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# Effect of Oxygen and $Zn^{2+}$ on the Thermal Transitions and $Cu^{2+}$ Complexation in Amine-Terminated Telechelic Polybutadiene: DSC and ESR Studies

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ABSTRACT: Complexes of amine-terminated telechelic polybutadiene (ATPB) with $Cu^{2+}$ and $Zn^{2+}$ were studied by ESR and DSC. The effect of annealing, presence of oxygen, and $Zn^{2+}$ content on the thermal transitions and $Cu^{2+}$ complexation have been investigated. This study has indicated that $Zn^{2+}$ is not only a diamagnetic diluent but can also significantly affect the ionic distribution, the degree of ionic clustering, and the appearance of the glass transition. The ESR signal from the cupric ion disappears on annealing to 523 K and reappears at ambient temperature only when ATPB/$Cu^{2+}$ is exposed to oxygen. $Zn^{2+}$ accelerates the rate of disappearance of the $Cu^{2+}$ signal for annealing in air or in vacuo. These results have been explained by a mechanism based on the formation of allyl radicals on annealing, reaction of these radicals with $Cu^{2+}$, reduction of $Cu^{2+}$ to $Cu^{+}$, and reoxidation to $Cu^{2+}$. Formation of allyl radicals is enhanced by $Zn^{2+}$. The glass transition of ATPB measured by DSC (heating rate 20 K/min) is not affected by the presence of $Cu^{2+}$ *or* $Zn^{2+}$; the transition in ATPB/$Cu^{2+}$ ($x(\mathrm{Cu}) = 0.02$) is weaker in the presence of $Zn^{2+}$ and is not detected for $x(\mathrm{Zn}) \geq 1.98$. An exothermic transition around 360 K accompanies the changes in the glass transition region induced by $Zn^{2+}$; the corresponding $Q_{\mathrm{exo}}$ (J/g) is enhanced in ATPB containing both cations, compared to ATPB containing $Cu^{2+}$ only. This transition, which is absent in ATPB/$Zn^{2+}$ (no copper), is assigned to the formation of ionic domains. Swelling experiments and $T_g$ measurements at heating rates lower than 20 K/min indicate the formation of a reversibly cross-linked network in ATPB containing $Cu^{2+}$ and $Zn^{2+}$. We explained these results based on the combined effects of the two cations: $Zn^{2+}$ cations provide the cross-links by acting as Lewis acids, and $Cu^{2+}$ cations connect the end groups by complexation of the piperazine groups.

## Introduction

Telechelic ionomers such as α,ω-dicarboxylic polybutadiene (CTPB) and polyisoprene (CTPI), amino-terminated polydienes, and sulfonated telechelic polystyrene have been extensively studied by relaxation, scattering, and spectroscopic methods.[1–7] The main goal of these studies has been to understand and model the process of ion aggregation and to generalize the results obtained from the relatively simple telechelic ionomers to more complicated ionomer structures. Small-angle X-ray scattering (SAXS) studies of dry and solvent-swollen CTPB and CTPI have suggested that the average size of the ionic domains is not sensitive to the nature of the neutralizing cation.[2] Moreover, the glass transition temperatures $T_g$ measured by differential scanning calorimetry (DSC) for CTPB, CTPI, and the corresponding amine-terminated polymers are constant for a range of cation types and contents. It has been suggested that this behavior is due to the relatively small amount of polymeric material in the vicinity of the cations; this part of the sample is not reflected in the $T_g$, which is an average over the entire system.[8] The rheological behavior is, however, sensitive to the amount and nature of the cations, thus providing a simple method for the control of these properties.[4]

In previous publications we have presented a study of amine-terminated telechelic ionomers based on α,ω-dicarboxylated polybutadiene (ATPB) containing various amounts of $Cu^{2+}$ (up to 6 times the theoretical amount needed to complex all the amine groups), using electron spin resonance (ESR) and DSC.[9,10] The local environment of the cation has been deduced from ESR spectra of $Cu^{2+}$, either in samples with a low $Cu^{2+}$ content or at higher $Cu^{2+}$ concentration, using $Zn^{2+}$ as the diamagnetic diluent. The presence of amine-nitrogen ligation to $Cu^{2+}$ was detected in the ESR spectra from an analysis of the ESR parameters of the paramagnetic cation ($g$ and $^{63}$Cu hyperfine tensors). The increase in the line width with cation content was taken as an indication of cation clustering.[9] The temperature stability of the ionic domains has been studied in ATPB/$Cu^{2+}$ annealed in air to 523 K. In addition to the glass transition at 200 K, an exothermic peak was detected above 300 K. This peak becomes more pronounced and shifts to higher temperatures as the $Cu^{2+}$ content increases; for $x(\mathrm{Cu}) = 3.0$ this transition is centered at 420 K. The high-temperature DSC peak is absent in the telechelic ionomer with no cations, becomes more intense as the amount of cation increases, is not detected in a second run taken immediately after the first run, and reappears in samples left at ambient temperature for several days. Based on these results, we have suggested a reversible process for the formation of ionic clusters when the temperature increases.[10]

In this report we present ESR and DSC measurements on the effect of oxygen, annealing conditions, and variation of $Zn^{2+}$ content on the thermal transitions and $Cu^{2+}$ complexation in ATPB. As will be shown below, these experiments indicate that $Zn^{2+}$ is not only a diamagnetic diluent but can also significantly affect the ionic distribution, the degree of ionic clustering, and the behavior of the system in the presence of solvents. We will also show that the presence of oxygen is essential for the recovery of the ESR signal from $Cu^{2+}$ after annealing and for the formation of the ionic clusters.

