

Mechanical Properties of Complexed α,ω -Diamino Polybutadiene

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SYNOPSIS

α,ω -Dipiperazino polybutadiene (PBD) was complexed with the hydrated forms of copper chloride, iron chloride, and nickel chloride in methanol. The polymers were recovered and compression molded into films and properties investigated. In particular, the tensile stress-strain behavior as well as stress relaxation behavior were monitored with time at ambient conditions. It was observed that the polybutadiene material showed a strong association with copper providing a pseudo network behavior. The association for the iron and nickel components were considerably weaker than that of copper. Comparisons of the data obtained from these systems were also made with earlier data obtained from the same laboratory on carboxylated or sulfonated telechelic ionomers based on polyisoprene and polyisobutylene. It was concluded that the copper complex with the α,ω -dipiperazino polybutadiene has comparable or better behavior than some of the carboxylate systems. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

The utilization of ionic bonding in polymers has been of interest for a number of years because it offers an additional variable by which polymer structure and properties may be modified and controlled.¹⁻⁵ Ionomers typically have less than about 15 mol % ionic groups attached to an otherwise nonpolar chain. In this nonpolar environment, the ionic groups associate quite strongly, resulting in what is essentially a thermally labile ionic cross-link. The fact that the association may become weaker at higher temperatures means that these materials can often be melt-processed. In the case of elastomeric ionomers, the potential thus exists for the material to be a thermoplastic elastomer.

Traditional ionomers have the ionic groups distributed randomly along the polymer chain. Although such a structure may lead to a useful material with desirable physical and mechanical properties, the complex network structure, which has a wide

distribution of molecular weights between effective cross-links, makes the development of structure-property relationships more difficult. Recent work from our laboratories has focused on what may be termed telechelic ionomers, which have the ionic groups located only at the chain ends.⁶⁻³⁷ Such a chain microstructure leads to a more well-defined network structure for which structure-property relationships are somewhat more straightforward. It is important to note that the basic effect of ionic association in the random and telechelic ionomers is somewhat different. Association of two ionic groups on different chains of a random ionomer system results in the formation of a tetrafunctional ionic cross-link, whereas such an association in a telechelic ionomer system leads to an end-linking of chains or simple chain extension. Thus, for a telechelic ionomer system to form an ionic cross-link, the formation of at least triplet associations is required.

Polymers may thus be cross-linked via the traditional covalent cross-links, in which case the resulting network structure is permanent, or via ionic cross-links, which are thermally labile and thus offer the potential for one to shape or form the material

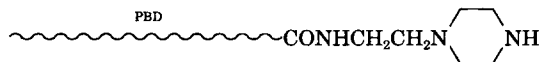
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using traditional polymer processing techniques. In addition to these two extreme types of chemical bonding, it is well known that transition elements having incompletely filled *d*-orbitals are capable of forming coordination compounds.³⁸ Because of their electronic structure, transition metals are able to form such coordination complexes when neighboring atoms or molecules (ligands) are present that can donate electrons to them. Thus, coordination complexes are distinguished from any other type of chemical compound in that both the central metal atom and the coordinating ligands are capable of independent existence as stable chemical species. Such a coordination mechanism has been utilized by Lundberg and co-workers to compatibilize polymer blends.^{39,40}

Charlier et al.³⁵ recently examined the dynamic viscoelastic properties of aminotelechelic polydienes that were cross-linked by such a coordination mechanism utilizing the transition elements copper(II), nickel(II), and iron(III). In this work, we report the stress-strain, stress relaxation, and creep behavior of these materials and compare them to the properties of similar materials in which ionic bonding is used.

EXPERIMENTAL

α,ω -Dipiperazino polybutadiene (PBD) was supplied by BFGoodrich under the trade name Hycar ATB. The main molecular features were: $\overline{M}_n = 4000$ (vapor-pressure osmometry), $\overline{M}_w / \overline{M}_n = 1.8$ (size-exclusion chromatography), average functionality = 2 piperazines/chain (according to the manufacturer), and *cis/trans*/vinyl ratio = 20/65/15 (NMR). The structure of the piperazine endgroup was



Thus, each endgroup consisted of one secondary and one tertiary amine function.

