Direct Detection of Ionic Clustering in Telechelic Ionomers by DSC and ESR

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ABSTRACT: Complexes of amine-terminated telechelic polybutadiene with Cu^{2+} have been studied by electron spin resonance (ESR) and differential scanning calorimetry (DSC). In addition to the glass transition temperature at 200 K, an *exothermic* peak was detected by DSC in the temperature range 350-450 K. This peak, which is absent in the telechelic polymer without metal cations, becomes more intense and shifts to higher temperatures as the amount of cation in the sample increases, is not detected in a second run taken immediately after the first measurement, and reappears in samples left at ambient temperature for several days. The glass transition region is not affected by heating the samples to 450 K. We suggest that the exothermic peak is due to the organization of the cation into ionic clusters, even when the Cu^{2+}/amine molar ratio is only 0.02. The reappearance of the high-temperature DSC peak in samples left at ambient temperature after measuring the exothermic transition suggests that the cluster formation is reversible. ESR spectra of Cu^{2+}-polymer complexes provide additional support for this interpretation: ESR signals from complexed Cu^{2+} cations decrease in intensity on annealing above ambient temperature, disappear almost completely on heating at 523 K for 1 h, and gradually reappear in samples left at ambient temperature. These results are interpreted in terms of the formation of ESR-silent diamagnetic or paramagnetic species with very broad ESR lines upon cluster formation and support the suggestion that the clusters form on heating and disappear at ambient temperature. A narrow (6 G) ESR singlet detected in the annealed samples is tentatively assigned to *small* metallic copper particles with a diameter <100 Å.

Introduction

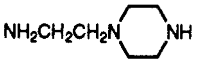
Telechelic ionomers, which contain ionic groups only at the chain ends, have been recently studied, in an attempt to verify and model the process of ionic clustering.[1] Extensive studies have been reported on dicarboxylic telechelic polybutadiene (CTPB) and polyisoprene (CTPI), on sulfonated telechelic polystyrene, and also on cationic telechelic ionomers, using in most cases scattering and relaxation methods.[2-7]

In a previous publication we have presented results obtained in an ESR study of the paramagnetic Cu^{2+} as counterion, complexed by amine-capped ionomers based on α,ω-dicarboxylated polybutadiene (ATPB).[8] The broadening of the ESR signals as a function of cation content was assigned to dipolar interactions between neighboring cations. The distance between the cations was estimated from simulation of the spectra and deconvolution of the line widths into contributions from the natural width of isolated cations and, in addition, from dipolar interactions between neighbors. These simulations have suggested that for the ratio Cu^{2+}/amine = 0.5 the intercation distance is less than that calculated from a homogeneous distribution, indicating some degree of ionic aggregation. This distance is, however, significantly larger than the Cu-Cu distance in $CuCl_2$ (7-8 vs 3.8 Å).

In this report we present evidence for the formation of ionic clusters with Cu-Cu distances smaller than 7 Å when the ATPB-Cu^{2+} complexes are annealed above ambient temperature. The evidence is obtained from DSC experiments and ESR spectra of Cu^{2+} in samples annealed between 300 and 523 K. The results obtained in the present study explain the drastic change in the viscoelastic properties of ATPB upon complexation of Cu^{2+} and Fe^{3+} cations reported by Charlier et al.[4]

Experimental Section

The α,ω-dicarboxylic polybutadiene (CTPB), trade name Hycar CTB *2000 × 162* (M_n = 4200, functionality = 1.9, and specific gravity at 25 °C = 0.907), was supplied by B.F. Goodrich. The diamine-terminated ionomer (ATPB) was prepared by reaction with the amine 1-(2-aminoethyl)piperazine from Aldrich (structure I) according to published methods.[9] The percentage



1-(2-aminoethyl)piperazine (I)

of unreacted acid groups was determined by dissolving ATPB in a mixture of toluene and 2-propanol (60:40 by volume) and titrating with a standard KOH solution. We deduced that only 3.8% of the initial acid groups remained unreacted with the amine; this value is within normal limits for the reaction.

To prepare the polymeric complexes, a solution of $CuCl_2 \cdot 2H_2O$ 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. The cation/amine molar ratio is x(Cu). For $x(Cu) \leq 1.0$ no precipitation occurred and the solution was homogeneous during the complexation process. For $x > 1.0$ a red-brown precipitate was formed. The color of the complex solution changed gradually from green to green-yellow to brown to red-brown as x(Cu) increased from 0.02 to 3.0. The Cu^{2+}-polymer complexes were separated from the solvents by distillation in vacuo at ambient temperature, drying in vacuo for 3 days, washing three times with methanol, and finally drying again as before to constant weight.

