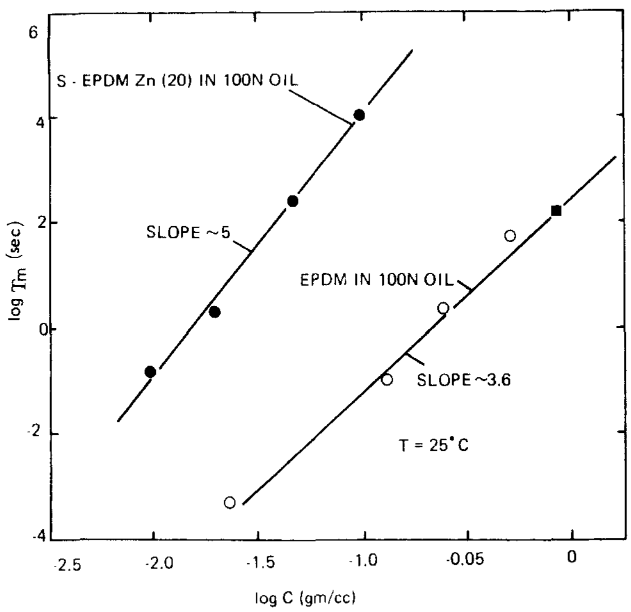

Figure 18. Maximum relaxation time τ_m (in s) vs. concentration (in g/cm^3) at 25 °C for sulfo-EPDM Zn salt and EPDM system.

function of the metal counterion, the concentration, and the degree of sulfonation.

Acknowledgment. We are pleased to acknowledge the experimental assistance of Richard Garner and the many useful comments of Dr. Gary Ver Strate.

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Viscoelastic Behavior of Concentrated Oil Solutions of Sulfo Polymers. 3. Magnesium and Barium Sulfo-EPDMs

Pawan K. Agarwal* and Robert D. Lundberg

Exxon Research and Engineering Company, Corporate Research Science Laboratories, Annandale, New Jersey 08801. Received June 3, 1983

ABSTRACT: The viscoelastic behavior of concentrated solutions of barium and magnesium sulfo-EPDM has been studied. Unlike the more weakly associating zinc sulfo-EPDM, the barium and magnesium salts exhibit a pronounced rubbery plateau over a wide temperature range (75–160 °C) in which G' is independent of temperature. On the basis of these measurements, it appears that the rate of relaxation is independent of temperature. The usual time–temperature superposition relationships for these samples do not hold. Various interpretations of these unusual phenomena are discussed. It is concluded that for strongly associating ionomers in concentrated solutions a state of transient ion pair aggregate exists. Near ambient conditions at any instance there is a balance of ionic linkages which are continuously forming and dissociating. However, for systems which interact sufficiently strongly, it is feasible for the ionic aggregate to increase in strength or persistence to some degree as temperature increases.

Introduction

Previous papers[1,2] in this series have been concerned with the viscoelastic behavior of ethylene–propylene–ethylidenenorbornene terpolymer (EPDM) and zinc sulfonated EPDM in bulk and when dissolved in paraffinic oils. The viscoelastic behavior of EPDM in oil is unremarkable in that a suitable entanglement plateau is observed for the storage modulus in very concentrated (>50 wt %) solution and in the bulk polymer. However, when diluted to 5 wt % polymer, there is no evidence for an entanglement plateau in G' over the frequency range studied. Sulfonated EPDMs, on the other hand, can display marked evidence of such a plateau at low sulfonate contents (10–30 mequiv/100 g) and even at polymer concentrations as low as 1 or 2 wt % polymer. It is clear that the ion-pair association in these systems manifested at extremely low ionic levels.