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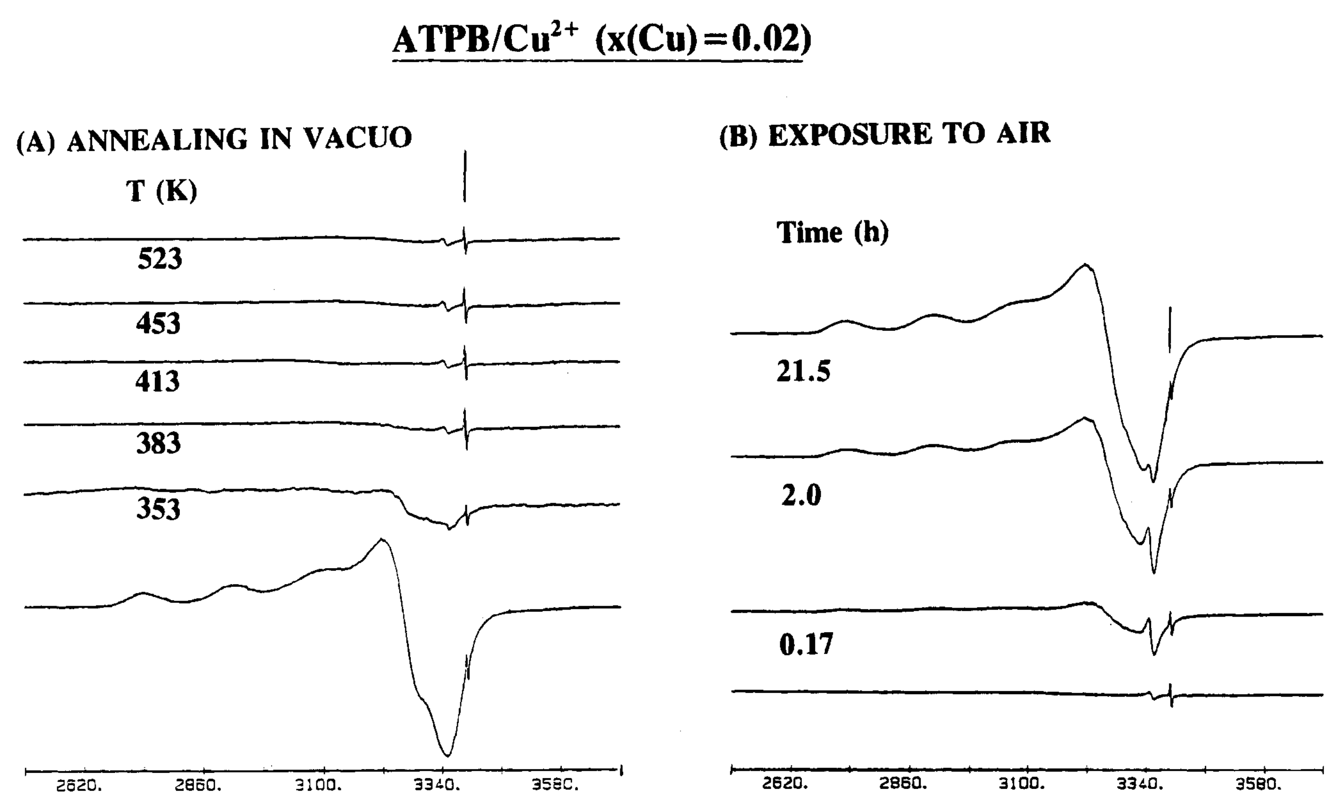
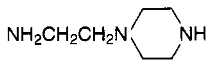


**Figure 1.** X-band ESR spectra at 110 K of ATPB/Cu$^{2+}$ complexes ($x$(Cu) = 0.02): (A) as a function of annealing temperature (1 h at each temperature) in vacuo; (B) as a function of time exposed to air at ambient temperature after annealing in vacuo to 523 K. The vertical bars point to the $g$ standard (Cr$^{3+}$, $g$ = 1.9796).

## Experimental Section

The α,ω-dicarboxylic polybutadiene (CTPB), trade name Hycar CTB 2000×162 ($M_n$ = 4200, functionality = 1.9, and specific gravity 0.907 at 25 °C), was supplied by B. F. Goodrich. The ratio of cis/trans/vinyl conformers, determined by NMR, is 20/65/15.[4] The diamine-terminated ionomer (ATPB) was prepared by reaction of CTPB with the amine 1-(2-aminoethyl)-piperazine (from Aldrich, structure I) according to published methods. The percentage of unreacted acid groups was determined by dissolving ATPB in a mixture of toluene and 2-propanol (60:40 by volume) and titration with a standard KOH solution. Only 3.8% of the initial acid groups remained unreacted with the amine, a value within the normal limits expected for the reaction.[11]



1-(2-aminoethyl)piperazine (I)

A solution of CuCl$_2$·2H$_2$O in methanol, containing also ZnCl$_2$ in the case of diamagnetic dilution, was added dropwise (≈5 mL/h) while stirring to 100 mL of a polymer solution in toluene (3–5% by weight) at ambient temperature under nitrogen. In order to maintain a constant volume ratio of the chloride solution to the polymer solution (≈7/100), the concentration of the chloride in methanol was varied, depending on the Cu$^{2+}$/amine and Zn$^{2+}$/amine molar ratios, $x$(Cu) and $x$(Zn), respectively. The total cation/amine molar ratio is $x$(total). To prepare the polymeric complexes, a solution of CuCl$_2$·2H$_2$O and ZnCl$_2$ (if required) in methanol was added dropwise (≈5 mL/h) while stirring to 100 mL of a polymer solution in toluene (3–5% by weight) at ambient temperature under nitrogen. For $x$(Cu) ≤ 1.0 no precipitation occurred and the solution was homogeneous during the complexation process. For $x$ > 1.0 a red-brown precipitate was formed. For complexation of the ionomer with a mixture of Cu$^{2+}$ and Zn$^{2+}$ ions, the precipitate appears to depend only on the amount of Cu$^{2+}$. In preparing samples containing $x$(Cu) = 0.02 and various amounts of Zn up to $x$(Zn) = 2.98, a fluid solution was obtained for $x$(Zn) = 0.48. The viscosity of the solution increased for higher Zn contents, and for $x$(Zn) = 2.98 a very hard gel was obtained. The polymer complexes were separated from the solvents by distillation in vacuo at ambient temperature (in the case of solutions), followed by drying in vacuo for 3 days, washing three times with methanol, and finally drying again as before to constant weight. The distillation step was omitted for the gels; the solvents (toluene and methanol) were removed by evaporation at ambient temperature, followed by drying as above.

ESR spectra at X-band were measured with Bruker 200D SRC and ESC106 spectrometers operating at 9.7 GHz (empty cavity at ambient temperature) and 100 kHz magnetic field modulation. Cr$^{3+}$ in a single crystal of MgO was used as a $g$ standard ($g$ = 1.9796).

Thermal transitions in the range 150–500 K were measured with a DuPont 9900 differential scanning calorimeter calibrated with mercury (mp 234.28 K) and indium (mp 429.71 K). Additional experimental details have been published.[9,10]

## Results

The results obtained in this study will be described as a function of cation content: $x$(Cu), $x$(Zn), and $x$(total). We note that for $x$(total) = 0.5 all the amine groups are theoretically complexed by the metal cations, assuming four nitrogen ligands from the piperazine group per cation.

**ESR Spectra.** In Figure 1A we present ESR spectra at 110 K for Cu$^{2+}$ in ATPB ($x$(Cu) = 0.02), on annealing in vacuo ($10^{-4}$ torr) for 1 h at the indicated temperatures. All ESR spectra in a given set are normalized to the same detector gain and can therefore be compared directly. Only a weak singlet at $g$ = 2.0030 ($H$ = 3340 G for the typical frequencies of the experiment) was detected after annealing at 523 K, and no further changes were observed in samples kept in vacuo at ambient temperature.

