Viscoelastic Behavior of Sulfonated Polymers: Sulfonated Ethylene–Propylene Terpolymer

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ABSTRACT: The dynamic mechanical properties of various sulfonated EPDM polymers were evaluated. The samples studied varied both in the type of counterion and in the degree of sulfonation. A series of modulus–temperature measurements showed that the introduction of as little as 0.5 mol % of metal sulfonate groups into the EPDM polymer produced a very strong and durable physical cross-link network which persisted up to 150 °C. The cross-link density and durability of the network were found to be a function of the nature of the counterion and were strongly dependent upon the degree of sulfonation. Profound effects of both were found in the case of the barium sulfonate, whose network behavior approached that of a covalently cross-linked system. The glass temperature was also found to increase moderately, in approximately linear fashion with increasing sulfonate content. An analysis of a series of isothermal modulus–frequency measurements on various zinc sulfonated EPDM polymers showed that the time–temperature superposition principle was applicable to these polymers. The maximum sulfonate content sample studied had about 1.5 mol % metal sulfonate groups. The WLF and Vogel parameters of sulfonated samples differed from each other and from the base EPDM. The rates of primary relaxations were found to depend upon the metal sulfonate content. These relaxations decreased with an increase in the ionic group concentration. The effect of an ionic plasticizer, zinc stearate, was also investigated. It was found that this plasticizer has a profound effect on the ionic group associations. At temperatures of about 100–150 °C zinc stearate diminished the strong ionic associations, and the sample behaved very much like a high molecular weight amorphous polymer. The rubbery modulus and glass temperature were a function of the plasticizer loading. It is suspected that the zinc stearate is present both in the form of a filler and in the associated form with the polymer matrix through sulfonate groups. The physical cross-linking due to sulfonate groups diminishes at the higher temperatures, where zinc stearate starts to melt.

Introduction

In recent years a considerable amount of research has been focused on the properties of ion-containing polymers, both in the solid state and in solution. The extensive industrial use of water-soluble, ion-containing polymers, i.e., the polyelectrolytes, for various applications has led to an enormous amount of interest among researchers, and various aspects of these systems have been studied.[1,2]

Much less attention has been given to the study of the solid state of ion-containing polymers, primarily due to limited commercial use. The introduction of Surlyn by du Pont in 1964 intrigued various academic and industrial research institutions because of the unique properties, and publications on such systems have been growing ever since.[3,4] Surlyn is a random copolymer of ethylene and methacrylic acid partially neutralized with either the zinc or sodium salt. The metal ion concentration of these materials is low but sufficient enough to form a thermally reversible network structure, thereby resulting in a very tough, strong, and clear material at ambient condition. Such tough, clear materials are well suited to a variety of applications, notably film packaging. The resultant systems are such that they can be successfully processed by conventional plastic-fabricating techniques, for example, injection molding and extrusion.

Early studies on ethylene-based ionomers and polyphosphates[3] indicated that ionic association is responsible for their unique, improved properties. It was soon realized that the extent and nature of this aggregation was very complex.[4] In spite of difficult problems various researchers, in both industry and academe, have attempted extensive and optimistic studies on the solid-state properties of ion-containing polymers.

Ionomers can be broadly considered to be noncovalently cross-linked polymers containing low levels of ionic functional groups. The ionomers which have been most studied are those containing metal carboxylate groups. Such polymers have almost invariably been prepared through copolymerization of vinyl monomers and monomers bearing carboxylic acid or carboxylate ester groups containing other kinds of acidic functionality.

This paper is concerned with the viscoelastic behavior of a new class of ionomers based on metal sulfonates recently developed in our laboratories.[5–7] Studies conducted to date show that sulfonate ionomers differ significantly from the corresponding carboxylate ionomers in both physical and solution properties. The sulfonates exhibit ionic association which results in a stronger physical network, and one which is more temperature resistant than is the case with the carboxylates. In light of these differences the viscoelastic behavior of the sulfonate ionomers is especially intriguing and is the focus of this paper.

With the exception of two papers by MacKnight and co-workers[9,10] the viscoelastic behavior of sulfonated polymers has not been reported in the literature.

In this paper we report on the viscoelastic properties of sulfonated EPDM as a function of (i) sulfonate content and (ii) type of cation borne by the sulfonate group. The effect of ionic domain plasticization with certain nonfugitive additives on sulfonate group aggregation and viscoelastic properties is also discussed.

In order to provide a suitable perspective for the discussion of the viscoelastic properties of sulfonate-containing ionomers, we briefly review the viscoelastic behavior of the carboxylate-containing ionomers. Comprehensive studies of the physical state of carboxylate-containing polymers have been made by various groups of workers and include those of the du Pont group, Otocka and Davis,[11] MacKnight,[12] Eisenberg,[13] and their coworkers. Various experimental tools were employed in these studies. At times the results were at variance and subject to different interpretations. There is still general disagreement about the solid-state structure of carboxylate-containing polymers.

The particular question regarding the state of aggrega-

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Table I
Composition and Characterization of Zinc Sulfonate EPDM's

sample no.	approx sulfonation content, mol %	sulfonation content,[a] mequiv/100 g of polymer	wt % sulfur	wt % zinc	zinc level in mmol/100 g of polymer
48-A	0.69	18.1	0.58	1.25	19.1
48-B	0.93	24.4	0.78	1.48	22.6
48-C	1.19	31.3	1.00	2.33	35.6
48-D	1.47	38.8	1.24	3.02	46.2

[a] All samples were neutralized with sufficient base to completely neutralize the sulfonic acid.

Table II
Composition and Characterization of Various Metal Sulfonate EPDM's

sample no.	approx sulfonation content, mol %	sulfonation content,[a] mequiv/100 g of polymer	wt % sulfur	metal ion	wt % metal (or amine)	mmol of cation/100 g of polymer
47-B	0.86	28.8	0.76	Mg	0.56	23.1
47-C	0.70	19.4	0.62	Ba	3.19	23.4
47-D	0.76	20.9	0.67	Li	0.18	25.9
47-E	0.72	20.0	0.64	Pb	3.50	16.9
47-F	0.66	18.4	0.59	NH_4	0.16	11.4
47-G	0.77	21.3	0.68	Cs	4.06	30.5

[a] All samples were neutralized with sufficient base to completely neutralize the sulfonic acid.

tion of ions and associated hydrocarbon polymer molecules in organic polymer systems is complicated due to the inapplicability of any directly available analytical tools.