The viscoelastic behavior for zinc sulfo-EPDM in oil has been studied in some detail.[2] We have observed a substantial difference in the viscoelastic behavior of bulk sulfo-EPDM that is dependent upon the type of cation used to neutralize the sulfonate.[1] For example, magnesium,

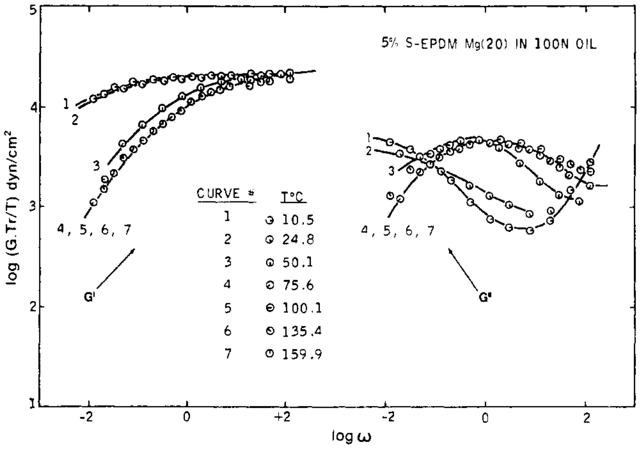

Figure 1. Plots of moduli $G'(T_r/T)$ and $G''(T_r/T)$ (in dyn/cm^2) vs. frequency (in rad/s) as a function of temperature for the 5% sulfo-EPDM salt solution in 100N oil.

barium, and calcium exhibit an apparently stronger ionic network, or at least a more persistent network than do zinc or lead. In the case of zinc sulfo-EPDM the weaker ionic association is manifested as a marked change in G' and G'' as a function of temperature when this polymer is dissolved in oil at a concentration of a few percent. For example, such a solution can behave similarly to a covalently cross-linked network at 0 °C but as a Newtonian fluid at 135 °C.

In the case of more strongly associating polymers, such as magnesium sulfo-EPDM, viscoelastic behavior is substantially different from that of the zinc salt. This paper is concerned with the study of magnesium and barium sulfo-EPDM as representative polymers possessing very strong ionic associations.

Experimental Section

Magnesium sulfo-EPDM (sulfonation level 20 mequiv) was prepared from the same batch of EPDM that was used for preparing zinc sulfo-EPDM discussed in the previous paper in this series, and solutions of Mg sulfo-EPDM in 100N oil were also prepared as discussed in that paper.[2] Since Mg sulfo-EPDMs are significantly much stronger than the zinc sulfo-EPDMs, their dissolution in the solvent is extremely slow. It took several months to obtain homogeneous samples, and the physical form of the final solution was a highly elastic gel.

During the past few years we have conducted a variety of measurements on various strongly associating sulfonated EPDMs and have found their time-dependent solution behavior to be very complicated. This facet of these polymers is discussed in the following paper in this series.[3]

In view of the complex behavior of metal sulfo-EPDM polymers, the present studies focused on the investigation of the viscoelastic behavior of limited samples. A 5 wt % solution of magnesium sulfo-EPDM was studied in detail. Measurements were also made on a 2 wt % solution of Mg sulfo-EPDM(20) and on a 5 wt % solution of Ba sulfo-EPDM(20). Viscoelastic measurements were made on a Rheometrics mechanical spectrometer. Dynamic moduli data were taken over a frequency range 2×10^{-3} to 20 Hz from about 10 to 160 °C.

Results and Discussion

A typical series of isothermal dynamic moduli measurements of a 5 wt % solution of Mg sulfo-EPDM polymer is shown in Figure 1. Both in-phase and out-phase shear modulus data are shown as a function of frequency on a log–log graph from 10 to 160 °C. The sulfonation level of this polymer was the same as that of the zinc salt of sulfo-EPDM, 20 mequiv.[2]

Several features are noteworthy. First, as seen in the previously reported case of the zinc salt of EPDM,[2] a rather flat, rubbery plateau can readily be observed in the shape of curves 1 and 2, indicating the existence of a three-dimensional, network-like structure. A close look at these curves suggests that relaxations are taking place, which are more evident in the corresponding G'' curves.

The second interesting phenomenon of the sample's behavior is observed at higher temperatures. The data for curves 4–7, which represent measurements from 75 to 160 °C, all fall on a single line. The viscoelastic response of this solution throughout the entire frequency region appears to be independent of temperature. In a broad sense the structure of the sample remains essentially unaltered at least up to 160 °C; the ionic linkage appears to be stable, resulting in a (stable) network. Just from these curves it could be concluded that at least in this temperature range the rate of the relaxation processes is independent of temperature. This is certainly a surprising result since to our knowledge this kind of observation has not been reported for any high molecular weight polymers. The G'' curves demonstrate that at each temperature rapid relaxations are taking place (in the experimentally covered frequency region). This leads one to think that perhaps the ionic linkages are continuously forming and dissociating.

