

# The Preparation and Properties of Chelates of Transition Metal Ions with the Homopolymer and Copolymers of *p*-Vinylbenzoylacetone

EARL C. CHAPIN, ELIZABETH FESTA TWOHIG,\* LOREN D. KEYS III,\* and KATHLEEN M. GORSKI,\* *Department of Physical and Biological Sciences, Western New England College, Springfield, Massachusetts 01119*

## Synopsis

*p*-Vinylbenzoylacetone (VBA) was prepared by the condensation of *p*-vinylacetophenone and ethyl acetate. This monomer was homopolymerized and copolymerized with acrylamide or maleic anhydride to produce polymers which would chelate substantial amounts of transition metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Eu}^{3+}$ , and  $\text{VO}^{2+}$ . In the case of the  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  chelates, about 80–90% of the metal ion could be eluted by dilute mineral acids. The resulting eluted products apparently have a somewhat porous structure because they are capable of rechelating these ions from water solution, even though the solid homopolymer which had not been chelated and eluted is too hydrophobic to chelate very much metal ion from water solution. The eluted  $\text{Cu}^{2+}$  chelate readily reaccepted  $\text{Cu}^{2+}$  ions from water solution and discriminated against  $\text{Ni}^{2+}$  almost completely. However, the eluted  $\text{Ni}^{2+}$  chelate would reaccept both  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions, but exhibited a strong preference for  $\text{Cu}^{2+}$  ions in competitive batch experiments. The  $\text{VO}^{2+}$  chelate was an effective heterogeneous phase catalyst for the epoxidation of allyl alcohols such as geraniol with *tert*-butylhydroperoxide. The chelate was stable under these oxidative conditions and could be recovered unchanged and reused.

## INTRODUCTION

Polymers bearing pendant  $\beta$ -diketone groups have been previously prepared<sup>1</sup> and the infrared<sup>2</sup> and ultraviolet spectra<sup>3</sup> as well as the stability constants<sup>1c,d</sup> of chelates of these polymers with transition metal ions have been studied. We wish to report here some additional work on these polymers which relates to their potential utility as ion exchangers and on the behavior of one of the chelates as a catalyst for the epoxidation of allyl alcohols. For our work we have chosen to investigate the preparation and chelating properties of a polymeric analog of benzoylacetone, namely poly(vinylbenzoylacetone) which is designated here as PVBA.

Monomeric *p*-vinylbenzoylacetone (VBA) was readily prepared by the Claisen condensation of ethyl acetate and *p*-vinylacetophenone as shown in the following scheme. The *p*-vinylacetophenone was prepared by a modification of the procedure reported by Baddelay, Wrench, and Williamson.<sup>4</sup> Monomeric VBA polymerizes easily to give homopolymers which chelate a variety of metal ions under certain conditions to be described. The monomer also copolymerizes with other active monomers such as acrylamide or maleic anhydride to give copolymers whose chelating behavior has also been investigated.

\* Undergraduate research participant.

## EXPERIMENTAL

The NMR spectra were recorded on a Varian T-60 spectrometer. Chemical shifts are reported in ppm downfield from  $\text{Me}_4\text{Si}$  as an internal standard. Infrared spectra were obtained on a Beckman IR-8 grating spectrometer using KBr pellets, cast films, or neat liquids as appropriate. The spectra were calibrated with the  $1601\text{ cm}^{-1}$  band of polystyrene film. Melting points were taken on a Thomas Electrothermal Capillary melting point apparatus and are uncorrected. Viscosity determinations were made using a Cannon-Ubbelohde viscometer in a water bath at  $25 \pm 0.1^\circ\text{C}$ .  $\text{Cu}^{2+}$  in solution was determined by electrodeposition on Pt electrodes using an Eberbach electrodeposition apparatus, and  $\text{Ni}^{2+}$  was determined gravimetrically as the complex with dimethylglyoxime. Elemental microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