Eisenberg[13] has extensively and thoroughly studied styrene-based carboxylate-containing ionomers. In a series of papers reporting on styrene–methacrylic acid copolymers he showed that, in neutralized systems containing about 6 mol % metal carboxylate groups, ion clustering occurred, while below this critical concentration a lower degree of aggregation, coined "multiplet formation", was found. A multiplet is defined as a spherical drop consisting of a group of ion pairs with the polymer chain outside the drop. The maximum number of ion pairs in a multiplet was calculated to be about 8. The structure of the ion cluster proposed by MacKnight et al.,[12b] based on X-ray data on carboxylate ionomers, consists of a small (8–10 Å) spherical cluster of ions, due to the coordination nature of metal ions. This cluster is surrounded by a shell of hydrocarbons chains up to a preferred distance of about 20–30 Å, due to the remaining matrix ions linked to polymer chains.

Thus a cluster may be viewed as a loose association of multiplets. At the core the multiplets are held together by electrostatic forces, but outside of the core they are separated by hydrocarbon chains. Several questions can be raised in the hypothesis of the existence of clusters and multiplets. The driving force for the formation of a cluster is not very clear. In spite of the coordinating tendency of metal ions extra work is required to overcome the steric hindrance imposed by polymer chain segments in bringing together the randomly distributed ion pairs. Further, if strong ionic bonds are formed within a cluster, it seems highly unlikely that viscoelastic relaxation mechanisms attributable to clusters can be expected in the experimentally accessible regions. The experimental relaxations observed in some systems at relatively higher temperatures are probably due to the slipping or breaking of primary ionic forces holding the structure together.

The extensive viscoelastic and X-ray studies of styrene-based carboxylate-containing ionomers by Eisenberg and co-workers strongly supported the viewpoint that a substantial change in the morphology of these systems takes place at about 6 mol %.[15,17] Above this critical ion concentration the time–temperature superposition principle was inapplicable, and X-ray data on a cesium salt showed a new peak at low angles. Among all the variables the effect of ion concentration on the viscoelastic properties was found to be most important. The effect of the degree of neutralization and the type of counterion borne by the carboxylate group was neglibible. The effect of free carboxylic acid groups was minimal, but they were found to affect the efficiency and lifetime of ionic clusters.

The ethylene-based ionomers have been extensively studied by MacKnight and co-workers.[12] Their studies on the sodium, lithium, and calcium salts of ethylene–methacrylic acid copolymers indicate that, in addition to the crystalline and amorphous polyethylene phase, an additional phase consisting of ionic domains exists. The existence of this ionic phase was found at the lowest acid concentration studied, about 2 mol %. It appears that in these systems the lowest ionic group concentration above which clusters exist is very low, perhaps below ~1 mol %, as pointed out by Eisenberg.[4] From these and other studies[8] it is evident that the nature of the polymer backbone plays an important role in determining the minimum concentration at which ionic aggregation occurs.

This paper is the first of several dealing with the viscoelastic behavior of sulfonated ionomers. Specifically the sulfonated EPDM ionomers of low sulfonate level (0.5–1.5 mol %) will be examined here. In the course of this discussion comparisons will be made with the carboxylate ionomers described previously.

Experimental Section

Sample Preparation. Sulfonated EPDM samples were prepared by procedures reported previously by the reaction of EPDM containing 5-ethylidene-2-norbornene (ENB) with acetyl sulfate.[7a]

All the sulfonated samples were prepared from the same base EPDM. In subsequent graphs and tables the base EPDM polymer is designated as sample 48-O. The number-average molecular weight of the polymer was 40 000, and its heterogeneity index $M_w/M_n \sim 2.10$, as determined from gel permeation chromatography with trichlorobenzene (TCB) solvent at 147 °C. The ethylene and ENB contents of this materials were 55 and 4.4% by weight, respectively.

Two groups of sulfonated samples were prepared. These are listed in Tables I and II. Table I lists four zinc sulfonate EPDM's

which vary only in sulfonate content. In Table II five metal sulfonate EPDM's and an ammonium sulfonate EPDM are listed which vary only in cation type. All six samples were intended to have the same sulfonation level. However, as can be noted from the second and fourth columns of Table II, the sulfur and metal analyses of the final products indicated slight differences in the level of sulfonation among these samples.

The samples in Table I were prepared through sulfonation of EPDM and direct neutralization of the resultant cement, i.e., without prior isolation of the sulfonic acid. Samples were synthesized as follows: To a solution of EPDM in hexane were added acetic anhydride and concentrated sulfuric acid at room temperature with good agitation. After 30 min the sulfonation reaction was terminated and the product was neutralized by adding a methanol–water solution of zinc acetate. Antioxidant (0.5%) was added, and the solvent was flashed off the neutralized cement by pouring into boiling water (steam stripping). The resultant polymeric mass was washed and pulverized with water in a Waring blender, filtered, and finally dried in a laboratory Aerometic fluid bed dryer at 100 °C. The samples in Table II were prepared from a master batch of the sulfonic acid which was isolated by steam stripping and drying on a rubber mill. Various samples were made by dissolution of the free acid in a mixture of hexane and 2-propanol and by addition of an aqueous solution of the neutralizing agent. The neutralized product was recovered as described above.

The sulfonation chemistry of these systems has been previously described.[7a] On the basis of elemental analysis the conversion of the sulfuric acid to polymer sulfonic acid is uniformly greater than 90%. The neutralization of the polymer sulfonic acid is effected by the addition of the appropriate metal acetate. To ensure complete neutralization 2.4 equiv of metal acetate was added per mol of sulfuric acid added. In the case of monovalent cations this stoichiometry is straightforward; however, in the case of divalent cations this level of neutralization agent is substantially in excess of that required to create solely metal sulfonate linkages. The structure of the neutralized species is not unambiguous and may consist of a mixture of disulfonates and monosulfonate–acetate species for the multivalent cations. The elemental analyses of the sulfonate EPDM products are shown in Tables I and II. Sulfonation content is indicated both in mol % and in mequiv of sulfonic acid per 100 g of polymer. The former figure assumes an average monomer repeat molecular weight of 38 corresponding to the EPDM composition and therefore is a somewhat artificial number, while the second figure is unambiguous. Both values are provided, since ionic functionality in the prior art has often been cited in mole percent.

All of the neutralized samples prepared in this study were observed to be soluble in suitable mixed solvents and therefore devoid of covalent cross-linking. Some viscoelastic studies were conducted on partially neutralized sulfonate EPDM samples. It should be emphasized that the thermal stability of partially neutralized samples is marginal and special precautions must be taken to avoid covalent cross-linking during fabrication. Those results will be the subject of a future paper.

The zinc stearate plasticized samples were prepared by incorporating the desired loadings of zinc stearate into the sample on a hot two-roll mill. The mill temperature was about 350 °F, and the mixing time varied from 15 to 25 min, depending upon the amount of zinc stearate added. Two levels of zinc stearate, corresponding to about 10 and 20 g/100 g of the polymer, were used.

Measurements. All viscoelastic measurements were made on a commercial mechanical rheometer manufactured by Rheometrics, Inc. The instrument can be used both for steady-state and transient measurements over a wide range of deformations. All measurements reported in this paper were made under unsteady deformations in a sinusoidal shear oscillation with a torsional geometry.

