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# Halato-Telechelic Polymers. 4. Synthesis and Dilute-Solution Behavior

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ABSTRACT: Halato-telechelic polymers (HTP) result from the complete ionization of both ends of telechelic prepolymers. Their behavior in nonpolar solvents is characterized by a very abrupt increase of viscosity at increasing concentration, so that gel formation is noted at concentrations as low as 1.5 g·dL$^{-1}$. The nature of the ion pairs, polarity of the medium, and temperature influence significantly the gel formation and prove its electrostatic origin. The depressive effect of any polar additive on the gelation requires drastic conditions in the synthesis of reproducible materials. In this respect, an efficient synthetic pathway has been proposed. The influence of molecular weight and end-to-end distance of the prepolymer shows the determinant role played by the polymeric backbone on the ion aggregation process.

## Introduction

In the past 2 decades, ion-containing polymers have attracted increasing attention, thanks to the dramatic modifications induced in the properties of polymeric materials by strongly interacting ions. A large range of potential applications is, of course, the primary source of this interest.[1] Books and reviews published recently give an excellent outline of their synthesis, structure, properties, and applications.[2–6]

Network glasses and polyelectrolytes have been known for a long time, whereas ionomers are now also recognized as very attractive materials. They consist of mainly nonpolar polymeric backbones carrying pendant ionizable groups (carboxylate or sulfonate), more or less randomly distributed along them. As a typical example, polyethylene-based ionomers are commercially available from DuPont under the trade name Surlyn. They can be processed on conventional equipment for plastics and offer improved properties in comparison to the corresponding base polymer.[4,5]

Eisenberg has paid attention to the role played by the strong coulombic interactions in controlling the supermolecular structure of ionomers. In media of low dielectric constant, the ionic groups can aggregate not only into multiplets but also into clusters, depending on the ion content.[5,7] Multiplets contain a few ion pairs, whereas clusters consist of 30–100 ion pairs, including some polymeric chains; they are responsible for a multiphase structure in ionomers. Rheological behavior, X-ray and neutron diffraction, electron microscopy, and NMR, IR,

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and Raman spectroscopy give relevant experimental evidence for the formation of clusters,[4,5,8–11] the internal structure of which is still questionable.[11]

The poorly controlled molecular structure of ionomers does not favor an unambiguous characterization of their supermolecular structure and general behavior. Their insolubility in common nonpolar solvents[12] is another drawback limiting their study. A search for model ion-containing polymers, the molecular parameters of which could be largely controlled, appears therefore to be a very attractive goal.

As already pointed out, carboxy-telechelic polymers offer a very attractive approach, as they form an ionic polymer $[-^{-}OOC-P_x-COO^{-}Met^{2+}-]_n$ when neutralized by a metal cation.[13–15] The nature of both $P_x$ and the cation (alkali, alkaline earth, etc.), as well as the length and the polydispersity of $P_x$, is easily modified. Thus the halato-telechelic polymers (HTP) form a family of materials with a potentiality of carefully matched molecular characteristics.

Previous communications have reported the first experimental information concerning morphology[13] and behavior of HTP in nonpolar solvents[14] and in bulk.[15] This paper describes HTP synthesis and the production of materials displaying well-reproducible properties. The in-depth investigation of the HTP behavior in nonpolar solvents is also reported and discussed in relation to the molecular parameters of these model compounds. It is to be mentioned that several years ago, Pineri et al.[16,17] and Otocka et al.[18] also considered the preparation of similar materials, as explained hereafter.

## Experimental Section

**Telechelic Polymers.** When not commercially available, telechelic polymers were prepared by anionic polymerization. Pure and carefully dried monomers and solvents were used. Polymerization was performed in previously flamed and nitrogen-purged flasks equipped with rubber septums. Hypodermic syringes and stainless steel capillaries were used to handle liquid products under a nitrogen atmosphere.

Benzene and toluene (pure grade) were dried by refluxing over $LiAlH_4$ and $CaH_2$, respectively, and distilled under a nitrogen atmosphere. Tetrahydrofuran (THF) (pure grade) was dried by refluxing over benzophenone–sodium and distilled under a nitrogen atmosphere. Styrene, α-methylstyrene, *tert*-butylstyrene, and isoprene (pure grade) were dried over $CaH_2$ at room temperature and distilled under reduced pressure just before use. Isoprene was mixed with *n*-BuLi and again distilled before polymerization.

Carboxy-telechelic polyisoprene (PIP), poly(α-methylstyrene) (PMS), and poly(*tert*-butylstyrene) (PTBS) were anionically prepared in THF at −78 °C. α-Methylstyrene sodium tetramer was used as a difunctional initiator, whereas the living macrodianions were deactivated by anhydrous carbon dioxide.[19] PIP microstructure was characterized by a 3,4/1,2 ratio of 65/35.

Poly(α-methylstyryl) dianions were also deactivated by propanesultone[20] and 1-chloro-3-(dimethylamino)propane,[21] respectively, to form α,ω-sulfonic acid or *tert*-amino-PMS. Molecular weights of telechelic PIP, PMS, and PTBS were controlled by adjusting the monomer/catalyst molar ratio. Polydispersity did not exceed 1.2 and the functionality was better than 1.95 (1.9 for disulfonic acid terminated PMS). This functionality was determined by potentiometric titration of the acid end groups with tetramethylammonium hydroxide and of the *tert*-amino end groups by *p*-toluenesulfonic acid in a 9/1 benzene–methanol mixture.

α,ω-Hydroxyl-terminated polyoxirane (PO) ($\bar{M}_n$ = 6000, $\bar{M}_w/\bar{M}_n$ = 1.15, and functionality = 2.0) was obtained from Hoechst AG and converted to dicarboxylic acid terminated PO by reaction with a twofold molar excess of succinic anhydride in toluene. After refluxing for 16 h, the polymer was precipitated in hexane and purified by three reprecipitations from benzene in hexane. Its functionality was higher than 1.95.

