant (2.1×10^{21}). It results that

$$\left[\frac{\langle r^2 \rangle}{M} \right]^{1/2} = \left[\frac{[\eta]}{2.1 \times 10^{21} M^{1/2}} \right]^{1/3} \qquad (22)$$

The intrinsic viscosity $[\eta]$ of the nonneutralized α,ω-carboxylic prepolymers has been measured in toluene at 25 °C,[1] and the calculated values of $[\langle r^2 \rangle / M]^{1/2}$ are reported in Table III. Figure 4 confirms that the experimental relation between $k^{-1/3}$ and $[\langle r^2 \rangle / M]^{1/2}$ is linear, in accordance with the theoretical relation (eq 20). From the slope of this graph, K is estimated to 227 ± 29.

The critical value of $\bar{n}_{gel}$ for the magnesium carboxylate ion pair in toluene at 25 °C would accordingly be near 2.3. This value is proper but assumes that the ratio $[\langle r^2 \rangle / M]^{1/2}$ is unmodified by the neutralization of the α,ω-carboxylic prepolymers and the occurrence of the gelation. However, SAXS measurements on a gel of barium α,ω-carboxylato-1,4-polybutadiene ($\bar{M}_n = 4600$) in toluene (50%) at 25 °C support this hypothesis. The observed lamellar structure has a periodicity of 74 ± 3 Å, whereas the nonneutralized prepolymer (see Table III) has a root-mean-square end-to-end distance of 77.6 Å. Recently, this agreement has been confirmed with a telechelic 1,2-polybutadiene ($\bar{M}_n = 4800$) under the same experimental conditions except for the gel content (10% toluene). The lamellar thickness of the gel is 61 ± 2 Å and $\langle r^2 \rangle^{1/2}$ of the nonneutralized prepolymer is 66.5 Å. The SAXS technique has been described elsewhere,[8] and the results will be published in more detail in the near future.

VI. Conclusions

In media of low dielectric constant, ion aggregation lowers significantly the potential energy of the system. However, the energy gained through formation of multiplets higher than a sextet decreases rapidly. In ionomers, the ionic multiplets can aggregate into clusters, the structure of which is not very clear-cut.[5,6] In Ba α,ω-carboxylato-PBD, mesomorphic phases are observed in the

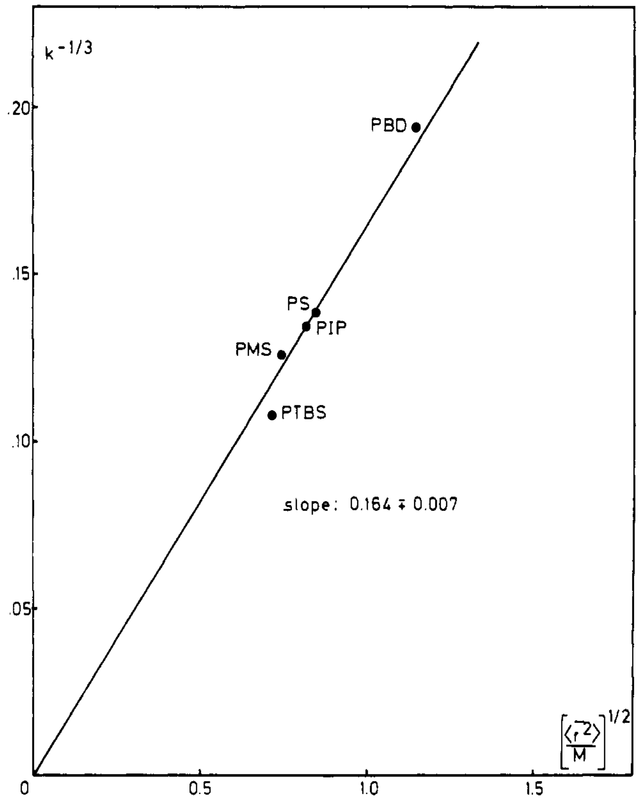

Figure 4. Dependence of the proportionality constant k (eq 19) on the conformation $[\langle r^2\rangle/M]^{1/2}$ of the nonneutralized telechelic prepolymer.

solid state; the aggregation of ionic multiplets into lamellar and probably localized structures has also been observed at high concentrations, but more studies on other systems are needed.

When model distributions of multiplets in HTP solutions (ideal lattices) are used, the experimental relationship between the critical concentration of gelation and the reciprocal square root of the prepolymer molecular weight can be confirmed theoretically. For a given ion pair, solvent, and temperature, the occurrence of the gelation phenomenon is essentially controlled by the conformational characteristics of the polymeric carrier. The first experimental results agree with a very limited extension of the α,ω-carboxylic acid prepolymer upon neutralization and gelation. In ionomers, cluster formation depends on the balance between the elastic forces, which prevent multiplets from approaching each other, and the attractive forces between multiplets. In HTP, practically no stretching of the prepolymer chains would occur on multiplet formation, and the energy released at this moment would be determinant. The large independence of the end groups of each prepolymer chain could also explain the likelihood of the formation of at least partially ordered structures as observed in barium α,ω-carboxylato-polybutadienes.

The gelation of alkaline earth α,ω-carboxylato prepolymers dissolved in toluene at 25 °C occurs when the mean number of cations per multiplet ($\bar{n}_{\text{gel}}$) is higher than the theoretical value. This behavior is due to the thermoreversibility of the ionic bonds, the average lifetime of which controls the stability of the multiplets. Any increase in the cation size, dielectric constant of the solvent, or temperature is responsible for less stable multiplets and accordingly for a higher $\bar{n}_{\text{gel}}$ or C_{gel} (eq 18). The theoretical value $\bar{n}_{\text{gel}} = 1$ should, however, be observed only for an infinitely short measurement time of gelation. The time dependence of the gel formation makes the study of the viscoelastic behavior of HTP solutions and gels very attractive. These results will be reported in the near future.

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