

# New Monomers and Polymers Derived from $\alpha$ -Hydroxymethyl Methyl Vinyl Ketone

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**ABSTRACT:** 2-Hydroxymethyl-*but*-1-ene-3-one [ $\alpha$ -hydroxymethyl methyl vinyl ketone (HMKV)] was synthesized from methyl vinyl ketone using paraformaldehyde and a tertiary amine catalyst. Free-radical polymerization of this monomer created transparent, tough polymers that were insoluble in organic solvents. HMKV was converted to trimethylsilyl, acetate, and chloride derivatives. When the hydroxyl group was thus protected or removed, all these monomers could be free radically polymerized in bulk to make soluble polymers. The chlorination reaction is complicated by the formation of 1,1-bischloromethylacetone, which dehydrohalogenated unexpectedly to the desired  $\alpha$ -chloromethyl methyl vinyl ketone. HMKV will self-condense to an ether dimer in the presence of a catalytic acid. This reagent is capable of crosslinking many alkene monomers through hydrolytically stable ether bonds. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 509–516, 2000

**Key words:** difunctional alkene monomers; 1,6-dienes; crosslinking agents

## INTRODUCTION

In our continuing efforts to synthesize new free radically polymerizable alkene monomers with various functional groups on the  $\alpha$ -carbon,<sup>1,2</sup> we worked on numerous derivatives of methylvinyl ketone. Among these derivatives, the  $\alpha$ -hydroxymethyl derivative 2-hydroxymethyl-*but*-1-ene-3-one ( $\alpha$ -hydroxymethyl methyl vinyl ketone; HMKV) (**1**) is interesting because it is a substituted allyl alcohol and because reactions of its hydroxyl and carbonyl groups can lead to further derivatives. HMKV has been previously synthesized by Grimme through high-temperature pyrolysis of 1,1,1-tris(hydroxymethyl) acetone<sup>3</sup> and by Saito through hydroxymethylation of methyl vinyl ketone with formaldehyde and  $\text{Ph}_3\text{P}$  catalyst.<sup>4</sup> Both syntheses involve difficulties and low yields. Concurrently with our work was the re-

ported synthesis of HMKV using formaldehyde in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO).<sup>5</sup> The homopolymer of HMKV has been synthesized<sup>7</sup> but not well characterized. The patent literature contains one disclosure, in which the polymers of methyl and ethyl ethers (**3a**) were synthesized and reported to be partially soluble.<sup>7</sup> No copolymers of HMKV are known.

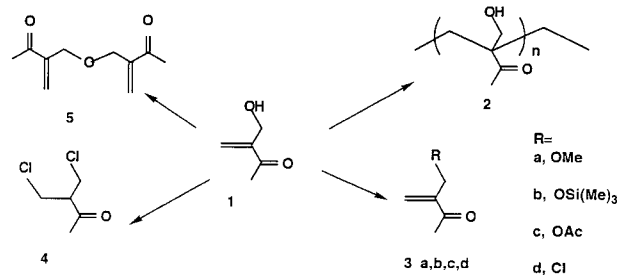
We report here an improved synthesis of HMKV (**1**) and its polymer (**2**); new monomers derived from HMKV by trimethyl silylation (**3b**), acetylation (**3c**), mono- and dichlorination (**3d** and **4**), and ether dimerization (**5**). These reactions are shown in Figure 1. We also report the synthesis and characterization of homo- and copolymers made from these new monomers and the use of the ether dimer as a crosslinking agent.

## EXPERIMENTAL

1,4-Diazabicyclo[2.2.2]octane (DABCO), paraformaldehyde, calcium chloride, pyridine, sodium

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**Figure 1** Reactions of HMVK.

sulfate, sodium carbonate, sodium bicarbonate, H<sub>2</sub>SO<sub>4</sub>, carbon tetrachloride, ether, chloroform, dimethyl sulfoxide, acetone, and diethyl ether were purchased from Merck. Thionyl chloride, triethyl amine, and styrene were obtained from Fluka, and trimethylsilyl chloride was received from Atabay. Petroleum ether was purchased from Baker; hydroquinone was received from Eastman Kodak Company; while p-toluenesulfonic acid, and benzoyl peroxide were purchased from Fischer Scientific Company and used as obtained. 2,2'-Azobisisobutyronitrile (AIBN) was received from BDH Chemicals, Ltd., and was crystallized from methanol before use. All <sup>1</sup>H-NMR spectra were run on a Varian T-60A NMR spectrometer operating at 60 MHz. All NMR data are reported as chemical shift  $\delta$  with respect to standard tetramethylsilane. All IR spectra were obtained by using KBr or NaCl windows on a Perkin-Elmer 1600 FTIR spectrometer.