The ESR signal of paramagnetic Cu$^{2+}$ reappears gradually at ambient temperature only on exposure of

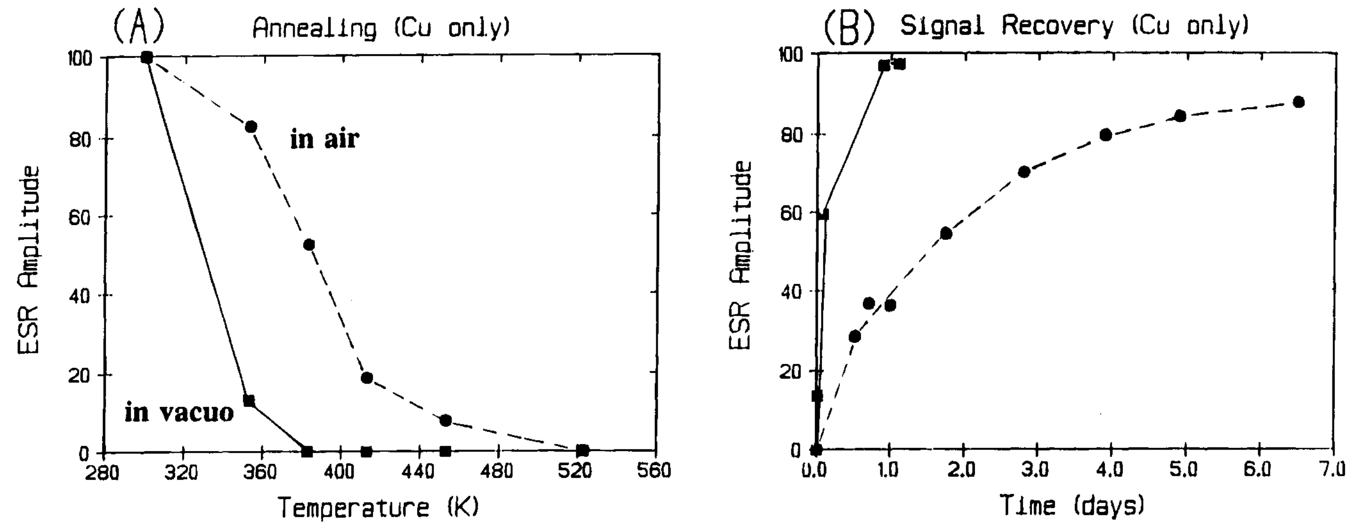


**Figure 2.** Effect of annealing conditions on the ESR signal from $Cu^{2+}$ in ATPB/$Cu^{2+}$ complexes ($x$(Cu) = 0.02): (A) the disappearance of the signal on annealing at the indicated temperatures for 1 h in air (●) and in vacuo (■); (B) the reappearance of the signal on exposure to air for the indicated time in days.

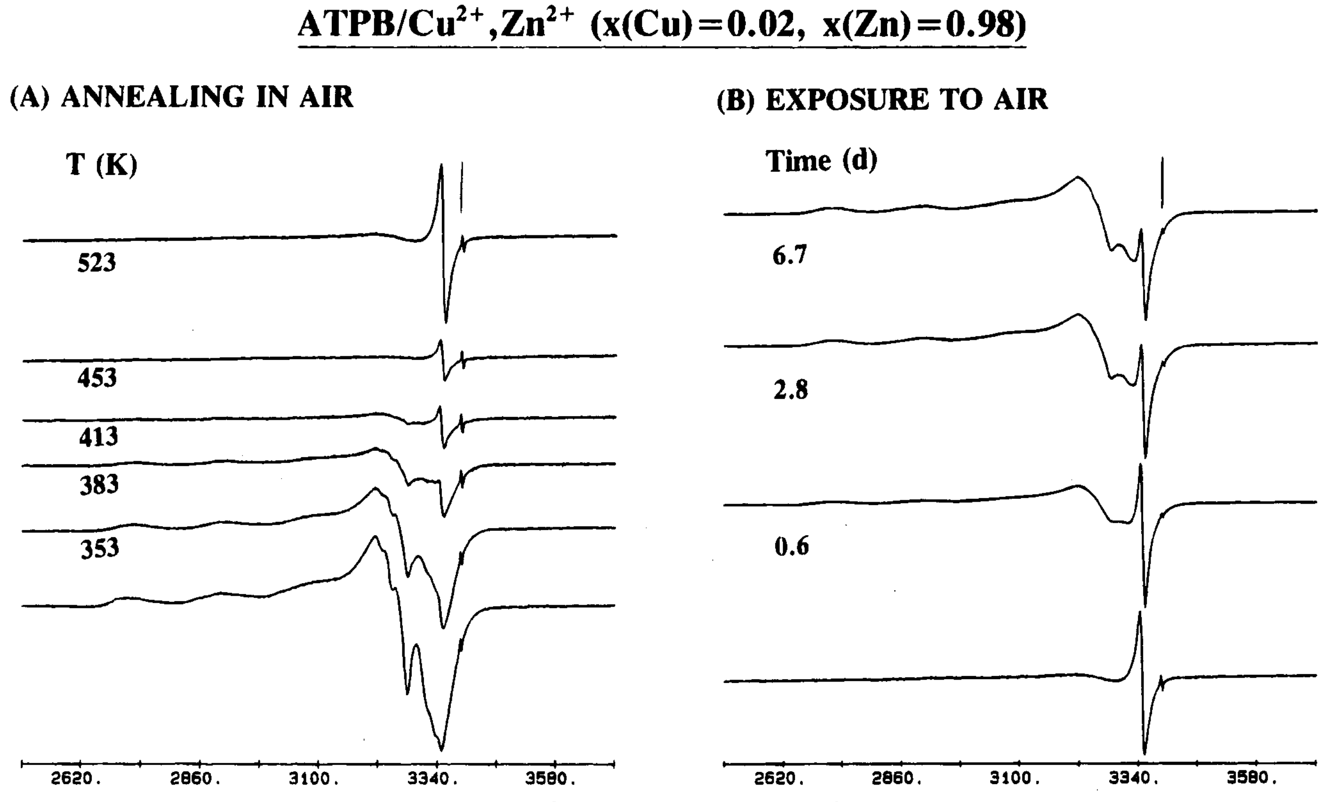


**Figure 3.** X-band ESR spectra at 125 K of ATPB/$Cu^{2+}$ complexes containing $Zn^{2+}$ ($x$(Cu) = 0.02, $x$(Zn) = 0.98): (A) as a function of annealing temperature (1 h at each temperature) in air; (B) as a function of time exposed to air at ambient temperature after annealing in air to 523 K. The vertical bars point to the $g$ standard ($Cr^{3+}$, $g$ = 1.9796).

the sample to air; the normalized ESR spectra for the indicated exposure time in hours are shown in Figure 1B. The decrease of the $Cu^{2+}$ signal intensity for annealing in air[10] and in vacuo as a function of annealing temperature and its increase with time of exposure to air are plotted in Figures 2A and 2B, respectively. We note that the ESR signal from $Cu^{2+}$ disappears at a lower temperature when heated in vacuo, compared to heating in air. For example, after annealing to 383 K in air the amplitude of the $Cu^{2+}$ signal has decreased by a factor of 2; in samples annealed in vacuo this signal disappears completely after annealing at 383 K. Moreover, the rate of reappearance of the $Cu^{2+}$ signal is considerably greater for samples that have been annealed in vacuo (Figure 3B): *hours* for samples annealed in vacuo and *days* for annealing in air. For samples annealed in vacuo, the full intensity of the ESR signal is recovered; the recovery for samples annealed in air is only ≈85%.