Carboxy-telechelic polybutadiene (PBD) commercially available from BFGoodrich under the trade name Hycar CTB2000×156 was also used. Its principal molecular characteristics were $\bar{M}_n$ = 4600, $\bar{M}_w/\bar{M}_n \simeq 1.8$, functionality = 2.01, and cis/trans/vinyl ratio = 20/65/15.

**Synthesis of Halato-Telechelic Polymers.** α,ω-*tert*-Amino-PMS was quaternized by a fivefold excess of benzyl chloride in chloroform solution (10% w/v) at room temperature. After purification by three successive precipitations into hexane, the product was free from any basic residue.

Zinc and magnesium pivalates were prepared in aqueous solution by double decomposition between the corresponding soluble chlorides and sodium pivalate. The insoluble alkaline earth pivalates were recovered by filtration and dried under vacuum to constant weight.

Metal methoxides were freshly prepared just before use by reaction of the pure metal with anhydrous methanol.

Carboxy-telechelic polymers were dissolved in decahydronaphthalene (DHN) (10% w/v) and mixed with the stoichiometric amount of metal pivalate. The reaction proceeded under nitrogen in a distillation apparatus equipped with an antifoaming head. Thanks to self-sealing accessories, fresh DHN could be introduced in the distillation flask or aliquots taken from it. When 20% of the DHN volume was distilled off under reduced pressure, it was replaced by fresh solvent and a further distillation run was carried out. Aliquots were precipitated into methanol, purified by reprecipitation, and finally dried to constant weight. These samples were analyzed by infrared (IR) spectrometry or viscometry.

Neutralization with metal methoxides proceeded similarly in toluene (instead of DHN) under strictly anhydrous conditions. The telechelic polymers were previously dried by three successive azeotropic distillations of benzene and finally dissolved in dry toluene (5% w/v). After two or three distillation runs of toluene, the absorption at 1700 cm$^{-1}$ (carboxylic acid) had completely disappeared in favor of a new absorption at 1560 cm$^{-1}$ (carboxylate). The relative viscosity of the product was also unmodified by further distillation.

Dialkyltin carboxylate containing polymers were prepared by refluxing the benzene solution of the carboxy-telechelic polymer and the dialkyltin oxide for 3 days in a Soxhlet apparatus, the thimble of which contained $CaH_2$. The tin oxide was found to be much more reactive than the corresponding alcoholate.

Metal α,ω-carboxylato polymers will be designated by $P_x$-Met-$Y$, where $P_x$ is the prepolymer, Met the metal, and $Y$ the carboxylate content in mol %.

**Viscometry.** Relative viscosity was determined in toluene at 25 °C with a Desreux–Bischoff capillary viscometer.[22]

Viscosity measurements vs. temperature were obtained using a sealed capillary viscometer originally designed by Desreux.[23] The viscometer was assembled on a horizontal axis and completely immersed in a thermostated bath (±0.1 °C) of dibutyl phthalate. The capillary was filled with the liquid by a rocking motion of the viscometer. The flow time measurements could be repeated at will. The solvent flow time was measured previously at different temperatures (25, 40, 60, and 80 °C), whereas the flow time of solutions was determined in a second run of measurements.

The vertical asymptote of the log $\eta_{rel}$–concentration plot defines the critical gelation concentration ($C_{gel}$).

## Results and Discussion

**Synthesis of Halato-Telechelic Polymers.** HTP formation takes place according to the general equation

$$n\mathrm{HOOC{-}P}_x\mathrm{{-}COOH} + (2n/v)\mathrm{Met{-}A}_v \rightleftharpoons [\mathrm{{-}OOC{-}P}_x\mathrm{{-}COO{-}Met}_{2/v}\mathrm{{-}}]_n + 2n\mathrm{HA} \quad (1)$$

Pineri et al.[16,17] have performed this neutralization of carboxy-telechelic polybutadiene (PBD) by using hydroxides of alkaline metals, acetates of divalent metals, or aluminum acetylacetonate. The metal derivative was dispersed in bulk PBD in a Brabender Plastograph at 150 °C whereas the reaction product (water, acetic acid, or acetylacetone) was volatilized. This technique allows only fair control of the reaction.[16] The authors observed indeed a difference between the theoretical and experimental degree of ionization; they noted a maximum torque for

Table I
Neutralization of Carboxy-Telechelic Polybutadiene (Hycar CTB) by Zinc Pivalate in DHN

| no. of dist runs | rel viscosity[a] | conversion, % |
|---|---|---|
| 0 | 1.6 | 0 |
| 2 | 3.8 | 75 ± 5 |
| 4 | 5.0 | 95 ± 5 |
| 6 | 6.1 | >95 |
| 10 | 8.6 | |
| 16 | 10.5 | |

[a] In toluene, at 25 °C; concentration = 2.5 g·dL$^{-1}$.

quantities of metal reagent exceeding (2–5 times) the stoichiometric amount. Finally, oxidative degradation can hardly be avoided and disturbs the specific effect of ionization.

Otocka et al.[18] used a more attractive technique. The carboxy-telechelic polybutadiene was dissolved in benzene and mixed at 55–60 °C with methoxides of group 1 and 2 metals (in solution in methanol). The aluminum derivative was prepared from aluminum isopropoxide in benzene, but particles of gelatinous material form even at low overall conversion.

Equation 1 is formally characteristic of a stepwise (polycondensation) process wherein maximum molecular weight and related properties are only reached in reactions carried very near the end point (>98–99%) and almost entirely free from undesirable side reactions.