### Synthesis of $\alpha$ -HMVK (1)

Paraformaldehyde (15.0 g, 0.5 mol), DABCO (5.6 g, 0.05 mol), and 35 mL diethylether were mixed and stirred, as freshly distilled methyl vinyl ketone (35.0 g, 0.5 mol) in 140 mL of diethylether was added over 16 h. After an additional 10 h of stirring at room temperature, the reaction mixture was filtered to remove insoluble by-products and unreacted paraformaldehyde. HCl gas was passed through the reaction mixture to convert DABCO to its ammonium salt, which was removed by filtration. The diethylether was evaporated. Crude product was distilled under vacuum in the presence of 1% hydroquinone, and HMVK was collected at 75°C at 4 mm Hg (yield 28–30%). <sup>1</sup>H-NMR (CCl<sub>4</sub>)  $\delta$ : 2.3 (s, 3H, CH<sub>3</sub>CO); 4.16 (s, 2H, CH<sub>2</sub>—O); 6.0 (s, 2H, CH<sub>2</sub>=C).

IR (NaCl): 3473 cm<sup>-1</sup> (OH); 2973 cm<sup>-1</sup> (C—H); 1682 cm<sup>-1</sup> (C=O), 1646 cm<sup>-1</sup> (C=C).

### Synthesis of Poly(HMVK) (2)

After purging with nitrogen, HMVK (0.5 g, 0.005 mol) was polymerized in bulk at 60°C with 2% AIBN (0.01 g, 6.1 × 10<sup>-5</sup> mol) for 7 h. Poly(HMVK) was obtained as a clear, hard polymer and purified by triturating with chloroform and acetone. It was insoluble in all available organic solvents, such as dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide, CCl<sub>4</sub>, CHCl<sub>3</sub>, tetrahydrofuran (THF), 1,4-dioxane, 2-propanol, ethyl alcohol, methyl alcohol, acetone, ethylacetate, petroleum ether, and isooctanol.

IR (KBr): 3474 cm<sup>-1</sup> (O—H); 2894 cm<sup>-1</sup> (C—H); 1710 cm<sup>-1</sup> (C=O).

### Synthesis of $\alpha$ -Trimethylsilyloxymethyl Methyl Vinyl Ketone (3b)

HMVK (0.5 g, 0.005 mol) was dissolved in 10 mL of dry CCl<sub>4</sub>; Et<sub>3</sub>N (0.7 g, 0.007 mol) was added followed by dropwise addition of (CH<sub>3</sub>)<sub>3</sub>SiCl (0.7 g, 0.007 mol) with rapid stirring at 0°C. When HCl evolution ended (15 min), triethylammonium chloride salt was separated by filtering. After evaporation of excess Et<sub>3</sub>N, excess (CH<sub>3</sub>)<sub>3</sub>SiCl, and CCl<sub>4</sub>, the trimethylsilyloxy derivative was purified by vacuum distillation at 98°C at 3 mm Hg (yield 80%).

<sup>1</sup>H-NMR (CCl<sub>4</sub>)  $\delta$ : 0.1 [s, 9H, (CH<sub>3</sub>)<sub>3</sub>Si]; 2.22 (s, 3H, CH<sub>3</sub>CO); 4.15 (s, 2H, CH<sub>2</sub>—O); 5.92 (s, 2H, CH<sub>2</sub>=C).

IR (NaCl): 2959 cm<sup>-1</sup> and 2893 cm<sup>-1</sup> (C—H); 1678 cm<sup>-1</sup> (C=O); 1389 cm<sup>-1</sup> (Si—(CH<sub>3</sub>)<sub>3</sub>); 1252 cm<sup>-1</sup> (Si—(CH<sub>3</sub>)<sub>3</sub>); 1088 cm<sup>-1</sup> and 1056 cm<sup>-1</sup> (Si—O—C); 869 cm<sup>-1</sup> and 844 cm<sup>-1</sup> (Si—C).

### Polymerization of $\alpha$ -Trimethylsilyloxymethyl Methyl Vinyl Ketone

After purging with nitrogen, the ketone (0.5 g, 2.9 × 10<sup>-3</sup> mol) was bulk-polymerized with 2% AIBN (0.01 g, 6.1 × 10<sup>-5</sup> mol) by heating at 65°C for 6 h. The product was obtained as clear, rigid polymer and was purified by reprecipitating from 1 mL of CHCl<sub>3</sub> into 3 mL of CCl<sub>4</sub>.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>)  $\delta$ : 0.1 [s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>]; 1.5 (broad, 2H, CH<sub>2</sub>—C); 2.35 (broad s, 3H, CH<sub>3</sub>CO); 4.0 (broad s, 2H, CH<sub>2</sub>—O).

### Synthesis of $\alpha$ -Acetoxymethyl Methyl Vinyl Ketone (3c)

To HMVK (0.2 g, 0.002 mol) and pyridine (0.3 g, 0.004 mol) in 3 mL of CCl<sub>4</sub>, acetyl chloride (0.4 g, 0.005 mol) was added dropwise with stirring at

0°C. After 30 min of additional stirring, the white pyridinium hydrochloride salt was separated by filtering. Excess acetylchloride was evaporated under vacuum at room temperature. Crude product was further purified by vacuum distillation in the presence of hydroquinone. Pure  $\alpha$ -acetoxymethyl methyl vinyl ketone was obtained as a colorless liquid by distilling at 65°C and at 4 mm Hg (crude yield quantitative).

