polymers via the γ effect method. Such detailed assignment of resonances permits an accurate assessment of vinyl polymer microstructure and polymerization statistics and should aid in our search to understand their structure-dependent physical properties.

Acknowledgment. We are grateful to F. J. Padden, who provided the sample of atactic polypropylene.

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Copper(II) Ion Binding in Poly(glutamic acid)

N. Imai and J. A. Marinsky*

Physics Department, Nagoya University, Nagoya, 464, Japan, and the State University of New York at Buffalo, Buffalo, New York 14214. *Received June 28, 1979*

ABSTRACT: The complexation of the Cu(II) ion by poly(1-glutamic acid) (PGA) has been studied potentiometrically as a function of its initial degree of dissociation. Two different species, one with Cu bound to the carboxylate group in the repeating functional unit and the other with Cu bound to two repeating functional units through attachment to two carboxylate groups and the nitrogen of the chromophoric peptide group in one or both units, have been observed. The formation constant of CuA^+, the first species, is 4.0×10^1 in 0.05 M Na_2SO_4. A unique formation constant has not been established for the second species, CuA_2; with the first addition of Cu^{2+}, the formation constant, β_2^S, of the second species is approximately 2×10^4. The Cu appears to be bound more effectively with addition of more Cu until a second constant formation quotient that is unaffected by further addition of Cu is resolved. This second quotient, β_2^S, is larger when the PGA is initially more highly dissociated ($\beta_2^S \approx 7 \times 10^5$ at $\alpha > 0.45$, $\beta_2^S \approx 3.6 \times 10^5$ at $\alpha = 0.35$, and $\beta_2^S \approx 2 \times 10^5$ at $\alpha = 0.18$ and 0.25). The variability of β_2^S has been ascribed to (1) the contraction of the molecule with the addition of Cu(II) from a dimensionally stable expanded molecule to a dimensionally stable contracted molecule and (2) to a change in the accessibility of the repeating functional units for simultaneous interaction of carboxylate and peptide (A^{*-}) with Cu. Restraint of the accessibility of (A^{*-}) has been assumed to be smaller the larger the initial dissociation of the macromolecule.

The complexities that are encountered in the quantitative examination of metal-ion binding in weakly acidic (basic) polyelectrolyte systems have been fully discussed.[1-4] Their source is (1) the high and variable electric field at the surface of the polymers and (2), when more than one functional unit is bound to the metal ion, the inability to express the concentration of polymer species, charged and

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* Address correspondence to this author at the State University of New York at Buffalo.

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uncharged, relative to the changing volume of the polymer domain in these two-phase systems.

The first of these problems has been shown to be eliminated by an experimental demonstration that the magnitude of deviation from ideality that is measured potentiometrically for the H^+ ion by means of eq 1 given below

$$\mathrm{pH} - \log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]} - \mathrm{p}K_{\mathrm{HA}}{}^{\mathrm{int}} = \mathrm{p}K_{\mathrm{HA}}{}^{\mathrm{app}} - \mathrm{p}K_{\mathrm{HA}}{}^{\mathrm{int}} = -0.4343 \frac{\epsilon\psi_{(\mathrm{a})}}{kT} \quad (1)$$

applies to the metal counterion as well. In eq 1 $\psi_{(\mathrm{a})}$ corresponds to the potential at the surface of the polyion, $K_{\mathrm{HA}}{}^{\mathrm{int}}$ to the intrinsic dissociation constant, and A^- and HA to the molar concentration of the dissociated and undissociated species expressed on a monomer basis with respect to the total volume of the colloidal dispersion. The free, mobile, metal ion in these systems is exposed to the same field, $\psi_{(\mathrm{a})}$, as the hydrogen ion. The effect of this field on the concentration of metal ions at the reaction site, accounting for their higher charge, is thus equal to the product of the deviation term, $0.4343(-\epsilon\psi_{(\mathrm{a})}/kT)$, and z, its charge.

The second problem is more formidable. It was shown to be an important factor in our earlier examination[2,4] of the binding of Cu^{2+} by poly(acrylic acid). In this system the dominant species that is formed has Cu attached to two functional units as CuA_2. An estimate of a unique formation constant was unresolvable with the expression of the concentration of the various species (HA, MA_2, and A^-) in molarity units based on the solution volume, V. At low Cu concentrations relative to HA, the representation of the mass-action expression

$$\beta_{\mathrm{MA}_2}{}^{\mathrm{S}} = \frac{(\mathrm{MA}_2)}{(\mathrm{M})(\mathrm{A}^-)^2} \frac{(V, \mathrm{L})^2}{(\mathrm{mol})^2(\exp[-2\epsilon\psi_{(\mathrm{a})}/kT])} \quad (2)$$

yielded a constant value. With addition of Cu^{2+} to the system, the computed value $\beta_{\mathrm{MA}_2}{}^{\mathrm{S}}$ began to increase; at the highest Cu^{2+} concentrations another plateau in the value of $\beta_{\mathrm{MA}_2}{}^{\mathrm{S}}$ was reached. This result was attributed to the contraction of the macromolecule as the quantity of Cu^{2+} bound increased. The two plateaus were considered to be a consequence of volume stabilization in the Cu-uncrowded and Cu-crowded systems.