The effect of $Zn^{2+}$ on the annealing behavior of samples containing $Cu^{2+}$ is shown in Figures 3 and 4. In Figure 3 we present the changes in the ESR spectra of a sample containing $x$(Cu) = 0.02 and $x$(Zn) = 0.98 on annealing in air up to 523 K (Figure 3A) and on exposure to air at ambient temperature (Figure 3B). The main effect, compared with the spectra of samples without $Zn^{2+}$ (Figure 2, broken lines), is the disappearance of the $Cu^{2+}$ signal at a lower temperature in the

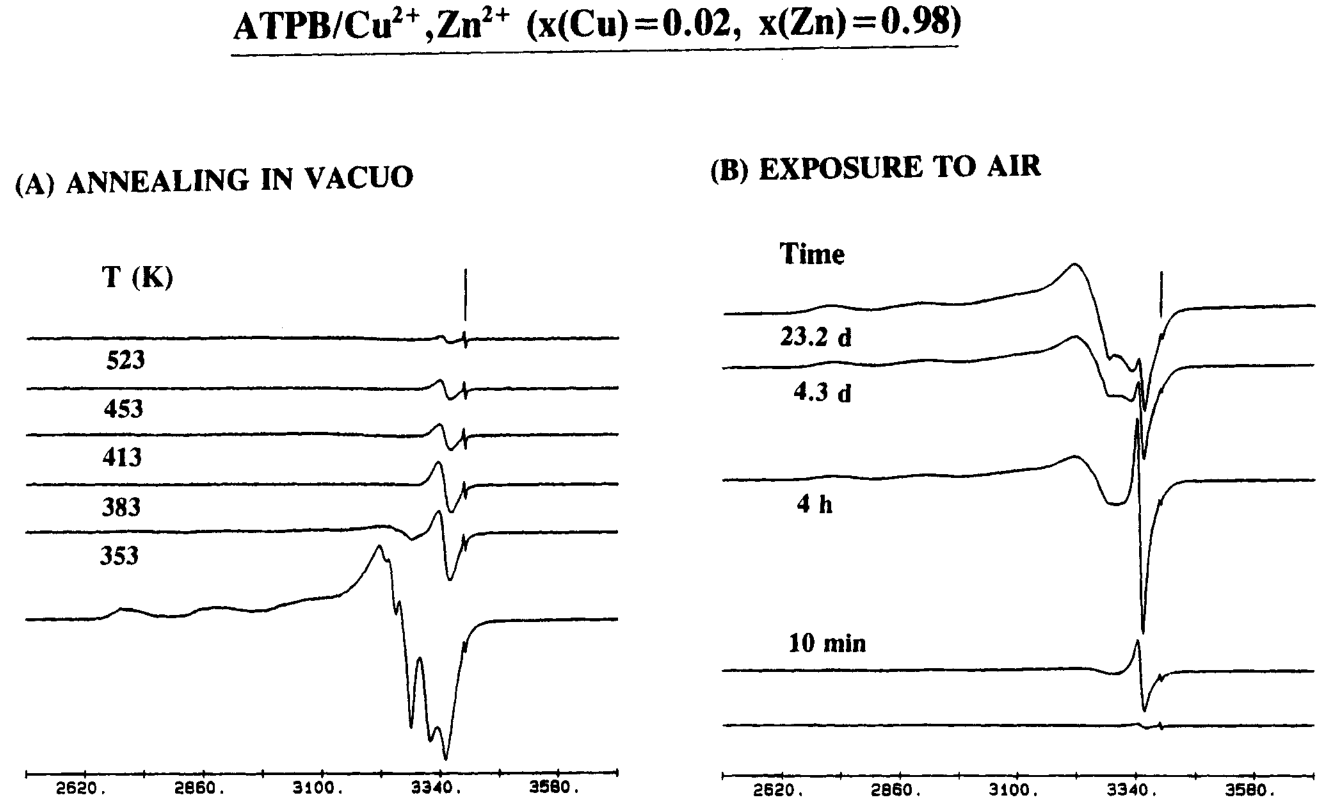


**Figure 4.** X-band ESR spectra at 125 K of ATPB/$Cu^{2+}$ complexes containing $Zn^{2+}$ ($x$(Cu) = 0.02, $x$(Zn) = 0.98): (A) as a function of annealing temperature (1 h at each temperature) in vacuo; (B) as a function of time exposed to air at ambient temperature after annealing in air to 523 K. The vertical bars point to the $g$ standard ($Cr^{3+}$, $g$ = 1.9796).

presence of $Zn^{2+}$; for example, ≈50% of the signal remains after annealing at 383 K in the absence of $Zn^{2+}$, compared to <20% for $x$(Zn) = 0.98. The rates of signal reappearance are similar.

The effect of annealing in vacuo on the evolution of ESR spectra for a sample containing $x$(Cu) = 0.02 and $x$(Zn) = 0.98 is shown in Figure 4A. We note that the disappearance of the $Cu^{2+}$ ESR signal in samples containing $Zn^{2+}$ occurs at a lower temperature, and the rate of reappearance is slightly slower, compared to samples containing $Cu^{2+}$ only (Figure 1). It is important to mention that the ESR spectra of $Cu^{2+}$ in the presence of $Zn^{2+}$ (for instance the lowest spectra in Figures 3A and 4A) are slightly different from those of $Cu^{2+}$ in the absence of $Zn^{2+}$ (compare with the lowest spectrum in Figure 1A), especially in the perpendicular region. This effect is due to the well-documented tetrahedral distortion induced by relatively large amounts of $Zn^{2+}$.[12]

The singlet at ≈3340 G detected after annealing to 523 K is considerably weaker for samples annealed in vacuo, compared to annealing in air, in the presence of $Cu^{2+}$ only or a mixture of $Cu^{2+}$ and $Zn^{2+}$ cations. This effect is clearly seen by comparing spectra in Figures 1A and 4A (very weak singlet) with the top spectrum in Figure 3A (strong singlet). The signal is considerably stronger during the signal recovery process after annealing in vacuo in samples containing $Cu^{2+}$ *and* $Zn^{2+}$ (Figure 4B), compared to samples containing $Cu^{2+}$ only (Figure 1B).

**DSC Measurements.** The DSC thermograms for ATPB/$Zn^{2+}$ in the glass transition region and in the 300–500 K range are shown in Figures 5A and 5B, respectively, as a function of $Zn^{2+}$ content. The glass transition region, which was scanned before (solid lines) and after (dashed lines) the high-temperature measurements, is not measurably affected by the cation content or by the high-temperature heating. The thermal behavior of ATPB/$Zn^{2+}$ and ATPB/$Cu^{2+}$ [10] ionomers in the $T_g$ range are identical, and the $T_g$ measured, 200 K, is that of polybutadiene. In the high-temperature region, however, the exothermic peak detected in the presence of $Cu^{2+}$ [10] and assigned to ionic clustering is not detected for ATPB/$Zn^{2+}$.