ESR spectra at X-band were measured with a Bruker 200D SRC spectrometer operating at 9.7 GHz (empty cavity at ambient temperature) and 100-kHz magnetic field modulation, interfaced with a data acquisition system based on an IBM PC/XT and the software EPRDAS (Mega Systems Solutions, Rochester, NY). Cr^{3+} in a single crystal of MgO was used as a g-value marker (g = 1.9796). Additional experimental details have been published.[8]

Thermal transitions in the range 150-500 K were measured with a DuPont 9900 differential scanning calorimeter calibrated with mercury (mp 234.28 K) amd indium (mp 429.71 K).

Results

DSC Measurements. In Figure 1 we present DSC thermograms obtained at a heating rate of 5 K/min for amine-capped telechelic polybutadiene in the range 300-450 K as a function of Cu^{2+} content expressed as x(Cu).

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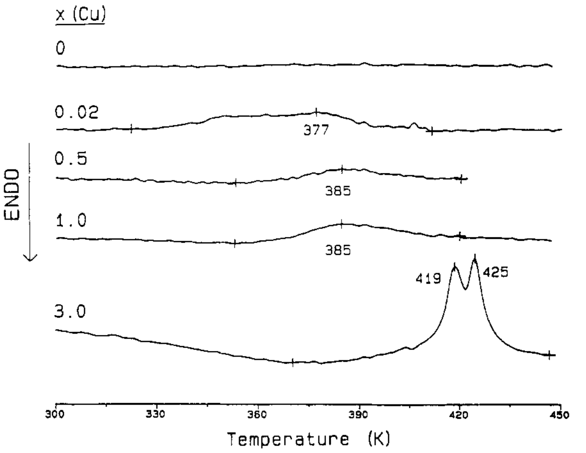

Figure 1. High-temperature DSC thermograms of Cu^{2+} complexes of ATPB as a function of cation content $x(Cu)$, obtained at a heating rate of 5 K/min.

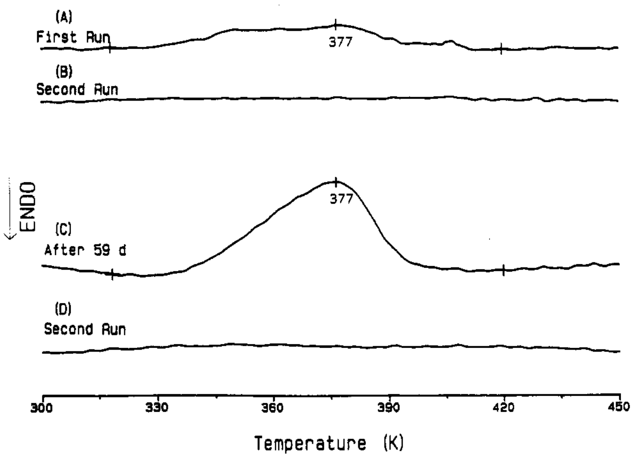

Figure 2. High-temperature DSC thermograms of Cu^{2+} complexes of ATPB with $x(Cu) = 0.02$ as a function of time, obtained at a heating rate of 5 K/min: (A) first run; (B) second run; (C) after 59 days at ambient temperature; (D) second run after (C).

The exothermic peak is absent for $x(Cu) = 0$ but becomes more pronounced and shifts to higher temperatures as the Cu^{2+} content increases. The heat of transition Q_{exo} increases with increasing $x(Cu)$ and is 6.4, 10.0, and 28.8 J/g for $x(Cu) = 0.5$, 1.0, and 3.0, respectively. The glass transition region measured after the high-temperature measurements is virtually unchanged, indicating that the polymer chains retain their mobility during the process responsible for the high-temperature DSC transition.

In Figure 2 we present the evolution of the high-temperature DSC peak with time for a sample with $x(Cu) = 0.02$. The peak is absent in a second run (indicating that the process is complete at the end of one cycle), reappears after 59 days at ambient temperature (Figure 2C), and is not detected in a run taken immediately after the third run (Figure 2D). Subsequent experiments indicated that the signal reappears even after several days. We note that the exothermic peak in Figure 2C is narrower than the original peak, suggesting more order. A similar behavior has been detected for samples containing a larger amount of Cu^{2+}.

