The Preparation and Properties of Zinc Coordination Complexes of Poly(4-Vinylpyridine-co-*n*-Butyl Methacrylate) Copolymers

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Synopsis

Two poly(4-vinylpyridine-co-*n*-butyl methacrylate) copolymers containing 14.2 and 30.0 mol% of 4-vinylpyridine residues were prepared by free radical copolymerization reactions. Insoluble complexes were obtained for each copolymer by reaction with zinc chloride. The coordination complexes obtained had a molar ratio of 4-vinylpyridine residues to zinc atoms close to 2 in both cases. The rheological behavior of each of these complexes has been compared to that of the corresponding metal-free copolymers, which were recovered by decomplexation. The metal complexed polymers exhibited much higher glass transition temperatures and much longer high temperature relaxation times than the corresponding uncomplexed copolymers.

INTRODUCTION

The poly(4-vinylpyridine) homopolymer is known to form complexes with a series of transition metal ions.[1,2] All of these complexes have been described as infusible solids whose polymer chains are believed to be crosslinked through coordinated metal chloride bridges between 4-vinylpyridine residues.

The complexation of a styrene, butadiene, and 4-vinylpyridine statistical terpolymer with nickel (II) and iron (III) chlorides has also been studied.[3,4] These complexes were considered to be similar to ionomers; that is, polymers composed of a hydrocarbon backbone containing pendant salt groups as the minority component. As in the case of ionomers consisting of a hydrocarbon backbone with pendant acid groups, which have been neutralized partially or completely to form salts, it was demonstrated that the main feature of the complexed 4-vinylpyridine terpolymer was a phase separation of the metal coordinated units into multiplets and a further aggregation of multiplets in clusters. The association of the coordinated unit aggregates was strong enough to act, at lower temperatures, as a physical crosslink. At higher temperatures a slow relaxation was observed, which was explained as a chemical exchange of the ligands, which was related to the proposed exchange of ion pairs in the ionic aggregates of ionomers. Unfortunately, the melt viscosities of these polymers were too high for melt processing.

The purpose of the present study is to examine the synthesis and rheological behavior of ionomerlike polymers obtained by complexation of the 4-

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vinylpyridine units in n-butyl methacrylate statistical copolymers with zinc chloride. In this study our attention was focused on several important questions including: (1) what is the stoichiometry of complexation, (2) what is the complexation-solubility relationship, (3) what is the minimum concentration of ion coordinating groups for ion clustering, (4) how does the glass transition temperature change with ion content, (5) is there an enhancement of the rubbery plateau modulus with ion content, and (6) what are the characteristics of the high temperature relaxation and viscous flow behavior of these metal coordinated copolymers?

EXPERIMENTAL

Synthesis of Copolymers

Monomers. 4-Vinylpyridine and n-butyl methacrylate, supplied by Fluka AG, were reagent grade and were purified by vacuum distillation after storage over potassium hydroxide pellets, washing the distillate with a 5% sodium hydroxide solution and with water, and drying over anhydrous sodium sulfate.

Poly(4-Vinylpyridine-co-n-Butyl Methacrylate)s. The copolymers for this study were prepared by free radical polymerization of 4-vinylpyridine and n-butyl methacrylate mixtures in bulk to high conversion. Two reaction mixtures, containing 10 and 20% by weight of 4-vinylpyridine each with 1% by weight of azo-bis(isobutyronitrile), were sealed in glass tubes under nitrogen and heated at 60°C for 72 h. The products of each reaction mixture were dissolved in diethyl ether to form approximately 10% solutions, which were added dropwise to a fivefold volume of n-heptane. The precipitated swollen polymer was collected by decantation and dried in air, and the purification procedure was repeated. After final drying at 80°C in vacuum for 24 h the yield was 88 and 81% for each of the two reaction mixtures. These copolymers are designated CVPBMA 14 and CVPBMA 30 in the following discussion.

Preparation of Coordination Complexes

Complexation of CVPBMA 14 with Zinc Chloride. A solution of 4 g of anhydrous $ZnCl_2$ in 80 mL of diethyl ether was added dropwise to a stirred solution of 40 g of CVPBMA 14 in 80 mL of diethyl ether. After addition of the first few drops, a precipitate appeared, the quantity of which increased with continuing addition. However, the quantity of zinc chloride used in this experiment was evidently largely in excess of the quantity necessary for precipitation, so that the last portion of the zinc chloride solution added caused no further precipitation. The white precipitate was collected by filtration, thoroughly washed with diethyl ether, and dried in air at room temperature. After drying at 80°C in vacuum for 10 h, 32 g of the complex of CVPBMA 14 with $ZnCl_2$ was obtained.