To improve Pineri's results, the neutralization of carboxy-telechelic PBD by metal salts is performed under homogeneous conditions and especially in decahydronaphthalene (DHN) solution. Metal pivalates are selected first for their solubility and used in stoichiometric amount (eq 1). The pivalic acid (PA) formed is displaced by continuous distillation of solvent under reduced pressure. ($T_{eb}$(PA) = 154 °C, $T_{eb}$(DHN) = 180 °C under 1 atm); when about 20% DHN is recovered, the initial volume is completed by addition of pure DHN and the distillation is resumed. After each distillation run, an aliquot is taken from the flask and the conversion is analyzed by IR spectroscopy; the relative viscosity ($\eta_{rel}$) of the polymer recovered is also measured in toluene solution (2.5 g·dL$^{-1}$) at 25 °C. Table I shows that after six distillation runs, the conversion is higher than 95%; nevertheless, a very significant increase in $\eta_{rel}$ is still observed upon further distillation. This observation confirms the expected important effect of the last stages of the reaction on the properties of the HTP formed. As the pivalate-based technique is very time-consuming, the use of highly reactive metal derivatives is to be recommended, provided that they are inactive toward the polymeric backbone and form a molecule (HA in eq 1) which can be easily eliminated. The choice of metal methoxides proposed by Otocka et al. is suitable but the experimental conditions described are insufficiently drastic. Table II reports indeed the relative viscosity of $\alpha,\omega$-carboxylato-Mg-PBD obtained by neutralizing carboxy-telechelic PBD in toluene (5%) by magnesium methoxide in methanol. Methanol is eliminated by solvent distillation as reported for the pivalate-based procedure, and a very sharp increase of $\eta_{rel}$ is observed after complete removal of methanol. After two distillation runs, no further modification of $\eta_{rel}$ is observed. It is to be noted that the same product prepared with magnesium pivalate in DHN has rather low $\eta_{rel}$ values compared to those obtained by the methoxide-based technique (Table II). In this case, either the reaction is incomplete (after 15 distillation runs) or the pivalic acid is not completely eliminated.

Table II
Relative Viscosities at Different Concentrations in Toluene at 25 °C for $\alpha,\omega$-(Carboxylato)magnesium Polybutadienes[a] Prepared Differently

| | metal reagent | | |
|---|---|---|---|
| concn, g·dL$^{-1}$ | $Mg(OCH_3)_2$ without dist | $Mg(OCH_3)_2$ after 2 dist runs | $Mg(O_2CC(CH_3)_3)_2$ |
| 1.0 | 1.4 | 2.9 | 1.7 |
| 1.5 | 2.0 | 41 | 3.0 |
| 1.8 | 2.5 | 224 | 4.9 |

[a] Polybutadiene: Hycar CTB from BFGoodrich.

In conclusion, Otocka's procedure is efficient only when the alcohol formed is carefully removed from the reaction medium. Under these conditions, the reaction equilibrium is continuously displaced toward HTP formation, but a powerful solvating agent of the ionic groups is eliminated. The depressive role of any polar compound on the properties of HTP will be clearly illustrated in the next section. This effect is also useful in the synthesis of homogeneous aluminum-based HTP. According to Otocka et al., the addition of aluminum isopropoxide to the polymer (33% solids) is responsible for the formation of particles of gelatinous material; however, the addition of anhydrous alcohol ($\simeq$1 mL) followed by its elimination by solvent distillation is efficient and yields a completely homogeneous system. Similarly, heterogeneity takes place spontaneously when highly reactive compounds such as alkylmetals (i.e., diethylzinc) are used. Nevertheless, overnight refluxing (toluene) or the transient addition of dry methanol can easily overcome this drawback. Anyhow, $\eta_{rel}$ of the recovered Zn-based HTP is the same whatever the procedure. This agrees with the complete elimination of the methanol added in the second pathway.

Thanks to the experimental conditions herein defined, a large variety of HTP can be prepared with reproducible characteristics in less than 1 h and at temperatures lower than 100 °C. Therefore, the forthcoming conclusions of our extensive investigation of HTP structure and properties can be drawn with reliability.

**Dilute-Solution Properties of HTP.** Otocka et al.[18] report the results of solution viscosity studies on carboxy-telechelic PBD and its ester terminated and sodium salt terminated forms. They mention that sodium $\alpha,\omega$-carboxylato-PBD is not soluble in benzene but soluble in trichlorobenzene (TCB) with difficulty. The viscosity values of the salt form in TCB increase more quickly with concentration than the nonneutralized PBD because of the association of the salt end groups. Besides these very partial results, no other information is available on the dilute-solution behavior of HTP. To fill this gap an extensive study has been undertaken and its more significant results are now reported.

Once completely dried, HTP require a prohibitively long time to dissolve again. Therefore, they are systematically prepared in the solvent for study. The concentration is then adjusted by addition or elimination of solvent and determined by evaporating an accurate aliquot to dryness and weighing the polymer recovered.

This investigation focuses mainly on the gel formation which occurs in dilute solutions at increasing concentrations. This phenomenon is characterized by viscosity measurements and is related not only to the nature of the ion pair, polymeric chain, and solvent but also to temperature and molecular weight of the telechelic polymer.

**Dependence of Dilute-Solution Viscosity on Concentration.** The dilute-solution viscosity of HTP is

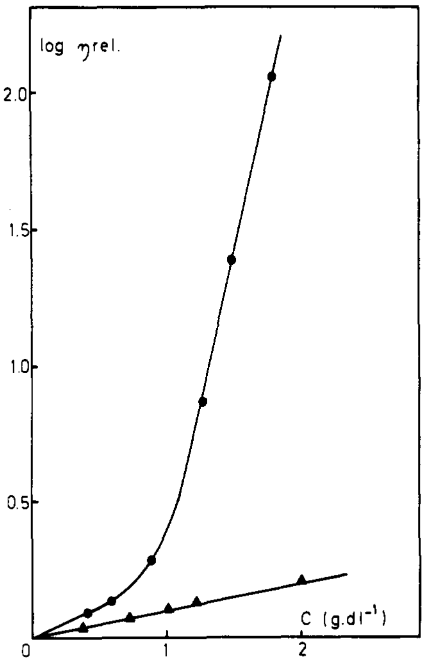

**Figure 1.** Relative viscosity of both $\alpha,\omega$-carboxylato-Mg-PBD (●) and nonneutralized $\alpha,\omega$-carboxy-PBD (▲) vs. concentration in toluene at 25 °C.

strongly dependent on concentration, as shown in Figure 1 for PBD-Mg-2,3 in toluene at 25 °C. At very low concentrations (<0.6 g·dL$^{-1}$) the relative viscosity of PBD-Mg-2.3 seems to vary like that of the corresponding carboxy-telechelic PBD (Hycar CTB), but with a slightly steeper slope. Beyond these concentrations, $\eta_{rel}$ increases abruptly and gelation occurs. This behavior is, of course, an obvious consequence of interactions between the carboxylato groups in a nonpolar solvent (dielectric constant $\epsilon = 2.38$). This conclusion agrees qualitatively with the observations of Otocka et al.[18] who do not mention however, any gel formation.