The PBD was dissolved in toluene (5%), and an amount of 1 wt % of antioxidant (Irganox 1010) was added to the polymer solutions prior to complex formation. A solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ in methanol (0.2 mol/L) was added dropwise to the polymer solution under vigorous stirring at 25°C. The solution was stirred for at least 24 h. The molar ratio of the metal chloride-to-butadiene chain was 1.0, and, thus, the molar ratio of the metal chloride-to-piperazine

endgroup was 0.5. No precipitation occurred, and the solution remained homogeneous throughout the process. The complexed polymers were recovered by solvent distillation under vacuum at room temperature and were dried at 60–70°C for at least 1 month to a constant weight.

Films of about 0.6 mm thickness were prepared for mechanical testing by compression molding at 100–120°C. Care was taken during compression molding to minimize the molding time and thus the potential for cross-linking or thermal degradation. Microdumbbell specimens, measuring 5.75 mm long in the linear region (10 mm overall) and 2.55 mm wide, were cut from these films.

Stress-strain experiments were performed on an Instron Model 1122 at room temperature (approximately 23°C). Experiments were conducted at a constant initial strain rate of 100%/min based on the length of the linear region of the specimen prior to deformation.

Long-term stress relaxation experiments were performed on a Tensilon/UTMII (Toyo Measuring Instruments Co. Ltd.) because of the excellent stability of this instrument over long periods of time. Samples were strained to 25% at an initial strain rate of 400%/min. The decay in stress was monitored for up to 10^4 min.

Creep experiments were conducted at room temperature by applying a load and monitoring the distance between two gauge marks located within the linear region of the microdumbbell sample about 5 mm apart. The distance between the two gauge marks was measured as a function of time with a cathetometer. To maintain a constant initial stress among samples, a 4 g load was applied to a 20 mil (0.02 in., 0.05 cm)-thick sample and was adjusted appropriately for other sample thicknesses. The creep compliance, $D(t)$, was calculated using the relationship

$$D(t) = \epsilon(t)/\sigma = \epsilon(t)(A/F) = \epsilon(t)(A_0/\lambda F) \quad (1)$$

where $\epsilon(t)$ is the time-dependent strain; σ , the engineering stress; A , the instantaneous cross-sectional area; A_0 , the original cross-sectional area; F , the measured force; and λ , the extension ratio. All creep data were obtained at extension ratios less than 1.20.

RESULTS AND DISCUSSION

Figure 1 shows the stress-strain behavior of α,ω -diamino polybutadiene complexed with CuCl_2 , FeCl_3 , and NiCl_2 . Clearly, the copper material dis-

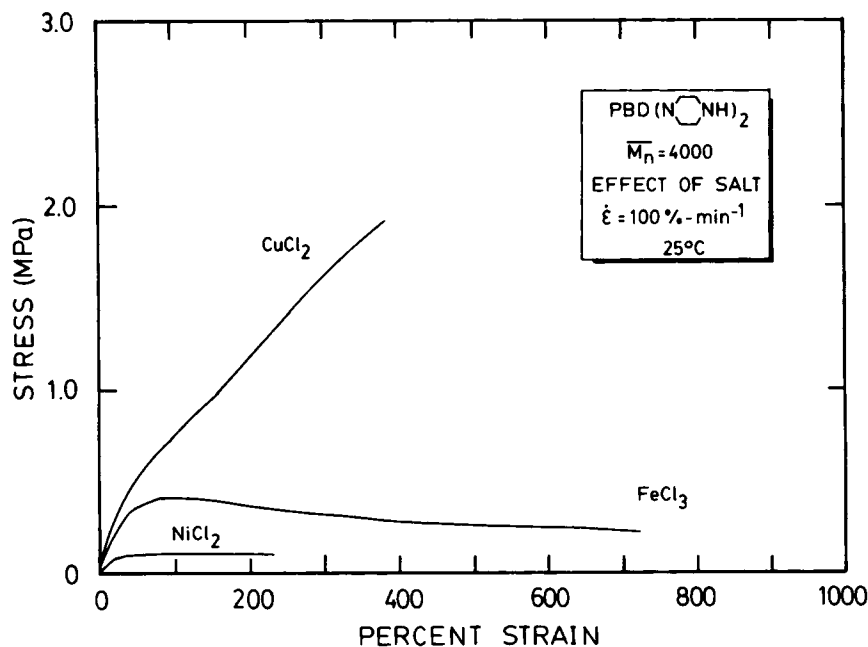
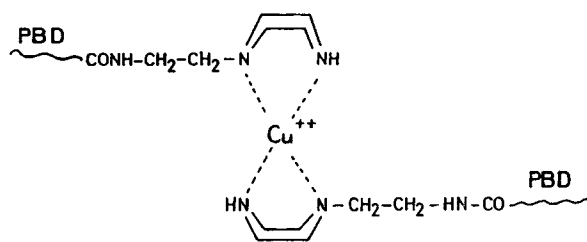