The deduction that volume change in the macromolecule led to the observed variation in the value of the formation constant was based on the following argument. By expressing the concentration of the polymer species as moles of species per total volume of polymer, υ, contained in the solution volume, V, the formation constant, $\beta_{\mathrm{MA}_2}{}^{\mathrm{v}}$, is

$$\beta_{\mathrm{MA}_2}{}^{\mathrm{v}} = \frac{\mathrm{MA}_2}{(\mathrm{M})(\mathrm{A}^-)^2} \frac{(\upsilon V, \mathrm{L})^2}{(\mathrm{mol})^2(\exp[-2\epsilon\psi_{(\mathrm{a})}/kT])} \quad (3)$$

so that

$$\beta_{\mathrm{MA}_2}{}^{\mathrm{v}} = \beta_{\mathrm{MA}_2}{}^{\mathrm{S}} \frac{\upsilon}{V} \quad (4)$$

The experimental observation that the value of $\beta_{\mathrm{MA}_2}{}^{\mathrm{S}}$ in the dimensionally stable regions, Cu crowded and Cu uncrowded, was inversely proportional to the initial quantity of the polyacid[2] was believed to justify this explanation of the experimental results.

Of course the formation of the simplest complex, MA^+, is unaffected by the unit employed in expressing the concentration of the polymer species and the complexation of $\beta_{\mathrm{MA}^+}{}^{\mathrm{S}}$ should normally lead to a unique value at every experimental condition.

It must be remembered, however, that in the computation of β_{HA} and $\beta_{\mathrm{MA}^+}{}^{\mathrm{S}}$ as well as $\beta_{\mathrm{MA}_2}{}^{\mathrm{S}}$ all deviation from ideality in these systems has been ascribed to electrostatic interaction of the mobile counterions with the polyion. This is an oversimplification. Certainly, because of the more limited accessibility of the polymer units, their effective concentration in these systems must be lowered appreciably relative to their effective concentration in the equilibria of the same functional units in small molecule systems. For example, if we compare isobutyric acid and PMA whose repeating functional unit closely resembles isobutyric acid, the activity coefficient of A^- and HA must indeed be smaller than that in the isobutyric acid since their freedom of motion is limited to fluctuations restricted by their attachment to the polymer matrix. The $\mathrm{p}K_{\mathrm{HA}}{}^{\mathrm{int}}$ measured for both acids under the same experimental conditions is the same within experimental error to suggest that the deviation terms, though probably a good deal smaller, cancel in the same way in both kinds of systems.

Because the relative accessibility of molecular aggregates attached to the polymer matrix is a potential source of variability in β^{S}, the possibility of such variability must be taken into account in the mass action expression for the formation of species such as HA, MA^+, and MA_2. Equation

$$\beta_{\mathrm{MA}_2}{}^{\mathrm{S}*} = \frac{(\mathrm{MA})_2}{(\mathrm{M})(\mathrm{A}^-)^2} \frac{(\gamma_{\mathrm{MA}_2})(V, \mathrm{L})^2}{(\gamma_{\mathrm{A}^-})^2(\exp[-2\epsilon\psi_{(\mathrm{a})}/kT])(\mathrm{mol})^2}$$

$$\beta_{\mathrm{MA}_2}{}^{\mathrm{S}*} = \beta_{\mathrm{MA}_2}{}^{\mathrm{S}} \frac{(\gamma_{\mathrm{MA}_2})}{(\gamma_{\mathrm{A}^-})^2} \quad (2a)$$

2 is modified to illustrate this aspect where γ represents species accessibility. Equation 4, in which any change observed in $\beta_{\mathrm{MA}_2}{}^{\mathrm{S}}$ is attributed to volume change in the effective domain of the macromolecule, must in turn be modified as shown to demonstrate as well the potential perturbation arising from changes in the relative freedom of motion of the polymer attached species.

$$\beta_{\mathrm{MA}_2}{}^{\mathrm{v}} = \beta_{\mathrm{MA}_2}{}^{\mathrm{S}} \frac{(\gamma_{\mathrm{MA}})_2}{(\gamma_{\mathrm{A}^-})^2} \frac{\upsilon}{V} \quad (4a)$$