**Dependence of Gel Formation on the Nature of the Ion End-Capping the Telechelic Polymer.** Both ends of anionically prepared poly($\alpha$-methylstyrene) ($\bar{M}_n = 6000$) are capped with a carboxylic acid (PMS-$(COOH)_2$), a sulfonic acid (PMS-$(SO_3H)_2$), and a tertiary amine (PMS-$(NMe_2)_2$). After complete neutralization by $Mg(OCH_3)_2$, the dicarboxylic and disulfonic acid terminated PMS have practically the same behavior (Figure 2), gelation appearing earlier for the sulfonate-based HTP. When quaternized with benzyl chloride, the $\alpha,\omega$-*tert*-amino-PMS exhibits a still greater trend to gelation (Figure 2). Ionic bonding prevails in the ammonium salt end groups whereas the ionicity of the sulfonate end groups is higher than that of the carboxylate salts, as a sulfonic acid is stronger than a carboxylic acid.

The attractive force $f$ between anion ($e_A$) and cation ($e_C$) varies inversely as both the dielectric constant ($\epsilon$) and the square of their distance ($a$)

$$f = \frac{1}{\epsilon}\frac{e_A e_C}{a^2} \qquad (2)$$

When $f$ is low, the ionic groups attached to a polymeric backbone set up an electrostatic repulsion, resulting in the well-known polyelectrolyte behavior. When $f$ is high, i.e., in media of low dielectric constant, net charges on the polymer molecule tend to disappear in favor of dipoles, the interaction of which can stabilize a chain network. Furthermore, at a constant and low dielectric constant ($\epsilon$(toluene) = 2.4), the higher the effective charges $e_A$ and $e_C$ are, the higher their attractive force $f$ is and the earlier the gel formation takes place.

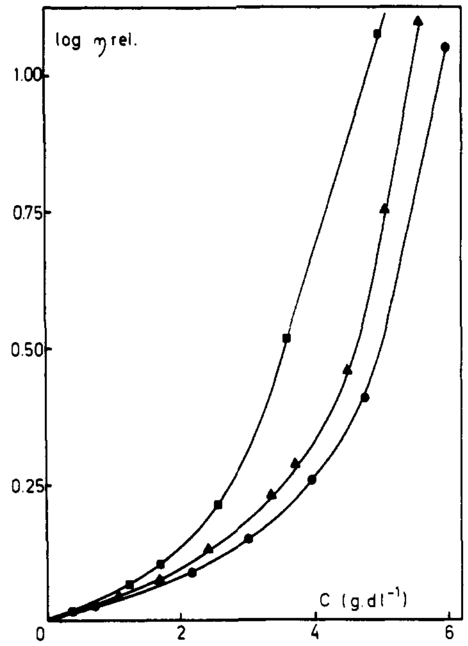

**Figure 2.** Relative viscosity–concentration plots in toluene at 25 °C for poly($\alpha$-methylstyrene) ($\bar{M}_n = 6000$) $\alpha,\omega$ end-capped with different ion pairs: (●) Mg carboxylate; (▲) Mg sulfonate; (■) dimethylbenzylammonium chloride.

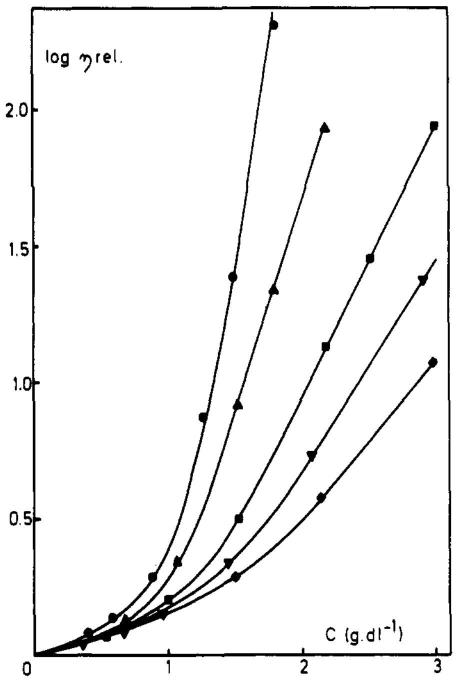

**Figure 3.** Relative viscosity–concentration plots in toluene at 25 °C for $\alpha,\omega$-carboxylato-polybutadiene containing different metal ions: (●) Mg; (▲) Ca; (■) Ba; (▼) Cu; (♦) Mn.

**Dependence of Gel Formation on the Metal Ion in Carboxylate-Containing Polymers.** The carboxy-telechelic PBD commercially available from BFGoodrich Co. (Hycar CTB) is neutralized by a series of alkaline earth cations. Again, a sharp increase of $\eta_{rel}$ is observed at decreasing concentration when the size of the cation decreases (Figure 3). As an example, an $\eta_{rel}$ value of 3 (or log $\eta_{rel} = 0.48$) is observed at 1.12 g·dL$^{-1}$ for Mg (ionic radius $r = 0.65$ Å), 1.25 g·dL$^{-1}$ for Ca ($r = 0.99$ Å), and 1.48 g·dL$^{-1}$ for Ba ($r = 1.35$ Å). This observation agrees with eq 2; $f$ increases indeed as $a$ decreases, all the other con-

Table III
Dependence of the Gelation of Different α,ω-(Carboxylato)magnesium Polymers on the Average End-to-End Distance $\langle r^2\rangle^{1/2}$ of the Corresponding Nonneutralized Prepolymer

| polymer ($\bar{M}_n$) | $C_{gel}$,[a] g·dL$^{-1}$ | ion content mol % | ion content wt % | flexibility[25] $(r_0^2/r_0{}^2{}_f)^{1/2}$ | $\langle r^2\rangle^{1/2}$, Å |
|---|---|---|---|---|---|
| PBD (4600) | 2.1 | 2.3 | 2.4 | 1.45[b] | 78 |
| PO (6000) | 2.5 | 1.5 | 1.9 | 1.42 | 66 |
| PMS (6000) | 6.3 | 3.9 | 1.9 | 2.29 | 57 |

[a] Critical gel concentration. [b] Value for PBD containing 71% trans and 25% cis units.

