Acknowledgment. We thank the NSF for support of this work.

Registry No. PMA, 25087-26-7; O_2, 7782-44-7; $TlNO_2$, 10102-45-1; CH_3NO_2, 75-52-5; pyrene, 129-00-0.

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Complex Formation in Polymer–Ion Solutions. 1. Polymer Concentration Effects

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ABSTRACT: We have studied the complexation of ions in polymer solutions and argue that when complexation leads to the formation of intramolecular cross-links (2:1 complexes) the usual law of mass action scheme adequate for small molecules must be revised. This limits the use of potentiometric methods in studying polymer–ion complexation. ^{11}B NMR spectroscopy on a suitably chosen borate–polyhydroxy compound (poly(glyceryl methacrylate)) system enables us to determine the concentration of free borate 1:1 and 2:1 complexes in a saline solution and to compare with a model system. The concentration of 1:1 complexes seems to be proportional to the free ligand concentrations, as for small molecule complexation. However, the formation of 2:1 complexes from 1:1 complexes (dicomplexation step) in dilute polymer solutions seems to be essentially independent of the global ligand concentration, contrary to the situation in model systems. Only when interchain 2:1 complexes are formed (in semidilute regime), a ligand concentration dependence appears. The number of intrachain complexes could be governed by the local polymer properties, e.g., chain stiffness.

I. Introduction

Metallic cations (Cu^{2+}, Cr^{3+}, ...) or basic anions ($B(OH)_4^-$, $Sb(OH)_6^-$) may be complexed by synthetic polymer (poly(vinyl alcohol), polyacrylamide, ...) or natural polymers (polysaccharides, proteins) bearing functional groups (i.e., ligands). Such water-soluble ion–polymer complexing systems are used in many applications including catalysis and petroleum or food industries.[1,2] The original properties[3-5] of these systems, such as gelation, demixing, or unusual rheological behavior, are governed by the complex formation. Various complexation equilibria have been studied for a long time mainly by potentiometric methods. Most of the time, the analysis of the polymer–ion complexation has been entirely inspired by analogy with reactions between ions and small model molecule.[6,7] In particular complexation is supposed to proceed by successive steps; each stage is controlled by the global ligand concentration in the solution and associated to a complexation constant k_i

$$M^- + L \overset{k_1}{\rightleftharpoons} ML^- \qquad k_1 = |ML|^-/|M^-||L| \tag{1}$$

$$ML^- + L \overset{k_2}{\rightleftharpoons} ML_2^- \qquad k_2 = |ML_2^-|/|ML^-||L| \tag{2}$$

$$\vdots \qquad\qquad \vdots$$

$$ML_{n-1}^- + L \overset{k_n}{\rightleftharpoons} ML_n^- \qquad k_n = |ML_n^-|/|ML_{n-1}^-||L| \tag{3}$$

where M^- denotes the free ion, L is the free ligand site, and ML^-, ML_2^-, and ML_n^- are respectively the 1:1, 2:1, and n:1 coordinated complexes.

However, macromolecular systems exhibit some very particular features arising from the very fact that ligands are connected on the polymer chain, which greatly limits the analogy with classical complexation between small molecules. Two major problems come from polyelectrolyte effects and intrachain complex formation.

In order to realize the importance of the polymer nature of complexing species it is convenient to view the chains as random copolymers with some units bearing charges

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(complexes).[8] These systems differ somewhat from classical polyelectrolyte carrying fixed charged groups because the number of charges on the chain is determined by chemical equilibria. Moreover, free ions are always present in the solution and partially screen out electrostatic interactions even in the absence of passive salt. Thus charge effects are strongly influenced by complexation equilibria and vice versa: the probability of the complex formation may be strongly decreased by repulsions between complexes already formed. We will present an experimental analysis of polyelectrolyte effects in a forthcoming paper.[9] Here we focus on the situation when a large excess of passive salt is present and electrostatic repulsions are screened out.

Another essential feature of polymer complexation comes from the very fact that multicoordinated complexes act as tie-points: mostly internal cross-links in dilute polymer solutions, both intra- and interchain cross-links in semidilute polymer solution. This study deals with the influence of the polymer concentration on complex formation. It can be argued that in a dilute polymer solution the first complexation step (monocomplexation) is ruled by the global change of entropy of mixing, as in the case for the complexation between small molecules. The number of monocoordinated 1:1 complexes should then be essentially proportional to the concentration of polymer chains or polymer sites. However, the situation is different in the second step (dicomplexation) when an ion fixed on an isolated macromolecule in a dilute solution by monocomplexation is expected to react with a free site belonging to the same polymer chain. Hence the polymer chain configurational entropy change principally determines the formation of di- (or multi-) coordinated complexes in very dilute solutions. In this picture, the number of multicoordinated complexes per polymer site should therefore be independent of the global monomer concentration in the solution. In the semidilute regime the number of multicoordinated complexes per polymer site should vary with the polymer site concentration since interchain complexes are formed.