The DSC thermograms obtained for ATPB containing a small amount of $Cu^{2+}$ ($x$(Cu) = 0.02) and various amounts of $Zn^{2+}$ are given in Figures 6A and 6B. The total amount of cations, $x$(total), parallels that in Figure 5. It is evident that while the glass transition is not affected by the presence of *either* $Cu^{2+}$ [10] or $Zn^{2+}$ (Figure 5A), the transition is not detected in ATPB/$Zn^{2+}$ for large $Zn^{2+}$ contents (for instance $x$(Zn) = 2.98) when a small amount of $Cu^{2+}$ ($x$(Cu) = 0.02) is added. We note the appearance of an exothermic peak in the high-temperature range; this transition is particularly strong in samples with a large $Zn^{2+}$ content, $x$(Zn) = 1.98 and 2.98. The heat of transition $Q_{exo}$ increases with increasing $x$(Zn), as seen in Figure 7. $Q_{exo}$ is considerably lower in samples containing $Cu^{2+}$ only,[10] as also shown, for comparison, in Figure 7.

Over a period of several months ATPB samples containing $Cu^{2+}$ and $Zn^{2+}$ changed from an elastic to a hard and brittle material. The effect of ageing is presented in Figure 8 for ATPB/($Cu^{2+}$,$Zn^{2+}$) containing $x$(Cu) = 0.02 and $x$(Zn) = 0.98. The glass transition, clearly seen in freshly prepared samples (Figure 6A), becomes weaker after 120 days and is not detected after 300 days in air at ambient temperature, as seen in Figure 8A. The changes in the high-temperature thermograms are also significant: $Q_{exo}$ increases from 0 immediately after sample preparation to 57 J/g after 120 days and levels off at 150 J/g after about 300 days. For the same storing time, $Q_{exo}$ increases with the molar

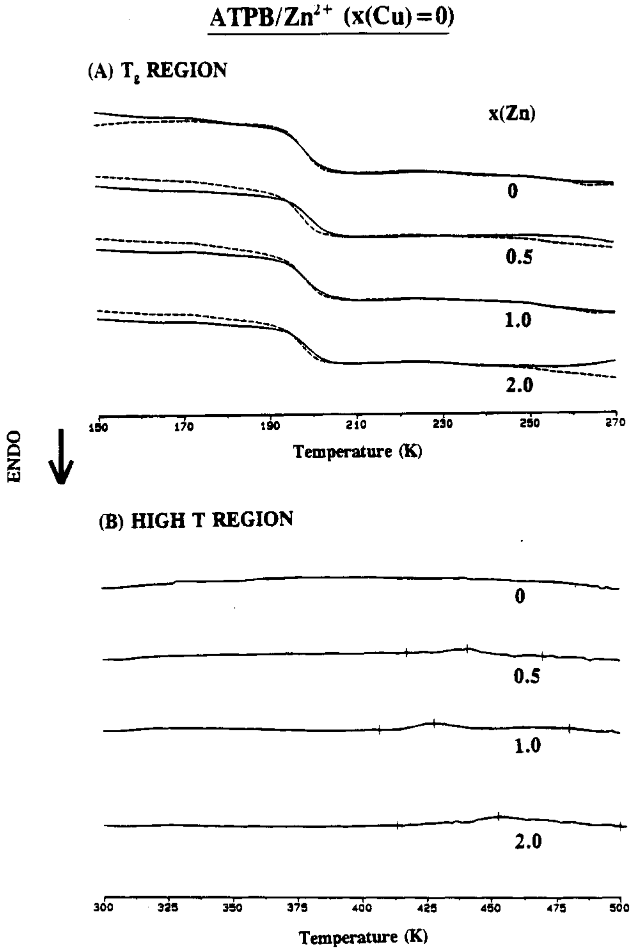


**Figure 5.** DSC thermograms for ATPB/$Zn^{2+}$ ($x$(Cu) = 0) as a function of $x$(Zn): (A) the glass transition region, recorded at a heating rate of 20 K/min (solid and dashed lines represent data collected before and after the high-temperature measurements, respectively); (B) high-temperature DSC thermograms obtained at a heating rate of 5 K/min.

ratio $Zn^{2+}$/amine. There seems to be a direct correlation between the disappearance of the glass transition and the appearance of the exothermic transition around 356 K, as shown in Figure 8B. Annealing accelerates the changes observed in the glass transition region. In samples that have been annealed for 1 h at 523 K and stored in air at ambient temperature, $T_g$ is not detected after 15 days. At the same time, the high-temperature DSC transition appears at 358 K, and $Q_{exo}$ increases as a function of time (5.8, 21, 24, 55, and 99 J/g after 1, 2.1, 3.1, 5.2, and 15.2 days). Similar results have been obtained when samples were annealed in vacuo ($\approx 10^{-4}$ torr) and exposed to air. In all cases the high-temperature transition is not observed in a second run taken immediately after the first run and is absent in the polymer that contains no cations.

We must emphasize that exposure to oxygen is necessary for the disappearance of the glass transition temperature (for a heating rate 20 K/min) on annealing and ageing, and for the corresponding appearance of the high-temperature peak.

## Discussion

In this section we will discuss the decay of ESR signals from $Cu^{2+}$ in ATPB as a function of the annealing conditions (in air or in vacuo) and the accelerating effect of $Zn^{2+}$ on the decay rate, the thermal transitions in ATPB containing *either* or *both* cations, and the origin of the narrow singlet ($g$ = 2.0030) and the possible role of the amino groups in the reactions thought to occur on annealing and ageing of the ATPB complexes.

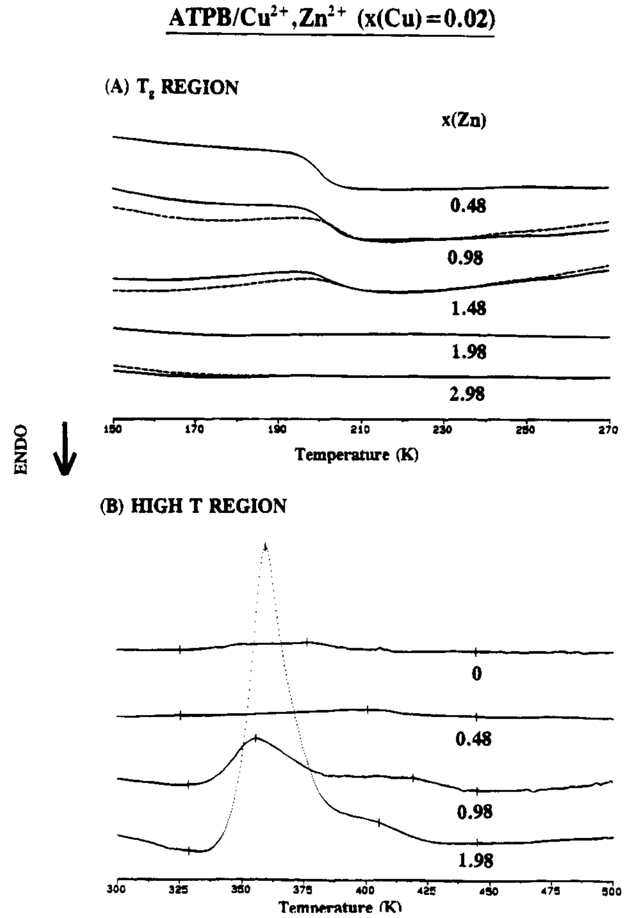


**Figure 6.** DSC thermograms for ATPB/$Cu^{2+}$ ($x$(Cu) = 0.02) as a function of $x$(Zn): (A) the glass transition region, recorded at a heating rate of 20 K/min (solid and dashed lines represent data collected before and after the high-temperature measurements, respectively); (B) high-temperature DSC thermograms obtained at a heating rate of 5 K/min.