Details of the operating procedure of the instrument are described elsewhere.[23] In brief the test sample is oscillated sinusoidally by a dc torque motor with position feedback from a rotary variable differential transformer. The data are analyzed through a device called a rheophaser, which produces a sinusoidal reference signal for the position loop to follow. The device analyzes the input strain and output stress signals for the amplitude and phase shifts. Quantities proportional to the in-phase modulus (G') and out-of-phase modulus (G'') are obtained. These quantities in turn are then processed through a data processor to obtain G' and G''.

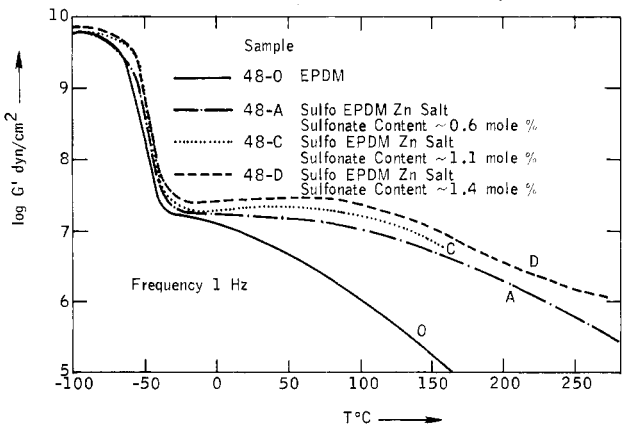

Figure 1. Semilogarithmic plot of in-phase modulus G' (in dyn/cm²) vs. temperature (in °C) of various zinc sulfonate EPDM's of varying sulfonate content.

Prior to measurements, the samples, which were in the form of coarse crumb and flakes, were compression molded at 350 °F in the form of 1 in. × 4 in. pads of varying thickness. Samples of the desired dimensions were cut with appropriate dies. The samples were then annealed in vacuo at 60–80 °C for 2 days and were then stored in a desiccator until the measurements were made. This conditioning of the samples was found to be necessary in order to obtain reproducible results. Unless the samples were properly conditioned, isothermal measurements were found to be nonreproducible Atmospheric moisture and, to a lesser extent, the molding conditions were found to affect the sample response.

Both isothermal and nonisothermal dynamic shear data were taken over a wide range of temperature and/or frequency. Typically the temperature range was from about −100 to +250 °C and the frequency ranged from 0.01 to 10 Hz. During measurements the sample chamber was constantly purged with dry nitrogen. The temperature was controlled within ±0.2 °C above the glass temperature of the samples and better than ±0.1 °C near and below T_g. Two check runs were made after the sample had been exposed to high-temperature measurements in order to assess the thermal stability of the sample and to check the reproducibility of the data during the measurement of each sample. During the period of measurement most of the samples were found to be thermally stable up to 250 °C, as judged from the reproducibility of the data, which was about ±5%.

All measurements were made in the linear range of viscoelasticity. Linearity was checked at and above room temperature at various frequencies. When the rectangular sample geometry was used the sample coefficient corrections due to the clamping of the specimen were less than 5% and hence were ignored in the analysis of data.

Results and Discussion

Sulfonation Effect. Typical nonisothermal dynamical modulus data are shown in Figure 1, where the logarithm of the in-phase modulus is plotted against temperature at 1 Hz for four samples. The curves designated A, C, and D correspond to sulfonated EPDM zinc salts varying in the degree of sulfonation from about 0.5 to about 1.5 mol %. The curve O is that of the base EPDM. The response of the base polymer is that of a typical amorphous high molecular weight polymer. The glass transition of the base EPDM is in the neighborhood of −50 °C, where a drop of about 3 orders of magnitude in the modulus of EPDM is evident. EPDM shows only a rather short pseudorubbery plateau near room temperature, which is not very surprising in view of its low molecular weight which precludes the formation of a well-developed entanglement network. Increasing the temperature lowers modulus and, above 100 °C, the sample rapidly approaches the viscous flow region.

Table III
Characterizing Parameters of Zinc Sulfonate EPDM's

sample no.	log G', dyn/cm^2	ν, cross-link density $\times 10^4$ mol/cm^3	cross-link density based on sulfonation concn $\times 10^4$ mol/cm^3
48-A	7.22	6.69	1.45
48-C	7.33	8.63	2.65
48-D	7.46	11.60	3.37
48-O[a]	7.10		

[a] Value at log $\omega \sim -2.0$; $\nu_e = 5.08 \times 10^{-4}$ mol/cm^3.

The incorporation of sulfonate groups into EPDM is primarily manifested by the development of a well-defined rubbery plateau, as seen from curves A, C, and D. Only about 0.5 mol % sulfonate (curve A) enables the polymer structure to remain intact up to a temperature of 150 °C. The modulus from about 0 to about 150 °C remains essentially constant at about 10^7 dyn/cm^2. On the basis of the position of the primary softening region, it appears that the effect of zinc sulfonate groups on the glass transition is small. T_g increases by about 5 °C.

The increase in sulfonate content results in an increase in the magnitude of the rubbery plateau, as exhibited by curves C and D. In the neighborhood of room temperature the rubbery modulus increases by a factor of 2 as the sulfonate concentration increases from 0.6 to 1.4 mol %. At temperatures above 150 °C the effect of the presence of ionic sulfonate groups is also evident. The modulus decreases slowly with increasing room temperature, and the higher the sulfonate content, the slower the decrease in modulus.

At the higher sulfonate levels in the intermediate temperature region G' increases moderately with increasing temperature, in accord with the theory of rubber elasticity.[25] This type of behavior is typically observed in covalently cross-linked elastomers at moderate-to-high cross-link densities.[26] To our knowledge such behavior has not been observed with physically cross-linked elastomers, such as the block copolymers.[27] Certainly this behavior is different from that observed with carboxylate-based ionomers.[3,4] In any event the relative persistence of the ionic sulfonate cross-links as a function of temperature results in a system very analogous to that containing covalent cross-links. Because of this similarity in these different systems, it was of interest to calculate the number of ionic cross-links present in these polymers in a fashion analogous to that done with covalently cross-linked elastomers. This permits an assessment of the efficiency of the metal sulfonate cross-links. We assume that all cross-link sites are $-SO_3-Zn-SO_3-$ and that they all participate and contribute equally to the modulus. The number of cross-links, ν, per unit mass was calculated according to equation $G = \nu kT$ from the ideal theory of rubber elasticity.[25] These calculated cross-link densities are shown in the third column of Table III. The actual values of the in-phase modulus used in calculations are shown in the second column of Table III. In the fourth column of this table are given the number of cross-links per sulfonate groups introduced into the polymer. Solely on the basis of these two sets of numbers it is clear that the cross-link efficiency of metal sulfonate groups in the zinc sulfonated EPDM's is 3–4 times higher than theoretically expected.