The aim of this work is to test the validity of this simple picture and to compare the ion complexation of the polymer with that of a corresponding small model molecule. The paper is organized as follows. In section II we discuss the choice of an adequate ion-complexing polymer system. In section III we describe experimental methods, and in section IV the experimental results are presented and discussed.

II. Choice of the Ion-Complexing Polymer System

The study of many complexing systems is based on pH measurements.[6,7] Such methods seem well adapted to the case of small complexing molecules but are more difficult to interpret when dealing with polymers as explained in the Introduction. In particular an ambiguity arises because pH measurements do not distinguish between the various kinds of complexes and cannot test the validity of the concept of complexation "constants" summed up in eq 1–3. In this context, direct spectroscopic observation of the ionic species (free ions and complexes) provides an efficient way of overcoming these drawbacks.

Another difficulty comes from "parasite" reactions which complicate the complexation chemistry and compete with the complex formation in numerous systems. For instance hydrated metallic ions such as Al^{3+} or Cu^{2+} behave like acids and undergo hydrolysis, releasing protons.[2] Other ions may form hydroxide and precipitate (e.g., $Cu(COH)_2$) or exist in solution as polynuclear species (e.g., Ti–O–Ti–O–...). The polymer itself is in many complexing systems a polyacid (e.g., poly(acrylic acid)) or a polybase (e.g., poly(vinylpyridine)), and consequently its structure becomes very sensitive to the solvent (pH, ionic strength). These requirements and constraints lead us to study borate–polyhydroxy compound systems whose complexation chemistry is relatively simple any may be well followed by ^{11}B NMR.

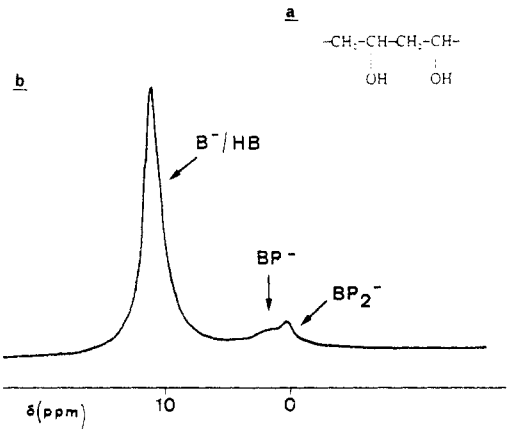
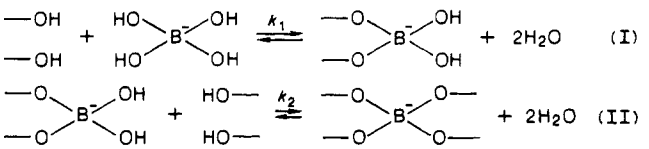


Figure 1. (a) Poly(vinyl alcohol). (b) Examples of ^{11}B NMR spectrum of an poly(vinyl alcohol)–borax solution.

Borate–Polyhydroxy Compound Systems. Borate ions have long been known for their ability to form complexes with *cis*-diol groups according to the scheme described below involving only two successive reactions: monocomplexation (I) and dicomplexation (II).[10]



In addition, ^{11}B NMR has proved to be an elegant and powerful method to detect any change in the environment of the boron nucleus and so to characterize diol–borate complexes.[11,12] Two neutral polymers systems, involving poly(vinyl alcohol)[13,14] and galactomannans,[15,16] have recently been examined by ^{11}B NMR, but they present some drawbacks for our purposes.

Poly(vinyl alcohol) possesses 1,3-diol groups which may form six-membered monodiol–borate (1:1) or didiol–borate (2:1) complexes. Unfortuantely, poly(vinyl alcohol)–borate systems do not offer, usually, a good resolution on the ^{11}B NMR scale between the two resonance signals assignable to complexes (see Figure 1). The interpretation of ^{11}B NMR data sometimes gives rise to ambiguities.[13]

Galactomannans are polysaccharides bearing two kinds of sites: 1,2-diols and 1,3-diols. Galactomannan–borate systems are in fact inconvenient systems for this problem. First, many different complexes may be formed (six-membered monodiol (1:1)—and didiol (2:1)—borate complexes, five-membered 1:1 and 2:1 complexes). Second, polysaccharides solutions are very viscous even at low concentrations,[16] NMR peaks are large, and it is a complex matter[15] to observe and account quantitatively for all the complexes formed (especially didiol–borate) (see Figure 2).