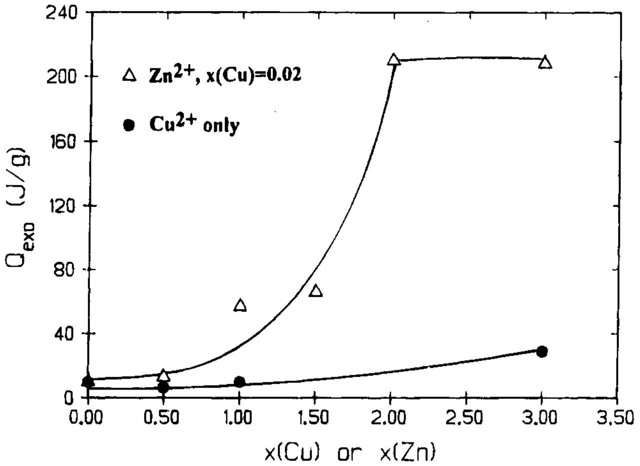


**Figure 7.** Heat of transition $Q_{exo}$ as a function of cation content for ATPB containing Cu only (●) and for ATPB containing $x$(Cu) = 0.02 and the indicated values of $x$(Zn) (△). Full lines are drawn as a guide to the eye.

**Evolution of the ESR Signal from $Cu^{2+}$.** The results presented in Figures 1–4 suggest three main conclusions: (a) The ESR signal from the cupric ion disappears at a lower temperature when annealing is done in vacuo, compared to annealing in air. (b) The

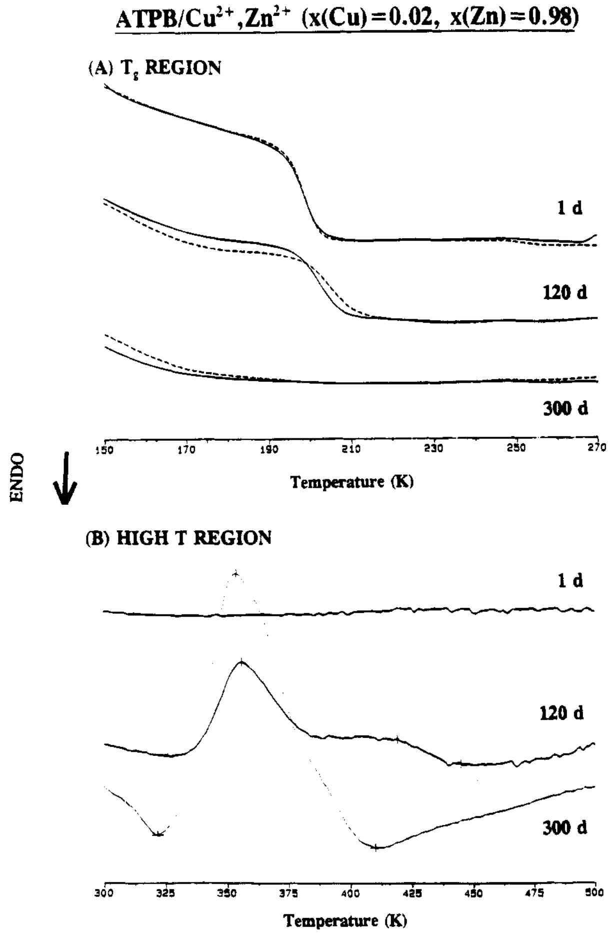
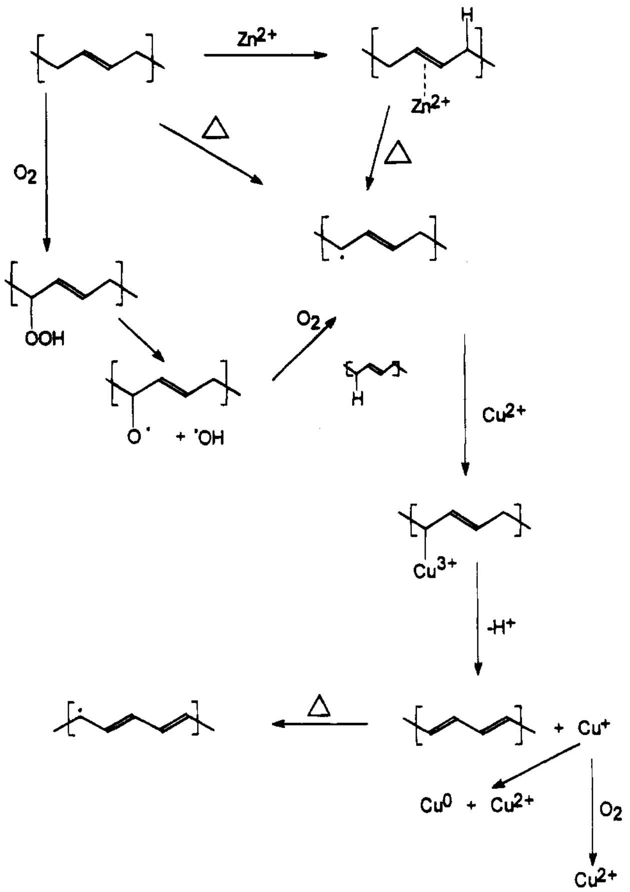


**Figure 8.** DSC thermograms for ATPB containing $x(\mathrm{Cu}) = 0.02$ and $x(\mathrm{Zn}) = 0.98$ as a function of ageing time (days): (A) the glass transition region, recorded at a heating rate of 20 K/min (solid and dashed lines represent data collected before and after the high-temperature measurements, respectively); (B) high-temperature DSC thermograms obtained at a heating rate of 5 K/min.

signal reappears at ambient temperature only when ATPB is exposed to air (oxygen); the *rate* of reappearance is significantly enhanced in ATPB that has been annealed in vacuo, compared to annealing in air (hours versus days). (c) $Zn^{2+}$ accelerates the rate of disappearance of the signal from $Cu^{2+}$ for annealing in air or in vacuo.

