Halato-Telechelic Polymers. 6. Viscoelastic Properties of Solutions of Alkaline Earth α,ω-Dicarboxylatopolybutadiene

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ABSTRACT: Alkaline earth α,ω-dicarboxylatopolybutadienes dissolved in a nonpolar solvent ($\bar{M}_n$ = 4600) display an attractive thermorheological simplicity and exhibit a secondary relaxation characteristic of the ionic component. The shear-thickening character of these solutions is to be outlined. Their deformation mechanism is controlled by the stability and the mean size of the ionic multiplets formed by the carboxylate end groups. The electrostatic origin of the viscoelastic behavior observed is well established by its dependence on solvent, temperature, and cation size.

Introduction

In the past 2 decades ion-containing polymers have received increasing attention. Network glasses and polyelectrolytes have been known for a long time, but more recently it appeared interesting to introduce a few percent ions into traditional low-polarity polymeric materials.[1,2] Strong intra- and intermolecular electrostatic interactions developing in such systems are responsible for dramatic changes in the properties of the base polymer and for new ranges of application. "Ionomer" materials asserted the potentialities of ion-containing polymers when Du Pont launched the marketing of "Surlyn".

In ionomers, the ionic groups are more or less randomly distributed along the polymeric backbone. They associate in media of low dielectric constant to form at least two types of aggregates, which basically determine the supermolecular structure and deeply modify the physical properties. Small multiplets would act as transient cross-links, whereas large clusters would give the materials a phase-separated character.[3] In either case, the morphology and behavior of ionomers largely depend on their molecular structure, which controls the ion aggregation process. As the distribution of ionic groups in ionomers can hardly be controlled and modified at will, the study of model ion-containing polymers is very attractive. In that respect, we have recently shown that halato-telechelic polymers (HTPs) really represent a family of materials with a broad range of carefully matched molecular characteristics.[4-7] The neutralization of carboxy-telechelic polymers is an example:

$$n\text{HOOC–P–COOH} + (2n/v)\text{MeA}_v \rightarrow -[{}^-\text{OOC–P–COO}^- \text{M}^{2+}{}_{2/v}-]_n + 2n\text{HA} \quad (1)$$

where A is a monovalent anion associated to the metal M, the valency of which is v. The nature of both prepolymer (P) and cation (M) can be substantially modified and the prepolymer length and polydispersity easily controlled. An efficient pathway has been proposed for the synthesis of such materials.[7]

When HTPs are dissolved in nonpolar solvents, a gelation process occurs at low concentrations.[4] This critical gelation concentration (C_{gel}) can be as low as 1.5 g dL^{-1}, but mainly depends on the molecular characteristics of the prepolymer and on the extent of the electrostatic interactions.[7] Theoretical considerations explain this kind of behavior well,[8] but they cannot account for the time dependence of the solution properties. The aim of this paper is to inquire into the rheology of HTP solutions.

Experimental Section

All the halato-telechelic polymers herein studied resulted from the neutralization of the carboxy-telechelic polybutadiene commercialized by B.F. Goodrich under the trade name HYCAR CTB 2000x156 ($\bar{M}_n$ = 4600 and $\bar{M}_w/\bar{M}_n$ = 1.8). The neutralization was carried out in dry chloroform, toluene, xylene, or Decalin by adding a stoichiometric amount of a highly reactive metal derivative: magnesium, calcium, or barium methoxide and di-n-butylberyllium, respectively. Complete reaction was ensured by distilling off the resulting alcohol or n-butane. The synthesis is described in detail elsewhere.[7]

Metal methoxides were prepared just before use by the reaction of the pure metal with anhydrous methanol. Di-n-butylberyllium was obtained by reacting n-BuLi with BeBr$_2$, prepared according to the procedure of Richards and Burgers for MgBr$_2$.[9] The synthesis of BeBr$_2$ was, however, carried out in refluxing tetrahydrofuran.

Once completely dried, HTPs needed a prohibitively long time to dissolve again, so they were prepared in the solvent in which they were studied. The concentration was adjusted by partial addition or elimination of solvent and determined by evaporating an accurate amount to dryness and weighing the recovered polymer.