$^1\text{H-NMR}$  ( $\text{CCl}_4$ )  $\delta$ : 2.07 (s, 3H,  $\text{CH}_3\text{COO}$ ); 2.33 (s, 3H,  $\text{CH}_3\text{CO}$ ); 4.7 (s, 2H,  $\text{CH}_2\text{—O}$ ); 5.92 and 6.1 (s, s, 2H,  $\text{CH}_2\text{=C}$ ).

IR (NaCl): No hydroxyl group absorption was detected at 3300–3600  $\text{cm}^{-1}$ ; 2924  $\text{cm}^{-1}$  (C—H); 1743  $\text{cm}^{-1}$  (C=O for ester); 1678  $\text{cm}^{-1}$  (C=O for ketone); 1230  $\text{cm}^{-1}$  and 1047  $\text{cm}^{-1}$  (C—O acetate); 1632  $\text{cm}^{-1}$  (C=C).

### Synthesis of Poly( $\alpha$ -Acetoxymethyl Methyl Vinyl Ketone)

After purging with nitrogen, HMVK acetate ester (0.2 g, 0.0014 mol) was bulk-polymerized at 60°C with 2% AIBN (0.004 g,  $2.43 \times 10^{-5}$  mol) for 16 h to make poly( $\alpha$ -acetoxymethyl methyl vinyl ketone). A clear, light yellow solid polymer was obtained that is soluble in chloroform.

### Synthesis of HMVK–Styrene Copolymer

Copolymerization of HMVK (0.1264 g,  $1.26 \times 10^{-3}$  mol) with styrene (0.22 g,  $2.1 \times 10^{-3}$  mol) was performed at 60°C in bulk using 2% AIBN (0.0067 g,  $4.1 \times 10^{-5}$  mol) after purging with  $\text{N}_2$ . The copolymer 7 obtained was insoluble in toluene (in which polystyrene is soluble) and was purified by triturating with toluene. The IR spectrum is essentially similar to that of polystyrene except for the presence of hydroxyl absorption.

IR (KBr): 3441  $\text{cm}^{-1}$  (O—H); 1697  $\text{cm}^{-1}$  (C=O); 675–900  $\text{cm}^{-1}$  (C—H aromatic ring); 1000–1300  $\text{cm}^{-1}$  (C—H aromatic ring); 1585–1600  $\text{cm}^{-1}$  and 1400–1500  $\text{cm}^{-1}$  (C=C) aromatic ring.

### Synthesis of $\alpha$ -HMVK Ether (5)

HMVK (0.5 g, 0.005 mol) and 1% *p*-toluene sulfonic acid (0.005 g,  $2.62 \times 10^{-5}$  mol) were heated at 60°C for 2 h. The product was dissolved in 10 mL of  $\text{CCl}_4$  and extracted with 2.5% aqueous  $\text{Na}_2\text{CO}_3$  (pH = 10) to remove *p*-toluene sulfonic acid. The  $\text{CCl}_4$  layer was dried with  $\text{CaCl}_2$  for 1 h, filtered, and evaporated. HMVK ether was purified by vacuum distillation at 110°C and 3 mm Hg

in the presence of 1% hydroquinone as polymerization inhibitor (yield 65%).

$^1\text{H-NMR}$  ( $\text{CCl}_4$ )  $\delta$ : 2.23 (s, 3H,  $\text{CH}_3\text{CO}$ ); 4.1 (s, 2H,  $\text{CH}_2\text{—Cl}$ ); 5.93 (s, 2H,  $\text{CH}_2\text{=C}$ ).

IR(NaCl): No hydroxyl group absorption was detected at 3300–3600  $\text{cm}^{-1}$ ; 2885  $\text{cm}^{-1}$  (C—H); 1677  $\text{cm}^{-1}$  (C=O); 1106  $\text{cm}^{-1}$  and 1057  $\text{cm}^{-1}$  (C—O—C).

### Polymerization of HMVK Ether

HMVK ether (0.15 g,  $7.58 \times 10^{-4}$  mol) was polymerized in bulk with 2% (AIBN) (0.003 g,  $1.82 \times 10^{-5}$  mol) at 60°C after purging with nitrogen. Poly-HMVK ether was obtained as transparent, clear, and extremely tough polymer and purified by triturating with chloroform. It was insoluble in all available organic solvents.

IR (KBr): 2944  $\text{cm}^{-1}$  and 2889  $\text{cm}^{-1}$  (C—H), 1699  $\text{cm}^{-1}$  (C=O), 1106  $\text{cm}^{-1}$  (C—O—C).

### Synthesis of HMVK Ether–Crosslinked Polystyrene

Copolymerization of HMVK ether (0.0184 g,  $1 \times 10^{-4}$  mol) with styrene (0.5 g,  $4.8 \times 10^{-3}$  mol) was done at 60°C in bulk using 1% AIBN ( $5.3 \times 10^{-3}$  g,  $3.23 \times 10^{-4}$  mol) after purging with  $\text{N}_2$ . The copolymer obtained was swollen but insoluble in toluene, in which polystyrene is soluble.