Such large differences in the calculated and expected cross-link densities strongly suggest possible contributions

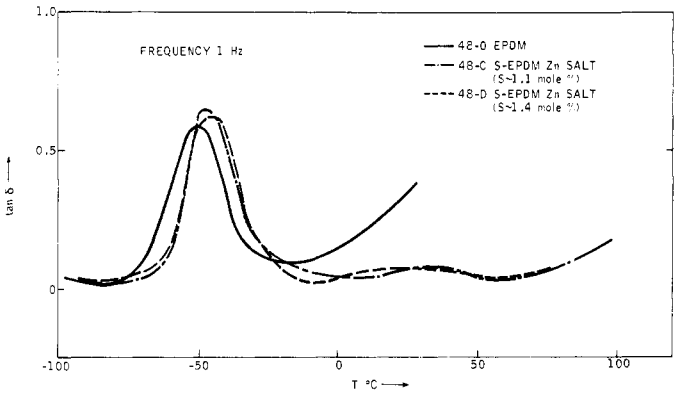

Figure 2. Plot of tan δ vs. temperature (in °C) of various zinc sulfonate EPDM's shown in Figure 1.

of the topological constraints of the nonionic sections of the EPDM chains to the elastic behavior. In stress relaxation experiments on a variety of high molecular weight amorphous polymers the existence of a rubbery plateau attributable to the entanglements has been experimentally observed. A rather short rubbery plateau observed below 0 °C in the base EPDM (curve O of Figure 1) hinted at the coexistence of a network-like structure retarding the relaxation processes in that temperature region. In view of the low molecular weight of this material this was at first a little surprising. Subsequent isothermal measurements on this sample clearly showed the existence of entanglement network formation in the intermediate frequency range (see the master curve of EPDM in Figure 4). The cross-link density ν_e associated with the entanglement modulus was calculated from the low-frequency region modulus value and was found to be 5×10^{-4} mol/cm^3. It is very interesting that, if this value of entanglement cross-links is added to the theoretically expected values of ionic cross-links (Table III, column 4), cross-link density values are obtained which are very close to those experimentally observed (Table III, column 3). Such agreement could be fortuitous. Nevertheless the interpretation of this observation could be worth discussing in view of the present entanglement concepts.[24] It appears that in the metal sulfonate EPDM's essentially all entanglements initially present in the base EPDM are trapped upon the introduction of metal sulfonate groups. These trapped entanglements play a significant role in determining the elasticity and modulus of these polymers.

Overall the viscoelastic behavior of all the three zinc sulfonate containing EPDM's is reminiscent of a typical covalently cross-linked rubber. These samples appear to form a network in a manner similar to covalent cross-linking, but which could only be due to some sort of ionic association. The constant rubbery plateau over a wide temperature range and the stability of the network up to more than 300 °C above the glass temperature demonstrate the strength of sulfonate group association. The strength of ionic association in these systems thus appears to approach that of covalent linkages.

In Figure 2 the tan δ–temperature curves of these samples are illustrated. In all samples, including the base EPDM, only one major peak, corresponding to the primary transition, was found. The effect of zinc sulfonate groups on the tan δ value is insignificant. All the zinc sulfonate EPDM's, as well as the base EPDM, are relatively low-loss materials with more or less identical tan δ values of about 0.6. Upon sulfonation there are hardly any changes in either the width or height of the main transition peak. This suggests that there have not been any significant changes in the nonionic phase of these polymers. In the

Table IV
Free-Volume Parameters of Various Zinc Sulfonate EPDM Samples

sample	T_g, °C	T_∞, °C	C_1^g	C_2^g	$(\Delta H)_{a,T_g}$,[a] kcal/mol
48-O; base EPDM	−58	−108	14.5	52.9	58.0
48-A; S-EPDM Zn salt ([S] ~ 0.6 mol %)	−53	−96	15.4	43.0	79.3
48-D; S-EPDM Zn salt ([S] ~ 1.4 mol %)	−50	−102	16.3	52.0	71.3
EP copolymer[b] ([ethylene]:[propylene] = 56:44)	−57	−98	13.1	40.7	68.7

[a] Using the relation $(\Delta H)_a = 2.303R(C_1/C_2)T_g^2$. [b] Reference 24a.

zinc sulfonate EPDM's there is a faint hint of a secondary transition in the vicinity of room temperature, where the tan δ curve shows a very small diffuse peak. Keeping in mind the limit and sensitivity of the instrument and the peak's rather low magnitude, it is difficult to say whether the peak is real. However, if it is real, it is quite conceivable that this peak indicates some sort of relaxation phenomemon occurring in the regions rich in ionic groups.

The detailed study on styrene-based carboxylate ionomers by Eisenberg and co-workers showed very clearly that in these systems two different types of morphologies exist below and above a critical ion concentration. They found that above about 6 mol % an extensive ion clustering occurred while below that a lower degree of ionic group association, referred to as a multiplet, was encountered. It was observed that above the critical ion concentration typical viscoelastic relaxation mechanisms were altered, and the usual time–temperature superposition principle was not obeyed. The critical ionic group concentration was found to depend upon the nature of the backbone. In polyethylene ionomers, for example, the critical ionic group concentration is about 1 mol %.

A series of isothermal dynamic modulus measurements were made as a function of frequency in order to critically assess the effect of sulfonate groups on the viscoelastic behavior of sulfonate-containing systems, especially on the primary relaxation mechanisms. Because of the similarity of the EPDM and polyethylene backbones, it was suspected that, similar to carboxylate-containing polyethylene, any structural changes due to the incorporation of about 1 mol % of sulfonate groups would result in variations in the viscoelastic behavior. Typical modulus–frequency data are shown in Figure 3. On the left half of the figure the data for the base EPDM are shown while on the right the data for the zinc salt of the 1.4 mol % sulfonate content sample are presented. Although the temperature range shown is from −75 °C to room temperature, some high-temperature measurements were made, especially for the sulfonate-containing samples. With the exception of a very small rubberlike vertical correction all the high-temperature curves for the sulfonate-containing sample overlapped. These high-temperature data are not illustrated to avoid unnecessary clustering of data. As can be noted the shapes of various curves are similar and nothing unusual is observed. The curves could be shifted along the frequency scale to obtain master curves. A good time–temperature superposition was obtained for the zinc sulfonate EPDM, as shown in the upper half of Figure 4, suggesting that the behavior of this material is thermorheologically simple, at least in the frequency region studied.[28]

In the bottom half of Figure 4 the master curves for the lowest and highest zinc sulfonate samples are compared with each other and with that of the base polymer at a reference temperature of −40 °C. The shift factors in generating these curves were of the WLF type, although the WLF constants differed slightly from each other and from those of universal numbers. The numbers are listed in Table IV. For comparison the WLF and Vogel constants of an EP copolymer studied by Ferry and co-workers[24a] are also included. This EP copolymer was very similar in its ethylene and propylene contents to the base EPDM polymer described herein.