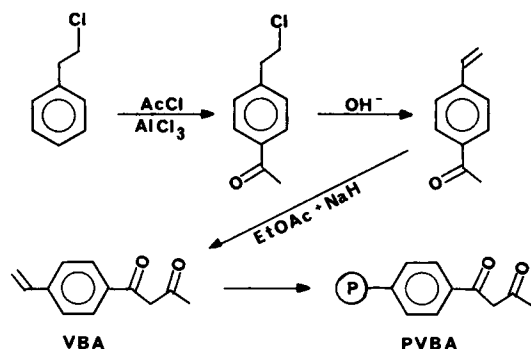
Sodium hydride was obtained as a 50% suspension in mineral oil (Alfa) and was washed free of the mineral oil with dry benzene under a nitrogen atmosphere prior to use. Reagent grade benzene, anhydrous ethyl ether, and ethyl acetate were dried by storing over Type 3A molecular sieves for several days. THF (Fisher Certified grade) was used from newly opened bottles or was stored for short periods under nitrogen in the refrigerator. All other chemicals were reagent grade and were used as received.

***p*-Vinylbenzoylacetone (VBA)**

A solution of *p*-vinylacetophenone (98 g, 0.67 mol) in 50 mL of dry ethyl ether was added dropwise over a period of 2.5 h to a stirred suspension of sodium hydride (35 g, 1.46 mol) in 200 mL of benzene, 100 mL of ethyl ether, and 140 g (1.6 mol) of ethyl acetate. The reaction mixture was maintained under an atmosphere of nitrogen until the evolution of hydrogen became vigorous. During the first 0.5 h, the reaction mixture was heated to  $35^\circ\text{C}$ , but as the rate of hydrogen evolution increased, the temperature was lowered to  $20\text{--}25^\circ\text{C}$ . The reaction mixture was stirred at room temperature for an additional 3 h until the evolution of hydrogen had essentially ceased. During this time the mixture became a very thick paste, and 150 mL more of dry ether was added to facilitate stirring. The reaction mixture was then added to a solution of 100 mL of concd  $\text{H}_2\text{SO}_4$  in 1 L of water. The benzene-ether layer was separated and washed with  $2 \times 500\text{ mL}$  of water. After drying ( $\text{MgSO}_4$ ), the solvents were removed using a rotary evaporator. The crude crystalline product was twice recrystallized from 400 mL of ligroine (bp  $90\text{--}120^\circ\text{C}$ ): yield 74.5 g (59%); mp  $67\text{--}68^\circ\text{C}$ ; IR (KBr)  $1608\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.16 (s, 3 H), 5.31 (m,  $\text{H}_\text{B}$  of an ABX vinylic system,  $J_{\text{AB}} = 2\text{ Hz}$ ,  $J_{\text{BX}} = 11\text{ Hz}$ ), 5.75 (m,  $\text{H}_\text{A}$ ,  $J_{\text{AB}} = 2\text{ Hz}$ ,  $J_{\text{AX}} = 17\text{ Hz}$ ), 6.11 (s, 2 H,  $\text{—CO—CH}_2\text{—CO—}$ ), 6.73 (m,  $\text{H}_\text{X}$ ,  $J_{\text{BX}} = 11\text{ Hz}$ ,  $J_{\text{AX}} = 17\text{ Hz}$ ), 7.58 (m, 4 aryl H's on a para disubstituted ring).

ANAL. Calcd for  $\text{C}_{12}\text{H}_{12}\text{O}_2$ : C, 76.57; H, 6.43. Found: C, 76.47; H, 6.38.

The filtrate from the two recrystallizations from ligroine was evaporated to 250 mL and cooled. An additional 20.4 g of product was obtained, making the total yield 75%.



Scheme I

The first crop of crystals were slightly yellow, and they were twice recrystallized from 400 mL of methanol to give 62.8 g of very light yellow material which was used in subsequent polymerizations. This material was shown by TLC on Whatman LK6DF silica plates to be free of trace amounts of minor products which were not identified, and which were present in the sample before the final recrystallization from methanol.

### Polymerization of VBA in Ethyl Acetate

VBA (6.5 g, 34.6 mmol) was dissolved in ethyl acetate (20.0 g), AIBN (0.10 g, 0.6 mmol) was added, and the solution was placed in two 1.5 × 13 cm glass culture tubes. These tubes were flushed with nitrogen, sealed with PTFE-lined caps, and placed in a silicone oil bath at 60 ± 1°C for 197 h. The polymer which had separated as a viscous layer was dispersed in the solvent by vigorous shaking and the reaction mixture was poured into 300 mL of 95% ethanol. The polymer was recovered on a filter, dissolved in 50 mL of THF to give a clear light yellow solution, and reprecipitated in 300 mL of 95% ethanol to give a finely divided polymer sample: yield 6.3 g (97%) after drying in a desiccator over Drierite at room temperature; limiting viscosity number  $[\eta] = 0.157$  dL/g in THF; IR (KBr) 1608 cm<sup>-1</sup>.