Complexation of CVPBMA 30 with Zinc Choride. In an analogous manner, starting from 40 g of CVPBMA 30 in 800 mL of diethyl ether and 8 g of $ZnCl_2$ in 160 mL of diethyl ether, 45.5 g of the CVPBMA 30 · $ZnCl_2$ complex was obtained.

Recovery of Copolymers from Their Complexed Form

Decomplexation of CVPBMA 16 · ZnCl$_2$. A homogeneous, stable emulsion was obtained by addition of 16.5 g of the CVPBMA 16 · ZnCl$_2$ complex to a vigorously stirred mixture of 35 mL concentrated ammonia, 35 mL water, 50 mL acetone, and 200 mL diethyl ether. This emulsion was added dropwise to 250 mL of concentrated ammonia diluted with 750 mL of water. The precipitated, swollen polymer was collected by decantation and dried in air. After further drying at 50°C in an air circulating oven for 24 h, 14.5 g of the copolymer CVPBMA 14′ was obtained.

Decomplexation of CVPBMA 30 · ZnCl$_2$. Using the procedure described above and starting with 23 g of CVPBMA 30 · ZnCl$_2$, 19 g of CVPBMA 30′ was recovered.

Polymer Characterization

The content of 4-vinylpyridine residues in the copolymers was determined by measurement of the UV absorption at 257 nm using a Varian instrument Model Super Scan 3. Poly(4-vinylpyridine) was taken as a standard for calibration. The content of zinc in the complexed copolymers was determined by calcination of a sample wetted with sulfuric acid and weighing the zinc oxide residue. The chlorine content was measured by standard elemental analysis. Limiting viscosity numbers were determined in chloroform solution at 25°C. The microcalorimetric measurements were made with a Perkin-Elmer instrument DSC-2 under nitrogen at a rate of 10°C/min.

Mechanical spectra were recorded with a Rheometrics mechanical spectrometer RMS-605 in the dynamic torsional mode at constant temperature by scanning the frequency from 0.1 to 100 rad/s through 14 values equidistant on a logarithmic scale. The temperature was increased stepwise from 30°C to the softening point of the sample, in increments of 15°C. The samples, 63.5 mm long, 12.7 mm wide, and 3.2 mm thick, were obtained from polymer powders by compression molding at 180–220°C under 10 MPa pressure.

RESULTS AND DISCUSSION

Copolymerization

The two poly(4-vinylpyridine-co-*n*-butyl methacrylate) copolymers, which were prepared for this study by free radical copolymerization reactions carried out to high conversion, are designated as CVPBMA 14 and CVPBMA 30 in the data of Table I according to their content of 4-vinylpyridine residues of 14.2 and 30.0 mol %, respectively. In both cases, the contents of the 4-vinylpyridine residues of the copolymers were higher than the contents of the 4-vinylpyridine in the monomer mixture, which can be attributed to an incomplete conversion of the copolymerization and a higher reactivity of 4-vinylpyridine, and possibly also to fractionation occurring during the isolation and purification of the copolymers.

These glassy, transparent copolymers must be considered to be highly heterogeneous with respect to their composition and the size distribution of

TABLE I
Copolymerization of 4-Vinylpyridine with n-Butyl Methacrylate

	CVPBMA 14	CVPBMA 30
Initial weight ratio of monomers (4-VP : BMA)	10 : 90	20 : 80
Yield of copolymer (wt %)	88	81
4-VP residue content in copolymer (wt %)	10.9	24.1
4-VP residue content in copolymer (mol %)	14.2	30.0
Limiting viscosity number in chloroform at 25°C (mL/g)	143	156

the macromolecules. Analysis of their UV absorption spectra is a reliable method for determination of the average 4-vinylpyridine residue content, and for solutions in chloroform, and with a cell path length of 1 cm, the following relationship was found between 4-vinylpyridine residue concentration c (μg/mL) and absorbance A at 257 nm: $c = 58.0 \times A$. The reproducibility of this measurement was $\pm$ 0.2 mol % of vinylpyridine content, and the position of the absorption peak was independent of the polymer structure, being the same for the 4-vinylpyridine homopolymer and for all of the copolymers.