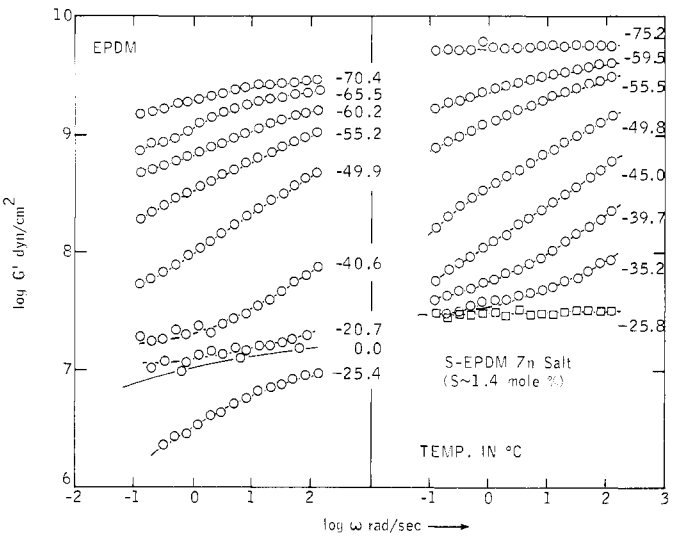

Figure 3. Logarithmic plot of in-phase modulus (in dyn/cm²) vs. frequency (in rad/s) of base EPDM and its sulfonated zinc salt (1.4 mol % sulfonation level) at various indicated temperatures.

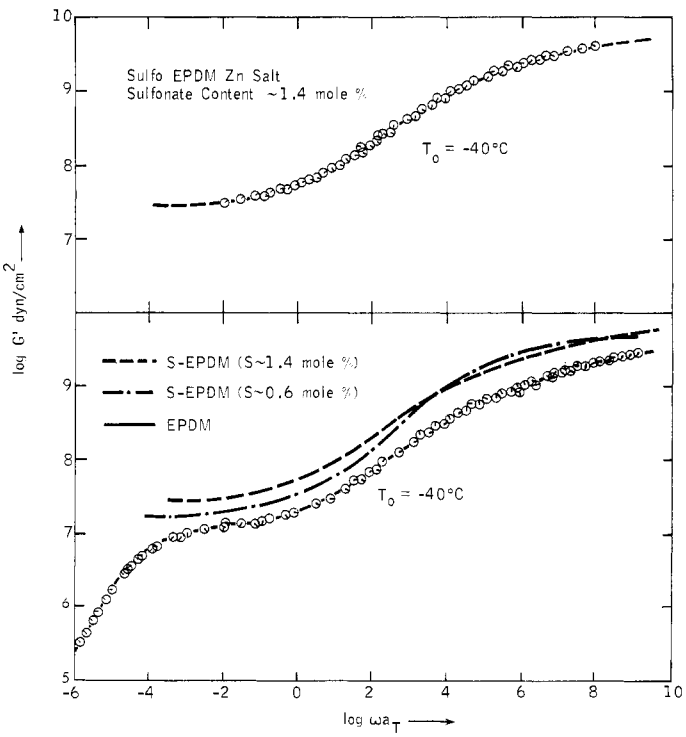

Figure 4. (Top) Logarithmic plot of in-phase modulus (in dyn/cm²) vs. reduced frequency (in rad/s). (Bottom) Plot of various master curves. Reference temperature T_0 = −40 °C.

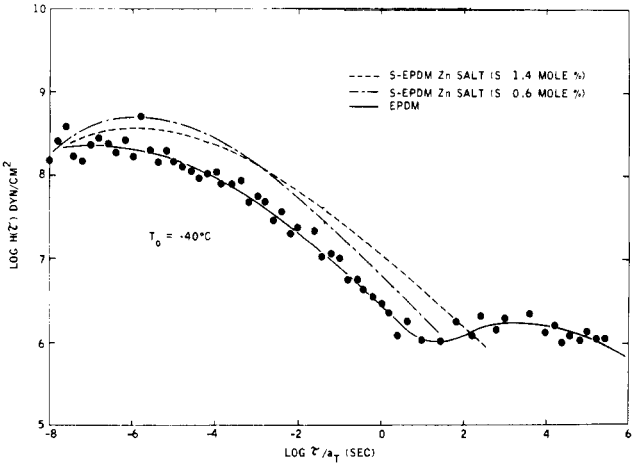

Figure 5. Logarithmic plot of the relaxation time ($H(\tau)$ (in dyn/cm^2) vs. reduced frequency at −40 °C for various zinc sulfonated EPDM samples of varying sulfonate content.

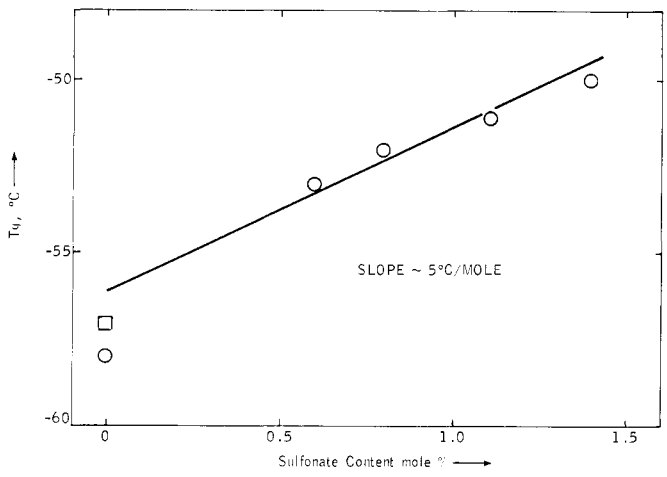

Figure 6. Plot of glass temperature (in °C) vs. sulfonate content (in mol %) of various zinc sulfonated EPDM samples [(□) EP copolymer, ref 24a].

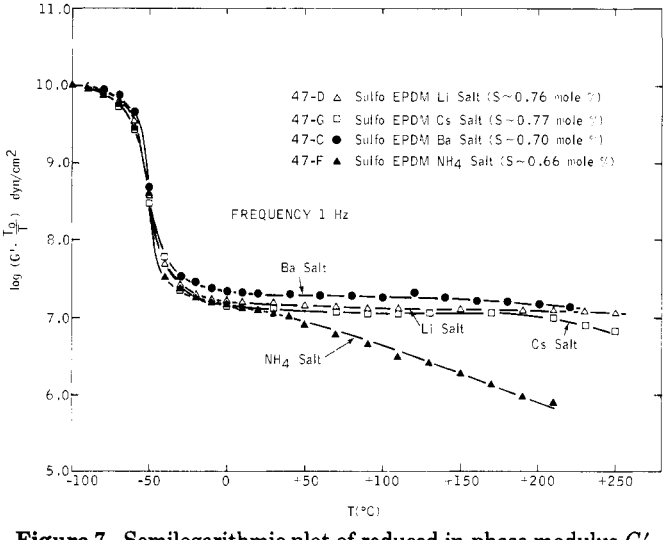

Figure 7. Semilogarithmic plot of reduced in-phase modulus G' (in dyn/cm^2) vs. temperature (in °C) of various sulfonated EPDM samples neutralized with various monovalent cations.