The disappearance of the ESR signal from $Cu^{2+}$ during annealing (in air, in vacuo, and in the presence or absence of $Zn^{2+}$) can be explained if we assume the plausible reaction steps presented in Scheme 1. The key step is the generation of an allyl radical, a relatively facile process for the polybutadiene chain under the annealing conditions. A similar mechanism has been proposed for thermooxidative degradation of either poly(vinyl chloride) or poly(vinyl fluoride) and for the generation of the polyene structure in the polymer chain.[13,14] Several avenues for the allyl radical formation are indicated in Scheme 1. In the absence of oxygen, the radical can be formed by reaction with a radical $R^\bullet$; as suggested previously,[14] the source of the radical $R^\bullet$ is difficult to pinpoint and might change with the history of the sample and annealing conditions. Higher than ambient temperatures are expected to promote the anaerobic formation of the allyl radical, due to the dissociation of the allylic C−H bond,[15] as suggested in the case of polyethylene.[16] In the presence of oxygen, formation of a hydroperoxide followed by its decomposition and reaction with an allylic proton also leads to the formation of the allyl radical. In the presence of $ZnCl_2$, the complexation of $Zn^{2+}$ with the π-bonds in the polybutadiene chain can provide a suitable pathway for the additional generation of an allyl radical and for promoting olefin polymerization, especially above ambient temperatures.[17]

**Scheme 1**



In contrast to $ZnCl_2$, $CuCl_2$ is known to be a strong inhibitor of olefin polymerization, because $Cu^{2+}$ combines with the radicals formed during polymerization.[18] Therefore the allyl radical is expected to react with $Cu^{2+}$ and to generate the transient Cu(III) complex, which subsequently loses a proton with the formation of Cu(I) and an additional double bond, conjugated with the double bond in the polybutadiene chain. This reaction is well documented in the literature, especially in the case of $Cu^{2+}$ complexes with nitrogen ligands[19,20] and accounts for the disappearance of the ESR signal from paramagnetic $Cu^{2+}$. The reduced copper species Cu(I) can be slowly reoxidized by oxygen, thus providing a mechanism for the experimentally detected reappearance of the ESR from $Cu^{2+}$ only in the presence of oxygen. This mechanism also provides an explanation for the faster disappearance of the $Cu^{2+}$ ESR signal in the absence of oxygen, because the reduced ESR-silent copper species Cu(I) is not reoxidized. The mechanism described in Scheme 1 can therefore explain the disappearance of the ESR signal from $Cu^{2+}$ on annealing (due to its reaction with the allyl radical) and the faster disappearance for annealing in vacuo (because the reduced copper species is not reoxidized) or in the presence of $Zn^{2+}$ (because more allyl radicals are formed).

At this time we do not have a firm explanation for the greatly enhanced rate of the reappearance of the

$Cu^{2+}$ signal after annealing in vacuo, compared to annealing in air. It is possible that the physical properties (for instance porosity) change in vacuo at high temperature, leading to more rapid diffusion of oxygen in these samples.

**Thermal Transitions in ATPB/($Cu^{2+}$,$Zn^{2+}$).** The most surprising result obtained in this study is the pronounced effect of $Zn^{2+}$ on the glass transition in ATPB/$Cu^{2+}$ ($x$(Cu) = 0.02) (Figure 6A). In parallel, the exothermic peak appears at ≈360 K, and $Q_{exo}$ for a constant $x$(Cu) increases with $Zn^{2+}$ content; for a given $x$(Zn), $Q_{exo}$ increases with ageing. The high-temperature transition detected in ATPB/$Cu^{2+}$ for large $Cu^{2+}$ contents was assigned to the formation of ionic domains;[10] a similar assignment is proposed in the corresponding systems containing $Cu^{2+}$ ($x$(Cu) = 0.02) and $Zn^{2+}$, especially at high $x$(Zn) values.

In order to understand the changes in the glass transition region, we studied in detail the swelling behavior of two samples with the same Cu content ($x$(Cu) = 0.02) but different Zn contents ($x$(Zn) = 0.98 and 2.98, respectively). For $x$(Zn) = 0.98, the dried polymer dissolved completely in toluene. For $x$(Zn) = 2.98, however, a soft gel was obtained in toluene. The solvent content at equilibrium swelling was 92 wt %, and the percentage of polymer soluble in toluene ("sol" %) was 11 wt %. These results indicate the formation of a cross-linked system at high Zn content; the high solvent content suggests a lightly cross-linked system.

In order to verify the nature of the cross-links, we "titrated" the toluene-swollen gel by dropwise addition of methanol, with the intention to observe the gel behavior after removing the cations by dissolution in methanol. We observed that the gel literally "melted" when a small amount of methanol was added and reappeared when more toluene was added; the transition gel ⟺ sol was completely reversible, indicating that the cross-linking is due to the presence of the ions and not due to reaction between allyl radicals in different chains. The presence of $Zn^{2+}$ in the methanol solution was determined indirectly by the precipitate formed with $AgNO_3$. Because gelation did not occur in ATPB/$Cu^{2+}$ even for high $Cu^{2+}$ contents,[10] we conclude that the chains are cross-linked by $Zn^{2+}$ and not by $Cu^{2+}$.

It is well known that cross-linking has important effects not only on the value of $T_g$ but also on the time scale of dynamical effects. For this reason we measured $T_g$ as a function of the heating rate for ATPB/($Cu^{2+}$,$Zn^{2+}$) ($x$(Cu) = 0.02, $x$(Zn) = 2.98) before and after removal of the cations by methanol as described above; the results are presented in Figures 9A and 9B. We note that for the original sample (Figure 9A) the $T_g$ is not detected at a heating rate of 20 K/min but reappears for slower heating rates (10, 5, and 2 K/min). After removal of the cations, the $T_g$ is observed even at the highest heating rate, as in the un-cross-linked polymer. These results suggest that the "disappearance" of the $T_g$ in the cross-linked samples for a relatively high heating rate is due to the time scale of molecular reorientations and thus provide additional proof for the cross-linking by $Zn^{2+}$. The variation of the $T_g$ with heating rate is ≈5 K, a normal range for this heating range.[21]

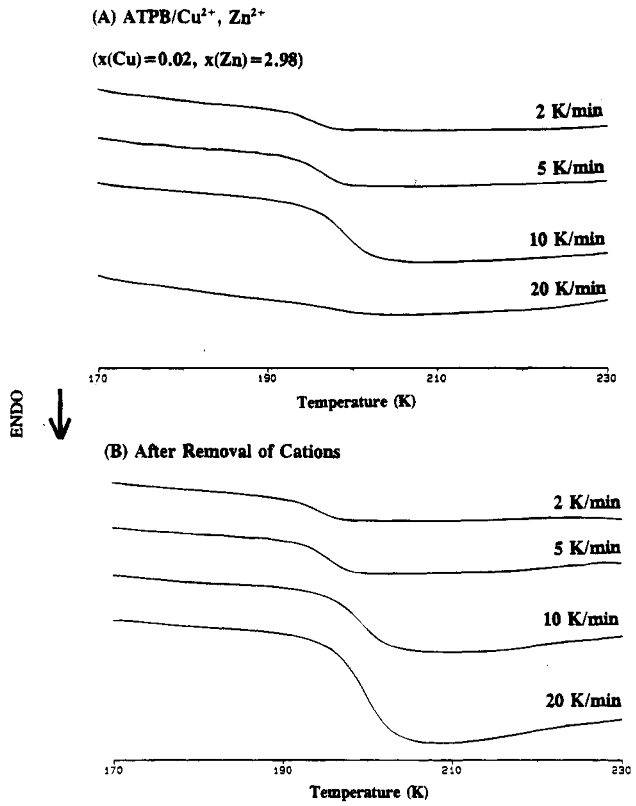
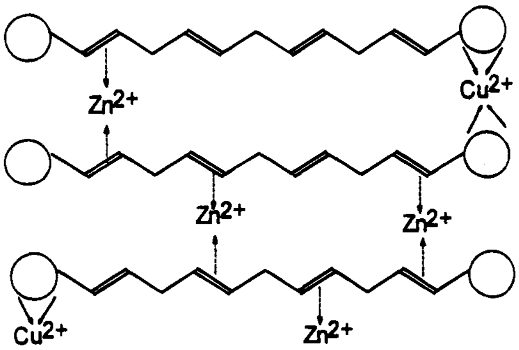


**Figure 9.** DSC thermograms for ATPB containing $x$(Cu) = 0.02 and $x$(Zn) = 2.98 for the indicated heating rate: (A) original sample; (B) after removal of the cations by addition of methanol.