In a separate study, which has not as yet been published, it was found that the reactivity ratios in this copolymerization are 2.56 for vinylpyridine and 0.60 for butyl methacrylate. For these reactivity ratios at a vinylpyridine content of about 16 mol %, this monomer should be present in the copolymer mostly (approximately 80%) as isolated units.

Complexation and Decomplexation

Zinc chloride complexes of the poly(4-vinylpyridine-co-n-butyl methacrylate) copolymers were obtained by adding a solution of the salt in diethyl ether to a solution of the copolymer in diethyl ether. The insoluble complex formed was washed with diethyl ether to eliminate the remaining soluble fraction of the reaction mixture, and the content of zinc chloride was directly determined by appropriate elemental analyses with the results shown in Table II. In order to measure the content of 4-vinylpyridine residues by UV analysis, the copolymer contained in the insoluble metal complex had to be quanitatively recovered. The recovery was accomplished by decomplexation with ammonia in diethyl ether, which dissolved the decomplexed copolymer. Because of the slightly different composition, the first of these copolymers is designated 16, instead of 14 in Tables II–IV.

It can be seen from the data in Table II that the molar ratio of 4-vinylpyridine residues to zinc atoms in both of the insoluble complexes was close to 2, despite the presence of an excess of zinc chloride during the formation of the complexes. That is, the composition of the zinc chloride in each of the complexes was close to the stoichiometric value to be expected for Zn^{+2},[2] although some chlorine atoms (less than 10% by elemental analysis) are certainly substituted by hydroxyl groups. Presumably, the insolubility of these metal coordinated polymers is caused by both crosslinking through the

TABLE II
Complexation and Decomplexation of
Poly(4-Vinylpyridine-co-*n*-Butyl Methacrylate) Copolymers

Starting copolymer	CVPBMA 14	CVPBMA 30
4-VP residue content (mol %)	14.2	30.0
Weight ratio CVPBMA : ZnCl$_2$	100 : 10	100 : 20
Molar ratio 4-VP residues : ZnCl$_2$		
for complexation	1.42 : 1	1.56 : 1

Insoluble complexed copolymer	CVPBMA 16 · ZnCl$_2$	CVPBMA 30 · ZnCl$_2$
Yield (wt %) (based on		
starting copolymer)	80	114
Zn content (wt %)	3.93	6.87
Cl content (wt %)	3.93	7.06
Molar ratio Zn : Cl	1 : 1.84	1 : 1.90
CVPBMA content (wt %)	91.98	85.89
Molar ratio 4-VP residues : Zn	1.74	1.88

	CVPBMA 16	CVPBMA 30
Decomplexed copolymer		
4-VP residue content (wt %)	12.0	24.1
4-VP residue content (mol %)	15.6	30.1
Limiting viscosity number in		
chloroform at 25°C (mL g)	134	154
Unprecipitated copolymer		
Quantity (wt %) (by difference)	26.4	2.30
4-VP residue content (wt %) (by		
difference)	8.0	
4-VP residue content (mol %) (by		
difference)	10.5	

TABLE III
Glass Transition Temperatures of Complexed and Decomplexed
Poly(4-Vinylpyridine-co-*n*-Butyl Methacrylate) Copolymers

	T_g (°C)			
Polymer	Max G''	Infl. G'	tan δ max	DSC
CVPBMA 16	42–44	53–56	61	63–64
CVPBMA 16 · ZnCl$_2$	113–117	132–135	142–144	102–103
CVPBMA 30	48–50	66–68	70	72–74
CVPBMA 30 · ZnCl$_2$	137–139	186–190	210–213	108–109

complex and clustering of the complexes. The unprecipitated copolymer fraction of Table II was apparently neither crosslinked nor clustered. For a copolymer with a statistical distribution of 4-vinylpyridine residues, for precipitation to occur by metal complex formation it is apparently necessary to have an average content of these complexing groups above some critical value. From the data shown in Table II, it can be concluded that this critical content is between 10.5 and 15.6 mol % of vinylpyridine units in the copolymer.

TABLE IV
Shift Factors a_T for Construction of Master Curves

Polymer	WLF parameters			Activation energies ΔH (kJ/mol)
	Temp (°C)	C_1	C_2	
CVPBMA 16[a]	> 30	17.4	79.5	
CVPBMA 16 · ZnCl$_2$	> 105	12.7	92.4	292.6[b]
CVPBMA 30[a]	> 30	19.2	72.4	
CVPBMA 30 · ZnCl$_2$	> 135	13.1	108.2	291.3[c]

[a] Polymer isolated after decomplexation.
[b] Below 105°C.
[c] Below 135°C.