ANAL. Calcd for (C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>)<sub>n</sub>: C, 76.57; H, 6.43. Found: C, 76.50; H, 6.59.

### Polymerization of VBA in Ethanol

VBA (40.0 g, 213 mmol) was dissolved in 200 mL of 95% ethanol by heating to 60°C with stirring under a nitrogen atmosphere and AIBN (0.40 g, 2.4 mmol) was added. A fine white precipitate of polymer began to form in a few minutes. Heating and stirring was continued for 8 h. The polymer was removed on a filter, washed with warm 95% ethanol, and placed in 200 mL of THF. This sample formed a highly swollen gel in this solvent, but no soluble fraction could be isolated. This suspension was slowly added to 600 mL of methanol with vigorous stirring. The finely divided white precipitate was collected on a filter, soaked in 200 mL of fresh methanol overnight, and again recovered and dried at 60°C for 4 h: yield 31.9 g (80%); IR (KBr) 1608 cm<sup>-1</sup>.

ANAL. Calcd for (C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>)<sub>n</sub>: C, 76.57; H, 6.43. Found: C, 76.60; H, 6.68.

### Polymerization of VBA in Emulsion

Distilled water (250 mL), sodium laurate (2 g, 8 mmol), and sodium dioctyl sulfosuccinate (2 g, 4.5 mmol) was heated to reflux under nitrogen, and VBA (26.6 g, 141 mmol) was added along with a potassium peroxydisulfate solution (0.088 g, 0.33 mmol in 10 mL of water). The reaction mixture was heated at reflux for 1 h and allowed to cool at room temperature. The emulsion was broken by freezing, and the granular polymer was recovered, washed with 1.5 L of hot distilled water and 400 mL of warm methanol. The polymer was dissolved in 400 mL of THF and filtered through a glass wool plug to remove a small amount of gel particles. The slightly yellow opalescent solution was added to 1.5 L of methanol with vigorous mechanical stirring. The finely divided polymer was collected on a filter, washed with 500 mL of methanol and dried at 110°C for 4 h: yield 23.3 g (87.8%);  $[\eta] = 1.26$  dL/g in THF; IR (KBr) 1608  $\text{cm}^{-1}$ .

ANAL. Calcd for  $(\text{C}_{12}\text{H}_{12}\text{O}_2)_n$ : C, 76.57; H, 6.43. Found: C, 76.65; H, 6.62.

After storage for several days in the air at room temperature, this polymer would no longer dissolve in THF but gave a very highly swollen gel, resembling that obtained from the polymerization of VBA in ethanol.

### Copolymerization of VBA with Acrylamide

VBA (2.64 g, 14.0 mmol), acrylamide (2.99 g, 42.0 mmol), and AIBN (0.0122 g) were dissolved in 20 mL of dioxane, and the solution was charged to a 22-mm glass tube which was flushed with nitrogen and sealed. The solution was heated 22 h at 60°C in a thermostatically controlled silicone oil bath. At this time the sample was an opaque gel which was removed from the tube, ground in a mortar, and soaked in dioxane. The light yellow granular product was collected on a filter and dried, first at room temperature and then at 105°C for 16 h: yield 4.0 g (71.0%); IR (KBr) 1608, 1668, 3205  $\text{cm}^{-1}$ ; 7.74% N, giving a mole ratio  $m_1/m_2 = 0.58$ . Since no soluble polymer was isolated, viscosity data could not be obtained.