The third very interesting observation in the behavior of this magnesium salt solution is the lack of any permanent deformation as distinguished from the zinc salt sample, which at 50 °C begins to show significant viscous flow (cf. Figure 1, curve 4, in the previous paper).[2] Even at such high temperatures at 160 °C, which is more than 200 °C above T_g, the sample response is nowhere near the Newtonian viscous flow region. The G'' curves do not even appear to be approaching a slope of 1 (at log $\omega \sim -2$ the slope is $\sim{}^1/_2$). Any interpretations suggesting that the system is approaching the terminal flow region because of the dip in G' at low frequencies would be misleading. Extending the viewpoint that ionic linkages are forming and dissociating, the complete lack of viscous flow in this system suggests that perhaps the new bonds form faster than they diffuse away from one another under the applied external excitation.

At any frequency, the modulus of this solution (gel) remains essentially constant from 75 to 160 °C. This could be understood in terms of the postulated ionic bond formation and dissociation model. As the temperature is increased the internal viscosity of the medium decreases. The thermal diffusional motions of polymer chain segments are facilitated, and the chain segments, initially being in "ionic charge sphere" multiplets or aggregates[4] of ion pairs, diffuse out. The newly formed ionic linkages "anneal", in the sense that the oppositely charged ions come closer to each other. Thus their electrostatic attraction increases, and the linkages become stronger. The net effects of all this is that the system itself becomes stronger and stronger, and it resists any permanent deformation.

One possible simple illustration of the interactions and ionic bond formation and dissociation phenomenon under an applied stress is schematically shown in Figure 2. At any given instant the number of network junction points remains constant, although the structure is continuously changing. Perhaps both inter- and intraionic molecular interactions[15] prevail in this system. However, because of the high polymer concentration, strong interionic molecular interactions would be expected to predominate.

Since the relaxation rates of magnesium sulfonated EPDM solutions are temperature independent, the usual time–temperature superposition of the various curves of Figure 1 does not hold. In view of the parallel nature of

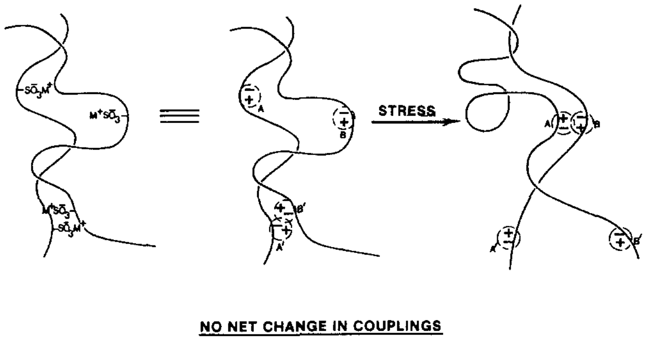

Figure 2. Schematic representation of ionic bond formation and dissociation in strongly associating ionomer networks, e.g., Mg or Ba sulfo-EPDMs at rest and under small deformations.

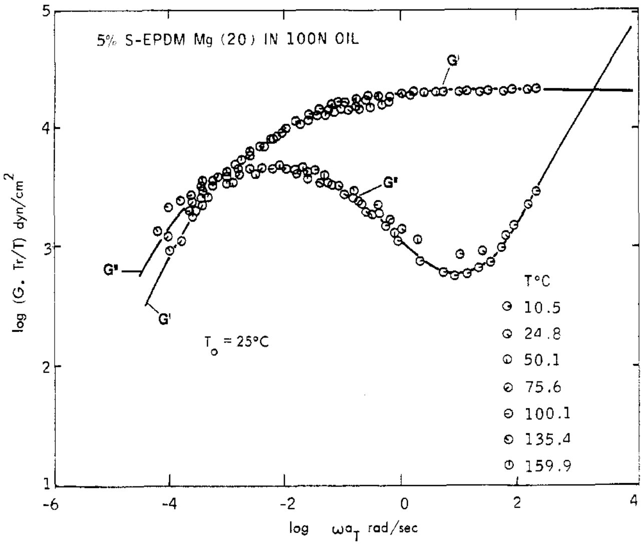

Figure 3. Plots of (apparent) reduced moduli $G'(T_r/T)$ and $G''(T_r/T)$ (in dyn/cm^2) vs. reduced frequency (in rad/s) for the 5% sulfo-EPDM Mg salt solution in 100N oil.