In the PAA system that we have studied the activity coefficient ratios in the acid $(\gamma_{\mathrm{HA}}/\gamma_{\mathrm{A}})$ and metal complexes $(\gamma_{\mathrm{MA}^+}/\gamma_{\mathrm{A}^-}$ and $\gamma_{\mathrm{MA}_2}/(\gamma_{\mathrm{A}^-})^2)$ apparently remain unchanged throughout the experimental range of study to yield constant values for $\beta_{\mathrm{HA}}{}^{\mathrm{S}}$, $\beta_{\mathrm{MA}^+}{}^{\mathrm{S}}$, $\beta_{\mathrm{MA}_2}{}^{\mathrm{S}}$(expanded), and $\beta_{\mathrm{MA}_2}{}^{\mathrm{S}}$(contracted). This result is easy to rationalize with the binding of ions along a single chain. Certainly the mode of fluctuation of functional units in the random coil remains essentially unchanged to assure the same accessibility of functional units.

One might expect this situation to be somewhat altered in a polyelectrolyte system which undergoes transformation. For example, PGA during neutralization with base changes from a helix configuration to a random coil. In such a system, functional units when bound by a metal ion, for example Cu(II), across the helix might be expected to lose additional freedom of motion thereby leading to changes in the activity coefficient ratios. If this should be the case one might expect that upon binding of Cu(II) to PGA to form MA_2 such bridging of the macromolecule could lead to differences in complexation behavior from that observed with the Cu(II)–PAA system.

In order to examine this possibility and to test further this approach to the interpretation of complexation reactions of metal ions by flexible polyelectrolytes, we have studied the binding of Cu^{2+} by poly(glutamic acid).

Experimental Section

A stock solution of poly(glutamic acid) (PGA) obtained from Pilot Chemical, Inc., Watertown, Mass. (mol wt ≈ 60 000), was readied for use by the methods previously described by one of us (J.A.M.) for the preparation of poly(acrylic acid) employed in an earlier study.[5] The PGA solution, placed in cellulose acetate tubing, previously prepared for use according to the procedure used by Reddy and Marinsky[6] was dialyzed against distilled-deionized water. After complete removal of the simple salt and low molecular weight fragments of the PGA, the solution was concentrated by evaporation at the ambient temperature through the surface of the acetate tubing exposed to the action of a fan. The PGA was then converted completely to the acid by the exchange of the Na^+ counterion for the H^+ ion released from Dowex-50 resin in the acid form. In the final equilibrations of the solution and the resin, the solution became slightly turbid.

Both forward and back titrations were employed to standardize the purified solution after reconcentration. During these standardizations of the PGA solution (made 0.05 M in Na_2SO_4) with standard NaOH or H_2SO_4, the potentiometric data obtained as a function of α, the degree of PGA dissociation, were identical, within experimental error limits, for the forward and reverse reaction.

The experimental procedures used to examine the Cu(II) ion binding properties of PGA were very much the same as those used in our earlier study of the Cu(II)-PAA-Na_2SO_4 system.[2]

The sodium hydroxide employed for standardization and potentiometric investigation of the various systems studied was prepared by diluting a saturated solution of NaOH with water previously boiled and cooled under nitrogen. It was standardized against potassium hydrogen phthalate and/or standard HCl certified reagent from the Fisher Scientific Corp. The H_2SO_4 was standardized with the NaOH. Standardization of the $CuSO_4$ used in the experimental program was by titration with EDTA, using murexide indicator or a Cu(II) ion selective electrode to detect the end point. Triply distilled water was used for the preparation of all solutions. The H_2SO_4, Na_2SO_4, and $CuSO_4$ were of reagent grade (Fisher Scientific Corp.) and were used without further purification.

In the series of experiments that were performed, a hydrogen ion glass electrode and a Cu(II) ion selective electrode from Orion were inserted in 50.0 mL of solution 0.05 M in Na_2SO_4 and containing a selected concentration of PGA (7.64×10^{-3} M) at a fixed degree of neutralization (α = 0.19, 0.26, 0.35, 0.45, 0.60, 0.75, and 0.90). The Pyrex glass cell was immersed in a lucite bath filled with 0.5 M KCl maintained at 25 ± 0.1 °C. The KCl solution was effective for electric shielding of the cell. A saturated calomel electrode contained in a separate vessel in the bath was connected to the cell by a KCl liquid junction tube containing a pin hole at its end to keep leakage of KCl into the cell imperceptibly small. Nitrogen gas, presaturated by bubbling through 0.05 M Na_2SO_4, was passed through the cell solution to prevent access of CO_2 from the air to the cell solution. Before initiation of a titration the entire system was allowed to equilibrate for at least 1 h, the solution being stirred constantly.