### Copolymerization of VBA with Maleic Anhydride

VBA (19.6 g, 0.102 mol), maleic anhydride (10.3 g, 0.104 mol), and AIBN (0.22 g) were dissolved in 400 mL of benzene and heated to reflux under nitrogen for 5.5 h. An additional amount of AIBN (0.2 g) was added, and refluxing was continued for 7 h. The polymer precipitated and adhered to the walls of the flask. After the benzene solution had been removed, the polymer was hydrolyzed by dissolving it in 200 mL of 6N NaOH, and reprecipitating it in 1.5 L of water containing 500 mL of concd HCl. The finely divided precipitate was collected on a filter, washed with large quantities of distilled water, and then soaked in water for 5 d. The product was again recovered on a filter and dried, first at room temperature, and then at 105°C for 3 days: yield 13.2 g (44%);  $[\eta] = 0.107$  dL/g in THF; IR (KBr) 1608, 1678, 1718, 1738, and 3430  $\text{cm}^{-1}$ ; 68.82% C, 5.88% H, giving a mole ratio  $m_1/m_2 = 2.18$ .

### Preparation of Cu<sup>2+</sup> PVBA in THF

PVBA (made in ethanol) (14.6 g) was allowed to swell in 300 mL of THF for 24 h and a solution of Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (8.6 g, 0.043 mol) in 125 mL of warm distilled water was added with stirring. A dark green granular precipitate formed immediately. The reaction mixture was stirred and allowed to stand for 24 h. The dark green precipitate was collected, washed with 2 L of distilled water, soaked for 24 h in 800 mL of distilled water, collected and dried at room temperature for 24 h, and then at 110°C for 54 h: yield 14.5 g; IR (KBr) 1390, 1419, 1500, 1520, 1548, and 1582 cm<sup>-1</sup>; 13.55% Cu (indicating that 92.7% of the β-diketone groups in the polymer had been chelated).

### Preparation of Ni<sup>2+</sup>PVBA in THF

PVBA (made in ethanol) (13.3 g) was allowed to swell in 300 mL of THF and a solution of Ni(OAc)<sub>2</sub>·4H<sub>2</sub>O (10 g, 0.4 mol) in 100 mL of distilled H<sub>2</sub>O was added. A lime-green precipitate formed immediately. The reaction mixture was stirred and allowed to stand for 24 h. The precipitate was collected, washed with 1 L of distilled water, soaked for 24 h in 800 mL of distilled water, collected and dried at room temperature for 24 h, and then at 110°C for 54 h (the color changed to a light yellow during this final drying step): yield 14.0 g; IR (KBr) 1390, 1418, 1498, 1548, and 1598 cm<sup>-1</sup>; 8.93% Ni (indicating that 62.8% of the β-diketone groups in the polymer had been chelated).

### Preparation of VO<sup>2+</sup> PVBA in THF

PVBA (2.5 g) was allowed to swell in 150 mL of THF, and 6.0 g of VO(acac)<sub>2</sub> in 400 mL of THF was added. After 2 h the entire reaction mixture had become a gel. This was stirred intermittently and allowed to stand for 24 h. During this time the gel became more granular but still highly swollen. This product was collected on a filter and washed with large quantities of warm methanol. The product was dried, first at room temperature and then at 105° for 16 h: IR (KBr) 1383, 1418, 1438, 1498, 1518, 1548, 1588, and 1608 cm<sup>-1</sup>; 10.33% V (indicating that 88.2% of the β-diketone groups had been chelated).

### Elution of Cu<sup>2+</sup> PVBA and Rechelation with Cu<sup>2+</sup> or Ni<sup>2+</sup>

5 g of Cu<sup>2+</sup> PVBA (containing 13.55% Cu) was ground to a fine powder and stirred with 100 mL of 3M H<sub>2</sub>SO<sub>4</sub> for 16 h. The eluted polymer was recovered on a fritted glass filter and washed with 500 mL of distilled water until the filtrate was essentially neutral. A small sample of this eluted chelate was dried at 110°C for 24 h and found to contain 2.66% Cu by microanalysis.

The remainder of the eluted chelate was divided into three portions while still wet. One portion was immediately suspended in 50 mL of 0.2 M Cu(OAc)<sub>2</sub> and allowed to remain in contact with this solution for 1 week. The chelate was recovered, washed, and dried: 8.86% Cu. The second portion was allowed to stand in contact with 50 mL of 0.02 M Ni(OAc)<sub>2</sub> solution for 1 week. The recovered chelated contained 1.10% Ni and 2.57% Cu. The third portion was further eluted with concd HCL and washed with 200 mL of distilled water. A dried sample of this eluted chelate contained 0.063% Cu.