The molar ratios of vinylpyridine to zinc in the copolymers given in Table II indicate that a substantial amount of these units exist as 1:1 complexes, which do not form crosslinks. For the CVPBMA 16 · ZnCl$_2$ complex, for example, the ratio of 1.74 indicates that 74% of the units are in 2:1 complexes and 26% in 1:1 complexes.

Rheological Study

It was expected that poly(4-vinylpyridine-co-n-butyl methacrylate) complexes with zinc chloride would behave in its rheological properties like an ionomer, as discussed in the Introduction. The two insoluble complexes, CVPBMA · 16 ZnCl$_2$ and CVPBMA · 30 ZnCl$_2$, were studied for these effects. However, it should be noted that because the complexation and precipitation of the heterogeneous copolymers were apparently accompanied by a compositional fractionation, one of the copolymers in the insoluble complexes differed significantly in composition from the starting copolymer. Therefore, in order to study the contribution of the complexation itself to the rheological behavior, the composition of the complexed copolymer is given by the compositions of the copolymer recovered after decomplexation, which was either 16 or 30 mol %, instead of the original 14 mol % for the former.

Samples of both complexed and decomplexed copolymers were subjected to dynamic torsion by scanning over a broad frequency and temperature range, and some of the results of these measurements are given in Figs. 1–3, in which only the values of moduli and G'' corresponding to a frequency of 6.28 rad/s are shown. All of the samples exhibited pronounced transitions from glassy to rubberlike behavior, and the storage modulus decreased in each case by 3–4 orders of magnitude over this range. The glass transition temperatures obtained from these measurements (corresponding to the maximum of G'', the inflection of G', and the maximum of the tan δ peak), which were all dependent on the time scale or frequency as expected, are shown in Table III, together with the results of the DSC measurements. It is clearly seen that the complexed copolymer had not only a much higher glass transition temperature, but also had a much higher rubbery plateau storage modulus and a longer high temperature relaxation time than the corresponding uncomplexed copolymer.

A more complete picture of each individual copolymer and a better comparison between various copolymers is given by the master curves shown in
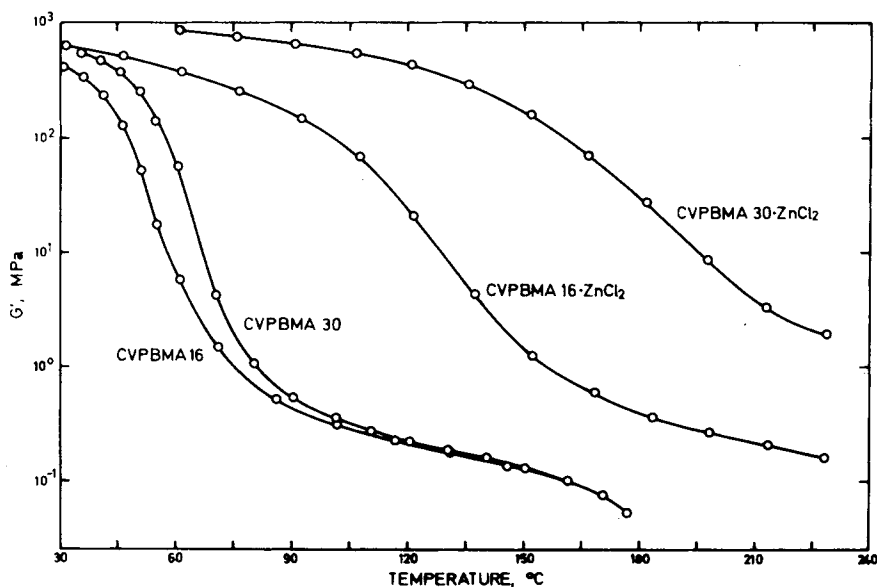
Fig. 1. Dynamic storage modulus G' vs. temperature for the two poly(4-vinylpyridine-co-*n*-butyl methacrylate) copolymers and their zinc chloride complexes.
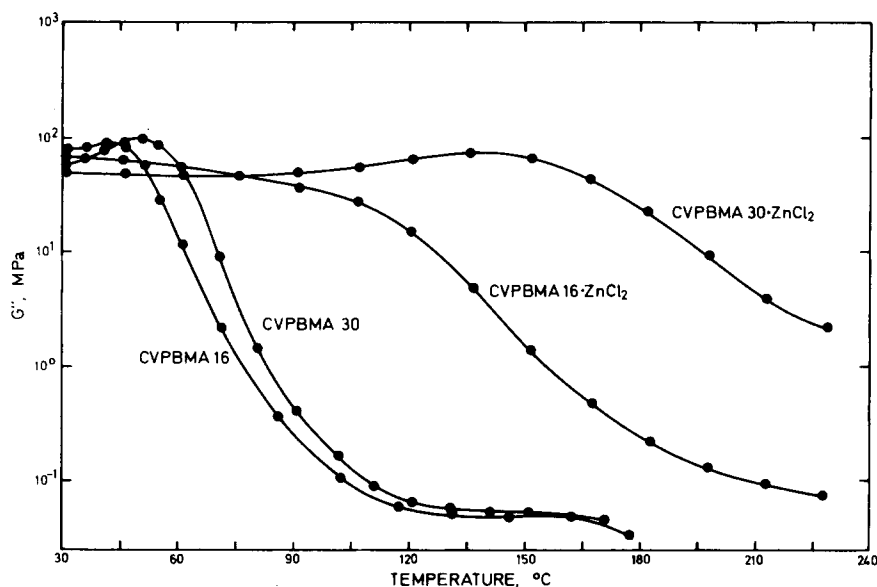