A 2.5-mL ultra precision microbutret (finest scale division of 1 μL) was used to control the addition of $CuSO_4$ to the cell. After the addition of each increment of titrant, the solution was agitated by a Teflon-coated bar controlled by a magnetic stirrer positioned underneath the bath. Equilibrium was ascertained by the constancy of the measured potential read with the stirrer stopped. Since light affected the Cu(II) ion selective electrode response (2 to 5 mV), the complete assembly was covered by a wooden box during each reading. The potential readings were precise to 0.02 mV under optimum conditions through the use of a Kiethley Model 603 high impedance amplifier connected to a Leeds Northrup K-3 potentiometer.

The reliability of the Cu(II) ion selective electrode and the complementary apparatus was assured by a plot of the potential vs. log [Cu(II)] values obtained in a PGA-free 0.05 M Na_2SO_4 solution. The Cu(II) ion concentration range investigated, while sufficient to provide a meaningful test of the electrode, was kept sufficiently dilute to keep the ionic strength of the system essentially constant. A straight line with the expected Nernstian slope (29.6 mV per tenfold Cu(II) concentration change) was always obtained. Calibration of the electrode system in PGA-free 0.05 M Na_2SO_4 solution was carried out before and after each experiment to provide an estimate of any deviation of the asymmetry potential of the electrode and to permit correct evaluation of Cu(II) ion concentrations in the PGA, $CuSO_4$, and Na_2SO_4 systems under investigation. A shift in the asymmetry potential was encountered from experiment to experiment.

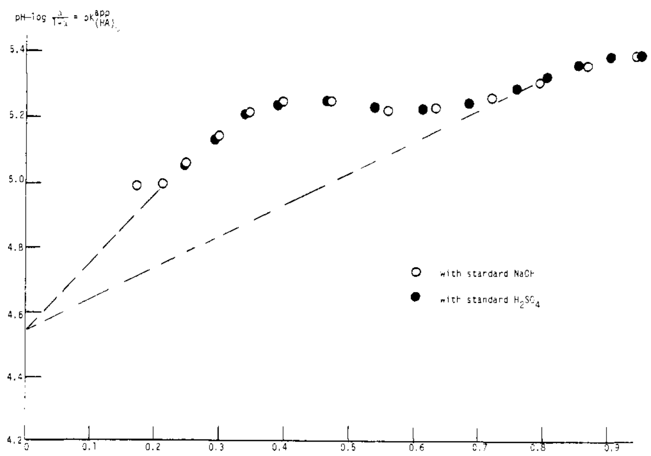

Figure 1. Potentiometric titration of PGA in 0.05 M Na_2SO_4.

Conversion of glass electrode potential readings to pH units was accomplished by standardizing the glass electrodes with NBS standard buffers. Two buffers (K phthalate, pH 4.008, and K-Na Phosphate prepared according to Bates,[7] pH 6.865) were normally used for this purpose.

The potentiometric properties of the Cu(II) free PGA, 0.05 M Na_2SO_4 system, determined during controlled addition of standard NaOH to the acid and standard H_2SO_4 to its Na salt during standardization, permitted evaluation of the intrinsic dissociation constant of PGA in the presence of Na_2SO_4.

Results

The potentiometric data obtained from the standardization of PGA in 0.05 M Na_2SO_4 with NaOH and H_2SO_4 are presented in Figure 1 to obtain the intrinsic pK (pK_{HA}^{int}) of the polyacid at the experimental condition of the Cu(II) ion binding studies. Extrapolation of these data to intercept the y axis (pH − log [$\alpha/(1-\alpha)$]) at α = 0 yields a pK_{HA}^{int} value of 4.56—error which can arise because of the distance through which the extrapolation must be carried is limited by the knowledge that the value resolved should approach closely the pK value of 4.51 reported for glutamic acid,[8] the repeating funtional unit of the polyelectrolyte. With this value of pK_{HA}^{int} so resolved, the evaluation of $(A^-)(\exp[-\epsilon\psi_{(a)}/kT])$ for each of the Cu(II) ion contained systems of the experimental study is facilitated with eq 1a. Because the relative abundance of MA^+ and MA_2 in the Cu(II)-PGA systems investigated is not easily accessible to permit accurate assessment of the concentration of A^- directly in each of the systems investigated, we require this approach.

$$\frac{HA}{[H^+][\beta_{HA}{}^{int}]} = (A^-)[\exp(-\epsilon\psi_{(a)}/kT)] \qquad (1a)$$

The following equation for the evaluation of the formation constants of M(II)-complexed species progressively formed in the polyelectrolyte system can now be employed in a limited way to facilitate interpretation of the Cu(II) ion binding data