The necessity in the present problem to clearly disginguish the different kinds of complexes (1:1 and 2:1) and to easily measure their concentrations has motived the synthesis of a water-soluble polymer bearing 1,2-diol groups: poly(2,3-dihydroxypropyl methacrylate) or poly(glyceryl methacrylate) (PGM). Indeed, 1:1 and 2:1 complexes of 1,2-diol groups can be easily distinguished by ^{11}B NMR (see Figure 3), and the complexing ability of the

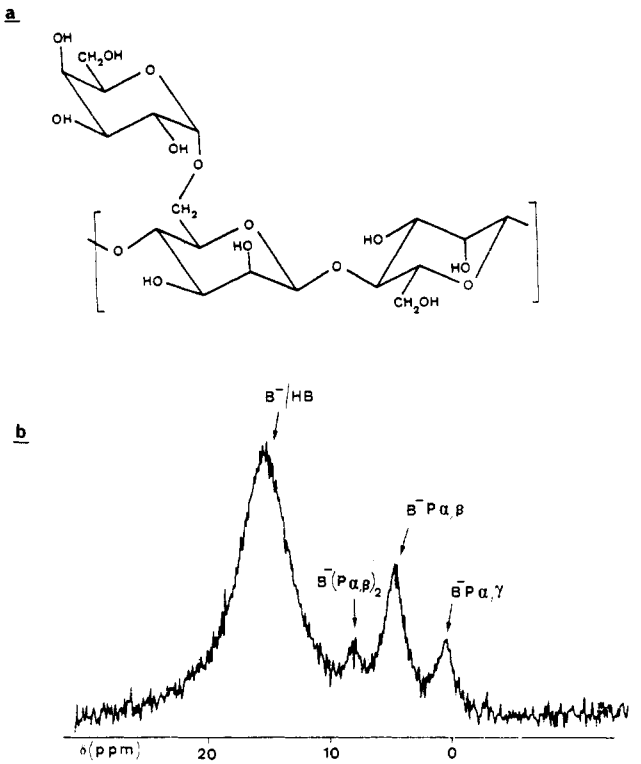


Figure 2. (a) Typical structural unit of a galactomannan. (b) Example of ^{11}B NMR spectrum of a galactomannan–borax solution.

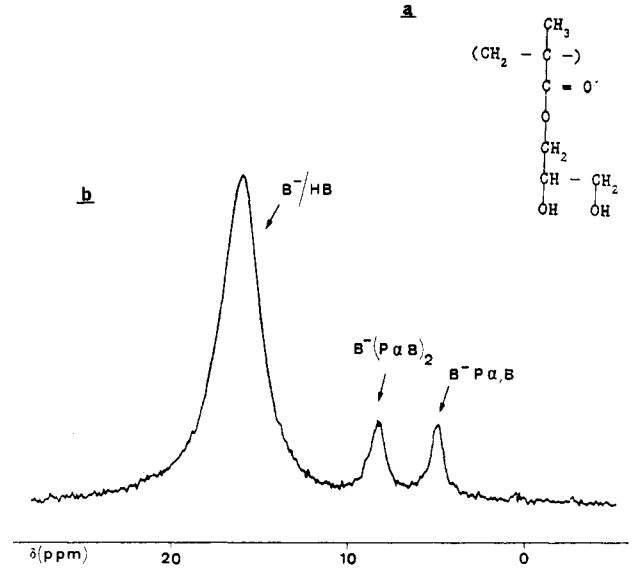


Figure 3. (a) Poly(glyceryl methacrylate) (PGM). (b) Example of ^{11}B NMR spectrum of a PGM–borax solution.

polymer can be compared with that of a corresponding small model molecule, 1,2-propanediol.