### Elution of Ni<sup>2+</sup> PVBA and Rechelation with Ni<sup>2+</sup> or Cu<sup>2+</sup>

5 g of Ni<sup>2+</sup> PVBA (containing 8.93% Ni by microanalysis) was ground to a fine powder and suspended in 100 mL of 3M H<sub>2</sub>SO<sub>4</sub> for 16 h. The eluted polymer was recovered on a fritted glass filter and washed with 500 mL of distilled water until the filtrate was essentially neutral. A small sample of this eluted chelate was dried at 110°C for 24 h and found to contain 0.65% Ni. The remainder of the eluted chelate was divided into two portions while still wet. One portion was suspended in 50 mL of 0.2M Cu(OAc)<sub>2</sub> and allowed to stand in contact with this solution for 1 week. The chelate was recovered, washed, and dried: 11.46% Cu. The other portion was allowed to stand in contact with 50 mL of 0.2M Ni(OAc)<sub>2</sub> solution for 1 week. The recovered chelate contained 6.60% Ni.

Ni<sup>2+</sup> PVBA (1.5012 g, 8.93% Ni) was placed in 50 mL of 1.0M H<sub>2</sub>SO<sub>4</sub> and allowed to stand for 15 days. The polymer was collected on a fritted glass funnel and washed with 100 mL of distilled water. The Ni<sup>2+</sup> in the filtrate was determined gravimetrically as the glyoximate, and it was found that 0.1329 g or 99.1% of the Ni<sup>2+</sup> had been removed from the polymer. The polymer sample was further washed with 400 mL of distilled water and placed in contact with a mixture of 10.0 mL of 0.2100M Cu(OAc)<sub>2</sub> and 10.0 mL of 0.2019M Ni(OAc)<sub>2</sub>. After standing for 9 days in this solution, the solids were collected on a fritted glass filter and washed with 150 mL of distilled water. The filtrate contained 0.0370 g of Cu by electrodeposition and 0.1148 g Ni by gravimetric determination of the glyoximate. This corresponds to an uptake of 0.0964 of Cu<sup>2+</sup> and 0.0036 g Ni<sup>2+</sup> by the polymer. From this it can be calculated that the resulting chelate contained 6.57% Cu and 0.25% Ni.

These values were confirmed by eluting the chelate with 1.0M H<sub>2</sub>SO<sub>4</sub> and again analyzing the filtrate by the methods used above. The filtrate contained 0.0945 g Cu and 0.0036 g Ni.

### Epoxidation of Geraniol Catalyzed by the VO<sup>2+</sup> Polymeric Chelate

The VO<sup>2+</sup> polymeric chelate (2 g) (containing 10.33% V) was suspended with stirring in a solution of geraniol (7.70 g, 0.05 mol) in 50 mL of benzene, and 24 g of a solution containing 6.75 g (0.075 mol) of dry tert-butylhydroperoxide in benzene was added dropwise over a period of 4 h. The temperature during this period increased from 23° to 28°C. The reaction mixture was allowed to stand overnight, the solid chelate was removed by filtration, and a solution of 16.7 g (0.163 mol) of acetic anhydride and 13.4 g (0.17 mol) of pyridine was added, keeping the temperature below 30°C. After standing for 24 h, the reaction mixture was poured onto ice, the benzene layer was separated and washed successively with 1% HCl, dilute NaHSO<sub>3</sub>, dilute NaHCO<sub>3</sub>, and saturated NaCl. The benzene solution was dried and the benzene allowed to evaporate at room temperature. The product was distilled (bp 74–80°C at 0.03 mm) to yield 6.9 g (65.1%) of a colorless liquid: IR (neat) 1738, 1228, 1034, and 878 cm<sup>-1</sup>; <sup>1</sup>H NMR (CCl<sub>4</sub>) δ 1.30 (s, 3 H), 1.57 (t, 2 H, *J* = 6 Hz), 1.64 (s, 3 H), 1.75 (s, 3 H), 2.00 (t, 2 H, *J* = 6 Hz), 2.07 (s, 3 H), 2.87 (t, 1 H, *J* = 5 Hz), 4.12 (t, 2 H, *J* = 5 Hz), 5.13 (t, 1 H, *J* = 6 Hz).