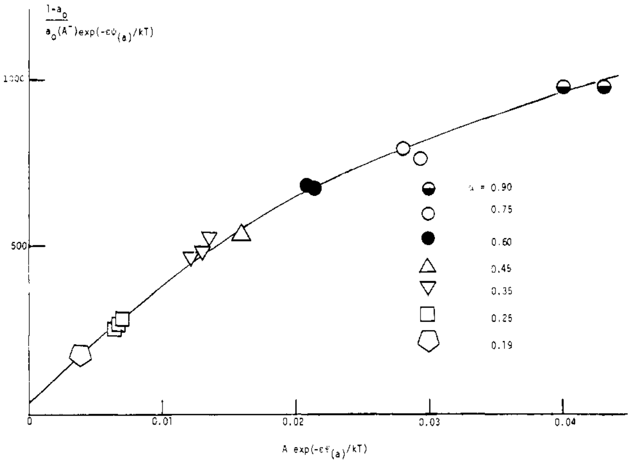

Figure 2. Analysis of binding data in the Cu-uncrowded region.

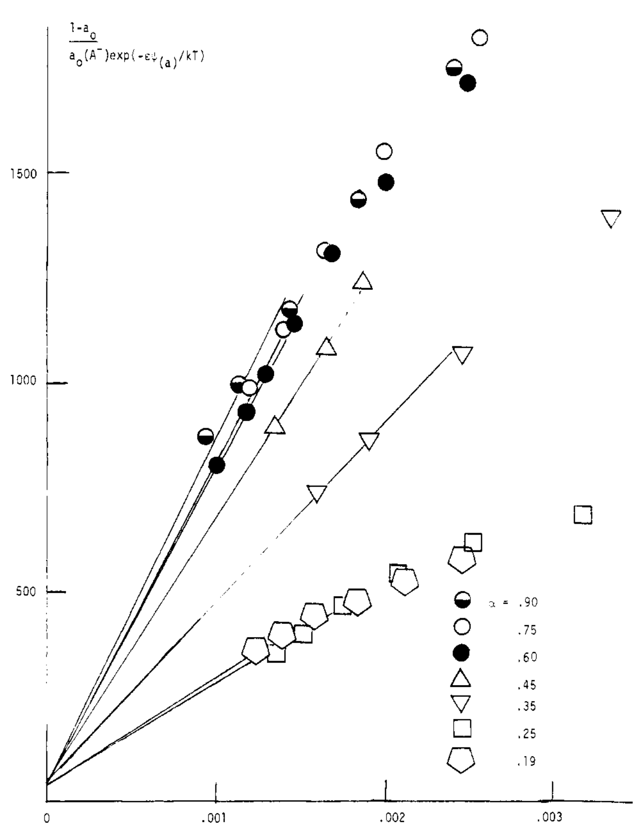

Figure 3. Analysis of binding data in the Cu-crowded region.

$$\frac{1 - a_0}{a_0(\mathrm{A}^-)[\exp(-\epsilon\psi_{(\mathrm{a})}/kT)]} = \beta_1{}^{\mathrm{S}}[\exp(-\epsilon\psi_{(\mathrm{a})}/kT)] + \beta_2{}^{\mathrm{S}}A[\exp(-\epsilon\psi_{(\mathrm{a})}/kT)] \quad (5)$$

In this equation a_0 is the fraction of the total metal present as free, mobile Cu(II) ion in each equilibrated solution.

In Figures 2 and 3 plots of $\{1 - a_0\}/\{a_0(\mathrm{A}^-)[\exp(-\epsilon\psi_{(\mathrm{a})}/kT)]\}$ vs. $(\mathrm{A}^-)[\exp(-\epsilon\psi_{(\mathrm{a})}/kT)]$ are presented for the binding data obtained with respectively the first and last increments of Cu(II) added to each of the systems studied (α = 0.19–0.9).

The smooth, gently curved line that can be drawn through the experimental points obtained with the first increments of added Cu^{2+} has been extended to intercept the ordinate axis in Figure 2. A $\beta_1{}^{\mathrm{S}}$ value of 4.0 × 10^1 is assigned from these data for the CuA^+ species formed. In the Cu-crowded case (Figure 3), the experimental data yield straight lines of different slopes, the slope being effected by a change in the intercept value introduced by the variable exponential. However, the lines converge and meet at the ordinate. At this point the exponential term reduces to unity for all the systems and a $\beta_1{}^{\mathrm{S}}$ value of 4 × 10^1 is again resolved for the formation constant of CuA^+.

With $\beta_1{}^{\mathrm{S}}$ made accessible in this way, it is now possible to compute the concentration of CuA_2 and A^- and the exponential term $(-2\epsilon\psi_{(\mathrm{a})}/kT)$ for evaluation of $\beta_2{}^{\mathrm{S}}$. This has been done and $(1 - a_0)/a_0(A)[\exp(-2\epsilon\psi_{(\mathrm{a})}/kT)]$ has been plotted vs. (A^-) in Figure 4, using data obtained at the different α values. The value of $\beta_2{}^{\mathrm{S}}$ increases rapidly from one region of constancy (as evidenced by the straight line drawn through the points) at low concentrations of Cu(II) to a second region of constancy at high concentrations of Cu.