The dynamic mechanical behavior was investigated with a Rheometrics mechanical spectrometer (RMS-7200). Steady-flow viscosity was measured by using a cone–plate geometry. The plate diameter was either 5.0 or 7.2 cm (for the less viscous solutions); the cone angle (β) was 0.04 rad. Dynamic mechanical properties were investigated with the plate–plate geometry (plate diameter 5.0 cm; plate-to-plate distance 0.2 cm).

Results

Perturbations are induced in the HTP solutions when they are introduced into the plate–plate geometry of the Rheometrics mechanical spectrometer. The equilibrium state of these solutions must be reached again; otherwise the meaning of the dynamic mechanical determinations is doubtful. In order to illustrate this point, the complex shear modulus of a 10 g dL^{-1} solution of magnesium α,ω-dicarboxylatopolybutadiene in decahydronaphthalene (DHN) has been measured just after introduction in the spectrometer. Figure 1 shows the time dependence of both storage and loss moduli recorded at constant frequency (1 rad s^{-1}) and constant temperatures (296, 312, and 327 K, respectively). After 35 min, the equilibrium values of G' and G'' are obtained at 327 K, whereas the point where

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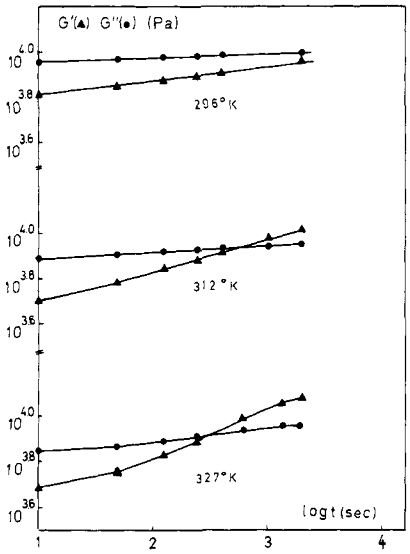


Figure 1. Shear storage (G') and loss (G'') moduli vs. time at constant frequency (1 rad s^{-1}) and different temperatures for a 10 g dL^{-1} solution of magnesium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ = 4600) in DHN. Time is recorded just after the introduction of the solution into the plate–plate geometry of the mechanical spectrometer.

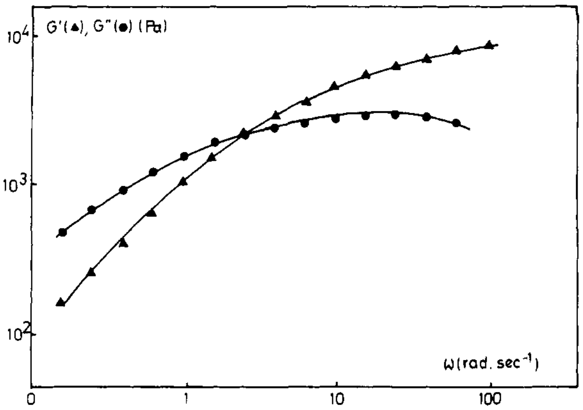


Figure 2. Shear storage and loss moduli as a function of angular frequency at 296 K for a 10 g dL^{-1} solution of magnesium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ = 4600) in DHN.

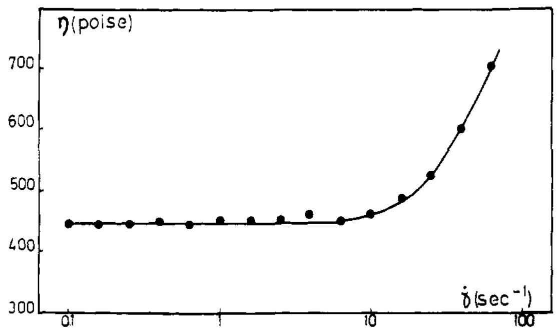


Figure 3. Shear-thickening behavior of a 10 g dL^{-1} solution of magnesium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ = 4600) in DHN, at 296 K.