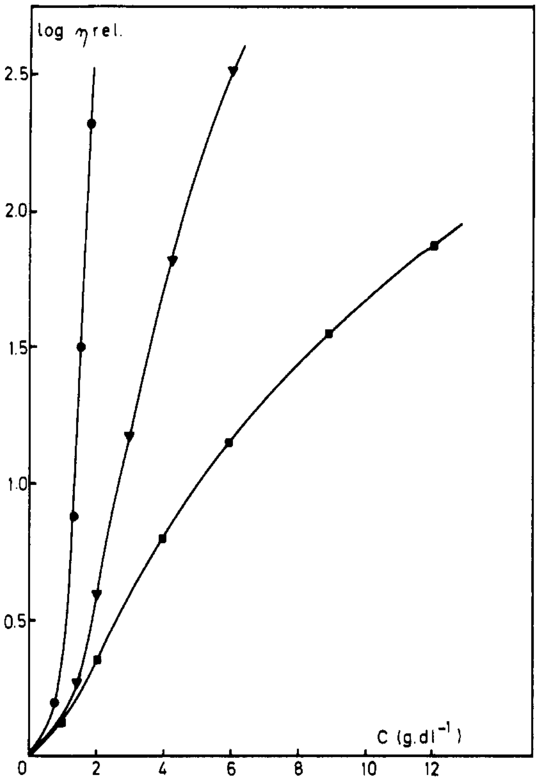

**Figure 4.** Relative viscosity–concentration plots in benzene at 25 °C for Mg and $R_2Sn$ α,ω-carboxylato-polybutadiene: (●) Mg; (▼) dimethyltin; (■) dibutyltin.

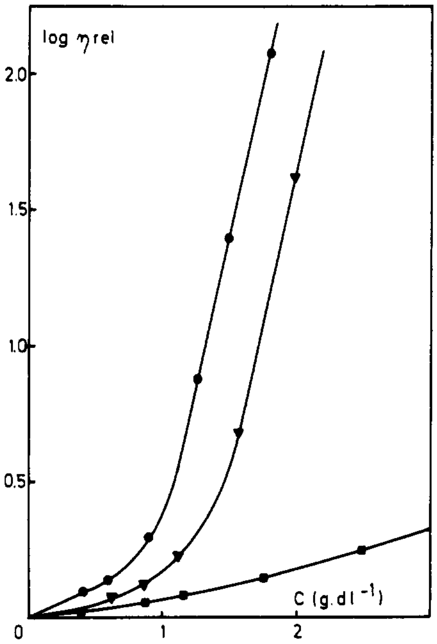

**Figure 5.** Relative viscosity–concentration plots in toluene at 25 °C: effect of the prepolymer nature in Mg α,ω-carboxylato polymers: (●) polybutadiene (PBD-Mg-2.3); (▼) polyoxirane (PO-Mg-1.5); (■) poly(α-methylstyrene) (PMS-Mg-3.9).

ditions being kept constant (i.e., alkaline earth carboxylates, in toluene at 25 °C). Cu ($r$ = 0.69) and Mn ($r$ = 0.80 Å), although smaller than Ba, are responsible for a delayed gelation; this may be a consequence of the less ionic, more coordinate character of the carboxylate–transition metal bonds. The formation of multiplets of increasing size is accordingly more difficult, as also observed for dialkyltin α,ω-carboxylato-PBD in toluene at 25 °C (Figure 4). The ionic character of dialkyltin carboxylate, is, of course, less pronounced than that of magnesium carboxylates whereas steric effects become significant in the aggregation process. The dibutyltin compound shows clearly a leveling-off in the $\eta_{rel}$ variation at increasing concentration (Figure 4).

When neutralized by tri- or tetravalent cations (Al ($r$ = 0.50 Å) or Ti ($r$ = 0.68 Å)) in toluene, Hycar CTB also forms homogeneous gels, but any attempt to "dilute" these gels at concentrations lower than 1 g·dL$^{-1}$ leads to demixing and prevents any $\eta_{rel}$ measurements in toluene at 25 °C. It is to be noted that Be ($r$ = 0.31 Å) α,ω-carboxylato-PBD also shows phase separation at high dilution. This phenomenon is quite reversible, since a homogeneous gel is again observed when solvent is partly recovered. Furthermore, the mixing of small amounts of alcohol homogenizes the two-phase system, which is noted again at the elimination of the alcohol while the overall polymer concentration is kept constant. No demixing has been noted with divalent cations other than Be at concentrations higher than 0.4 g·dL$^{-1}$ in toluene. The carboxylates of all these cations form less strong dipoles than Be carboxylates do, and the demixing is delayed or metastable solutions are obtained. The demixing of HTP solutions can accordingly be observed at increasing dilution and constant temperature. According to Joanny,[24] the demixing of ionomer solutions in nonpolar solvent is to be expected, but at decreasing temperature and constant concentration. This situation will be discussed in a forthcoming paper.

