may be possible to broaden the range of materials (copolyester composition) that will form mesogenic polymers: materials ruled out as candidates for liquid crystallinity at atmospheric pressures may be driven into ordered phases at elevated pressures. (Similarly, flow fields may also induce liquid crystallinity in isotropic polymer solutions.[18]) Moreover, as elevated pressures are routine during polymer processing no additional complications are required for practical application of these findings. For example, the evidence of a new pressure-induced crystalline phase could have significant potential technological importance in optical storage applications: refractive index changes are expected to parallel changes in density, and changes in the latter quantity might be achieved locally by initiating the transformation K2 → K1 via laser irradiation.

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Registry No. (HQ)(HBA)(IA) (copolymer), 112482-60-7.

References and Notes

(1) Chandrasekhar, S.; Ramaseshar, S.; Reshamwala, A. S.; Sadashiva, B. K.; Shashidhar, R.; Surendranath, V. *Proceedings of the International Liquid Crystal Conference*; Bangalor, Pramana. Suppl., 1975; Vol. 1, p 117.
(2) Chandrasekhar, S.; Shashidhar, R. *Adv. Liq. Cryst.* **1979**, *4*.
(3) Hiramatsu, N.; Karasz, F., private communications, 1985.
(4) Kiss, G. *J. Rheol. (N.Y.)* **1986**, *30*, 585–599.
(5) Hsiao, B. S.; Shaw, M. T.; Samulski, E. T. *Rev. Sci. Instrum.* **1987**, *58*, 1009; *SPE ANTEC Tech. Paper*, **1986**, *32*, 424.
(6) Hsiao, B. S. Ph.D. Thesis, The University of Connecticut, 1987.
(7) Jackson, W. J.; Kuhfuss, H. F. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2043.
(8) Joseph, E.; Wilkes, G. L.; Baird, D. G. *Polymer* **1985**, *26*, 703.
(9) Economy, J.; Storm, R. S.; Matkovich, V. I.; Cottis, S. G.; Nowak, B. E. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2207.
(10) Lieser, G. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1611.
(11) Economy, J.; Volksen, W.; Geiss, R. H. *Mol. Cryst. Liq. Cryst.* **1984**, *105*, 289.
(12) Gutierrez, G. A.; Chivers, R. A.; Blackwell, J.; Stamatoff, J. B.; Yoon, H. *Polymer* **1983**, *24*, 937.
(13) Chivers, R. A.; Blackwell, J.; Gutierrez, G. A. *Polymer* **1984**, *25*, 435.
(14) Chivers, R. A.; Blackwell, J. *Polymer* **1985**, *26*, 997.
(15) Chen, G.; Lenz, R. W. *Polymer* **1985**, *26*, 1307.
(16) George, E. R.; Porter, R. S. *Macromolecules* **1986**, *19*, 97.
(17) This number is extrapolated from η data of HIQ with different HBA compositions at 340 °C and 100 s^{-1} shear rate (see ref 4).
(18) Ciferri, A. In *Polymer Liquid Crystals*; Ciferri, A., Krigbaum, W. R., Meyer, R. E., Eds.; Academic: New York, 1982; p 63 and the references cited therein.

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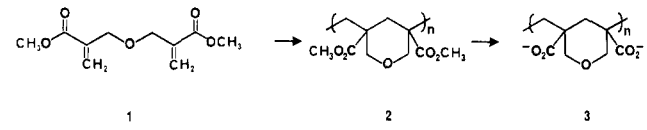
Cyclopolymerization of the Ether of Methyl α-(Hydroxymethyl)acrylate

We have elsewhere reported the synthesis, purification, and characterization of several ethers and acetals of methyl α-(hydroxymethyl)acrylate.[2] We have also reported their use as cross-linking agents in the polymerization of various vinyl monomers including hydrolysis of **1** to the dicarboxylate and its use in cross-linking water-soluble and water-dispersible monomers.[3] While bulk and solution polymerization of **1** generally leads to insoluble and highly cross-linked products,[2] we have discovered conditions leading to soluble polymer of structure **2**. We here report the synthesis and characterization of this new polymer and its partial hydrolysis to the water-soluble derivative **3**.