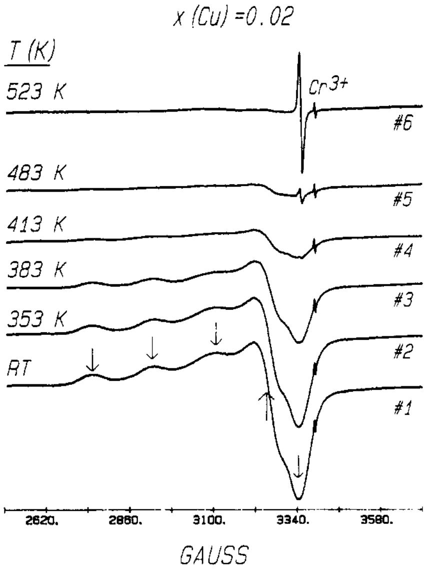

Figure 3. X-band ESR spectra at 125 K of ATPB complexes with Cu^{2+} for $x(Cu) = 0.02$ as a function of annealing temperature (1 h at each temperature). The parallel quartet and the perpendicular signal are indicated by downward and upward arrows, respectively, in spectrum 1.

ESR Spectra. X-band ESR spectra at 125 K of ATPB complexes heated for 1 h at the indicated temperatures are shown in Figure 3. The parallel quartet and the perpendicular component are indicated by downward and upward arrows, respectively. As discussed in ref 8, the **g** tensor and the hyperfine splittings of the Cu^{2+} signal measured for the sample prior to annealing (RT, or room temperature storing in Figure 3) indicate ligation of Cu^{2+} to ^{14}N ligands. To compare the ESR intensities for each heat treatment, the sample was introduced always in the same position in the ESR resonator. The spectra in Figure 3 are normalized to the same gain and can therefore be directly compared. Two important comments can be made on the evolution of spectra 1–6 as a function of annealing temperature. First, the signal for the isolated cupric cations decreases in intensity as the annealing temperature increases above ambient temperature and disappears almost completely after heating at 523 K. Second, a narrow singlet at $g = 2.0031$ appears during annealing and dominates the spectrum obtained after heating at 523 K.

Changes in the ESR spectra were monitored after annealing; 13 spectra were measured at 125 K in 7 days. Some of these spectra, measured after storage at ambient temperature for the indicated time in days, are presented in Figure 4. The spectra were taken at the same gain. We notice the gradual *reappearance* of the signal from the isolated cupric ions and the stability of the narrow singlet.

The peak-to-peak amplitude of the perpendicular component of the cupric signal, normalized to the same gain, is given in Figure 5. Because the line shape of the ESR spectra remains the same during the heat treatment, the amplitudes are proportional to the signal intensity. Within an error margin of ±10%, the plot suggests the disappearance of the ESR signal from the cupric complexes after heat treatment and the recovery of most of the signal (90%) in samples left at ambient temperature for about 7 days. Only minor intensity variations are detected after more than 7 days. The intensity of the narrow signal appears to remain stable after annealing at 523 K (spectrum 6 in Figures 3 and 4) and represents about 10% of the initial intensity of the Cu^{2+} signal.

Discussion

In this section we will discuss the evolution of the ESR signal from the Cu^{2+}–polymer complexes together with the DSC results and will offer some suggestions on the nature of the narrow ESR signal obtained on annealing.

Cu^{2+} Signal. The DSC and ESR results presented in Figures 1–5 can be rationalized by assuming that the cations phase-separate and organize into clusters in the temperature range 300–500 K. In support of this con-

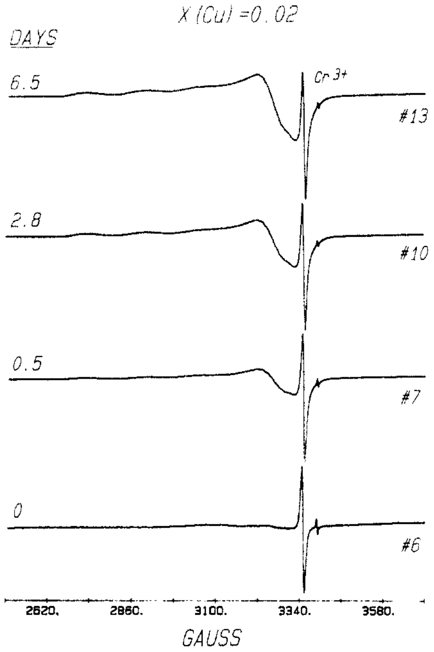

Figure 4. X-band ESR spectra at 125 K of ATPB complexes with Cu^{2+} for $x(Cu) = 0.02$ as a function of days stored at ambient temperature after annealing to 523 K.