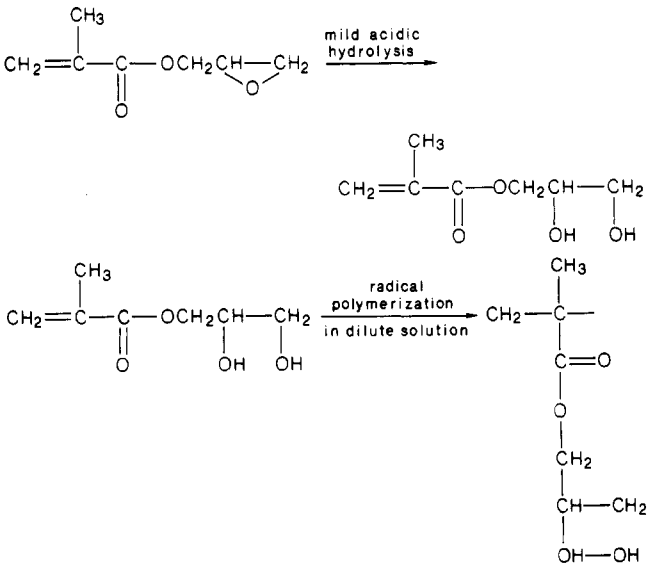
III. Experimental Section

Materials. Borax (or sodium tetraborate decahydrate: $Na_2B_4O_7{\cdot}10H_2O$) is a good buffer. In a aqueous solution at low concentrations it is totally dissociated into equal amounts of boric acid ($B(OH)_3$) and borate ion ($B(OH)_4^-$), so that the natural pH of a borax solution is close to the boric acid ionization constant (e.g., pH = $pK_a \simeq 9$). ^{11}B NMR spectra of borax solutions show only one pH-dependent average peak corresponding to the rapid acid–base exchange (on the ^{11}B NMR scale):

$$B(OH)_3 + OH^- \rightleftarrows B(OH)_4^-$$

All experiments in poly(glyceryl methacrylate) and 1,2-propanediol

Scheme I



systems are performed in basic conditions so that borax is present under its borate form.

Poly(vinyl alcohol) was obtained from Rhone Poulenc S.A. (Rhodoviol 4/20). This polymer was 98% hydrolyzed. The purification procedure included dissolution in hot water (80 °C), centrifugation, and precipitation in ethanol.

Guar galactomannan is a naturally occurring polysaccharide consisting of a chain of β-1,4-linked D-mannose units partially substituted at O-6 with α-D-galactopyranoside group (Figure 2a). The mannose to galactose ratio of guar galactomannan is less than 2. Our sample comes from Sigma Co. The essential purification procedure included dissolution in cold water, centrifugation, and precipitation. To obtain good ^{11}B NMR spectra from guar galactomannan–borate solution it was necessary to partially depolymerize the polysaccharide by hydrolysis in mild acidic conditions.

Poly(glyceryl methacrylate). The synthesis of this polyhydroxy compound inspired by Refojo's work[17] is summarized in Scheme I.

Monomer glyceryl methacrylate is prepared by mild acidic hydrolysis of glycidyl methacrylate, using dilute sulfuric acid.

Initiation. Ammonium persulfate, 12% aqueous solution, and sodium metabisulfite, 6% aqueous solution, are used as redox initiator for the polymerization (0.1 mL of each salt/mol of monomer).

Polymerization. The initiator is added to a dilute aqueous solution of glyceryl methacrylate (3%). The reaction is carried out at 60 °C in a glass tube. After 3 h the water-soluble viscous polymer solution is centrifugated, dialyzed 24 h against deionized water, and freeze-dried.

The intrinsic viscosity $[\eta]$ of the poly(glyceryl methacrylate) in aqueous solution, determined from an Ubbelohde-type capillary viscometer measurements at 25 °C, is 50 mL/g. The overlap concentration C^* of the polymer solution is then estimated to be around 20 g/L (from the relation $C^* \approx 1/[\eta]$). The polymer could be branched because of the presence of bifunctional monomers as impurities in the commercial glycidyl methacrylate.[18] Borax, 1,2-propanediol, and glyceryl methacrylate were obtained from Janssen Chimica. All other chemicals are commercial products of analytical grade.

^{11}B NMR. Spectra were recorded with a Bruker WP 250 spectrometer operating at 80.25 MHz. Boron 11 chemical shifts were referenced to external $BF_3O(C_2H_5)_2$. Samples were contained in 10-mm-o.d. quartz NMR tubes at the temperature of 20 ± 1 °C. Species concentrations and stability constants were calculated from the measure of the relative area of each signal.

Samples were prepared by dissolving appropriate amounts of the polyol (polyhydroxy compounds or 1,2-propanediol) and borax in deionized water (Milli-Q system of Millipore) and D_2O. The natural pH of samples corresponding to spectra of Figures 1–3 is slightly lower than 9. For poly(glyceryl methacrylate) and 1,2-propanediol samples (2.5 mL) (Figures 4 and 5), the pH was