### Synthesis of $\alpha$ -Chloromethyl Methyl Vinyl Ketone (3d)

Into HMVK (1 g, 0.01 mol) dissolved in 25 mL of  $\text{CCl}_4$ ,  $\text{SOCl}_2$  (1.2 g, 0.01 mol) was added dropwise at 0°C with rapid stirring. When HCl evolution ended, the reaction mixture was poured into 80 mL of 5% aqueous  $\text{NaHCO}_3$  and stirred for  $\frac{1}{2}$  h until  $\text{CO}_2$  evolution ceased. The  $\text{CCl}_4$  layer was separated and dried with  $\text{CaCl}_2$ , filtered, and evaporated to make  $\alpha$ -chloromethyl methyl vinyl ketone as a colorless liquid. This product has a pungent smell and is a lachrymator. The product was further purified by vacuum distillation at 66°C at 4 mm Hg in the presence of 1% hydroquinone as polymerization inhibitor (yield 40%).

$^1\text{H-NMR}$  (DMSO)  $\delta$ : 2.33 (s, 3H,  $\text{CH}_3\text{CO}$ ); 4.29 (s, 2H,  $\text{CH}_2\text{—Cl}$ ); 6.25 and 6.35 (s, s, 2H,  $\text{CH}_2\text{=C}$ ).

IR (NaCl): No hydroxyl group absorption was detected at 3300–3600  $\text{cm}^{-1}$ ; 2929  $\text{cm}^{-1}$  (C—H); 1679  $\text{cm}^{-1}$  (C=O); 946–1304  $\text{cm}^{-1}$  ( $\text{CH}_2\text{Cl}$ ); 768  $\text{cm}^{-1}$  (C—Cl).

### Synthesis of Poly( $\alpha$ -chloromethyl methyl vinyl ketone)

$\alpha$ -Chloromethyl methyl vinyl ketone (0.6 g, 0.005 mol) and benzoyl peroxide (0.06 g,  $3.6 \times 10^{-4}$  mol)

were purged with N<sub>2</sub> gas and polymerized at 70°C for 48 h. The crude product was dissolved in 1 mL of CHCl<sub>3</sub> and precipitated into 3 mL of CCl<sub>4</sub>. The precipitate was separated by centrifuging and vacuum-dried. The product was soluble in chloroform and acetone but insoluble in carbon tetrachloride.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ: 2.31 (broad s, 3H, CH<sub>3</sub>CO); 3.76 (broad s, 2H, CH<sub>2</sub>-Cl); 1.63 (broad, 2H, CH<sub>2</sub>C).

IR (KBr): 3019 cm<sup>-1</sup> (C-H); 1732 cm<sup>-1</sup> (C=O); 1037–1472 cm<sup>-1</sup> (CH<sub>2</sub>Cl); 759 cm<sup>-1</sup> (C-Cl).

#### Synthesis of 1,1-Bischloromethyl Acetone from HMVK (4)

Into HMVK (1 g, 0.01 mol), SOCl<sub>2</sub> (1.2 g, 0.01 mol) was added dropwise at 0°C in 15 min, and the mixture was stirred for 30 min at room temperature. The product was dissolved in 10 mL of CCl<sub>4</sub> and poured into 50 mL of 5% aqueous NaHCO<sub>3</sub> and stirred for  $\frac{1}{2}$  h until CO<sub>2</sub> evolution ceased. The mixture was extracted with an additional 50 mL of CCl<sub>4</sub> and dried with CaCl<sub>2</sub>. After filtration, CCl<sub>4</sub> was evaporated, and yellow-colored 1,1-bischloromethyl acetone was obtained (crude yield quantitative).

<sup>1</sup>H-NMR (d<sub>6</sub> acetone) δ: 2.25 (s, 3H, CH<sub>3</sub>CO); 3.21 (m, 1H, C-H); 3.9 (d, 4H, CH<sub>2</sub>-Cl).

IR (NaCl): No hydroxyl group absorption was detected at 3300–3600 cm<sup>-1</sup>; 1741 cm<sup>-1</sup> (C=O); 1241 cm<sup>-1</sup> and 926 cm<sup>-1</sup> (CH<sub>2</sub>Cl); 731 cm<sup>-1</sup> (C-Cl).

#### Dehydrohalogenation of 1,1-Bischloromethyl Acetone

1,1-Bischloromethylacetone and excess DMSO were reacted with stirring for  $\frac{1}{2}$  h at room temperature. Water, equal in volume to the DMSO, was added, and the lower liquid layer was separated. The product was purified by vacuum distillation at 66°C at 4 mm Hg in the presence of hydroquinone (yield 98%).

<sup>1</sup>H-NMR (DMSO) δ: 2.33 (s, 3H, CH<sub>3</sub>CO); 4.29 (s, 2H, CH<sub>2</sub>-Cl); 6.25 and 6.35 (s, s, 2H, CH<sub>2</sub>=C).