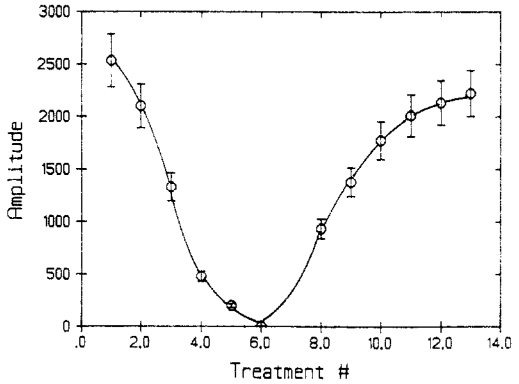

Figure 5. Variation of the amplitude of the Cu^{2+} perpendicular signal from the cupric complexes for the samples shown in Figures 3 and 4, normalized to a common gain. The error bars correspond to an estimated uncertainty of ±10%. The abscissa is the running number of the sample.

clusion is the absence of the exothermic peak in the polymer that has no cations and the observation of an unchanged glass transition after the sample undergoes the high-temperature cycle. The reappearance of the peak after annealing of the sample at room temperature (Figure 2) implies that the cluster formation is reversible.

The conclusions derived from DSC experiments are strongly supported by the ESR results presented in Figures 3–5. Formation of the cluster above 350 K is reflected in the disappearance of the ESR signal from isolated Cu^{2+} complexes upon annealing (Figure 3). The signal reappears after storing the samples at ambient temperature (Figure 4), indicating the breakup of the cluster. We suggest that cation clustering leads to the formation of diamagnetic and therefore ESR-silent species *or* to a very broad signal that is not detected at the low field modulation amplitudes used in the ESR measurements; the clusters break up at ambient temperature and re-form the ^{14}N-ligated cations. The changes of the ESR signal from Cu^{2+} complexes as a function of annealing time and temperature reinforce and complement the information obtained from the DSC data.

We are aware of one reported case for the appearance of ionic clusters as the temperature is increased, in a study of lightly sulfonated polystyrene (SPS) partially neutralized by Mn^{2+} by small-angle X-ray scattering (SAXS):[10] The ionic peak, which is considered diagnostic of the presence of ionic clusters, is absent at ambient temperature and appears when heating the sample above ≈448 K. It has been reported, however, that the process of cluster formation is not reversible, in contrast to the results presented in this study. In addition, recent NMR evidence suggests that the ionic clusters in α,ω-dicarboxylatopolybutadiene in the acid form and neutralized by Zr^{4+} exist at ambient temperature and partially break up at and above 360 K.[11] It appears that the process of ionic clustering is extremely sensitive to the details of the bonding of the ionic groups to the polymer chain. It is quite possible that the stronger complexing ability of the amine-terminated polymer is responsible for the detection of clustering only at elevated temperatures in ATPB, compared with the situation in the carboxylic-terminated telechelic polybutadiene (CTPB).

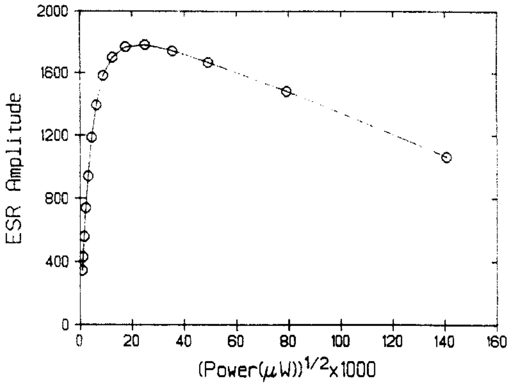

Figure 6. Microwave power saturation curve at 300 K for the narrow singlet (peak amplitude vs square root of the microwave power in μW).

Narrow Singlet. At this time we can only speculate on the source of the narrow ESR singlet detected on heating the samples. One possibility is the formation of an organic radical on high-temperature annealing; this assignment is supported by the *g* value, which is typical for such a radical. Another possibility is the formation of small metallic copper particles due to reduction of Cu^{2+}.[12–17] The stability of the signal as a function of temperature, which is hard to explain if the signal is due to an organic radical, is in support of this suggestion. The Cu^{2+} reduction might be initiated by the formation of a small amount of an organic radical at elevated temperatures; this radical can then react with Cu^{2+} to produce Cu^{+}, followed by disproportionation to Cu^{2+} and Cu^{0}.[18] The properties of the narrow signal in our system were studied by microwave power saturation at 300 K (Figure 6) and by following the intensity of the unsaturated signal with temperature; because the line width on the unsaturated signal is constant with temperature, the intensity is proportional to the signal amplitude, which is plotted in Figure 7 as a function of the inverse temperature. The saturation behavior is different from that of the signal from the cupric complex, suggesting a different type of signal.