these curves, however, a (false) frequency–temperature superposition from these curves can still be attempted. In this case for the first time, we observed clearly the failure of time–temperature superposition in sulfo-EPDM systems. The resulting master curves of G' and G'' are shown in Figure 3. These curves do not have their usual significance, but we generated them to make some qualitative comparisons with other metal sulfonated EPDM solutions. This will be discussed later. It is interesting that if the shift factor from the universal WLF equation was used in construction of the master curve, the length of the rubbery plateau would be extended to several decades.

The G' and G'' data obtained for the 2 wt % solution of Mg sulfo-EPDM(20) and the 5 wt % solution of sulfo-EPDM(20) barium salt are shown in Figures 4 and 5, respectively. Qualitatively, similar observations as discussed above were noted in these as well. First, taking the case of barium solutions from previous studies,[1] the barium salt system is stronger than magnesium, and hence it is not very surprising that the temperature-independent modulus behavior appears at low temperatures. In the case of the 2 wt % solution of Mg sulfo-EPDM(20), again above about 75 °C, the G' modulus becomes less dependent on temperature, consistent with the observations of the previous 5 wt % solution. Near room temperature, the (equilibrium) modulus G_e values for the 2 wt % sulfo-EPDM Mg salt and the 5 wt % barrium salt solutions are 1.26×10^3 and 1.51×10^4 dyn/cm^2, respectively.

During a literature search we found that the situation occurring in this system appears to be very much analogous to that observed some time ago by Tobolsky and coworkers in their study of the chemical stress relaxations of polysulfide rubbers. In a series of papers[5–7] on the study of chemical rheological behavior of such polymers, they reported the predominance of bond-exchange reactions of tri-, tetra-, and pentasulfide linkages. Following a simple single-element, Maxwellian stress-decay equation and analyzing the experimental data through an Arrhenius plot, these authors reported an activation energy of about 26 kcal/mol of polysulfide interchange reaction.

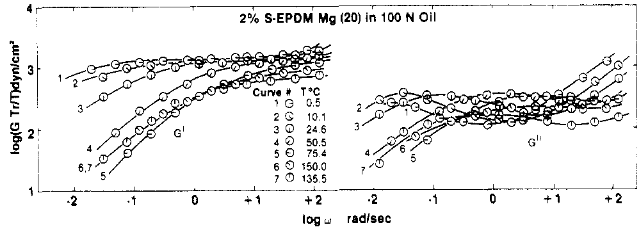

Figure 4. Plots of moduli $G'(T_r/T)$ and $G''(T_r/T)$ (in dyn/cm^2) vs. frequency (rad/s) as a function of temperature for the 2% sulfo-EPDM Mg salt solution in 100N oil.

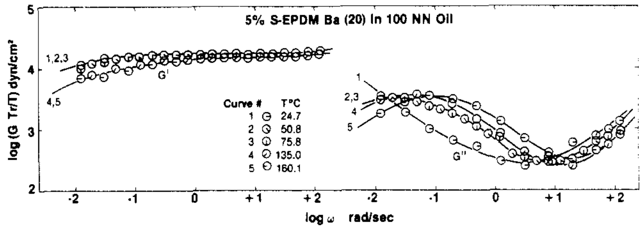

Figure 5. Plots of moduli $G'(T_r/T)$ and $G''(T_r/T)$ (in dyn/cm^2) vs. frequency (in rad/s) as a function of temperature for the 5% sulfo-EPDM Ba salt solution in 100N oil.

Experimental relaxation curves and activation energy data were taken on a variety of samples of varying cross-link densities and were found to fit reasonably well with the theory. However, the value of 26 kcal/mol reported by Tobolsky et al. from stress relaxation measurements for the homolytic scission of the polysulfide bond was somewhat lower than 35 kcal/mol (for breaking the S–S bond) determined from other kinetic and thermodynamic measurements.[8–10]

Because of the gross similarity between polysulfide bond-interchange interactions and ionic-bond-interchange reactions in strongly associative sulfonated EPDM polymers (e.g., Ba and Mg vs. Zn and NH_4 salts), we made an analysis along the lines of Tobolsky et al.[7] Assuming that at any time t the number of ionic linkages supporting the stress is $\nu_i(t)$, then from rubber elasticity theory

$$\frac{F(t)}{F(0)} \propto \left.\frac{G'(t)}{G'(0)}\right|_{t=1/\omega} = \frac{\nu_i(t)}{\nu_0(t)} \tag{1}$$

where $F(t)$ is the stress at time t: $G'(t)$ is the corresponding in-phase shear modulus, and $F(0)$, $G'(0)$, and $\nu_i(0)$ represent the initial state, i.e., at time zero.