This property of $\beta_2{}^{\mathrm{S}}$ resembles the observed property of $\beta_2{}^{\mathrm{S}}$ in the Cu(II)–PAA–$\mathrm{Na_2SO_4}$ system examined by us earlier.[2] However, in the case of PAA the value of $\beta_2{}^{\mathrm{S}}$ in the two regions of constancy was unaffected by the degree of dissociation of the polyacid. In the PGA system $\beta_2{}^{\mathrm{S}}$ at low Cu(II) concentrations is only slightly modified by an increase in the α whereas it is sizably affected in the high Cu(II) concentration range.

Discussion

In our earlier study of the binding of Cu(II) by poly(acrylic acid), regions of constancy in $\beta_2{}^{\mathrm{S}}$ were considered to indicate the existence of respectively both a dimensionally stable compact and expanded macromolecule. The transformation from the less compact to the more compact molecule, as indicated by the increase in the value of $\beta_2{}^{\mathrm{S}}$ with addition of more and more Cu(II), was attributed to contraction of the macromolecule with additional Cu(II) ion binding. An approximately five- to sixfold reduction in volume during the transformation from one dimensionally stable conformation to the other was estimated with eq 4.

For the PGA system the difference in $\beta_2{}^{\mathrm{S}}$ in the two regions of stability corresponds with this model to as much as a 40-fold decrease in volume in the high α region (0.455–0.90); in the lowest α region (0.18–0.255) a tenfold decrease in volume is indicated. Such a remarkable change in volume with Cu(II) ion binding is believed to be much too great to attribute exclusively to contraction of the macromolecule with increased binding of the Cu. Also, the observed dependence of the $\beta_2{}^{\mathrm{S}}$ value reached in the Cu(II) ion crowded region on the initial degree of dissociation of the PGA ($\beta_2{}^{\mathrm{S}} \approx 7 \times 10^5$ at the highest α values ranging from 0.9–0.45, $\beta_2{}^{\mathrm{S}} \approx 3.6 \times 10^5$ at $\alpha = 0.35$ and $\beta_2{}^{\mathrm{S}} \approx 2 \times 10^5$ at $\alpha = 0.185$ and 0.255) is not consistent with the results obtained in the PAA–Cu(II) system where the value of $\beta_2{}^{\mathrm{S}}$ in the Cu-crowded region is unaffected by the initial dissociation of the PAA macromolecule.

Another factor must contribute to the observed variation in $\beta_2{}^{\mathrm{S}}$. We have in the introduction already suggested the possibility that with the binding of Cu to one and two functional units, respectively, the accessibility, γ, of the various species (A^-, CuA^+, CuA_2, and HA) relative to each other may change. As a consequence, the difference in activity coefficient terms could contribute to the observed variation of $\beta_2{}^{\mathrm{S}}$ with its initial degree of dissociation and the quantity of Cu added.

In the case of PAA, the relative change in accessibility of the various species formed with the addition of the Cu(II) ion apparently is not altered, their magnitudes

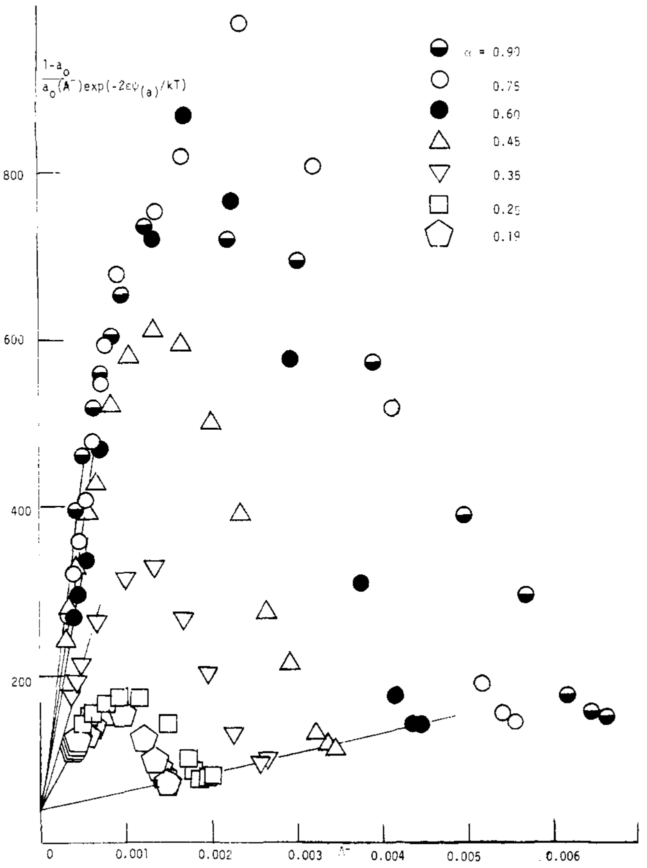

Figure 4. Complete analysis of binding data.