**Scheme 2**



Normally, cross-linking is accompanied by an increase in $T_g$.[21,22] If this increase $\Delta T_g = T_{g,c} - T_g$ (where $T_{g,c}$ is the glass transition for the cross-linked polymer) is estimated using the parameters for natural rubber,[21] we obtain $\Delta T_g \approx 25$ K for $x$(Zn) = 2.98. Comparison of Figures 9A and 9B indicates, however, that the glass transition measured at a given heating rate is the same for the linear and cross-linked material, within ±0.5 K. The constant glass transition measured suggests that not all $Zn^{2+}$ cations are involved in cross-linking; this suggestion is logical in view of the evidence for the participation of part of the $Zn^{2+}$ cations in the ionic domains. In support of the estimation of a low degree of cross-linking is the large amount of solvent in equilibrium with the network, 92 wt %. It is also possible that the expression used to estimate $\Delta T_g$, which was proposed for permanently cross-linked polybutadiene, is not valid in the case of reversible cross-linking.

The cross-linking of polymer chains with $Zn^{2+}$, together with complexation of the piperazine group by $Cu^{2+}$, is shown in Scheme 2. The complexation of $Zn^{2+}$ acting as a Lewis acid with the double bonds of the polymer chain[17,23] is enhanced by the formation of the conjugated double bonds shown in Scheme 1. The rigidity of the chain is enhanced by the complexation of the end groups via $Cu^{2+}$. The combination of chain connectivity (by $Zn^{2+}$) and complexation of the end groups (by $Cu^{2+}$) leads to slower dynamics and to the loss of $T_g$ at high heating rates for large $Zn^{2+}$ content. The cross-linking of the polymer chains is possibly facilitated by the presence of "pendant" vinyl groups, which amount to 15% of the total number of monomeric groups.[4]

The network formed might assist in the formation of ionic clusters and therefore in the exothermic transition by the cooperative effect of the two types of cations. The significantly higher $Q_{exo}$ in ATPB containing both cations compared to ATPB/$Cu^{2+}$ indicates the importance of cross-linking for the process of ionic clustering.

The cross-linking mechanism evident in aged samples (Figure 8) is not completely understood at present. Based on the possibilities shown in Schemes 1 and 2, it is possible to consider a combination of contributions from reversible (from $Zn^{2+}$) and permanent (through allyl radicals) cross-links.

In a recent and elegant experiment, Vanhoorne et al. reported on direct evidence for the restriction of the segmental motion in carboxylato-telechelic polystyrene in the vicinity of the ionic groups from high-resolution solid-state $^{13}C$ NMR;[24] such behavior is in agreement with the recent model for ionomer morphology.[25] The terminal polystyrene segment affected by the ionic groups consists of 5–6 styrene units and represents only ≈5% of the total number of chain units. For this reason the $T_g$ remains the same and is independent of the ion presence. To the best of our knowledge, the results presented here give the first evidence for the loss of $T_g$ in DSC studies at relatively fast heating rates in telechelic ionomers, due to the presence of ions that immobilize the end *and* and inner segments.

**Narrow ESR Singlet.** In a previous paper we have tentatively assigned the ESR singlet at $H = 3340$ G to small metallic copper particles with a diameter <100 Å.[10] The mechanism for the formation of metallic copper is disproportionation of Cu(I) to $Cu^{2+}$ and Cu(0) and is part of the mechanism shown in Scheme 1. We would like to comment on possible additional contributions to this signal.

The ESR singlet is significantly more intense after annealing in air at 523 K (Figure 3A), compared to annealing in vacuo (Figures 1A and 4A), in the presence or absence of $Zn^{2+}$. The line width is larger in the presence of $Zn^{2+}$ (Figure 4A), possibly due to a superposition of two types of signals. We suggest that an additional contribution to the narrow singlet comes from an organic radical. A possible candidate is the allyl radical generated on annealing, as shown in Scheme 1, which suggests that the allyl radical can be formed by the intercalation of oxygen to form a hydroperoxide, followed by abstraction of an allylic proton. The polyene radical shown in Scheme 1 is also a possibility.

An additional source of organic radicals is a nitrogen-containing radical formed via abstraction of a proton from the piperazine unit by the allyl radical.[26,27] A study of telechelic polybutadiene and polyisoprene with different end groups is in progress in our laboratory in order verify this alternative pathway and will be reported in a future publication.

## Conclusions

We have presented ESR and DSC measurements on the effect of oxygen, annealing temperature (up to 523 K), and variation of $Zn^{2+}$ content on the thermal transitions and $Cu^{2+}$ complexation in amine-terminated telechelic polybutadiene (ATPB). This study has indicated that $Zn^{2+}$ is not only a diamagnetic diluent but can also significantly affect the ionic distribution, the degree of ionic clustering, and the behavior of the system in the presence of solvents.

The ESR results (Figures 1–4) suggest that the ESR signal from the cupric ion disappears at a lower temperature when annealing is done in vacuo, compared to annealing in air; the signal reappears at ambient temperature only when ATPB is exposed to air (oxygen); the *rate* of reappearance is significantly enhanced in ATPB that has been annealed in vacuo, compared to annealing in air (hours versus days); and $Zn^{2+}$ accelerates the rate of disappearance of the signal from $Cu^{2+}$, for annealing in air or in vacuo. These results have been explained by a mechanism based on the formation of an allyl radical on annealing, reaction of this radical with $Cu^{2+}$, reduction of $Cu^{2+}$ to $Cu^{+}$, and reoxidation back to $Cu^{2+}$ (Scheme 1).

The DSC results (Figures 5–9) suggest that $T_g$ is detected at lower heating rates in ATPB/$Cu^{2+}$ for high Zn contents. A high-temperature exothermic transition at 360 K accompanies the changes in the glass transition region, and the intensity of this transition (i.e., the value of $Q_{exo}$, in J/g) is enhanced in ATPB containing both cations, compared to ATPB containing $Cu^{2+}$ only. This transition is absent in ATPB/$Zn^{2+}$. We have suggested that these results can be explained, based on the cross-linking of polymer chains with $Zn^{2+}$ that acts as a Lewis acid, together with complexation of the piperazine group by $Cu^{2+}$, as shown in Scheme 2. The cooperative effect of the two types of cations leads to cross-linking, to lower relaxation rates for the segmental motion, and to the formation of ionic clusters connected to the polymer chains.

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