Fig. 2. Dynamic loss modulus G'' vs. temperature for the two poly(4-vinylpyridine-co-*n*-butyl methacrylate) copolymers and their zinc chloride complexes.

Figure 3. The figures were obtained in the usual manner by multiplying the moduli by the factor T_0/T and the frequency by the empirical factor a_T. The reference temperature T_0 for these calculations was chosen as 30°C, which was the lowest temperature at which the experiments were carried out. The variation of the experimental shift factor a_T with temperature fits the WLF equation for both of the uncomplexed copolymers in the whole range of
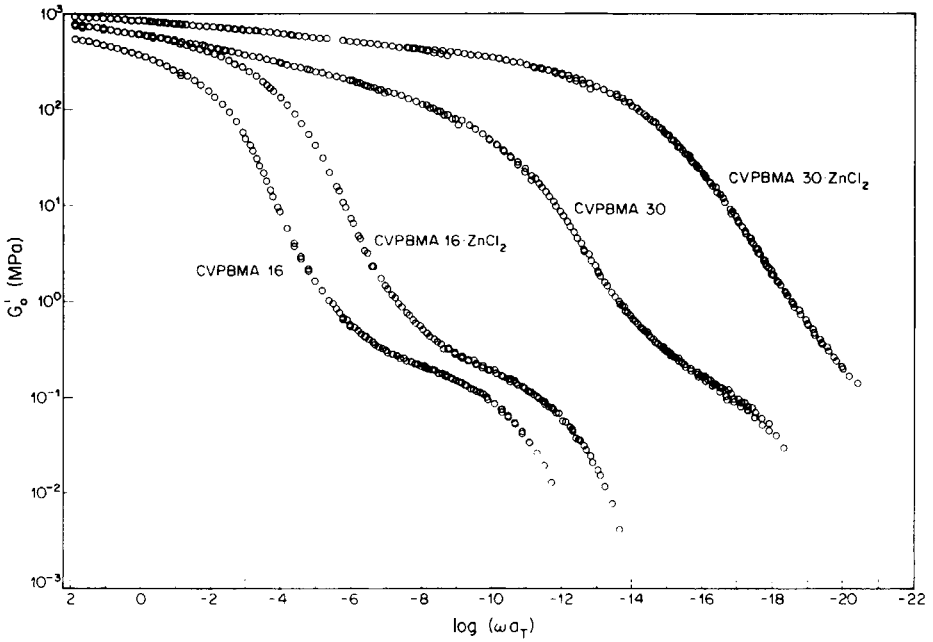
Fig. 3.   Master curves of reduced dynamic storage modulus G_0' vs. reduced frequency ωa_T for the two poly(4-vinylpyridine-co-n-butyl methacrylate) copolymers and their zinc chloride complexes. The reference temperature for each polymer, T_0, was 30°C.
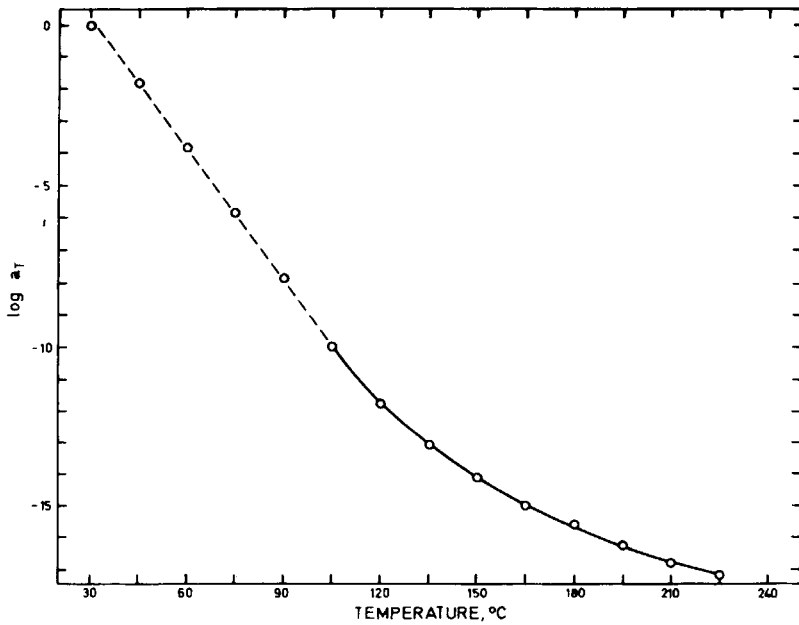