Figure 1 Stress-strain curves for α,ω -diamino polybutadiene complexed with various metal chlorides.

plays a higher modulus and much higher stresses than either of the other two materials, suggesting that the complex formed in this case is much stronger and/or is of a higher network functionality. Some insight can be obtained from the work of Charlier et al.,³⁵ in which the viscoelastic properties of the Cu(II) and Fe(III) materials, but not the Ni(II) material, were studied. That work demonstrated that the rubbery plateau modulus for the Cu(II) and Fe(III) materials were quite similar, suggesting similar cross-link functionalities, but that the rubbery plateau for the Cu(II) material extends to much higher temperatures, suggesting greater strength and stability of the Cu(II) complex. Thus, we expect that the differences in the stress-strain behavior result from differences in strength of the complex formed. Although information concerning the local environment of the copper atom in this material is not yet available, it is well known that Cu(II) cations coordinate at least four amino groups.⁴¹ That situation corresponds to the actual metal-to-piperazine endgroup molar ratio of 0.5 and is illustrated by Scheme 1. That piperazine can behave as a bidentate ligand has been proposed by Pagano et al.⁴² According to Scheme 1, a chain extension process should occur, resulting in the formation of long, entangled chains and/or entrapped cyclic molecules. The structure of the Cu(II) complexes might, however, be more complex than depicted in Scheme 1. First, the coordination number

of Cu(II) could be higher than four. Second, in addition to complexing with amine groups, the copper ions could complex with the double bonds in the polybutadiene chain. Although double bonds are weaker ligands than are amines, their population is much greater and such complexes may well exist. Figure 2(a) and (b) illustrate the effect of initial strain rate on the stress-strain behavior of the Cu(II) and Fe(III) materials, respectively. The greater strain rate dependence of the Fe(III) material also suggests that these complexes are weaker than those formed by Cu(II). The Ni(II) material also displays a high degree of strain rate dependence (not shown) and thus a weak association.

Stress relaxation and creep data are shown for the three materials in Figure 3. Again, the trend is similar. The Cu(II) material is by far the most stable, with Fe(III) and Ni(II) following. The complexes formed in the Ni(II) material are so weak