The results for the narrow singlet shown in Figures 6 and 7 can be compared with the behavior expected for metal particles.

The ESR signal from metals, known as conduction ESR (CESR), is expected to be broad and difficult to saturate. This is the reason for conducting most CESR studies at low temperatures, typically 4 K and below. The paramagnetism of bulk metals is expected to be of the Pauli type and independent of temperature. Both the temper-

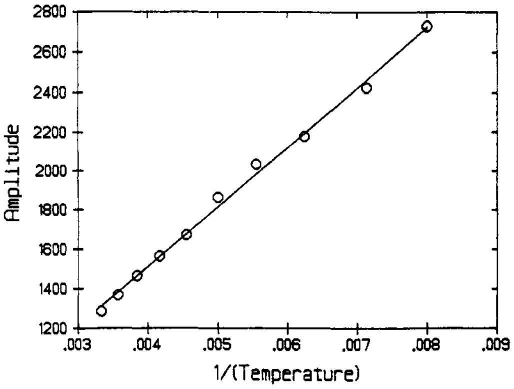

Figure 7. Amplitude of the narrow singlet in arbitrary units as a function of inverse temperature.

ature dependence and the saturation behavior of the narrow ESR signal formed in our system on annealing appear to be contrary to the behavior expected from metal particles. If the metal particles are small, however, it has been shown[17] that the paramagnetism follows the Curie law, with the signal intensity proportional to $1/T$; this dependence is in agreement with the temperature dependence detected for the narrow signal in our system and shown in Figure 7. Moreover, for metal particles of diameter <100 Å it is not unusual to detect narrow lines, of the order of several gauss, even at ambient temperature,[12-16] again in agreement with our results.

The saturation behavior presented in Figure 6 is very similar to that reported for small metal particles in alkaline-earth-exchanged zeolites, where the Mg, Ca, and Ba particles are formed by reduction with sodium metal.[16] It appears that the behavior of the narrow signal that forms in our system on annealing suggests the existence of small metal copper particles and is consistent with the results reported for metal particles in zeolites.[12-16]

Finally, we emphasize that the glass transition region is not affected by the annealing process. This is not surprising even in the absence of an antioxidant. $CuCl_2$ is known to be a strong inhibitor of olefin polymerization, due to its combination with the radicals formed during polymerization.[19]

Additional studies of ATPB complexes with a mixture of Cu^{2+} and Zn^{2+} cations are in progress. Preliminary results indicate that the high-temperature exothermic DSC peak is also observed in ATPB complexes containing a cation mixture and appears at lower temperatures in complexes containing Cu^{2+} and Zn^{2+}, compared to the complexes containing Cu^{2+} only.[20]

Conclusions

An exothermic peak was detected by DSC in the temperature range 350–450 K in complexes of amine-terminated telechelic polybutadiene with Cu^{2+}. This peak, which is absent in the telechelic polymer without metal cations, becomes more intense and shifts to higher temperatures as the amount of cation in the sample increases, is not detected in a second run taken immediately after the first, and reappears in samples left at ambient temperature for several days. We suggest that the exothermic peak is due to the organization of the cation into ionic clusters, even when the Cu^{2+}/amine molar ratio is only 0.02. The reappearance of the high-temperature DSC peak in samples left at ambient temperature after measurement of the exothermic transition suggests that the cluster formation is reversible.

ESR spectra of Cu^{2+}–polymer complexes provide additional support for this interpretation: ESR signals from complexed Cu^{2+} cations decrease in intensity on annealing above ambient temperature, disappear almost completely on heating at 523 K for 1 h, and gradually reappear in samples left at ambient temperature. These results are interpreted in terms of the formation of ESR-silent diamagnetic or paramagnetic species with very broad ESR lines upon cluster formation and support the suggestion that the clusters form on heating and disappear at ambient temperature.

A narrow ESR singlet detected in the annealed samples is tentatively assigned to *small* copper particles with a diameter <100 Å.

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