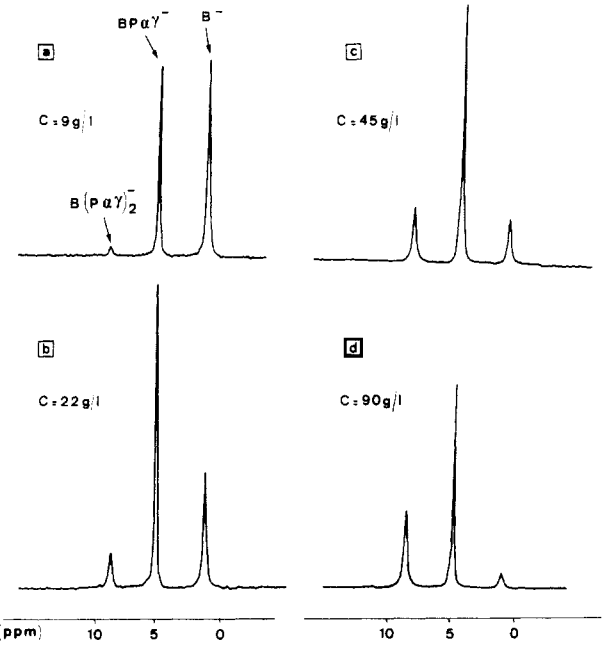


Figure 4. ^{11}B NMR spectra of 1,2-propanediol–borate solutions (0.2 M, NaCl, pH 12, T = 20 °C). Influence of the polyol concentration.

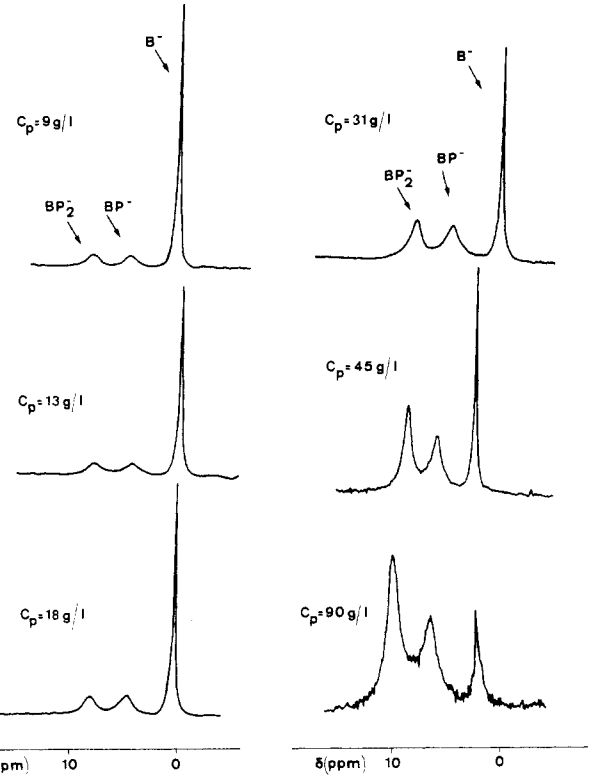


Figure 5. ^{11}B NMR spectra of poly(glyceryl methacrylate)–borate solutions (or gels; 0.2 M, NaCl, pH 12, T = 20 °C). Influence of the polymer concentration.

adjusted to 12 with aqueous sodium hydroxide so that the total borate concentration in all samples was $[B(OH)_4^-] = 2.10^{-2}$ M. The ionic strength was raised by the addition of 0.2 M sodium chloride to screen out electrostatic effects. These mixtures were vigorously stirred and spectra were recorded after 1 h.

IV. Results and Discussion

Two similar series of spectra were recorded in order to investigate the influence of the diol (ligand) concentration on the borate complexation for the small model molecule (1,2-propanediol) and the polymer (poly(glyceryl methacrylate)).

Table I
^{11}B NMR Data of Aqueous 1,2-Propanediol–Borate Solutions[a]

polyol C, g/L	borate ions (B^-) δ ($\Delta\nu_{1/2}$, Hz) area	1:1 complex (BP^-) δ ($\Delta\nu_{1/2}$, Hz) area	2:1 complex (BP_2^-) δ ($\Delta\nu_{1/2}$, Hz) area
9	0.6 (20) 55%	4.5 (15) 42%	8.2 (20) 3%
22.5	0.65 (20) 31%	4.5 (15) 58%	8.3 (25) 11%
45	0.6 (20) 17%	4.5 (15) 63%	8.3 (15) 20%
90	0.6 (24) 7%	4.5 (10) 52%	8.25 (25) 40%

[a] NaCl, 0.2 M,[b] pH 12; $[B^-]_0 = 2 \times 10^{-2}$ M; T = 20 °C.