IR (NaCl): No hydroxyl group absorption was detected at 3300–3600 cm<sup>-1</sup>; 2929 cm<sup>-1</sup> (C-H); 1679 cm<sup>-1</sup> (C=O); 946–1304 cm<sup>-1</sup> (CH<sub>2</sub>Cl); 768 cm<sup>-1</sup> (C-Cl).

## RESULTS AND DISCUSSION

Hydroxymethylation of activated double bonds with formaldehyde in the presence of the highly nucleophilic tertiary amine 1,4-diazabicyclo[2.2.2]octane

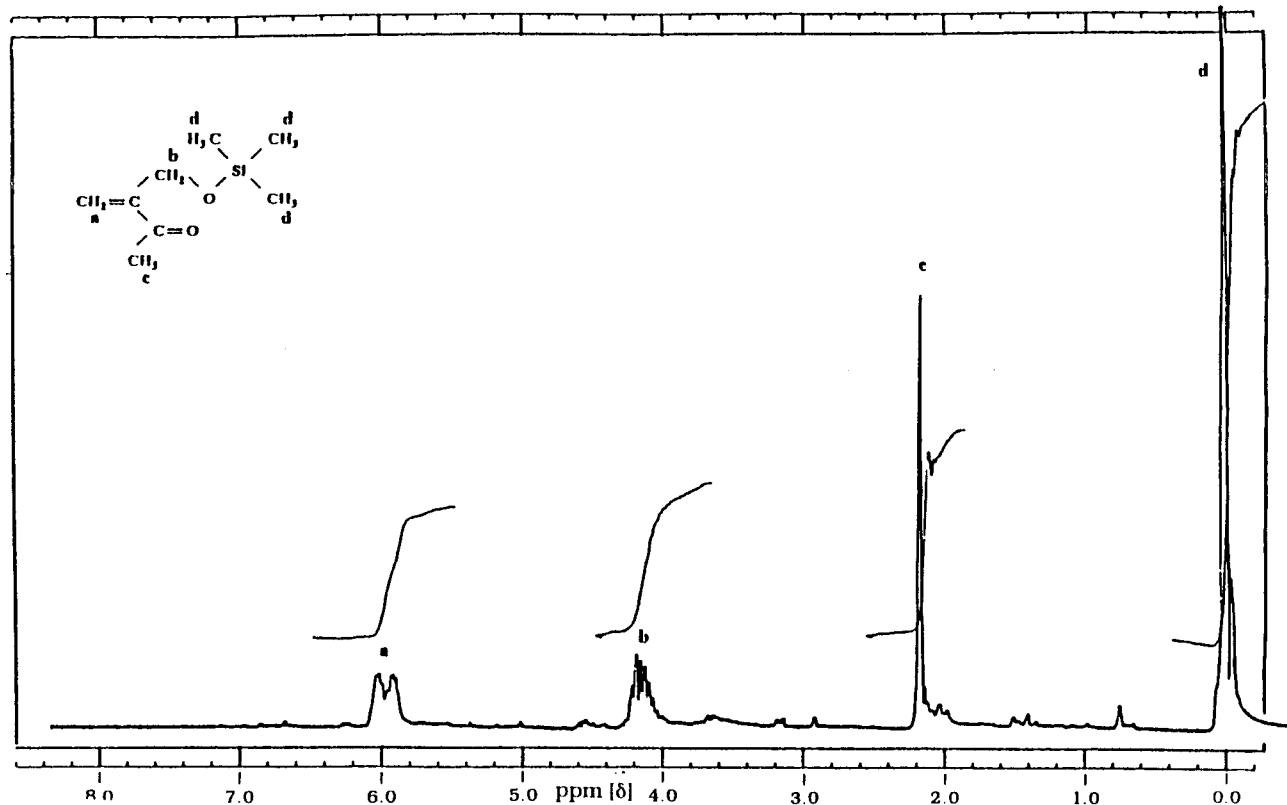
(DABCO) is well known.<sup>8,9,10</sup> It's been suggested that the reaction mechanism<sup>11</sup> is an initial Michael attack on the β-carbon by the tertiary amine, followed by attack of the newly formed anion on formaldehyde. Proton transfer and Hoffmann elimination regenerates the double bond. This is a unique and useful reaction of activated alkenes that is capable of substituting a carbon for a vinyl hydrogen. Ph<sub>3</sub>P probably behaves similarly as a catalyst. When the activated double bond is an acrylate, the reaction can be run with many different aldehydes and is referred to as the Baylis–Hillman reaction.<sup>12</sup> In our hands the reaction of methyl vinyl ketone with paraformaldehyde in ether solution in the presence of DABCO followed by an aqueous acid workup gave a 30% yield of HMVK. The IR and <sup>1</sup>H-NMR spectra were as expected.

Free-radical polymerization of HMVK in bulk initiated with 2,2'-azobisisobutyronitrile (AIBN) is very fast and makes insoluble transparent polymers. The known inability of allyl alcohol to give high molecular weight polymers is changed dramatically by the presence of the carbonyl group. In fact, very pure samples of this monomer will polymerize spontaneously at 4°C. Failure to remove all traces of the DABCO catalyst will also polymerize the monomer rapidly. The IR spectrum of poly-HMVK shows the disappearance of C=C stretching at 1630 cm<sup>-1</sup> and a shift in the carbonyl absorption from 1680 to 1725 cm<sup>-1</sup> due to loss of conjugation; otherwise, the spectrum is remarkably similar to that of the monomer.