The VO<sup>2+</sup> PVBA chelate which was recovered contained 9.99% V and gave an IR spectrum which was identical to that of the original sample. This catalyst was reused in the same manner described above with the same result. The VO<sup>2+</sup>

chelate which was recovered from this second run contained 10.09% V. The IR spectrum of this recovered chelate was again unchanged.

## RESULTS AND DISCUSSION

VBA was polymerized and copolymerized with acrylamide and maleic anhydride by a variety of methods using free radical initiators (Table I). Prolonged heating of a solution of VBA in ethyl acetate with 1.5 wt % AIBN resulted in a low-molecular-weight polymer as judged by its low solution viscosity in THF. This polymer was also soluble in DMF, dioxane, and chloroform. Polymerization of VBA in ethanol gave a product which did not dissolve in THF but formed very highly swollen gels which could be easily dispersed throughout a large volume of this solvent, thus facilitating its use in the preparation of chelates. VBA was also polymerized in emulsion to yield a soluble polymer containing only a small amount of gel. This polymer was initially purified by reprecipitation from a THF solution. However, on storage in air at room temperature for a few days, this polymer became loosely crosslinked and would no longer dissolve in THF but formed highly swollen gels in this solvent.

PVBA did not swell in water and was stable in dilute acid solutions at room temperature. Nongelled PVBA was soluble in dilute sodium hydroxide, and on warming the acetyl groups were cleaved, yielding a polymer having an infrared spectrum very similar to that of an authentic sample of poly(vinylacetophenone). Gelled samples gave similar results except that the resulting poly(vinylacetophenone) was also crosslinked.

It is apparent that VBA tends to give loosely crosslinked polymers, even though the monomer was very carefully recrystallized and care was taken to avoid contamination by multivalent metal ions which could serve as crosslinking agents. The observation that the emulsion polymer was soluble when first prepared but became crosslinked on storage suggests a free radical oxidative coupling mechanism. The monomer behaves as though it has a high chain transfer activity, and we believe that crosslinking may take place by free radical abstraction of

TABLE I  
Homopolymers and Copolymers of VBA

Mol % monomers in the charge	Polymerization conditions	% conversion	$[\eta]^a$ (dL/g)	Mol % comonomer in the copolymer
100 VBA	solution in ethyl acetate	97	0.157	— <sup>b</sup>
100 VBA	ethyl alcohol solvent-nonsolvent system	80	— <sup>c</sup>	— <sup>b</sup>
100 VBA	emulsion	87.8	1.26 <sup>d</sup>	— <sup>b</sup>
25 VBA				
75 Acrylamide	dioxane solvent-nonsolvent	71.0	— <sup>c</sup>	63.1 <sup>e</sup>
49.5 VBA				
50.5 Maleic anhydride	benzene nonsolvent	44.0 <sup>f</sup>	0.107 <sup>f</sup>	31.4 <sup>e,f</sup>

<sup>a</sup> Determined in THF at 25°C.

<sup>b</sup> Homopolymers.

<sup>c</sup> Polymer was completely crosslinked.

<sup>d</sup> Determined on the soluble polymer before gelation took place.

<sup>e</sup> Calculated from elemental analysis.

<sup>f</sup> Determined after hydrolysis to the corresponding maleic acid copolymer.

a methylene hydrogen between the two carbonyl groups followed by coupling of two of the resulting radicals. Cleavage of the acetyl group from the crosslinked polymer by base would not destroy this intermolecular bond, thus accounting for the observation that the poly(vinylacetophenone) which is formed in this case is also crosslinked. The copolymer of VBA with acrylamide was also crosslinked but did swell to some extent in water. The copolymer with maleic acid resulting from the hydrolysis of the VBA—maleic anhydride copolymer was soluble in THF, dioxane, and DMF, but it did not swell in water. It is interesting to note that, in both cases, the VBA entered the chain preferentially during the propagation step giving copolymers which contained a higher mol % of VBA than was contained in the monomer charge.