**Effects of Polymeric Chain Nature on Gel Formation.** Carboxy-telechelic PBD ($\bar{M}_n$ = 4600), PMS ($\bar{M}_n$ = 6000), and polyoxirane or PO ($\bar{M}_n$ = 6000) are completely neutralized by magnesium methoxide in toluene. Qualitatively, the corresponding HTP behave similarly, as shown in Figure 5; however their relative position does not depend at all on the ion content, but rather on the average end-to-end distance $\langle r^2\rangle^{1/2}$ of the carboxy-telechelic prepolymers (Table III). $\langle r^2\rangle^{1/2}$ can be calculated in toluene at 25 °C from the Flory relation ($[\eta] = \phi\langle r^2\rangle^{3/2}/M$, with $\phi = 2.1 \times 10^{21}$) and experimental $[\eta]$ values; Figure 5 would agree qualitatively with the inverse dependence of $C_{gel}$ on the real chain length of the nonneutralized prepolymer in solution. To be strictly valid, the comparison should, however, be based on materials with the same ion content. This point will be considered again in the discussion about the effect of the prepolymer molecular weight (i.e., $\langle r^2\rangle^{1/2}$).

**Effect of Solvent on Gel Formation.** The α,ω quaternary ammonium chloride PMS used in Figure 2 is studied in toluene, tetrahydrofuran (THF), and di-

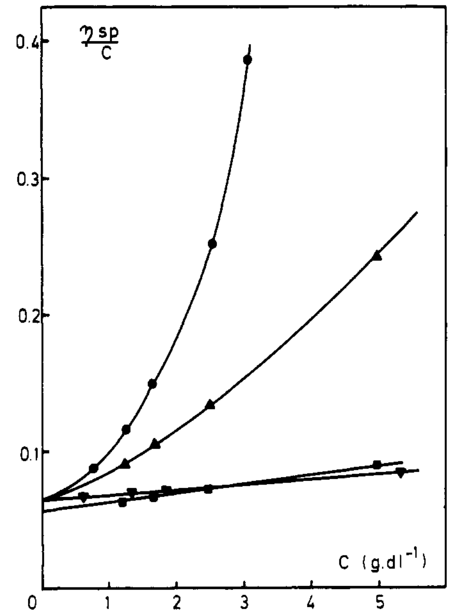

**Figure 6.** Effect of solvent on the reduced viscosity–concentration plots for $\alpha,\omega$ quaternary ammonium chloride PMS at 25 °C: (●) toluene; (▲) THF; (■) DMF; (▼) nonquaternized $\alpha,\omega$-*tert*-amino-PMS in DMF.

methylformamide (DMF), respectively. This HTP is not prepared in each solvent separately. After quaternization in chloroform, the product is evaporated to dryness and finally dissolved in the respective solvents, the $\eta_{rel}$ vs. concentration plots reported in Figure 6 are accordingly strictly comparable. In solvents of increasing dielectric constant ($\epsilon$), the dissociation of the ionic end group is enhanced and their aggregation depressed. In DMF ($\epsilon$ = 37), at around 5 g·dL$^{-1}$, HTP behaves rather as the nonquaternized prepolymer whereas in toluene ($\epsilon$ = 2.4) the gel is already well formed. THF ($\epsilon$ = 7.4) is, of course, an intermediate case. This solvent effect illustrates clearly the electrostatic nature (eq 2) of the gel-determining process. In the section "Synthesis of Halato-Telechelic Polymers", the depressive effect of trace polar compounds was suspected; Figure 7 is an unambiguous confirmation of that.

Toluene is mixed with 1% (v/v) THF, propylene carbonate, and triethylamine, respectively. A very large decrease of $\eta_{rel}$ is noted for PBD-Mg-2.3 at concentrations higher than 1 g·dL$^{-1}$. The depressive effect of 1% methanol on the gelation is particularly obvious; the shape of the $\eta_{rel}$ variation vs. concentration is, however, modified, evidencing a stronger action of methanol on the ion aggregation process.

**Temperature Effect on Gel Formation.** To obtain significant viscosity measurements vs. temperature, completely tight capillary viscometers are used (see Experimental Section). The viscosity of the nonneutralized carboxy-telechelic PBD vs. temperature (25–80 °C) was measured previously in toluene. The classical behavior of any polymer dissolved in a good solvent is observed, i.e., an intrinsic viscosity $[\eta]$ decreasing as the temperature increases.[26] The $[\eta]$ variation is, however, small and ranges from 0.22 to 0.18 dL·g$^{-1}$. The individual $\eta_{sp}/C$ vs. $C$ (0–1.25 g·dL$^{-1}$) plots are perfectly linear.

Figure 8 shows the effect of temperature on $\eta_{rel}$ of PBD-Mg-2.3 in toluene. This effect becomes increasingly higher beyond 1 g·dL$^{-1}$, i.e., in a range where the ions are gathering into multiplets. Moreover, an increase in temperature has the same effect as an increase in the size of alkaline earth cations (Figure 3).

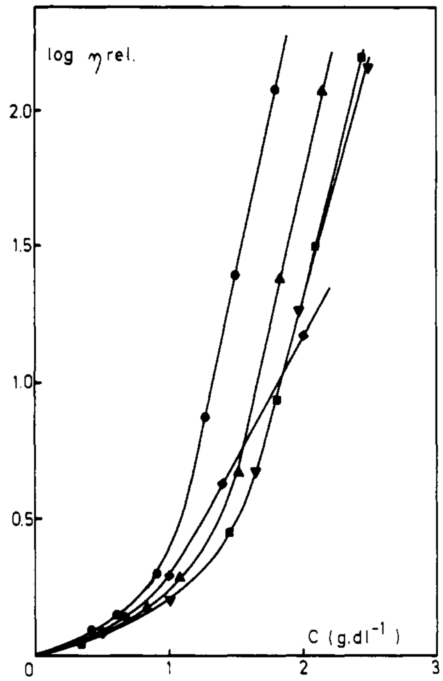

**Figure 7.** Relative viscosity–concentration plots for PBD-Mg-2.3 in toluene at 25 °C. Effect of the addition of 1% polar compounds into toluene: (●) pure toluene; (▲) addition of THF; (■) addition of propylene carbonate; (▼) addition of triethylamine; (♦) addition of methanol.