Now assuming that all the ionic linkages are equally responsible for stress supporting and that all are undergoing bond interchange, the rate equation for the ionic linkages that undergo change will be given by

$$-\mathrm{d}\nu_i(t)/\mathrm{d}t \propto \nu_i(t) \tag{2}$$

or

$$-\mathrm{d}\nu_i(t)/\mathrm{d}t = k\nu_i(t) \tag{3}$$

where k is the rate constant for the ionic bond formation and dissociation reaction. Integrating eq 2 gives

$$\nu_i(t) = \nu_i(0)e^{-t/\tau_{ex}} \tag{4}$$

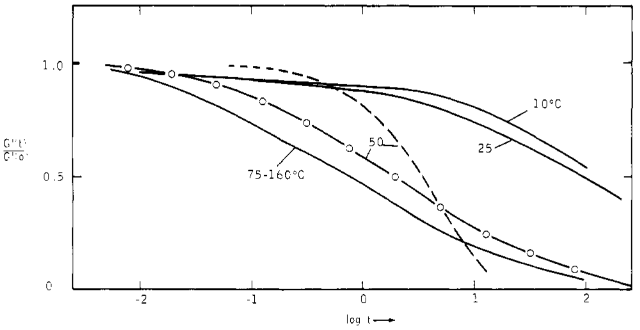

Figure 6. Plot of normalized modulus ($G'(t)/G'(0)$) vs. time as a function of temperature for the 5% sulfo-EPDM Mg salt in 100N oil.

where τ_{ex} is the exchange time constant and is equal to $1/k$. From eq 1 the corresponding equation for the stress decay is

$$G'(t)|_{t=1/\omega} = G'(0)e^{-t/\tau_{ex}} \quad (5)$$

which is the well-known, single-element Maxwell equation.

It is clear from eq 4 that when $t = \tau_{ex}$, $G'(t)/G'(0)$ is $1/e$; thus, τ_{ex} can be evaluated from experimental data. Although τ_{ex} is exactly the same as the relaxation time constant of a Maxwellian body, its physical significance as embodied in these equations is somewhat different.

Experimental relaxation data of the 5 wt % solution of 20-mequiv sulfo-EPDM Mg salt (Figure 1) were plotted according to eq 4 and are shown in Figure 6. The values of the exchange time constant τ_{ex} at various temperatures were obtained from this figure. The dotted curve represents eq 4 with $\tau_{ex} = 5.01$ at 50 °C.

The experimental data do not conform well to the theoretical curve. The poor fit of the data with an equation having a single time constant is not very surprising. In the case of highly entangled polymers such as ethylene–propylene copolymers, near the terminal-flow region, the contributions to the viscosity, besides the maximum relaxation time τ_{max}, due to other higher order terms of the relaxation spectrum could be substantial, since the dispersion region is a function of the overlapping mechanisms responsible for the plateau and flow regimes.

One way to overcome the problem practically is to subtract the viscous contributions of a corresponding unsulfonated EP polymer solution. However, we could not do this because in the case of sulfonated EP polymers the situation is further complicated by the presence of highly associative metal sulfonate groups. The bond-interchange reactions, if occurring with these polymers, can be expected to be somewhat restricted because of the sluggish diffusion rate of polymer chain segments, and hence, because of these restrictions on the rate of relaxations of bond-interchange reactions, equations with multiple exponential time constants are expected to improve the fit. Nevertheless, because of the reasonable fit of the data with eq 4, and especially in view of its simplicity, all the data were analyzed with this equation only.