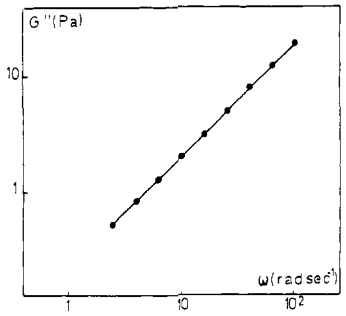


Figure 4. Dynamic modulus at 296 K of a 10 g dL^{-1} solution of magnesium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ = 4600) in chloroform.

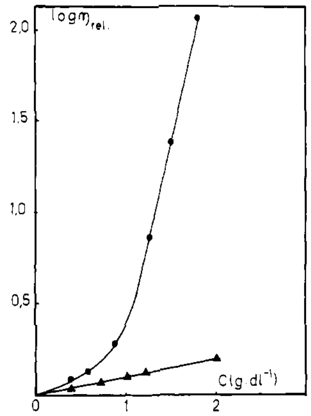


Figure 5. Relative viscosity of both magnesium α,ω-dicarboxylatopolybutadiene (●) and nonneutralized prepolymer ($\bar{M}_n$ = 4600) (▲) vs. concentration in toluene at 298 K.

$G' = G''$ is not yet reached at 296 K. The reorganization of the HTP solutions is therefore a thermally activated phenomenon, which must be taken into account to record reliable measurements.

The complex shear modulus vs. frequency isotherm, measured at 296 K for the same solution, is reported in Figure 2. At frequencies ω smaller than 0.45 rad s^{-1}, G'' is higher than G' and the system behaves as a viscous liquid. Above 0.45 rad s^{-1}, the situation is reversed and the system displays a gellike behavior. The steady-flow viscosity of this solution is clearly dependent on the $\dot{\gamma}$ shear rate when the latter is higher than 6 s^{-1} (Figure 3). In this shear rate range, a deviation from Newtonian behavior is observed, which confers a shear-thickening (or dilatant) character to the system.

At constant concentration and temperature, the complex shear modulus vs. frequency isotherm is dramatically modified when chloroform is substituted for DHN (Figure 4). A liquidlike behavior is then reported as the real part of the shear modulus is negligible with respect to the imaginary part, which varies proportionately to the frequency. In chloroform, the real part of the dynamic viscosity ($\eta' = G''/\omega$) is 2.1 P; it is independent of the frequency at least in the investigated range, whereas η' rises to 3.2×10^4 P in DHN at low frequency (0.1 rad s^{-1}). The steady-flow viscosity of the chloroform solution is about 350 times lower than that of the DHN solution; furthermore, up to a shear rate of 150 s^{-1}, no shear-thickening effect is detected in chloroform while it is effective in DHN from 6 s^{-1}. These results show the dramatic effect of solvent on the solution properties of HTP; it is significant that the dielectric constant of chloroform (4.4) is twice as high as that of DHN (2.2).

The effect of concentration has been partly discussed in a separate paper.[7] Briefly, at low concentrations (<1 g dL^{-1}), the relative viscosity of magnesium α,ω-dicarboxylatopolybutadiene (toluene, 298 K) varies in a manner similar to that of the nonneutralized prepolymer, whereas a sudden and sharp increase of viscosity appears at increasing concentrations (Figure 5). This gelation effect results from the association of the carboxylate end groups into multiplets. It occurs at decreasing polymer concentrations when the alkaline-earth cation size decreases. As both prepolymer and cation are difunctional,