Table II
^{11}B NMR Data of Aqueous Poly(glyceryl methacrylate)–Borate Solution[a]

polymer C, g/L	borate ions (B^-) δ ($\Delta\nu_{1/2}$, Hz) area	1:1 complex (BP^-) δ ($\Delta\nu_{1/2}$, Hz) area	2:1 complex (BP_2^-) δ ($\Delta\nu_{1/2}$, Hz) area
9	0.55 (16) 73%	4.8 (110) 13%	8.15 (100) 14%
13.5	0.55 (20) 66%	4.75 (110) 16%	8.15 (100) 18%
18	0.55 (20) 54%	4.8 (120) 21%	8.2 (110) 25%
32	0.55 (20) 40%	4.8 (110) 27%	8.1 (95) 32%
45	0.55 (20) 28%	4.75 (110) 28%	8.1 (95) 44%
66	0.55 (20) 22%	4.8 (100) 29%	8.15 (80) 49%
90	0.55 (40) 15%	4.7 (130) 31%	8.0 (130) 54%

[a] NaCl, 0.2 M; pH 12; $[B^-]_0 = 2 \times 10^{-2}$ M; T = 20 °C.

Model Molecule–Borate Complexes. ^{11}B NMR data for 1,2-propanediol borate solutions are gathered in Table I.

A borax solution at pH 12 presents only one resonance signal characteristic of the borate anion $B(OH)_4^-$ (δ = 0.6 ppm). When 1,2-propanediol is added to the borate solution, two new peaks appear (see Figure 4). The first one is relative to the monocomplexation (reaction I) and is assigned to five-membered ring monodiol–borate (δ = 4.5 ppm). The second one (δ = 8.3 ppm) is related to dicomplexation (reaction II) and is assignable to a five-membered ring didiol–borate. It is of importance to notice that monocomplexation largely predominates at low diol concentration whereas dicomplexation becomes significative for high diol amounts.

Polymer–Borate Complexes. ^{11}B NMR data for poly(glyceryl methacrylate)–borate solutions (or gels) are gathered in Table II.

Again two resonance signals are observed in addition to the free borate peak, for all polyhydroxycompound concentrations (see Figure 5). Gels were obtained for the two most concentrated polymer samples, whereas other samples were more or less viscous solutions. The chemical shifts indicate the formation of monodiol–borate 1:1 complexes ($\delta \approx$ 4.8 ppm) and didiol–borate 2:1 complexes ($\delta \approx$ 8.2 ppm). However, the comparison between the spectra of Figures 4 and 5 reveals an important difference between the complexing behavior of the small model molecule and the polymer. The ratio of didiol–borate to monodiol–borate complexes strongly increases with the diol concentration in the 1,2-propanediol case, while the dependence of this ratio on the poly(glyceryl methacrylate) concentration seem much weaker.

The quality of the spectra from Figures 4 and 5 allows the determination of the concentration of the different species, it is then possible to compare quantitatively the monocomplexation and dicomplexation steps in the polymer and model molecule cases.

Monocomplexation. For small molecules, complexation constants are defined from the mass action law. For