The insolubility of the polymer raises a question: Is the polymer insoluble due to strong hydrogen bonding or is it due to an unexpected crosslinking reaction? Removing the hydroxyl hydrogen by converting HMVK to trimethylsilyl ether was an obvious experiment; reaction with trimethylchlorosilane in a dry medium went smoothly, giving the silyl ether **3b** quantitatively.

The <sup>1</sup>H-NMR spectrum in Figure 2 shows the presence of a number of trimethylsilyl CH<sub>3</sub> at 0.1 δ and the intact alkene protons at 6.0 δ. Polymerization of the silylether with AIBN gave a transparent polymer that was readily soluble in chloroform, suggesting that hydrogen bonding may be the essential reason for the insolubility of poly-HMVK.

In a similar experiment, HMVK was acetylated to give acetoxymethyl methyl vinyl ketone (**3c**) by treating (**1**) with acetyl chloride in the presence of pyridine at 0°C. The product was a colorless liquid that boiled at 65°C at 4 mm Hg and was obtained in quantitative yield. The IR spectrum of



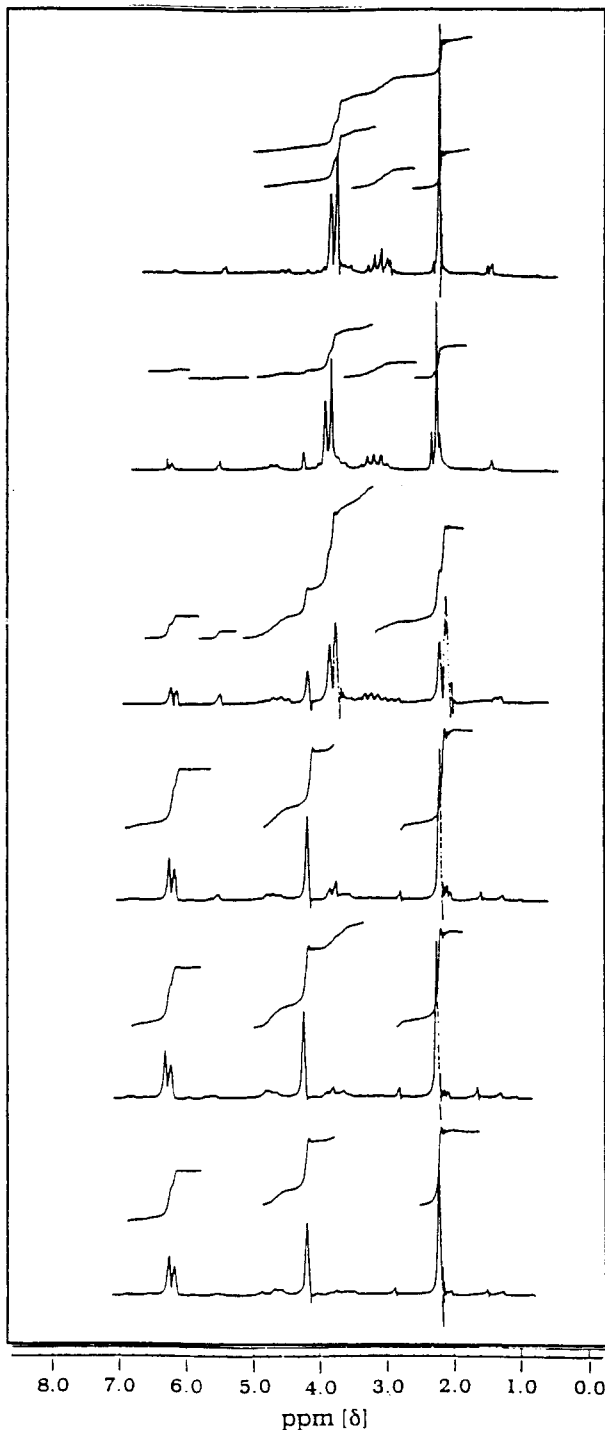
**Figure 2**  $^1\text{H-NMR}$  spectrum of  $\alpha$ -trimethylsilyloxymethyl methyl vinyl ketone (**3b**) in  $\text{CCl}_4$ .

**3c** shows the appearance of a second carbonyl and the disappearance of hydroxyl absorptions. The  $^1\text{H-NMR}$  is also consistent with the structure. Homopolymerization of the acetate **3c** with AIBN was slow and gave a chloroform-soluble colorless polymer.