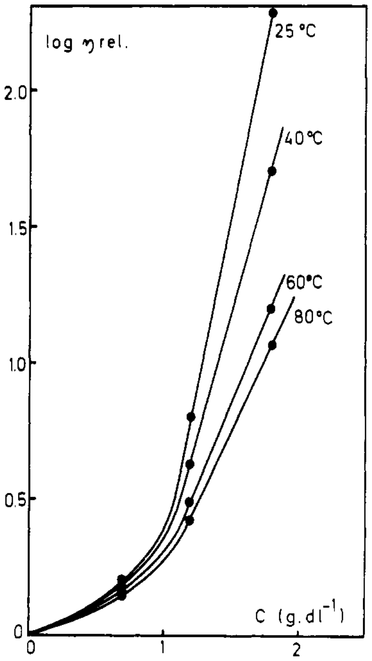

**Figure 8.** Temperature effect on the relative viscosity–concentration plot for PBD-Mg-2.3 in toluene.

Figure 9 differs from Figure 8 in the presentation of the experimental data but not in its conclusions. Figure 9 reports, however, additional information concerning Ca and Ba cations.

The excellent thermoreversibility of the HTP solutions in toluene must be noted. After a heating run up to 80 °C, the measurement of the relative viscosity at 25 °C is repeated with a reproducibility higher than 95%.

The observed temperature effects also agree with a dominant role for the ionic component on the gelation process. As long as the chain ends are largely free, the viscous flow of the solution shows no anomaly. When the

Table IV
Dependence of $C_{gel}$ upon $\bar{M}_n$ of Prepolymer in $\alpha,\omega$-(Carboxylato)magnesium Polymers (Toluene, 25 °C)

| PIP | | PMS | | PTBS | | PS | | PBD | |
|---|---|---|---|---|---|---|---|---|---|
| $\bar{M}_n$ | $C_{gel}$, g·dL$^{-1}$ | $\bar{M}_n$ | $C_{gel}$, g·dL$^{-1}$ | $\bar{M}_n$ | $C_{gel}$, g·dL$^{-1}$ | $\bar{M}_n$ | $C_{gel}$, g·dL$^{-1}$ | $\bar{M}_n$ | $C_{gel}$, g·dL$^{-1}$ |
| 15 500 | 3.2 | 6 000 | 6.3 | 11 000 | 7.8 | 10 500 | 3.7 (5) | 4 600 | 2.0 |
| 20 000 | 2.8 | 12 000 | 4.8 | 15 000 | 6.8 | 13 500 | 3.4 | | |
| 36 000 | 2.2 | 20 000 | 3.3 | 23 000 | 5.2 (5) | 20 500 | 2.9 | | |
| 69 000 | 1.5 | | | | | 37 000 | 2.2 | | |

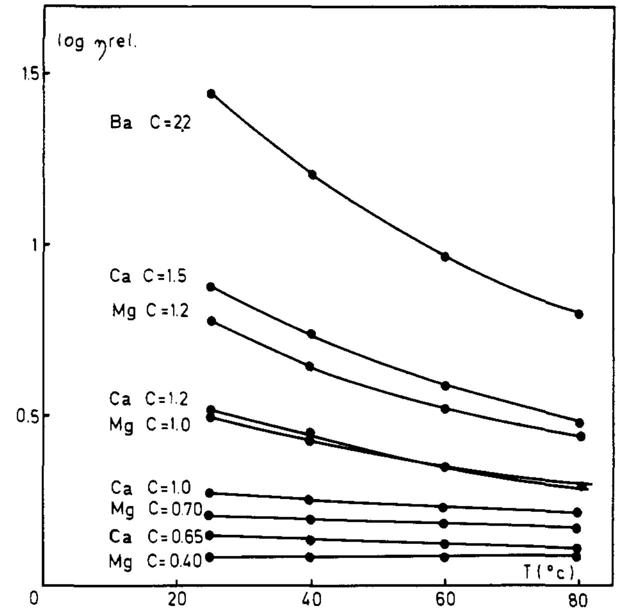

**Figure 9.** Temperature effect on the relative viscosity of alkaline earth $\alpha,\omega$-carboxylato-polybutadienes in toluene at different concentrations ($C$ = g·dL$^{-1}$).

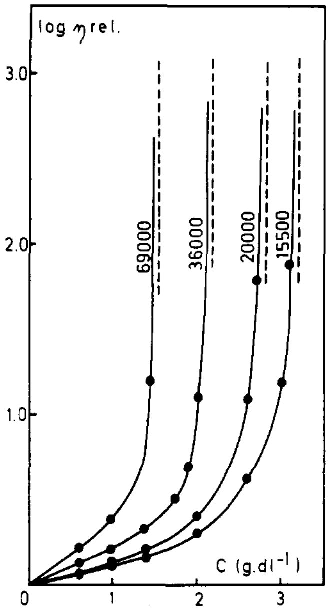

**Figure 10.** Relative viscosity–concentration plots in toluene at 25 °C for Mg $\alpha,\omega$-carboxylato-polyisoprenes with different molecular weights.

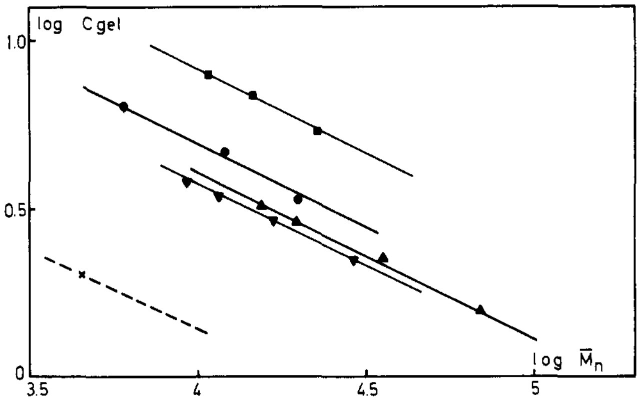

**Figure 11.** Dependence of the critical gel concentration ($C_{gel}$) upon the prepolymer molecular weight in Mg $\alpha,\omega$-carboxylato polymers (toluene, 25 °C): (●) PMS; (▲) PIP; (■) PTBS; (▼) PS; (×) PBD.

ionic chain ends are engaged into multiplets and the chains form a three-dimensional network, a potential barrier must be overcome to free them again; at this moment, the sharp increase of viscosity and the ultimate gelation are observed. The height of this barrier, which depends on a series of parameters (temperature, solvent, cation, etc.) is the factor controlling the gel formation.