Scheme 1

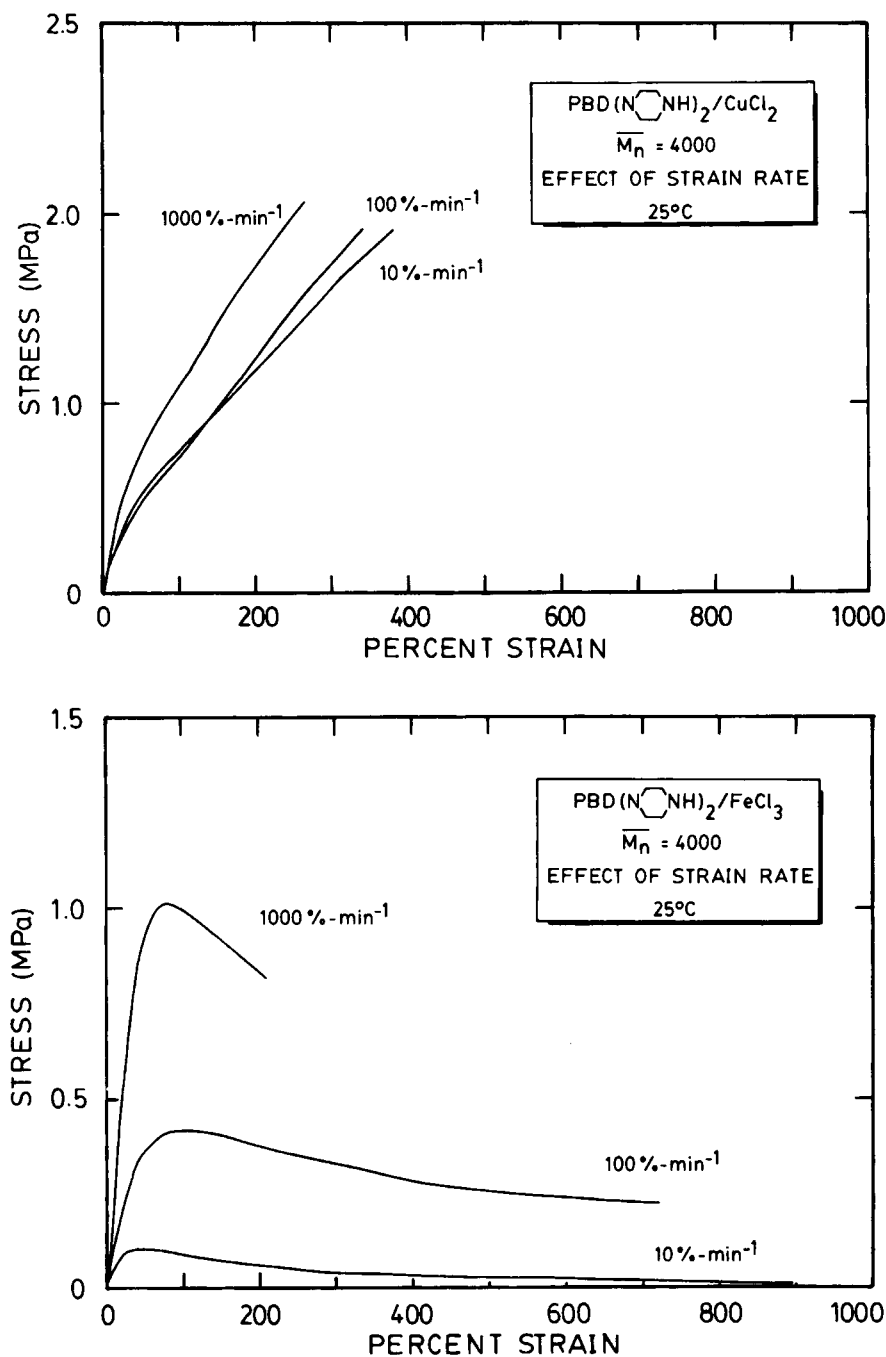


Figure 2 Effect of strain rate on stress-strain behavior of α,ω -diamino polybutadiene complexed with (a) CuCl_2 and (b) FeCl_3 .

that in the stress relaxation experiment stress falls to 10% of its initial value in only about 20 min. On the other hand, after about 10^4 min, the stress of the Cu(II) material has not yet reached 10% of its initial value. In the creep experiments, the Ni(II) material flowed so quickly that only one data point could be obtained before the strain became too great to provide usable data. Yet even after 10^4 min, the

Cu(II) material is just beginning to enter the viscous flow region.

It is of interest to compare the mechanical properties of these materials with those of similar telechelic ionomers, in which terminal carboxylic or sulfonic acid groups are neutralized with various metal ions. Table I compares the ultimate stress and ultimate elongation of the Cu(II)-complexed α,ω -