From the shapes and positions of the various master curves shown in Figure 4 various important conclusions can be drawn. Qualitatively the overall shapes of the master curves are similar to each other especially in the vicinity of the primary transition. The master curves of the zinc sulfonate EPDM's were obtained essentially by superimposing the data in the primary softening region. In view of the similar response behavior of the base EPDM it appears that the viscoelastic relaxation processes in zinc sulfonate EPDM's are due to the nonionic phase. The phase rich in ionic groups does not contribute to the primary relaxation processes except for slowing them down. Comparing the curves of the zinc sulfonate EPDM's it appears that the rate of relaxation as a function of sulfonate group content and is faster for the lower sulfonate sample.

Relaxation time distributions were calculated by using the appropriate approximation equations and are shown in Figure 5. Here again a broadening of relaxation times is obtained, indicating a decrease in the rate of relaxation as the sulfonate concentration increases. Intuitively it would be expected that an increase in the ionic group content would slow down the diffusional processes due to increased intermolecular interactions and thereby restrict configurational motions. The relaxation behaviors of these systems are similar to the behavior of those styrene-based carboxylate ionomers which follow WLF-type behavior.[15]

With zinc sulfonate EPDM's at very low frequencies a constant rubbery plateau is observed (cf. Figure 4), indicating the existence of cross-linking through ionic association. The magnitude of the rubbery modulus is affected by the introduction of sulfonate groups and increases with increasing sulfonate content. These effects were earlier observed in Figure 1. In the case of the base EPDM at very low frequencies the flow region is evident. Further, a close examination of the various curves reveals that the glassy moduli of zinc sulfonate EPDM's also appear to be a function of ionic group concentration. The higher glassy modulus observed at the highest sulfonate level is due to increased interaction between the polymer chains.

The glass temperature of EPDM is not strongly influenced by the incorporation of sulfonate groups. The glass temperatures of the zinc sulfonate EPDM's were back-calculated through the use of Vogel and WLF equations.[24a] The values were cross-checked from modulus–temperature data such as those in Figure 1. It was found that an increase of about 8 °C in T_g occurs by incorporating about 1.4 mol % of zinc sulfonate groups into the EPDM polymer. Within the experimental error of such measurements and calculations a linear relationship between T_g and sulfonate content was developed. This relationship is illustrated in Figure 6, and the numerical data therefore are given in the second column of Table IV.

Counterion Effect. The time–temperature principle was found to be applicable in salts other than zinc as well. These data will be published at a later date. Because of the ease of measurements extensive modulus–temperature data were obtained on various sulfonated polymers which differed only in the type of cation. Figure 7 compares the data for three monovalent cations and one divalent cation, barium. The data for the barium sulfonate EPDM are included for comparison. In the figure the modulus has been multiplied by the factor T_0/T to account for the temperature dependence of rubberlike behavior, in accordance with the kinetic theory of rubber elasticity. The sulfonate group contents of the samples were almost identical and in the neighborhood of 0.7 mol %. The results show that both the lithium sulfonate and cesium sulfonate EPDM's form a very stable and tight network. In both cases an extended rubbery plateau is observed. Within the uncertainty of the measurements it can be concluded that both the cesium and lithium salts contained the same concentration of sulfonate groups. The lithium salt has a higher modulus than the cesium salt, which is

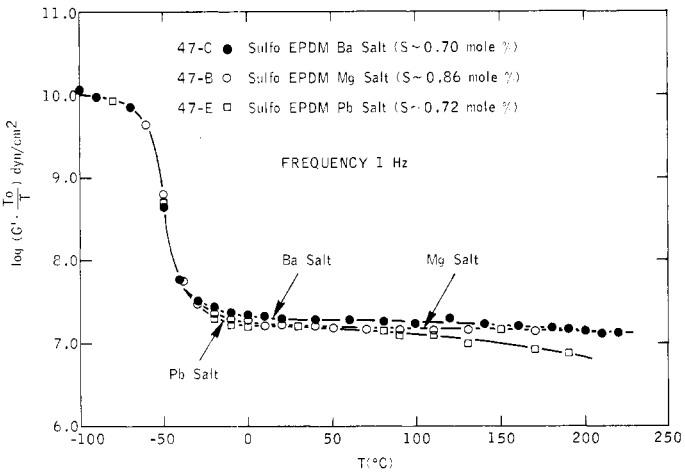

Figure 8. Semilogarithmic plot of reduced in-phase modulus G' (in dyn/cm^2) vs. temperature (in °C) of various sulfonated EPDM samples neutralized with various divalent cations.

indicative of a somewhat tighter network. The differences between the two materials are clearly manifested at higher temperatures. At 250 °C the modulus of the cesium salt is lower than that of the lithium salt by a factor of 2. On the basis of these results it seems clear that the strength of ionic associations in the lithium salt is higher than that of the cesium salt. The ammonium sulfonate EPDM, on the other hand, forms a much weaker pseudonetwork. In this material a very short rubbery plateau is obtained from about −30 °C to room temperature, but the ionic cross-links start to yield beyond room temperature. At higher temperature the modulus drops off more rapidly than for the lithium and cesium sulfonates. The effect of these counterions on the glass temperature is negligible. All the samples have more or less the same glass temperature of about −50 °C. However, from a close examination of the shapes of the curves in the transition region, it would appear that there are small differences in the primary relaxation rates of these materials. The stress relaxation master curves obtained on some of these materials substantiate this conclusion. These observations will be discussed in detail in a later publication.

In Figure 8 data are shown for metal sulfonate EPDM's containing the divalent cations barium, magnesium, and lead. Here also the glass temperature is not affected by the counterion. However, the rubbery modulus depends upon the nature of the counterion. The magnesium sulfonate, although at a somewhat higher sulfonate level than the barium sulfonate, exhibits a lower modulus. In both materials the ionic group interactions are very strong since the rubbery modulus remains essentially constant up to 250 °C. The lead sulfonate forms a weaker network than the other two sulfonates. The lead salt begins to lose its integrity above 100 °C, which indicates the onset of slow relaxation processes associated with the viscous flow region.