### Preparation and Properties of the Chelates of PVBA and VBA Copolymers

Some representative chelates of PVBA and VBA copolymers are listed in Table II. The  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{VO}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Eu}^{3+}$  chelates were all prepared from the swollen gels of PVBA in THF. Essentially the same results were obtained with either the polymer prepared in ethanol or that prepared in emulsion. It should be pointed out that the total capacity of PVBA would be 5.32 meq metal ion/g polymer, assuming that all of the  $\beta$ -diketone groups in the polymer were utilized in forming the chelate and no other ligands were involved. On this basis it can be seen that the  $\text{Cu}^{2+}$  and  $\text{VO}^{2+}$  chelates represent a very high utilization of the  $\beta$ -diketone groups.

The VBA—acrylamide copolymer swelled considerably in water, and chelates could be prepared from this copolymer directly from water solution. Likewise the VBA—maleic acid copolymer was soluble in dilute base, allowing chelates to be prepared from this copolymer in aqueous medium.

Several observations indicate that these products are chelates. Many of them contain a substantial amount of metal, approaching the theoretical chelate composition, as has been mentioned earlier. Incorporation of a transition metal ion into PVBA gives products which are very insoluble and nonswellable. This may be an inherent property of polymeric chelates of this type, but it may also indicate that some intermolecular crosslinking has occurred. All of these ma-

TABLE II  
Chelates of PVBA and VBA Copolymers

Polymer	Metal ion	Wt % metal ion in the chelate	Meq metal ion/g polymer	Method of preparation
PVBA	$\text{Cu}^{2+}$	13.55	4.93	THF $\text{Cu}(\text{OAc})_2$ (aq)
PVBA	$\text{Ni}^{2+}$	8.93	3.34	THF $\text{Cu}(\text{OAc})_2$ (aq)
PVBA	$\text{VO}^{2+}$	10.33	4.73	ligand exchange with $\text{VO}(\text{acac})_2$
PVBA	$\text{Co}^{2+}$	6.54	2.38	THF + $\text{Co}(\text{OAc})_2$ (aq)
PVBA	$\text{Eu}^{3+}$	9.82	2.16	THF + $\text{EuCl}_3$ + piperidine
VBA—acrylamide	$\text{Cu}^{2+}$	8.46	2.91	swollen gel in water + $\text{Cu}(\text{OAc})_2$ (aq)
VBA—maleic acid	$\text{Cu}^{2+}$	11.36	4.03	polymer was dissolved in dil. $\text{NH}_3$ (aq) + $\text{Cu}(\text{OAc})_2$ (aq)



terials (except the  $\text{Eu}^{3+}$  chelate) formed with transition metal ions were highly colored, and, in our preparative work, we came to rely on the intensity of color development as a qualitative measure of the extent of metal incorporation. The most convincing evidence, however, is the change in the IR spectrum which occurs when these polymers are converted to their metal ion containing derivatives. PVBA as well as the model compound, benzoylacetone, have a very strong absorption band at  $1608\text{ cm}^{-1}$  plus somewhat weaker absorption in the  $1300\text{--}1600\text{ cm}^{-1}$  region. On the other hand, the IR spectra of the chelates of these polymers as well as the spectrum of bis(1-phenyl-1,3-butanedionato) copper II lack the absorption at  $1608\text{ cm}^{-1}$  but have a least six very pronounced bands in the  $1400\text{--}1582\text{ cm}^{-1}$  region, giving the spectra of these chelates a completely different appearance from that of the starting material.

When these chelates are suspended in dilute mineral acids as much as 80–90% of the metal ion can be eluted. These eluted polymers must have a somewhat porous structure because they are capable of rechelating a substantial quantity of the metal ion from water solution. It should be emphasized that this behavior of the eluted polymers is in marked contrast to that of the solid PVBA which has never been chelated and which is a very ineffective chelating agent unless swollen by organic solvents. For example, solid samples of PVBA absorbed only very small amounts of  $\text{Cu}^{2+}$  (0.09 meq/g polymer) when suspended in a water solution of  $\text{Cu}(\text{OAc})_2$  for a prolonged period of time. Since the polymer does not swell in water, there is very limited contact between the two phases, and it is not surprising that very little chelation occurs under these conditions.