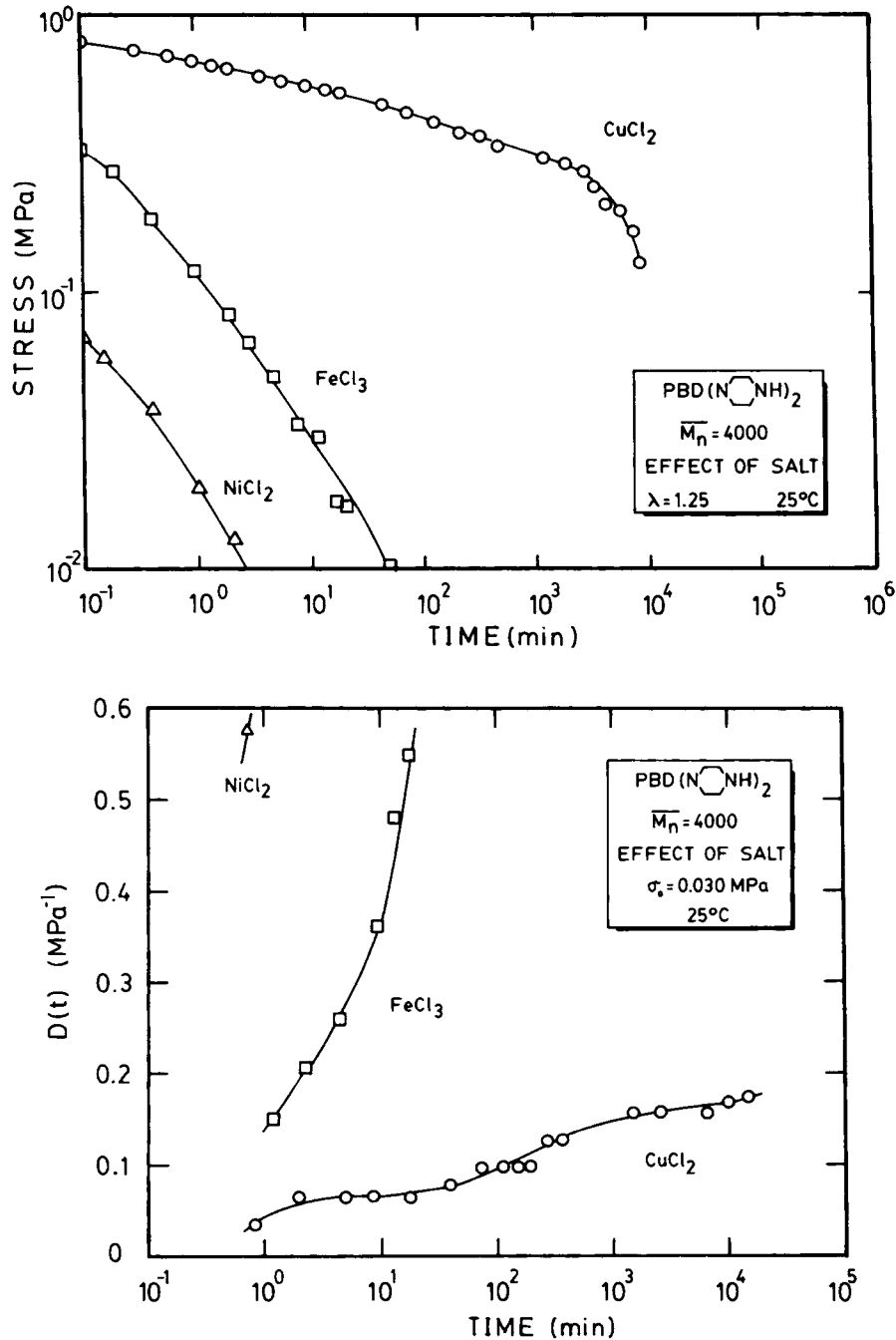


Figure 3 (a) Stress relaxation and (b) creep curves for α,ω -diamino polybutadiene complexed with various metal chlorides.

diamino polybutadiene with those of carboxylated polyisoprenes, sulfonated polyisoprenes, and sulfonated polyisobutylenes. The stress-strain experiments from which these data were obtained were all performed at the same strain rate and temperature. Unfortunately, all these materials with which we compare the properties of the α,ω -diamino polybutadienes are of higher molecular weight. Of course, the effect of increasing molecular weight on the

stress-strain behavior of such materials is usually to increase both the ultimate stress, due to the more extensive entanglement network, and ultimate elongation, due to a lower cross-link density. Clearly, the sulfonated polyisoprene displays much higher stresses than do the carboxylated polyisoprenes, as has been described by Venkateshwaran et al.³⁷ But, perhaps, it is more reasonable to compare the stress-strain behavior of the Cu(II)-complexed α,ω -dia-

Table I Comparison of Ultimate Mechanical Properties of Various Telechelic Polymers