The τ_{ex} values were fitted on an Arrhenius plot as shown in Figure 7. The data could be represented by two regions. From the lines drawn through these points, activation energies of 18.3 kcal/mol in the lower temperature region from 10 to 75 °C and only 5.0×10^{-2} kcal/mol above 75 °C were obtained (estimated error limits are ±15%). In a relatively less viscous medium (recall the concentration of polymer is only 5 wt %), the ionic-bond-exchange reaction could be facilitated. In view of this, intuitively at low temperatures an energy of aboout ~18 cal/mol for dissociating an ionic bond seems reasonable (since this value is typical of an ionic bond). At higher temperatures an abrupt change in the activation energy reflects changes in the mechanism of relaxations. As mentioned previously, at higher temperatures the annealing of the ionic linkages takes place, and they become stable. Above ~75 °C not much bond exchange takes place, and hence no relaxation of these ionic bonds occurs. The relaxations at higher temperatures reflect the mechanisms associated with the relaxations of segments of chains between these linkages. The near-zero activation energy values reflect these relaxations and are not surprising.

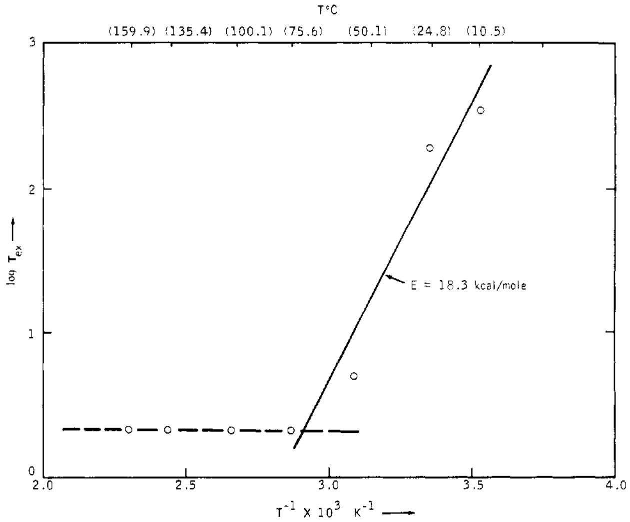

Figure 7. The exchange time τ_{ex} vs. temperature for the 5% sulfo-EPDM Mg salt solution in 100N oil.

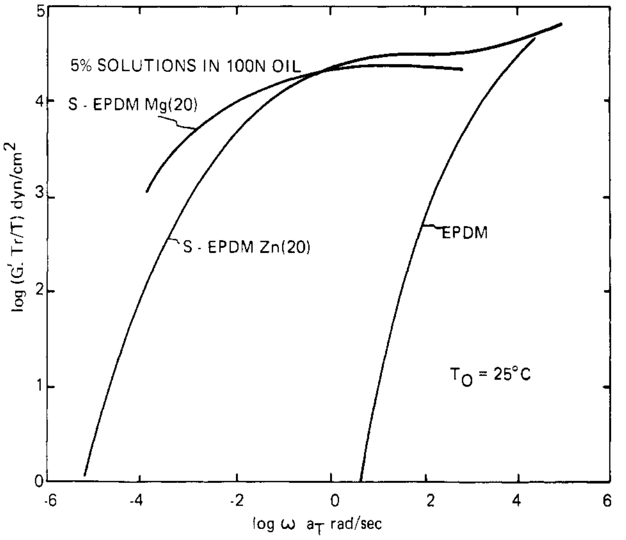

Figure 8. Plots of reduced G' curves vs. frequency (in rad/s) for 5% solutions of EPDM, Zn sulfo-EPDM(20), and Mg sulfo-EPDM(20) in 100N oil.

In Figure 8 the reduced curves of the 5 wt % solution of zinc- and magnesium-neutralized sulfo-EPDM (~20-mequiv sulfonation) in 100N oil are compared with each other. The behavior of the zinc sample has been discussed previously in detail.[2] The magnesium salt solution exhibits an extensive entanglement plateau, and the curve is shifted toward lower frequencies, i.e., to longer times. This is exactly what one would expect in view of the relatively stronger associations prevailing in magnesium systems.

The interesting feature is the level of the plateau (Figure 8) as compared to the zinc salt solution at ω ~10 rad/s. It is somewhat lower by about 25%. This result is somewhat surprising and is consistent with the $G_N{}^0$ values calculated from data using eq 8 of the previous paper in this series.[2] The exact reasons for this result are not clear. The nature of associations prevailing in the zinc and magnesium salt are significantly different from each other, as seen in Figure 8 and in other publications.[1,2,16] It is quite conceivable that owing to the rather strong ionic associations in the magnesium salt, an equilibrium network state, even in dilute solution, may not have been achieved, and consequently the rubbery plateau is somewhat lower than that of the zinc salt.