relative to each other remaining constant in the dimensionally stable expanded and contracted forms. This may not be the case in the PGA–CuSO$_4$ system where Cu is bound across helix spirals to restrict more effectively the fluctuation of bound units in the macromolecule. In order to examine the possibility that the change in the accessibility of functional units relative to each other is indeed a likely contributor to the observed variation of β_2^S with α, the potentiometric behavior of several of the CuSO$_4$–PGA–Na$_2$SO$_4$ systems studied (α = 0.18, 0.6, and 0.9) has been plotted vs. (A$^-$) in Figure 5 for this purpose by using the experimental value of pH and HA and the value of (A$^-$) computed by accounting for the presence of CuA$^+$ and CuA$_2$; the quantity of CuA$^+$ has been defined by the formation constant, β_1^S, of 4.0×10^1 that is unambiguously resolved for this species in this research program. The first points obtained with the first increments of Cu(II) at each fixed α studied are also included in the figure.

From Figure 5 we see that the intrinsic pK_{HA}^{int} derived from this treatment of the data is not affected by progressive binding of Cu, remaining 4.56 (see Figure 1). The ratio of γ_{HA} to γ_{A^-} is apparently unchanged in the presence of Cu. This result is consistent with the observed constancy of β_1^S at every experimental condition, and we must conclude that the change in accessibility (degree of freedom), i.e., the modification of the fluctuation of functional units in the macromolecule as Cu is increasingly bound, should not seriously affect the computation of the formation constants of CuA$^+$ and CuA$_2$ if only the carboxylate units are involved.

There is, however, one additional factor that could lead to the observed results. It has been shown that the spectral behavior of Cu–PGA mixtures at 260 mμ provides strong evidence for the existence of a Cu–PGA complex with charge-transfer properties.[9] This observation has been fully substantiated by spectroscopic data obtained for the CuS0$_4$–M$_2$S0$_4$–PGA systems in the laboratory of one of us (J.A.M.).[10] Concurrent binding of the Cu(II) ion to the N of the peptide chromophore, on binding to two carboxylate units, is apparently responsible for the charge-transfer band maximum observed at 260 mμ. One must anticipate that the simultaneous interaction of the peptide and carboxylate units of PGA with the Cu(II) ion will be extremely sensitive to the geometry of the macromolecule. The accessibility of this repeating unit (A* = carboxylate-peptide) for combination with Cu can be expected to change with experimental conditions as a consequence. At low α values (0.18 and 0.25) the ratio of $\gamma_{A^{-*}}$ to $\gamma_{CuA_2^+}$ must be 3.5 times smaller than that at the higher α (0.45–0.9) values. Such variation in accessibility ratios will account for the larger value of β_2^S at the higher α values.

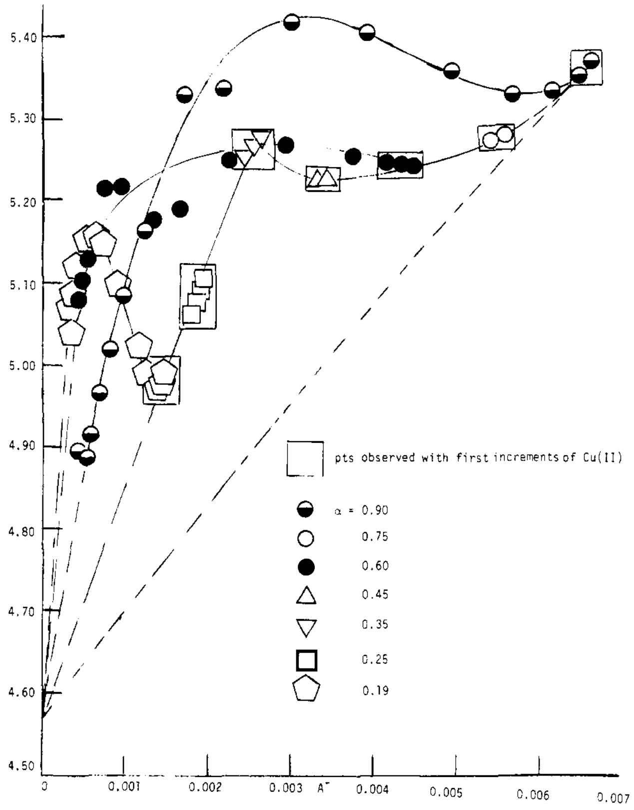

Figure 5. The effect of Cu(II) ion binding on the intrinsic pK of PGA.