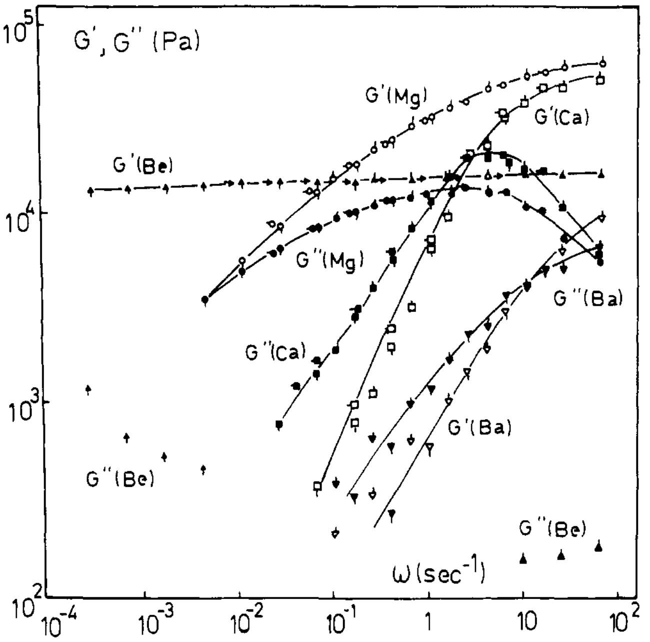


Figure 6. Master curves of shear storage and loss moduli for 10 g dL^{-1} solutions in xylene of beryllium, magnesium, calcium, and barium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ = 4600), reference temperature 297 K. For clarity only half the experimental points of maximum three isotherms have been plotted in the figure. Six isotherms have really been reported between 297 and 342 K and confirm the superposition shown by the partial results of this figure. Be: (▲) 297 K, (-▲) 324 K, (▲) 342 K. Ca: (□) 297 K, (-□) 323 K, (□) 342 K. Mg: (○) 297 K, (-○) 330 K, (○) 342 K. Ba: (▽) 297 K, (▽) 342 K.

this gelation would be expected when the multiplets contain a mean number of divalent cations ($\bar{n}$) just higher than 1. However, at the critical point of gelation in toluene at 298 K, $\bar{n}$ is calculated as 2.3 for magnesium α,ω-dicarboxylatopolybutadiene.[8] The rheological behavior of HTP solutions in nonpolar solvents is of course dependent on the concentration at constant temperature. It is experimentally observed that the higher the concentration, the higher the storage shear modulus and the lower the loss tangent ($\tan \delta = G''/G'$) whatever the frequency.

Both storage and loss shear moduli vs. frequency isotherms have been recorded for beryllium, magnesium, calcium, and barium α,ω-dicarboxylatopolybutadiene solutions in xylene (10 g dL^{-1}) at six different temperatures between 297 and 342 K. As temperature increases, the G' and G'' curves systematically shift toward higher frequencies. The usual procedure of shifting successive isotherms of log G' (or log G'') vs. log ω horizontally with respect to a reference isotherm (297 K) makes them fit with a maximum overlap (Figure 6). A good frequency–temperature superposition of the data is accordingly observed, except for the biggest cation, Ba, which shows some scattering of the experimental data. Since the loss moduli of the Be derivative are too small and much less accurate, the resulting master curve is ill-defined. The storage modulus isotherms of beryllium α,ω-dicarboxylatopolybutadiene are very flat and the accuracy of the shift factors a_T is accordingly limited.

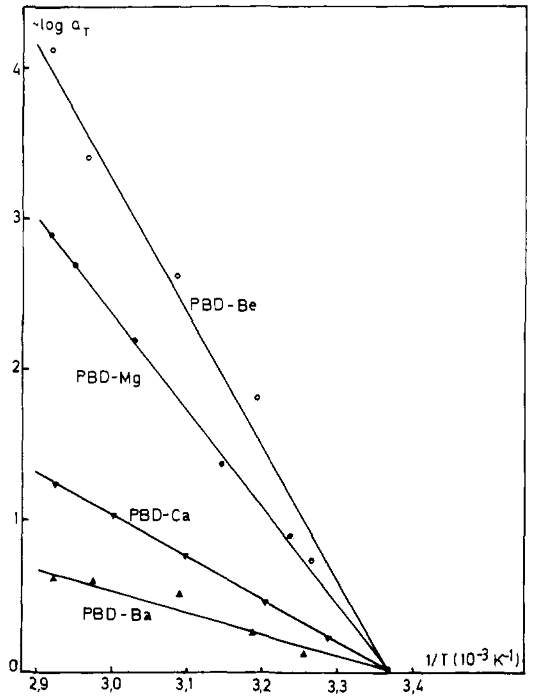


Figure 7. Shift factors (a_T) vs. $1/T$ for 10 g dL^{-1} solutions in xylene of beryllium, magnesium, calcium, and barium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ = 4600).