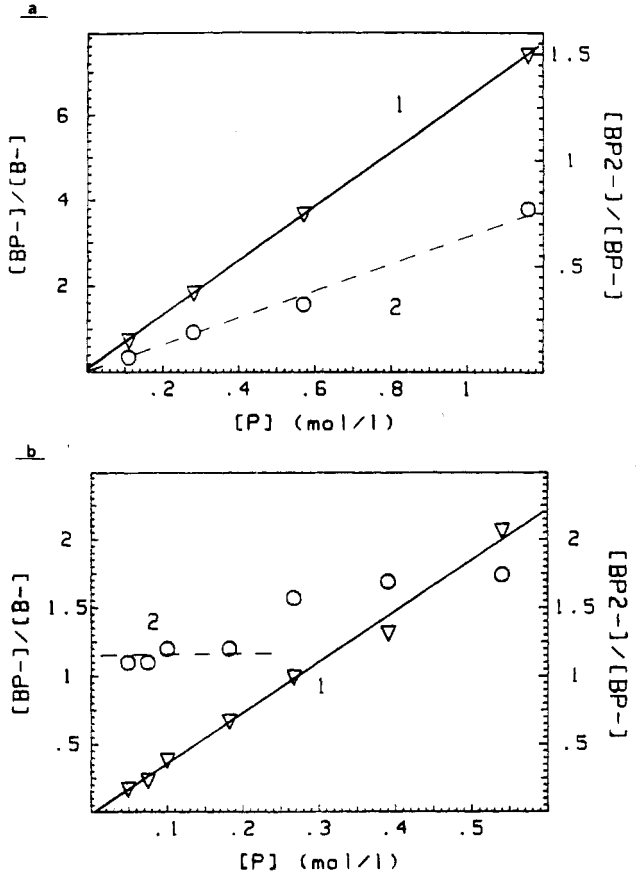


Figure 6. Variation of $|BP^-|/|B^-|$ and $|BP_2^-|/|BP^-|$ with the diol site concentration $|P|$. $|B^-|$, $|BP^-|$, and $|BP_2^-|$ concentrations in free borate ions, 1:1 complexes and 2:1 complexes, are determined from ^{11}B NMR spectra: (a) model molecule (1,2-propanediol)–borate systems; (b) polymer (poly(glyceryl methacrylate)–borate system. In the polymer case, the dicomplexation step (i.e., $|BP_2^-|/|BP^-|$) is very different from that of the small molecule case for which the usual dicomplexation constant $k_2 = |BP_2^-|/(|B^-||P|)$ may be defined. But in both cases (model molecule and polymer) the monocomplexation constant k_1 may be defined and given by the slopes of curves 1.

1,2-propanediol–borate systems, the monocomplexation constant k_1 is expressed as

$$k_1 = |BP^-|/|B^-||P| \quad (4)$$

where $|B^-|$, $|P|$, and $|BP^-|$ respectively denote the free borate ion concentration, the free diol concentration, and the monodiol–borate concentration. Figure 6 (curve 1) shows that in 1,2-propanediol–borate solutions the ratio of monodiol–borate complexes to free borate varies indeed linearly with the free propanediol concentration. The monocomplexation constant k_1 may then be determined from the slope: $k_1 = 6.0$ L/mol.

As a matter of fact, the monocomplexation step seems to be very similar for polymers and small molecules. Figure 5 shows that $|BP^-|/|B^-|$ varies linearly with the free polymer diol site concentrations. It is therefore possible to define a monocomplexation constant k_1 as in relation 4. For poly(glyceryl methacrylate)–borate systems k_1 is 3.6 L/mol, which is in the range of the monocomplexation constant measured for the corresponding model system.

It may be recalled, however, that any possible electrostatic effects are screened out thanks to an excess of added passive salt ($|NaCl|$ 0.2 M).

Dicomplexation. For 1,2-propanediol–borate systems, the stability constant k_2 relative to the dicomplexation step (reaction II) is written as

$$k_2 = |BP_2^-|/|BP^-||P|$$

where $|BP_2^-|$ is the didiol–borate complexes concentration. Plotting $|BP_2^-|/|BP^-|$ as a function of the free diol site concentration, we then obtain as expected a straight line passing through the origin. Its slope gives $k_2 = 0.7$ L/mol.

The dicomplexation step in polymer solutions is clearly different. First, the proportion of didiol borate complexes is higher; second, the ratio of the didiol–borate to monodiol–borate complexes ($|BP_2^-|/|BP^-|$) depends only slightly on the polymer diol site concentration. Figure 6b (curve 2) shows unambiguously that the ratio $|BP_2^-|/|BP^-|$ does not tend to zero even at very low ligand concentration. Hence the classical picture seems indeed to be inadequate for polymer dicomplexation and the meaning of the complexation constant k_2 must be revised. The dicomplexation step in poly(glyceryl methacrylate)–borate systems is not controlled by the global concentration of polymer diol sites.

For the lowest polymer concentrations ($C < C^*$), $|BP_2^-|/|BP^-|$ appears to be constant (≈ 1.2) and then independent of the diol site concentration. For higher polymer concentrations (typically $C > C^*$), $|BP_2^-|/|BP^-|$ slightly increases ($|BP_2^-|/|BP^-| \approx 1.7$). This extra dicomplexation seems to be related to the formation of didiol–borate intermolecular complexes. The gel formation observed when $C > C^*$ supports this interpretation. ^{11}B NMR spectra of poly(glyceryl methacrylate)–borate solutions do not allow any direct distinction between intra- or interchain didiol–borate complexes. Nevertheless the comparison of ratios $|BP_2^-|/|BP^-|$ at low and high polymer concentrations suggests that even when a gel is formed intrachain complexes can largely predominate.

Similar conclusions can be drawn from recent results of Sinton[13] for dilute poly(vinyl alcohol)–borax solutions. The ratio of the concentrations of the two kinds of complexes observed by ^{11}B NMR seemed to be essentially independent of the polymer concentration (and molecular weight).[13] Sinton interpreted this observation by attributing the NMR signals to two types of didiol–borates: intra- and interchain complexes. We rather suggest that (as usual for 1,3-diol–borax systems) the two resonance signal appearing on ^{11}B NMR spectra of poly(vinyl alcohol)–borate solutions are assignable to monodiol– and didiol–borate complexes. Therefore, although no particular care was taken to consider or eliminate polyelectrolyte effects (cf. ref 9), the observed constant ratio between the concentrations of both complexes would mean that the dicomplexation step is independent of the global polymer concentration. The situation would then be similar to our systematic observations of poly(glyceryl methacrylate)–borate systems for which it seems that there is not ambiguity in assigning ^{11}B NMR peaks.