Andrianova,[11] during his extensive studies on the effect of solvent on the melt viscosities of polystyrenes and polypropylenes, found that polystyrene samples, obtained from ~40 wt % concentration, had more than 1 order of magnitude lower melt viscosities than the bulk polymer. The viscosities of the solution-recovered samples were a function of the solvent and exhibited strong time-dependent properties, even at temperatures 100 °C higher than their glass-transition temperature. In an attempt to explain this phenomenon, he postulated the formation of a structure in the solution-recovered sample. Upon annealing, the structure is destroyed, the sample's random network of fluctuating entanglements starts dominating, and its viscosity returns to the bulk melt viscosity.

Recently, Plazek[12] et al. during their creep studies on a very high molecular weight polystyrene solution ($M_w \sim 4 \times 10^7$) found a higher degree of entanglements, determined from comparisons of the width and the level of entanglement plateaus in the solutions of this polymer with those of its bulk state. They attributed this to the lack of an entanglement equilibrium state in the bulk polymer because of the slow diffusion rate of polymer chain segments resulting from its very high molecular weight.

It is not quite clear what sort of structure could be formed in the magnesium and barium sulfo-EPDM solutions other than transient ion pair aggregates. Qualitatively the phenomenon in the magnesium and other strongly associating sulfonated EPDM systems appears to be similar to those in the polystyrene studies of Plazek et al., the difference being in the type of primary interchain interactions involved and their mechanism. Certainly any type of conventional entanglement concepts[13] and reptation mechanism[14] cannot be perceived to dominate the behavior in strongly ionic associative systems.

Acknowledgment. We gratefully acknowledge various helpful discussions with Prof. W. J. MacKnight.

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Synthesis of Pure Head-to-Tail Poly(trifluoroethylenes) and Their Characterization by 470-MHz Fluorine-19 NMR

Rudolf E. Cais* and Janet M. Kometani

AT&T Bell Laboratories, Murray Hill, New Jersey 07974. *Received August 29, 1983*

ABSTRACT: We report the first synthesis of poly(trifluoroethylene) (PF_3E) having a pure head-to-tail (isoregic) sequence of monomer units. The procedure involves reductive debromination or dechlorination of the precursor polymers poly(bromotrifluoroethylene) (PBF_3E) or poly(chlorotrifluoroethylene) (PCF_3E). We have also prepared a model for head-to-head:tail-to-tail (syndioregic) PF_3E by the copolymerization of 1,2-difluoroethylene with tetrafluoroethylene. Regioirregular (aregic) PF_3E samples have been obtained by free-radical polymerizations over a 160 °C temperature range. The chemical microstructures of these polymers have been analyzed by high-resolution 188- and 470-MHz fluorine-19 NMR, which show that PBF_3E, PCF_3E, and PF_3E are stereoirregular (atactic) polymers. There are no head-to-head structures in PBF_3E, but PCF_3E has about 2% of these defects. Free-radical PF_3E is far more regioirregular, with defect levels increasing from 10% at −80 °C to 14% at +80 °C. The stereochemical microstructure changes little with temperature.

Introduction

There are six fluoroethylenes which differ according to the number and position of their fluorine substituents. They are vinyl fluoride, vinylidene fluoride, *cis*- and *trans*-1,2-difluoroethylene, trifluoroethylene, and tetrafluoroethylene. When the substitution patterns of the carbons in a fluoroethylene monomer are different, then that monomer is capable of forming a regioirregular polymer. Such is the case for vinyl fluoride (VF), vinylidene fluoride (VF_2), and trifluoroethylene (F_3E), which give the aregic polymers PVF, PVF_2, and PF_3E, respectively.[1,2]

We have shown in part 1 of this series that isoregic PVF can be prepared by the reductive dechlorination of appropriate precursor polymers.[3,4] This approach is now extended to the synthesis of isoregic PF_3E. We have defined the terms isoregic, syndioregic, and aregic by analogy with the terms for stereochemical structure to describe

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