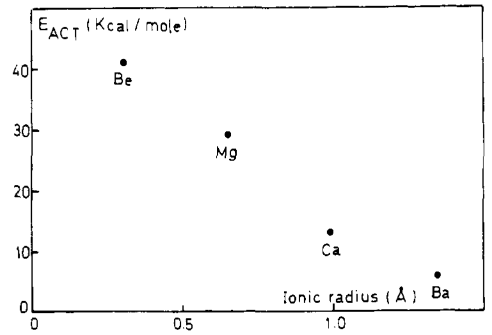


Figure 8. Dependence of the activation energy of the secondary relaxation on the ionic radius for 10 g dL^{-1} solutions in xylene of alkaline earth α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ = 4600).

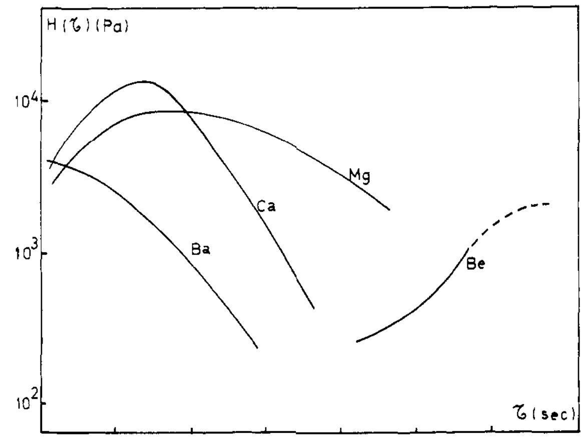
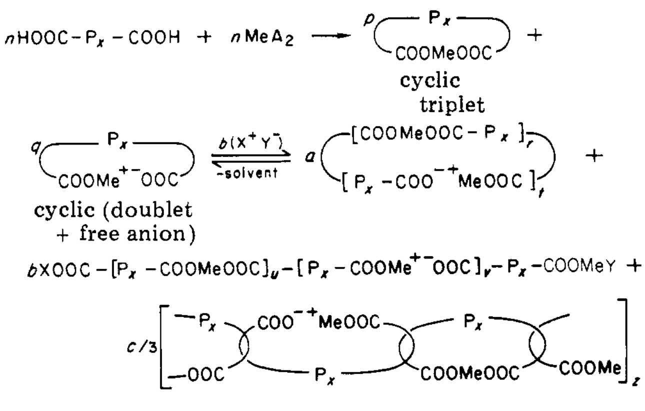


Figure 9. Relaxation times distribution of 10 g dL^{-1} solutions in xylene of beryllium, magnesium, calcium, and barium α,ω-dicarboxylatopolybutadiene ($\bar{M}_n$ = 4600) at 297 K.

It is noteworthy that the solution of the Be-based HTP displays a typical gellike behavior; G' is practically independent of frequency, whereas G'' is significantly smaller. The shift factors plotted on a logarithmic scale vs. the reverse of temperature support an apparent Arrhenius-like dependence (Figure 7), from which the activation energy of the observed secondary relaxation process can be calculated. The activation energy is 41, 29, 13, and 6 kcal mol^{-1} for Be, Mg, Ca, and Ba, respectively; therefore it decreases as the ionic radius increases (Figure 8). It is also observed that the relaxation spectrum calculated by the first-order approximation of Ninomiya and Ferry[10] is

Scheme I



displaced on the time scale as a function of the cation size (Figure 9).

In conclusion, the smaller the alkaline-earth cation and the lower the critical gel concentration, the longer are the relaxation time and the higher the activation energy.

Discussion

In nonpolar solvents at very high dilution (<0.75 g dL^{-1}) the ion pair end groups of HTP seem to be intermolecularly nonassociated and the individual chains to be practically independent of each other; a viscous flow is therefore the effective deformation mechanism. However, as soon as the concentration increases, the ionic groups aggregate into multiplets, the polymer chains build a tridimensional network, and gelation occurs. This sequence of events is clearly illustrated in Figure 5. The dynamic behavior of more concentrated solutions (10 g dL^{-1}) is obviously dependent on frequency: a regular transition from a viscous flow ($G' < G''$) to a gellike behavior ($G' > G''$) is noted at increasing frequencies. Similarly, a shear-thickening effect appears as the shear rate increases.