From Figure 9, it appears that at the same concentration (1.2 g·dL$^{-1}$) PBD-Ca-2.3 at 25 °C has the same behavior as PBD-Mg-2.3 at 62 °C. When the same solvent, prepolymer, and concentration are used, a relation between the effects of temperature and size of alkaline earth cations appears. The same frequency of jumping the potential barrier is therefore observed at temperatures depending on the electrostatic interactions.

**Effects of Prepolymer Molecular Weight on Gel Formation.** By modifying the prepolymer molecular weight, the ion content of the HTP formed is altered. Figure 10 shows this effect for Mg-$\alpha,\omega$-carboxylato-polyisoprene (PIP). The critical concentration for gelation ($C_{gel}$) corresponds to the vertical asymptote of the log $\eta_{rel}$ vs. *concentration curve.* The narrower the molecular weight distribution of the prepolymer, the sharper the viscosity increase or the more accurate the $C_{gel}$ determination. The comparison between PIP samples ($\bar{M}_w/\bar{M}_n$ < 1.2) and the commercial PBD ($\bar{M}_w/\bar{M}_n \simeq 1.8$, Figure 1) is convincing in this respect.

As the gelation is the consequence of the aggregation of the ionic end groups into multiplets, it should be expected that $C_{gel}$ decreases as the ion content increases. Table IV and Figure 11 show unambiguously an opposite behavior, since $C_{gel}$ varies inversely as the molecular weight of the prepolymers. For a given HTP, solvent, and temperature, a straightforward relation exists between $C_{gel}$ and $\bar{M}_n$ of the prepolymer. In toluene at 25 °C, this relation is deduced from Figure 11 and can be written

$$C_{gel} = 407M_n^{-0.5} \tag{3}$$

for $\alpha,\omega$-carboxylato-Mg-PIP,

$$C_{gel} = 490M_n^{-0.5} \tag{4}$$

for $\alpha,\omega$-carboxylato-Mg-PMS,

$$C_{gel} = 370M_n^{-0.5} \tag{5}$$

for $\alpha,\omega$-carboxylato-Mg-PS, and

$$C_{gel} = 800M_n^{-0.5} \tag{6}$$

for $\alpha,\omega$-carboxylato-Mg-PTBS. For polybutadiene (85% 1, 4), only one prepolymer (Hycar CTB, $\bar{M}_n = 4600$) was studied. Assuming the same relation as before,

$$C_{gel} = 136M_n^{-0.5} \qquad (7)$$

This unexpected result is to be compared to the apparent dependence of the gelation on the real chain length $\langle r^2\rangle^{1/2}$ of the prepolymer (Figure 5): the shorter the end-to-end distance, the less favorable the gelation. By analogy with eq 3–7, an equation type $C_{gel} = A\langle r^2\rangle^{-x/2}$ could be proposed.

In conclusion, there is no doubt that the gel results from dipolar interactions between the ionic end groups of the telechelic polymers, but the characteristics of the polymeric backbone ($\bar{M}_n$, $\langle r^2\rangle^{1/2}$) have a determining influence on the process. The higher the average end-to-end distance of a given polymer, the easier the simultaneous incorporation of both ionic ends in multiplets. This can explain why the $\eta_{rel}$ vs. concentration plots are sharper when the prepolymer heterodispersity is lower (Figure 1, $\bar{M}_\omega/\bar{M}_n \simeq 1.8$; Figure 10, $\bar{M}_\omega/\bar{M}_n \leq 1.2$). A theoretical interpretation of the experimental results reported herein will be presented in a future paper.

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# Scaling Analysis of Static Properties for Semidilute Solutions

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ABSTRACT: Low-angle scattered laser light from semidilute solutions of relatively monodisperse polystyrene in toluene is measured as a function of concentration and degree of polymerization. The excess chemical potential is observed to scale asymptotically as the $d\nu/(d\nu - 1)$ power of concentration, where $d = 3$ is the dimensionality of space and $\nu$ is measured to be 0.575. This value of $\nu$ is 4% smaller than that determined from dilute solution measurements and 2% smaller than the value predicted by renormalization group techniques. The excess chemical potential for polymers of molecular weight $M$ at concentration $c$ approaches this asymptote as a function of $(Mc^{1/(d\nu-1)})^{-1}$, in accordance with scaling theory. The data are more satisfactorily described by this model than a generalization of the Flory–Huggins theory that permits the interaction parameter to be a function of polymer concentration.

## Introduction

Scaling theory has given polymer scientists a new perspective on interpreting measurements made in semidilute or moderately concentrated solutions.[1] In this regime there is substantial overlap of individual polymer molecules, but the solvent molecules still constitute a significant volume fraction of the solution. Experimentally this corresponds to a concentration

$$c > c^* = M/N_{Av}R^3 \qquad (1)$$

where the overlap concentration $c^*$ specifies the condition where the average local concentration inside the polymer coil of molecular weight $M$ and average length $R$ equals the concentration of the solution. Avogadro's number is represented by $N_{Av}$.

Scaling analyses predict both the static and dynamic properties of molecules. Although dynamic predictions for polymers in good solvents have been investigated by light scattering techniques by several investigators,[2–6] static predictions have not been as widely studied. Elegant neutron scattering measurements have confirmed static scaling behavior,[7] but a relatively small number of samples have been studied by this complex method. Chu and co-workers[3,5] have observed some scaling relations by

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