The data presented in Figures 1, 7, and 8 strongly suggest that in metal sulfonate EPDM's ionic cross-link networks very similar to that of a covalent system exist. The cross-link density in these materials is a function of ionic group concentration. It also depends upon the counterion, but to a lesser extent. The cross-link density in the barium salt is significantly higher than that in the others. This is apparently in contrast to the behavior observed by Navratil and Eisenberg[16] on carboxylated polystyrene neutralized with barium and other monovalent cations. The barium salt of the carboxylated polystyrene showed a lower cross-link density than the cesium and sodium salts.

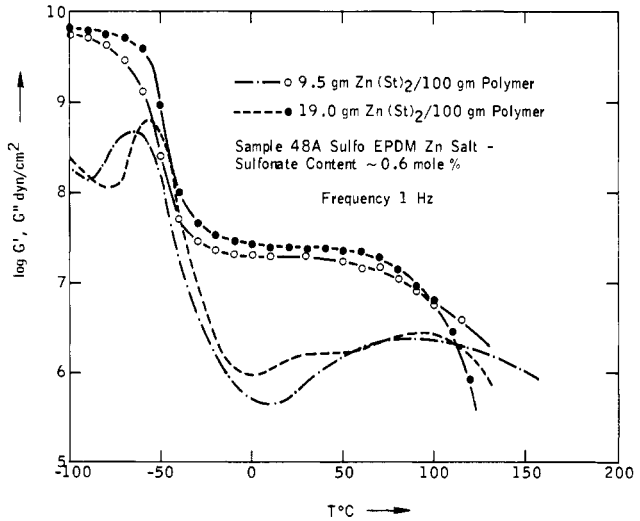

Figure 9. Semilogarithmic plot of in-phase modulus G' and out-of-phase modulus G'' (both in dyn/cm^2) vs. temperature (in °C) of plasticized zinc sulfonated EPDM (sulfonate content ~0.6 mol %) to various contents.

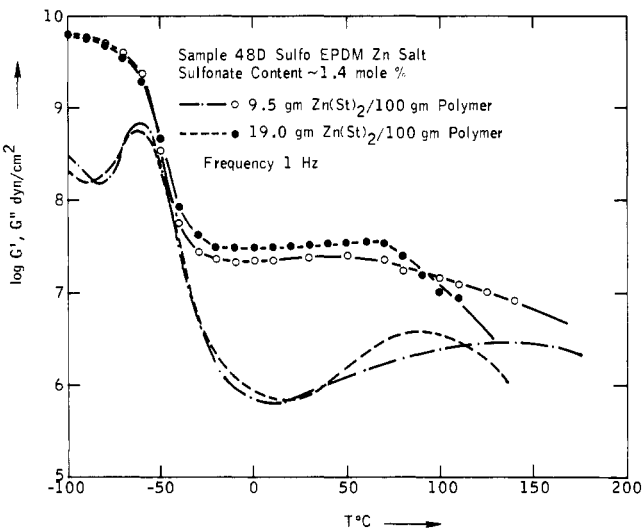

Figure 10. Semilogarithmic plot of in-phase modulus G' and out-of-phase modulus G'' (both in dyn/cm^2) vs. temperature (in °C) of plasticized zinc sulfonated EPDM (sulfonate content ~1.4 mol %) to various contents.

Plasticizer Effect. From the discussions presented above it is clear that even in the molten state at high temperature the sulfonate-containing EPDM's possess very high viscosities and are difficult to melt process. During the last few years a series of nonfugitive additives have been studied in an attempt to decrease melt viscosity and improve processability.[7] Basically two categories of plasticizer have been developed. The first category includes the conventional phthalate esters employed with lightly sulfonated polystyrenes which lower T_g and viscosity due to free-volume effects in the polymers. Such plasticizers effectively solvate the polymer backbone on a selective basis. In the case of sulfonated EPDM's, paraffinic oils can be employed in a similar manner. However, due to the strong ionic associations in these sulfonate-containing polymers such plasticizers are not very effective in lowering viscosity to a level which would be practical for melt fabrication. Substantial improvements in the melt flow of ionic polymers are achieved via the so-called "ionic plasticizers".

It was discovered in our laboratories that metal-neutralized EPDM's improved markedly in processability as well as in mechanical properties when plasticized with

certain metal derivatives of fatty acids, notably stearic acid. One of the most effective plasticizers is zinc stearate. Consequently, we decided to study the effect of zinc stearate on the viscoelastic behavior of sulfonate-containing EPDM's in detail. Figures 9 and 10 illustrate the modulus–temperature data for the lowest and highest zinc sulfonate EPDM's at various plasticizer loadings. Both the in-phase (G') and out-of-phase (G'') modulus data are shown. For clarity the experimental data points of G'' are eliminated. Several important features can be noted. The remarkable effect of the plasticizer on the ionic interactions is noteworthy, especially at higher temperatures. Figure 9 clearly shows that, above 100 °C at about 20% zinc stearate, the modulus of the 0.6 mol % zinc sulfonate EPDM sample drops precipitously and very rapidly approaches the flow region. Either the zinc stearate has virtually eliminated the ionic group associations or the ionic domains became mobile and permitted the flow of polymer molecules.

The G' curves of Figure 9 are reminiscent of a very high molecular weight, narrow-distribution, linear amorphous polymer. In these polymers it is now well established that the flow of polymer molecules takes place by the long-range coordinated motion of chain segments. In view of this it appears that in plasticized sulfonate-containing EPDM's at higher temperatures the ionic linkages are dissolved. The word "dissolved" is used in the sense that the ionic forces which kept the network structure intact are at least diminished. Consequently a structure very similar to that of amorphous high molecular weight polymers occurs in the plasticized sulfonate-containing EPDM's in which polymer chain segments are free to undergo coordinated deformations at higher temperatures. Alternatively, it might be argued that the effect of such plasticizers is to improve flow by promoting ionic bond interchange. At this time, it is not feasible to distinguish between these mechanisms.

Two other important features which are worth noting in Figures 9 and 10 are the effect of ionic group plasticizers on the glass transition temperature and the rubbery modulus of sulfonate-containing EPDM. The incorporation of about 10 parts of zinc stearate increases the glass temperature of the lowest (0.6 mol %) sulfonate content zinc sulfonate EPDM by about 3 °C. Doubling the amount of plasticizer further raises T_g by 5 °C. Similar effects on T_g are found at higher sulfonate contents, as shown in Figure 10. Compared to the behaviors of typical low molecular weight plasticizers in polymeric systems, which lower glass transition temperature by introducing extra free volume, zinc stearate plasticizer behaves differently.