The stability and mean size of the ionic multiplets will be the key parameters governing the deformation mechanism of the HTP solutions. The ionic multiplets are of course dynamic entities in which the average lifetime of the electrostatic interactions depends on solvent, temperature, and ion pair. In a highly diluted state, the initial telechelic macromolecules are quite independent of each other. Upon neutralization of the carboxylic acid end groups, the viscosity of the solution remains largely unmodified (Figure 5; $C < 0.1$ g dL^{-1}). The carboxylate end groups form only small-size multiplets from which a maximum of two chain segments emerge, i.e., triplet and/or doublet plus free anion. Larger multiplets would be responsible for the formation of a polymeric material with an infinite molecular weight, in disagreement with the viscometric behavior. The simplest situation is therefore the cyclization of the initial telechelic chains. It must be recalled that alkaline polydianions are known to be at least partially cyclic at high dilution in nonpolar solvents.[11,12] Thanks to that conformational state, cyclic polymers have been successfully prepared by deactivating these polydianions with a dibromo derivative.

As the concentration increases (up to ca. 0.6 g dL^{-1} in Figure 5), the initial macromolecules partially lose their mutual independence in a way which is not completely understood. The cooperation of several mechanisms may be assumed: the partial interlocking of the cyclic species into catenanes, the increase in their size due to a condensation process, and the potential opening of the cyclic macromolecules by "monoionic" compounds (X^+Y^-). Scheme I (a scheme of equilibria) attempts to account for that situation, where $p + q = a(r + t) + b(u + v + 1) + cz$; r, t, u, v, and z are expected to be low. Inside the extended macromolecules, the triplet and the doublet plus free anion entities are of course randomly distributed. The migration of these species in the medium controls the behavior of the highly diluted solutions, and viscous flow accordingly results.

At still higher concentrations, the formation of larger size multiplets is progressively favored (quadruplet, sextet, ...) and a chain network of increasing stability is formed. The deformation process is now controlled by the multiplets, which dissociate at a finite rate into temporarily moving species (triplet and doublet plus free anion). Of course, the dissociation process is controlled by electrostatic interactions, whereas the diffusion of moving chain segments obeys the free volume concept. As the experimental results agree with an Arrhenius type of activation, the deformation mechanism of HTP solutions must be controlled by thermal multiplet dissociation.

The constant scrambling of the multiplets (i.e., the redistribution of the electrostatic interactions) readily explains the discrepancy between the theoretical and the effective mean number of divalent cations per multiplet ($\bar{n}$) at the gel point. Although in theory multiplets with $\bar{n}$ just higher than 1 should be efficient in promoting gel formation, the Coulombic interactions appear indeed to be nonoperating under these conditions and a more or less viscous solution is observed; this means that the average lifetime of the electrostatic interactions is shorter than the time of measurement. It is only when multiplets are larger sized ($\bar{n}$ = 2,3 for magnesium carboxylate in toluene at 25 °C) that apparently stable "ionic cross-links" involve the polymer chains in an infinite network.

The dynamic behavior of HTP solutions can also be understood in terms of the average lifetime of the multiplets in comparison with the relaxation times that affect the viscoelastic properties. Similarly the shear-thickening effect is the consequence of intermolecular electrostatic interactions, which impede the relaxation of polymer chains as the deformation time decreases. Under the experimental conditions of Figure 3, the average lifetime of the ionic cross-links would be approximately 0.16 s. The gelation process is accordingly a multidimensional phenomenon; at constant rate of deformation it appears at a critical concentration, whereas at constant concentration a critical rate of deformation can be defined.

Because of their dynamic character, the structure of HTP solutions can easily be perturbed, as exemplified in Figure 1. When the solution is strained, the distribution of the ionic multiplets is modified in favor of smaller and more easily diffusing ionic entities. At rest, the solution tends to recover from perturbations thanks to the thermally activated redistribution of the ionic multiplets. The formation of an increasingly stable structure accounts for the more rapid increase of G' compared to G'' (Figure 1).