Although many studies devoted to complexing polymer–ion systems evoked intrachain complex formation,[7,19] the influence of the polymer concentration on the crosslinking has seldom been considered (cf. ref 19). The spectroscopic results obtained in this work on polyhydroxy compound–borate system seem to confirm the simple picture presented in the Introduction. In dilute solution, the number of complexes per polymer site does not depend on the polymer concentration, or in other words, the intrachain complex concentration $|BP_2^-|$ varies linearly with the polymer site concentration $|P|$ (rather than with $|P|^2$ as for small molecules).

In a dilute solution, there is a high probability for a 1:1 complex to react with a site of its own chain to form a 2:1 intrachain complex. In a mean-field approach, this probability of intrachain complex formation would be proportional to the average concentration in the polymer

coil, i.e., $C^* \approx M^{-4/5}$ (where M is the molecular weight of the macromolecules).[20] But the formation of internal cross-links in a polymer coil means the existence of loops.[20] Theoretical[21,22] studies have shown that in a good solvent where excluded-volume effects predominate, the probability that two given polymer sites on the same chain come into close contact decreases sharply with their distance on the chain. In a polyhydroxy compound–borate system where any polymer site is able to form a complex, intrachain complexes would then imply the existence of small loops whose size should be governed by the local structure of the chain (i.e., rigidity). In this "small loop" picture, the concentration of complexes is independent of the polymer molecular weight (as far as the chain is longer than a possible minimal loop length). Still the number of intrachain complexes per macromolecule increases with the molecular weight. As a consequence, for polyhydroxy compound solutions we may expect that intrachain borate complex formation is more easy for flexible polymers such as poly(vinyl alcohol) or poly(glyceryl methacrylate) than for rigid polysaccharides (e.g., galactomannans) although the complexation mechanism is very similar.

Registry No. 1,2-Propanediol, 57-55-6; borax, 1303-96-4; poly(glyceryl methacrylate), 28474-30-8; poly(vinyl alcohol), 9002-89-5; galactomannan, 11078-30-1.

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Kinetics and Mechanisms for Thermal Imidization of a Polyamic Acid Studied by Ultraviolet–Visible Spectroscopy

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ABSTRACT: The kinetics and the mechanisms of thermal imidization of polyamic acid made from a conjugated diamine (*p,p'*-diaminoazobenzene) and a nonconjugated dianhydride (6F-DA) were investigated both in dilute solution and in solid state in the temperature range 150–190 °C. UV–vis absorption spectroscopy was the main tool used even though IR spectroscopy was also used for comparison with the results from UV–vis studies. UV–vis spectral changes as a function of imidization time were analyzed on the basis of the previously reported model compound studies in order to obtain the composition of various imidization species (*Macromolecules* **1987**, *20*, 1414). In 1% *N*-methylpyrrolidone solution, dissociation and the first imide ring closure proceed faster than the second imide ring closure of polyamic acid/imide at all three temperatures studied (150, 170, and 190 °C). This trend is attributed to the reduced basicity of the amide group in polyamic acid/imide in comparison to the analogous group in polyamic acid. Activation energies for the fast process and the second ring closure were 11 and 18 kcal/mol, respectively. During the early stages of imidization in dilute solution, IR spectra suggest some dissociation of polyamic acid as well as imidization. On the basis of these findings, the mechanism of imidization for dilute solution has been proposed. In solid-state imidization, the apparent imidization rate was initially faster than in dilute solution due to the catalytic effect of the neighboring amic acid group but levels off probably due to vitrification. Therefore, the mechanism of solid-state imidization must take into account the catalytic effect of the neighboring amic acid groups and the decreasing mobility effect as a function of cure time. Modeling studies to predict spectral changes as a function of the ratio of the two imidization rate constants are consistent with the observed results in dilute solutions. The results are adequately modeled by assuming a first-order, two-step imidization reaction, assuming a small extent of dissociation. On the other hand, solid film results seem to be reasonably simulated by assuming a second-order reaction for the first step, followed by a first-order reaction for the second step to account for the decrease in the concentration of the conformationally favorable catalytic amic acid group. Finally, there is a good correlation between UV–vis results and IR results, in regard to the overall extent of reaction in solid films.

Introduction

Polyimides are an important class of high-performance polymers. Excellent mechanical and electrical properties as well as high-temperature stability make these polymers suitable for applications in the aerospace industry as high-performance composites and in the electronics industry as high-temperature coatings. Difficulty in processing, however, has slowed the widespread use of these

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