At room temperature zinc stearate is a crystalline solid with a melting point of about 125 °C. It seems unlikely that incorporating such a material would diminish free volume and raise T_g. It appears that the zinc stearate in sulfonate-containing EPDM's is present in the form of a filler which may or may not be bonded to the organic matrix through dipole interactions with the sulfonate groups. It is believed that it is probably present in both forms, depending upon zinc stearate concentration. The amount of zinc stearate that could be associated with the sulfonate groups should be governed by the level of sulfonate groups which is low in these modified EPDM polymers. It should be noted that the maximum ionic group concentration studied is about 1.5 mol %. The effect of filler in polymers on glass temperature and on modulus is well documented. Accordingly an increase in the rubbery modulus is found in both the low (Figure 9) and high (Figure 10) sulfonate systems. Also, as plasticizer loadings are increased, probably regions rich in ionic groups are solvated and increase in size, which also contributes to an increase in modulus. As expected, the onset of viscous flow is a function of plasticizer loading. In the low sulfonate content material (Figure 9) at higher plasticizer loadings flow starts at lower temperatures. The same is true for the higher sulfonate material (Figure 10). This also can be understood in terms of large solvated ionic regions which can be expected to dissociate at lower temperatures.

Conclusions

These studies have shown that sulfonated ionomers can approach covalently cross-linked elastomers in their viscoelastic behavior. In this respect sulfonated EPDM is markedly different from analogous carboxylate ionomers. It is presumed that there is a tendency for a stronger Coulombic association of the ion pairs with the sulfonate ionomers than with the carboxylates. It would be of interest to categorize the structure of metal sulfonated EPDM's in terms of multiplets and clusters as described by Eisenberg and co-workers,[4] but, as yet, insufficient information is available to permit this analysis.

Acknowledgment. We acknowledge with thanks the experimental assistance of Mr. Richard T. Garner in the measurements.

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Polymerization of 2-Methyltrimethylene Oxide with Organoaluminum Catalysts and a Microstructure Study of Its Polymer by ^{13}C NMR Spectroscopy

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ABSTRACT: The polymerization of 2-methyltrimethylene oxide and its optically active enantiomer was done with an aluminum coordination catalyst and some cationic catalysts. Only the coordination catalyst gave polymer with predominantly head-to-tail linkages. The microstructure of the polymers obtained was determined by ^{13}C NMR spectroscopy from the methine-carbon triads and the *O*-methylene-carbon dyads. The stereospecific ability of the catalysts was also evaluated.

Since the polymerization of trimethylene oxide and its derivatives with BF_3 catalyst was reported by Rose,[1] a large number of papers and patents have appeared on the polymerization of derivatives of trimethylene oxide, particularly 3,3-bis(chloromethyl)oxetane. There has been much research on the polymerization of propylene oxide but little investigation of the polymerization of 2-methyltrimethylene oxide in the past decade. We have reported microstructure results for poly(propylene oxide) by ^1H and ^{13}C NMR spectroscopic methods.[2] In this paper the ^{13}C NMR method was also used for the microstructure analysis of poly(2-methyltrimethylene oxide) obtained with some coordination and cationic catalysts.

Experimental Section

Materials. In general, purification of materials was carried out under a dry argon atmosphere. All solvents were purified by conventional methods, dried over calcium hydride, and distilled just before use. Diethylzinc and triethylaluminum were purified by distillation under reduced pressure.

2-Methyltrimethylene Oxide. This racemic compound was prepared with 1,3-butanediol as a starting material by the method reported by Searles et al.:[3] bp 60 °C; yield 54%. Optically active (+)-2-methyltrimethylene oxide was prepared by asymmetric reduction of methyl acetoacetate with Raney-nickel catalyst treated with D(+)-tartaric acid, followed by reduction with lithium aluminum hydride in dry ether and subsequently by Searles' procedure:[3] yield 46%; $[\alpha]^{22}_D$ −22.4 ° (neat), optical purity 76%.[4]

Polymerization Procedure. 2-Methyltrimethylene oxide was charged by distillation over calcium hydride into the polymerization ampule containing the catalyst solution. The ampule was sealed and allowed to stand at 60 °C for several days. Polymerization was terminated by adding a mixture of benzene and a small amount of methanol. The precipitated catalyst residue was removed by centrifugation and the raw polymer was obtained from the solution by freeze-drying. Intrinsic viscosity, $[\eta]$, was measured at 30 ± 0.1 °C in benzene solution.

Preparation of Catalysts. (a) Diethylzinc–Water (Molar Ratio 1:0.8) Catalyst. An ampule connected to a vacuum line was flushed several times with dry argon, and a solution of diethylzinc (3.0×10^{-4} mol) in benzene (5 mL) was introduced by distillation under reduced pressure; then, while the mixture was stirred at room temperature, water (5.04 μL) was added with a microsyringe. Stirring was continued at room temperature for 2 h and then at 60 °C 3 h. The resulting benzene solution was freeze-dried to remove unreacted diethylzinc. To the residue obtained toluene and monomer were added by distillation seperately in this order under reduced pressure from the graduated reservoirs.

Table I
Polymerization of Racemic 2-Methyltrimethylene Oxide with a Variety of Catalysts[a]

catalyst (molar ratio)	amt of catalyst, mol/mol of monomer	polymerization time, days	polymer yield, %	$[\eta]$,[b] dL/g
t-BuOK	2×10^{-2}	48	0	
BF_3·OEt_2	2×10^{-2}	44	52	0.05
$FeCl_3$	3×10^{-2}	44	62	0.02
$Al(O\text{-}i\text{-}Pr)_3$–$ZnCl_2$ (1:1)	3×10^{-2}	54	14	0.01
$ZnEt_2$–H_2O (1:1)	3×10^{-2}	23	16	0.20
$AlEt_3$–H_2O (1:1)	3×10^{-2}	5	24	0.11
$AlEt_3$–acac–H_2O (1:1:0.5)	3×10^{-2}	9	51	0.90

[a] Polymerization was carried out in toluene solution at 60 °C. The concentration of monomer was 11.8 mol/L. [b] Intrinsic viscosity was measured in benzene at 30 °C.

(b) Triethylaluminum–Water Catalyst. The procedure was the same as that described for the diethylzinc catalyst, except for the reagent used.

(c) Triethylaluminum–Acetylacetone (acac)–Water Catalyst. The preparative method was reported by Vandenberg[5] and the typical procedure in this work was as follows: Triethylaluminum (0.0235 mol) was reacted with an equimolar amount of acac in toluene (20 mL) at 60 °C for 2 h; subsequently, water (0.0118 mol) was added with stirring and the mixture was allowed to stand overnight at room temperature.

Measurement of ^{13}C NMR Spectra. ^{13}C NMR (25.1 MHz) spectra of the polymers in deuteriobenzene solution were measured with a Varian XL-100 FT spectrometer. The instrument conditions were as follows: spectrum width, 5 kHz; acquisition time, 2.0 s; transients, 6000; flip angle, 50°; temperature, 30 °C. Tetramethylsilane was used as an internal standard.

Measurement of Molecular Weight Distribution. Chromatographic measurements were performed on a Shimadzu-Du Pont Model 830 liquid chromatograph using a set of three Styragel columns designated 7×10^5–5×10^6, 4×10^3–1.5×10^5, and

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