The reported effects of solvent and temperature generally confirm the electrostatic origin of the behavior of HTP solutions. As estimated from the master curves (Figure 6), the influence of the alkaline-earth cation size provides further confirmation. The characteristic gellike behavior exhibited over the whole frequency range by the solution of Be-based HTP results from the very long lifetime of the electrostatic interactions. This feature also explains why the gel formed by this material in toluene cannot be diluted into a viscous solution, as reported for the Mg counterpart (Figure 5). In the case of Be, a phase separation occurs at high dilution.[7] As the ionic radius increases, $G' = G''$ is observed at increasing frequencies, and the average lifetime of the Coulombic interactions is accordingly decreasing. The four G' master curves of Figure 6 show at least the end of the rubberlike plateau, the height of which passes through a maximum from Be to Mg, Ca, and Ba, successively. It is noteworthy that, measured in bulk, the equilibrium storage modulus increases regularly with the ionic radius,[13] which means that the effective cross-link density is favored by the bigger cations. In consequence, Ba would form the largest size multiplets, which are however characterized by the weakest electrostatic interactions, whereas Be would exhibit just the opposite behavior. The mixing of the bulk HTP with a nonpolar solvent changes the conformational state of the polymeric backbone, and this perturbation could possibly modify the ion aggregation to an extent depending on the strength of the ion multiplets. Accordingly, a maximum multiplet size should be observed for intermediate-size cations, but this expectation needs experimental support.

The thermorheological simplicity of the HTP solutions is to be outlined, and the secondary relaxation observed is undoubtedly characteristic of the ionic component. These attractive features largely justify the choice of HTP as model compounds for ion-containing polymers. Furthermore, the rheological behavior, and especially the shear-thickening effect, could give to HTP solutions a real interest for applications.

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Reviews

Mechanism of Cyclic Acetal Polymerization. End of a Controversy?

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ABSTRACT: An analysis of the major controversies that have arisen in studies of cyclic acetal polymerization over almost 2 decades is presented. These controversies involve the structures of the polymers and the structures of the active species. Analysis of the published data has revealed that at least some polyacetals, e.g., poly(1,3-dioxolane), may be prepared either as almost exclusively cyclic or as predominantly linear macromolecules, depending on the starting monomer concentration. The initial (formed during initiation) and the final (formed during termination) end groups have clearly been observed in a number of systems. The earlier controversy whether polyacetals are linear or cyclic had at least partially been due to different starting concentrations of monomer used by various authors or different starting ratios of monomer to initiator. A new notion "critical monomer concentration" is introduced, describing a certain starting monomer concentration, below which practically all of the produced polymer must be cyclic. When, on the contrary, conditions are chosen to avoid a higher proportion of macrocycles, living polyacetals can be obtained; the dicationically living polyacetals were successfully used to prepare ABA block copolymers. Recent data on oxonium–carbenium ion equilibria have been analyzed and it is shown that the previous insistence of various authors on the uniqueness of structures of growing species cannot be sustained. Various species coexist in dynamic equilibrium and their role in the chain growth may vary according to the conditions of polymerization. For 1,3-dioxolane the carbenium–oxonium equilibrium suggests that growing species are predominantly the tertiary oxonium ions, although some alkoxycarbenium ions can also be present.

1. Origin and Nature of Controversy

There have been two major controversies in the polymerization of cyclic acetals. The first concerns the structure of the polymers, and the second the way the macromolecules grow.

Plesch,[1] following the idea expressed in Gresham's patent,[2] concluded that poly(1,3-dioxolane) (poly-**1**) and poly(1,3-dioxepane) (poly-**2**) are exclusively cyclic. This conclusion was based on studies of the end groups by chemical, IR, and ^{1}H NMR analyses. Plesch, assuming that the structure of the end groups should be related to the initiators and/or to the transfer reactions, was looking for these end groups. Not finding them, he assumed that growth proceeds by ring expansion: cationated rings add

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