Fig. 4.   Shift factor a_T vs. temperature for CVPBMA 16 · ZnCl$_2$: ○ experimental values for $T_0 = 30°C$; (—) WLF equation with $T_0 = 105°C$, $C_1 = 12.7$, and $C_2 = 92.4$.
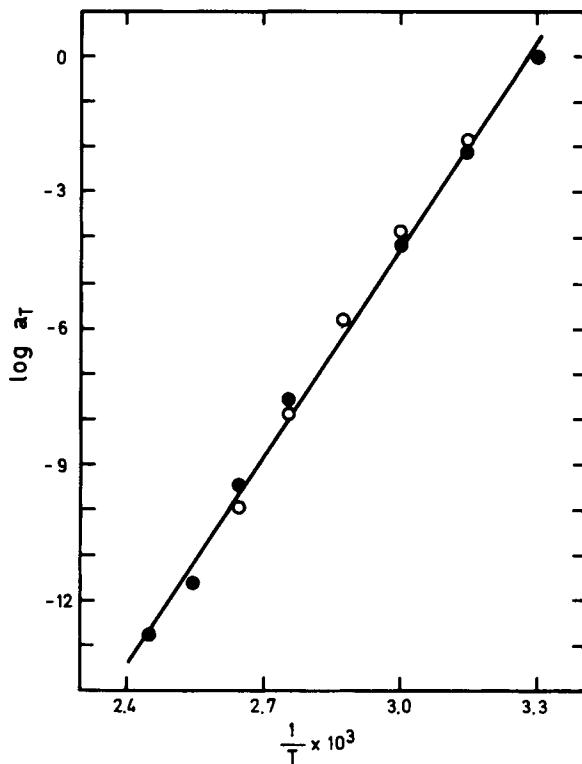
Fig. 5. Shift factor a_T for $T_0 = 30°C$ vs. reciprocal temperature for CVPBMA 16 · ZnCl$_2$ below 105°C (○) and for CVPBMA 30 · ZnCl$_2$ below 135°C (●): (—) the linear regression fit.

temperature, and for the two metal coordinated copolymers above the temperature close to their glass transition temperatures T_g (Table IV). Below T_g the factor a_T for the complexed copolymers obeyed the Arrhenius equation with an activation energy of about 290 kJ/mol as shown in Table IV and Figure 5.

The presence of the complexed zinc chloride in a 4-vinylpyridine statistical copolymer, and the apparent clustering of the salt molecules, postponed the onset of the segmental mobility to higher temperatures. Also, the complexation increased the temperature at which the relaxation processes involving entanglements became efficient. However, the relative increase of the glass transition temperature was more important, so that as a global result, the width of the rubbery plateau decreased with complexation. The result is certainly caused by the statistical distribution of the complexed 4-vinylpyridine residues.

It is clear from the large increase in T_g observed for the complexed copolymers that a simple two-phase structural model, consisting of hydrocarbon chains on the one hand and microphase-separated coordination clusters on the other, is inadequate. The distribution of vinylpyridine units and the compositional heterogeneity of the copolymers probably resulted in the formation of a mixture of multiplets and clusters, but, with these reservations, it may be concluded that the complexed poly(4-vinylpyridine-co-*n*-butyl

methacrylate)s studied here exhibited rheological behavior typical of that of ionomers, in general.[5]

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