Chlorination of HMVK with thionyl chloride at  $0^\circ\text{C}$  gave the unexpected dichloride (**4**) when the reaction was run without solvent. Apparently by-product HCl of the halogenation reaction hydrohalogenates the double bond in a secondary reaction. Attempts to remove the HCl in the presence of pyridine gave an uncontrollably vigorous reaction, and the double bond could not be kept intact. The behavior of the dichloride **4** was interesting: when dissolved in dimethylsulfoxide (DMSO), spontaneous dehydrohalogenation took place at room temperature to make the monochloride **3d** quantitatively. Figure 3 gives the  $^1\text{H-NMR}$  spectrum of a sample in  $\text{DMSO-d}_6$ , clearly showing the disappearance of half of the chloromethyl protons and the appearance of the vinyl protons. The dehydroha-

logenation does not occur in any other solvent. We have proposed a mechanism for this reaction (Fig. 4) in which the DMSO's oxygen acts as a nucleophile to displace chlorine and to make a sulfonium salt. Elimination of the sulfonium-leaving group regenerates the double bond and the DMSO. Although the dichloride **4** could be converted to the monochloride, the desired monomer **3d**, we were interested in finding the right conditions for the formation of the monochloride directly. To this end, various solvents were tried, and it was found that running the thionyl chloride reaction in  $\text{CCl}_4$  without any tertiary amine catalyst cleanly made the desired monochloride. We believe that very low solubility of HCl and the difficulty of formation of a charge-separated transition state in this nonpolar solvent probably prevents secondary hydrohalogenation reactions.

The polymerization of the chloride **3d** was very troublesome. As an allyl chloride derivative, it is expected to show chain transfer reactions.<sup>13</sup> The presence of even trace amounts of



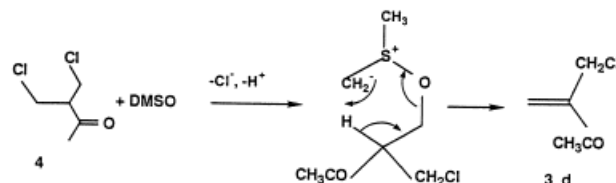
**Figure 3**  $^1\text{H-NMR}$  spectra showing the conversion of 1,1-bis(chloromethyl)acetone (**4**) to  $\alpha$ -chloromethyl methyl vinyl ketone (**3d**) in DMSO.

the dichloride would prevent polymerization, a fact that has been reported for the structurally similar ethyl  $\alpha$ -chloromethyl acrylate.<sup>14</sup> After

careful purification, the chloride **3d** could be bulk-polymerized at  $60^\circ\text{C}$  in the presence of benzoyl peroxide to make clear, hard polymer that is soluble in chloroform.

Gas chromatography of the crude reaction product of the DABCO-catalyzed hydroxymethylation of HMVK showed the presence of a compound that contained no hydroxyl groups and was water insoluble. Distillation of this fraction at  $110^\circ\text{C}$  at 3 mm Hg created a clear liquid that was identified as the ether dimer of HMVK, a new compound (**5**). NMR of the ether (**5**) (Fig. 5) indicates that the ether methylene protons are shifted about 0.1  $\delta$  units downfield compared to HMVK and that the hydroxyl proton is missing. The IR spectrum shows no hydroxyl absorption but a strong ether absorption appears at  $1080\text{ cm}^{-1}$ . Our previous experience with ethyl  $\alpha$ -hydroxymethyl acrylate (EHMA)<sup>15</sup> suggested that HMVK should be easily converted to its ether. In fact, a pure sample of HMVK treated with 1% *p*-toluenesulfonic acid at  $60^\circ\text{C}$  gave the ether (**5**) in quantities. The ease of this dehydration reaction is surprising. An ene-type mechanism has been suggested for a similar dehydration reaction of EHMA.<sup>16</sup> This mechanism involves a six-membered cyclic transition state with simultaneous transfer of a proton, loss of water, and ether bond formation, as shown in Figure 6. A study with deuterium-labeled EHMA proved this mechanism in the case of EHMA.<sup>17</sup> We believe that HMVK behaves similarly, but the etherification reaction goes even faster and at lower temperatures.

The ether (**5**) is a 1,6-diene and capable of acting as a crosslinking agent in free-radical polymerizations. The question of insolubility of poly-HMVK becomes complicated by some ether being formed during polymerization, rendering the polymer insoluble by crosslinking. That the silyl ether, the acetate, and the chloride made soluble polymers does not negate this argument. These



**Figure 4** Proposed reaction mechanism of dehydrohalogenation of 1,1-bis(chloromethyl)acetone (**4**) to  $\alpha$ -chloromethyl methyl vinyl ketone (**3d**) in DMSO.