	α,ω -Diamino Polybutadiene (4000 M_n) [Cu(II)]	α,ω -Dicarboxylato Polyisoprene (15,000 M_n)			α,ω -Disulfonated Polyisoprene (15,000 M_n)			α,ω - Disulfonated Polyisobutylene (6500 M_n)	
		[Mg(II)]	[Ca(II)]	[K(I)]	Mg(II)	Zn(II)	K(I)	[Ca(II)]	[K(I)]
Molar ratio ^a	0.5	0.5	0.5	1.0	0.5	0.5	1.0	1.0	2.0
Ultimate stress (MPa)	2.0	1.2	0.8	0.8	3.0	1.5	4.2	1.2	0.7
Ultimate elongation (%)	400	210	450	280	310	400	320	270	270

^a Molar ratio is given in moles of neutralizing agent per mole of endgroups, irrespective of the valence of the metal. The "degree of neutralization" for an ionic reaction is calculated using the valence of the neutralizing ion.

mino polybutadiene with that of the sulfonated linear polyisobutylene due to the similarity in molecular weight. The fact that the ultimate mechanical properties of the Cu(II)-complexed α,ω -diamino polybutadiene are higher than those of all of the other materials except the higher molecular weight sulfonated materials suggests that this particular coordination complex involving Cu(II) is very effective.

We can also compare the long-term network stability of the α,ω -diamino polybutadiene with that of the telechelic ionomers by examining the stress relaxation behavior. Referring to Figure 3(a), if lines are drawn to fit the two near-linear portions of the stress relaxation curve, their point of intersection may be used as an indicator of the time where significant viscous flow begins. For the Cu(II) material, this time is about 10^4 min. Referring to the long-term stress relaxation curves for the α,ω -dicarboxylato polyisoprene in Ref. 36, the two most stable materials, neutralized with Na(I) and Mg(II), began significant flow at less than 100 min. All the others began flowing at less than 10 min. The sulfonated polyisoprenes did not begin to flow significantly during the experimental time frame of 10^3 min. Referring to the long-term stress relaxation curves for the sulfonated polyisobutylene telechelic ionomers,⁴³ both the linear difunctional materials and the three-arm star trifunctional materials began to flow at about 10^3 min. However, the rate of relaxation of the three-arm star materials was much less than that for the linear materials. The point is simply that the network formed by the α,ω -diamino polybutadiene complexed with Cu(II) is quite stable compared to the carboxylated materials and the sulfonated linear difunctional polyisobutylene. The linear sulfonated polyisoprene and the trifunctional sulfonated materials are, however, the most stable of all, but both the much higher molecular weight and the difference in chain architecture undoubtedly

play a strong role in shifting the relaxation spectrum to longer times.

Another experiment was performed to compare the network stability of the α,ω -diamino polybutadiene with that of the α,ω -dicarboxylato polyisoprene. Tensile specimens were quickly stretched to 100% extension and that extension was maintained for 1 week. The tensile specimens were then released and strain recovery was monitored as a function of time. For the carboxylates, the material neutralized with Mg(II) fractured during the stretching. The K(I) material was found to recover only slightly, leaving 91% permanent set (i.e., only 9% of the 100% strain was recovered) after 10^4 min. None of the other carboxylates recovered at all, indicating very poor long-term network stability. Neither the Ni(II)- nor the Fe(III)-complexed α,ω -diamino polybutadiene displayed any recovery following 1 week at 100% extension. The Cu(II)-complexed material displayed 55% permanent set (i.e., 45% of the 100% strain was recovered) after 10^4 min, certainly much less permanent set (and more recovery) than displayed by any of the carboxylates. These results indicate that the complex formed by the CuCl₂ in these α,ω -diamino polybutadiene materials is quite strong compared to typical carboxylate ionic associations and is sustained at room temperature for longer periods of time.

CONCLUSIONS

This work has demonstrated that the formation of coordination complexes between functional units on polymer chains may be attractive as another means to create useful polymer networks. In particular, metal chlorides have been used to form coordination complexes with α,ω -diamino polybutadiene. Stress-strain, stress relaxation, and creep experiments indicate that the complex formed by CuCl₂ is much

stronger than that formed by either MgCl_2 or FeCl_3 . The network formed by complexation with CuCl_2 displays stress-strain behavior and long-term network stability that is superior to similar materials relying on carboxylate ionic associations. These materials are also similar to the typical ionomers in that they may be melt processed under appropriate conditions. Information on the specific structure formed in these complexes is not yet available, but is being pursued.

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