The observation that an eluted PVBA chelate would rechelate the metal ion which it had originally contained seemed to offer the possibility that PVBA could be conditioned to preferentially absorb this metal ion and exclude other ions. We elected to test this hypothesis by eluting the  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  chelates and determining their ability to reabsorb these ions. The eluted  $\text{Cu}^{2+}$  chelate did indeed preferentially absorb  $\text{Cu}^{2+}$  ions in batch experiments, but the eluted  $\text{Ni}^{2+}$  chelate absorbed either  $\text{Ni}^{2+}$  or  $\text{Cu}^{2+}$  ions depending on which solution it was placed in. In competitive experiments both the eluted  $\text{Cu}^{2+}$  chelate and the  $\text{Ni}^{2+}$  chelate preferentially absorbed  $\text{Cu}^{2+}$  ions with respect to  $\text{Ni}^{2+}$  ions, probably reflecting the greater stability of the  $\text{Cu}^{2+}$  complex. Thus preferential  $\text{Cu}^{2+}$  absorption is a chemical property of the polymer and not a "conditioning" effect.

### **Epoxidation of Allyl Alcohols Catalyzed by the $\text{VO}^{2+}$ Chelate of PVBA**

Polymer-bound catalysts<sup>5</sup> have advantages over homogeneous catalysts in that they can be easily recovered by simple filtration and reused providing they are not destroyed under the reaction conditions employed. Many such polymer supported catalysts have been studied for hydrogenation or hydroformylation reactions,<sup>6</sup> but very few such catalysts have been proposed for oxidation reactions because many of them are sensitive to oxidation.<sup>7</sup>

We have found that the reaction of tert-butylhydroperoxide with the allylic alcohol, geraniol, is catalyzed by the  $\text{VO}^{2+}$  PVBA chelate and that the chelate can be recovered unchanged and reused. The turnover number (mol product/mol V present-h) is only about  $2\text{ h}^{-1}$ , which may indicate that, because of the nonswellability of the chelate in the reaction mixture, only those  $\text{VO}^{2+}$  chelate

sites on the outside of the particles are effective as catalysts. The product of this reaction followed by acylation was identical to that obtained by a similar reaction catalyzed by  $\text{VO}(\text{acac})_2$ , which has previously been identified by Sharpless and Michaelson<sup>3</sup> as consisting of 98% 2,3-epoxygeranyl acetate and 2% of its isomer, 6,7-epoxygeranyl acetate.

We are grateful for support of this work from the Physical Sciences Research Budget and a grant from the Faculty Committee on Scholarship and Research of Western New England College.

### References

1. (a) P. Teyssie and G. Smets, *Macromol. Chem.*, **26**, 245–51 (1958); (b) A. R. Despic and Dj. Kosanovic, *ibid.*, **29**, 151–5 (1959); (c) G. K. Hoesele, J. B. Andelman, and H. P. Gregor, *J. Phys. Chem.*, **62**, 1239–44 (1958); (d) M. T. Teyssie and P. Teyssie, *J. Polym. Sci.*, **50**, 253–64 (1961); (e) R. C. Degeiso, L. G. Donaruma, and E. A. Tomic, *J. Appl. Polym. Sci.*, **7**, 1515–21 (1963); (f) T. R. Norton, U.S. Pat. 3,362,935 (1968).
2. J. Charette and P. Teyssie, *Spectrochim. Acta*, **16**, 689–95 (1961).
3. J. Charette, G. Neirynch, and P. Teyssie, *J. Phys. Chem.*, **65**, 735–9 (1961).
4. G. Baddeley, E. Wrench, and R. Williamson, *J. Chem. Soc.*, **1953**, 2114–5 (1953).
5. (a) Y. Chauvin, D. Commereuc, and F. Dawans, *Prog. Polym. Sci.*, **5**, 95–226 (1977); (b) C. U. Pittman, Jr., in *Polymer-Supported Reactions in Organic Chemistry*, P. Hodge and D. C. Sherrington, Eds., Wiley, New York, 1980, Chap. 5.
6. R. H. Grubbs, *Chemtech*, **7**, 512 (1977).
7. N. L. Holy, *Chemtech*, **10**, 366–71 (1980).
8. K. B. Sharpless and R. C. Michaelson, *J. Am. Chem. Soc.*, **95**, 6136–7 (1973).

Received February 27, 1981

Accepted September 3, 1981