The fact that the smallest β_2^S at low α is, in its compact form, an order of magnitude larger than the β_2^S value obtained for its dimensionally stable expanded configuration, exceeding by almost a factor of 2 the ratio of about 5.5 obtained for the β_2^S values resolved for the Cu–PAA system in its dimensionally stable contracted and expanded forms, is probably due to this factor and not to a relatively greater change in the volume of the PGA.

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Polymer Reaction. 9. Effect of Polymer-Bound Chromium on Oxidative Pyrolysis of Poly(propylene)[1]

James C. W. Chien* and Joseph K. Y. Kiang[2]

Department of Polymer Science and Engineering, Department of Chemistry, Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003.

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ABSTRACT: Poly(propylene) has been reacted with chromyl chloride (Etard reaction) to covalently bind chromium to the polymer. The thermal pyrolysis and oxidative pyrolysis of poly(propylene) with and without chromium have been compared, using an interfaced pyrolysis GC peak identification system. Between 388 and 438 °C the thermal pyrolysis of the two materials in an inert atmosphere have comparable reaction rates, but chromium tends to lower the pyrolysis activation energy of poly(propylene) from 51 to 44 kcal mol^{-1} while increasing the temperature of the maximum pyrolysis endotherm by 15 °C. Chromium does not alter the amount of major pyrolysis products but tends to increase the formation of methane, isobutylene, and 2,4,6-trimethyl-1-heptane. The effect of chromium on oxidative pyrolysis is more substantive by comparison. Chromium suppresses the formation of all major products, though no new product was detected. It increases the activation energy of oxidative pyrolysis by 10 kcal mol^{-1} and promotes char formation. The behavior suggests possible catalysis by chromium in the termination processes. The combustion properties of poly(propylene) are significantly modified by the bound chromium. At only a 1.5% level of chromium the poly(propylene) has a limiting oxygen index of 26.4 and a self-ignition temperature of 400 °C in air as compared to 17.4 and 250 °C, respectively, for normal poly(propylene).

Polymer combustion is an extremely complicated chemical process. In the condensed phase there is thermal decomposition as well as oxidative degradation of the polymer; the latter process is diffusion limited. The rate of oxidative pyrolysis should thus be dependent upon sample thickness and oxygen pressure.[3,4] In the gas phase the flame is sustained by these volatile decomposition products; the combustion process itself involves degenerative chain branching oxidations. The heat liberated by combustion in turn provides the energy needed for the condensed phase reactions. There are, therefore, several approaches to flame retardation. A flame retardant may decompose into free-radical scavengers to interfere with chain reactions in the gas phase or release noncombustible gases to lower the oxygen concentration at the polymer surface. Some flame retardants form intumescent coatings which act as a thermal insulating barrier. Current flame retardants for polymers are limited to compounds of a few elements. Bromine- and chlorine-containing compounds, especially those in synergistic combination with antimony oxide, have been demonstrated to be effective radical scavengers in the gas phase.[5] Some phosphorus compounds decompose to form phosphate glasses to reduce polymer flammability.[6] Less effective and of uncertain function are nitrogen- and boron-containing flame retardants. Even the best flame retardant formulations are relatively inefficient, up to 40 wt % of chlorine and antimony compounds being necessary to obtain a nondripping flame-retarded poly(propylene). At such high levels, the flame retardants tend to alter and decrease the material's physical properties.

In the past, most studies tried to differentiate the gas phase from the condensed phase mode of retardancy activity by some macroscopic criteria. For instance, if there is volatilization of the retardant element from the substrate and its activity is insensitive to the polymer structure or the nature of the oxidant, then the flame retardant is said to act in the gas phase. If contrary behavior is observed or there is evidence of char formation, then the flame retardant is thought to act in the condensed phase.

The research in our laboratories has two objectives: to find new elements which are effective in the flame retardation of polymers at levels much lower than those currently employed and to develop methods for the determination of whether a flame retardant acts primarily in the condensed or the gas phase. A candidate is introduced directly into a hydrocarbon flame, such as a CH_4–O_2 flame, and the lowering of the flame temperature or flame velocity is measured to assess its efficacy in the supression of gas phase reactions. The candidate's activity in the condensed phase is determined through its effects on the thermal pyrolysis and oxidative pyrolysis of the polymeric substrate under flameless conditions. In this paper we report the effect of covalently bonded chromium on the condensed phase degradation of poly(propylene). The choice of chemical binding of chromium to the polymer over simple blending of a chromium complex with poly(propylene) was made to avoid volatilization, incompatibility, and other complications.

The rationale of this work is predicated on the hypothesis that if chromium plays a role in the inhibition of thermal pyrolysis of poly(propylene), then its presence

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