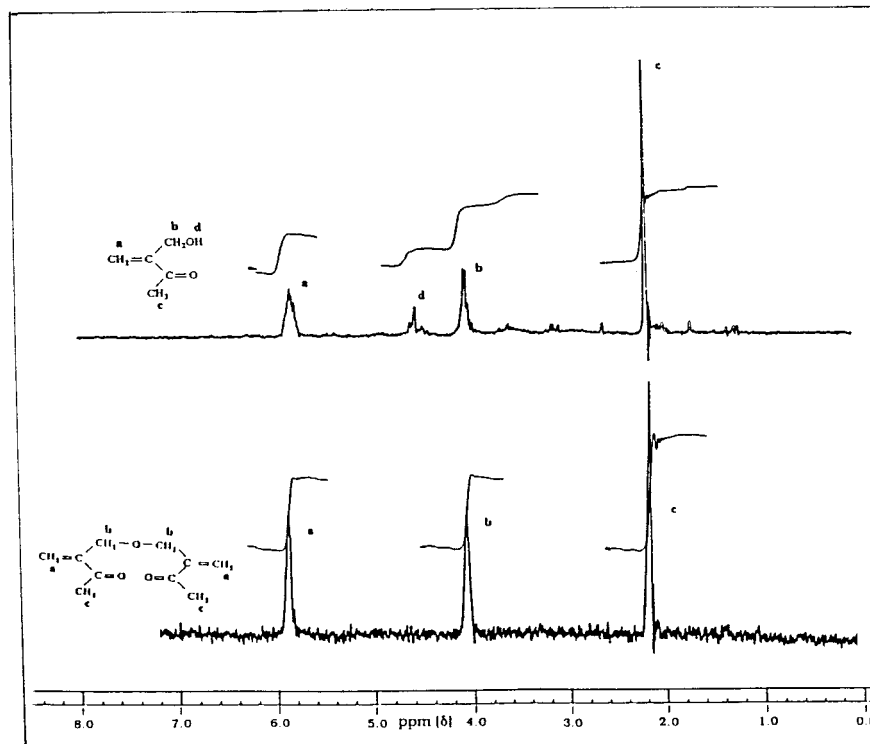


Figure 5  $^1\text{H-NMR}$  spectra of HMVK (1) and its ether (5).

derivatives not only do not show hydrogen bonding, but they are also incapable of dimer ether formation.

The homopolymer of ether (5) could be synthesized readily in bulk or in solution and, as expected, was insoluble. To test this compound's ability to crosslink other polymers, styrene, methyl acrylate, butyl acrylate, vinyl acetate, acrylonitrile, methacrylonitrile, and methyl methacrylate were radically polymerized in the presence of small amounts of the ether (5). The formation of the styrene copolymer is shown in Figure 7. In each case, a crosslinked polymer was obtained that swelled but did not dissolve in solvents that dissolve the parent, uncrosslinked polymer. For example, with polystyrene crosslinked

with a 20 : 1 weight ratio of the ether (5), the swelling behavior shown in Figure 8 was observed. Swelling reached a maximum at a  $V - V_0/V_0$  of 1.08 in toluene, clearly showing the effect of crosslinking.

Unlike a number of commercially used bis-acrylate crosslinking agents joined through ester groups, the crosslinking functionality in the ether (5) is a more hydrolytically stable ether group. This provides crosslinks that are resistant to hydrolysis as witnessed by the insolubility of crosslinked polystyrene upon prolonged heating in alkaline DMSO. In addition to its usefulness as a crosslinking agent, the ether (5) should be able to cyclopolymerize under appropriate conditions. This work is now in progress.

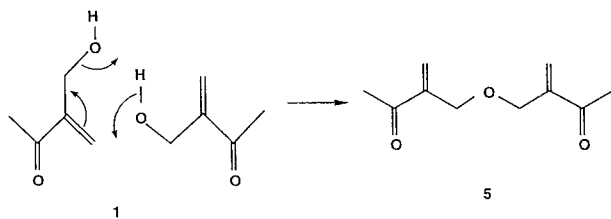


Figure 6 Proposed mechanism for the formation of ether (5) from HMVK (1).

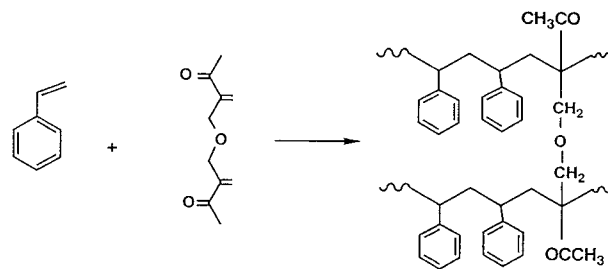
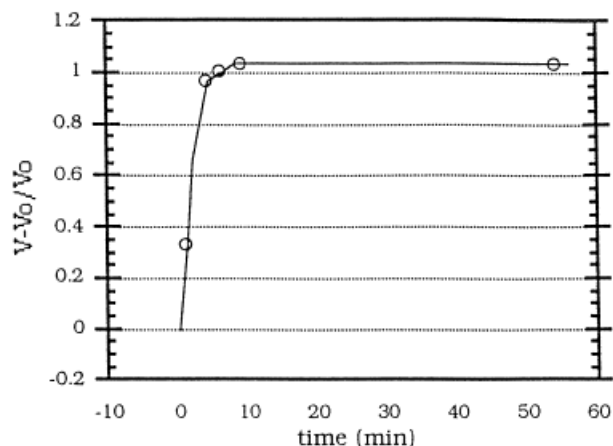


Figure 7 Polystyrene crosslinked with ether (5).



**Figure 8** Swelling behavior of *bis*-ether (5) crosslinked styrene in toluene.

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