1 **2** **3**

Radical and photoinitiated bulk polymerization and radical solution polymerization of ether **1** in dimethyl sulfoxide gave only insoluble products. Anionic polymerization has so far been unsuccessful in tetrahydrofuran and toluene with *n*-butyllithium as initiator. However, when a 3% benzene solution of **1** was polymerized with 2,2′-azobis(isobutyronitrile) at 60 °C, polymer precipitated that was subsequently soluble in chloroform and methylene chloride. Reprecipitation into ether gave cyclopolymer **2** as a white powder having a melt/decomposition temperature of 270–275 °C. DSC confirmed the melting transition at 270 °C and also showed a strong glass transition temperature at 160 (onset) or 165 °C (midpoint). Intrinsic viscosity of this polymer was found to be 0.43 dL/g in $CHCl_3$ at 25 °C. Polymerization was also successful in acetone, although both acetone and benzene gave insoluble material along with the soluble fractions. Chloroform gave good conversion to soluble polymer with viscosities of 0.15–0.45 dL/g.

The IR spectrum of **2** showed two distinct carbonyl peaks centered at 1752 cm^{-1} possibly corresponding to cis and trans carboxymethyl groups on the six-membered ring repeat units.[4] Strong ether and ester bands were observed at 1150 and 1270 cm^{-1}, respectively. The ^1H NMR spectrum contained only broad, overlapping peaks consistent with the proposed structure. The ^{13}C NMR spectrum is given in Figure 1. Peak assignment is based on comparison to monomer and model polymers as well as on the fully coupled spectrum also shown. The carbonyl carbons show a multiplicity which may be due to tacticity and/or cis/trans ring substitution. No residual unsaturation due to pendent vinyl groups was observed in the IR and NMR spectra of reprecipitated samples.

Cyclopolymer **2** was hydrolyzed under heterogeneous conditions in a 1:1 mixture of methanol and water containing 5% NaOH at 65–75 °C overnight. Dissolution during reaction gave a viscous polymer solution which was then acidified to precipitate the poly(carboxylic acid) polymer. The precipitated polymer was subsequently soluble in aqueous base. The IR spectrum of this material showed strong, broad peaks at 3350 and 1770 cm^{-1} attributed to the free acid groups. ^{13}C NMR in dilute base (see the figure) showed a greatly reduced peak for the ester methyl carbon and two peaks for the carbonyl groups, corresponding to hydrolyzed (downfield) and unhydrolyzed ester units. The ratio of these latter two peaks was approximately 3:1 indicating ca. 75% hydrolysis. Further work is under way to increase this to 100% and to completely characterize these polymers.

Proposed structure **3** is similar in overall composition to that of the pyran copolymer **4** obtained from the 2:1 copolymerization of divinyl ether and maleic anhydride,[5]

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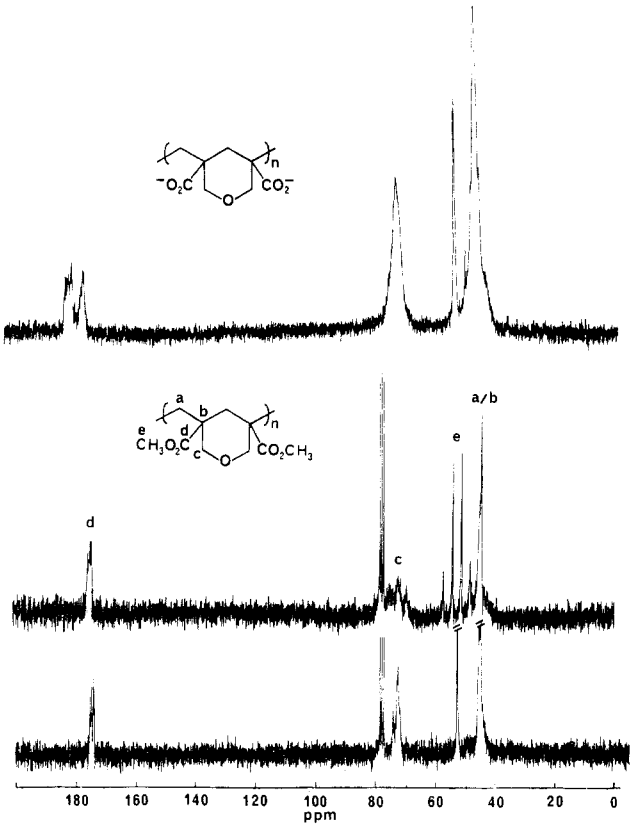
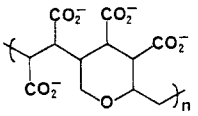
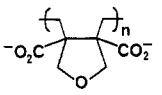


Figure 1. ^{13}C NMR spectra of cyclopolymer **2** proton decoupled (lower trace) and coupled (middle trace) in $CDCl_3$ and partially hydrolyzed polymer **3** proton decoupled in basic D_2O (upper trace).

although we have not ruled out possible formation of structure **5**. Selected molecular weight fractions of



4



5

polymer **4** have been found to exhibit high activity as antitumor and antimetastatic agents.[5-7] The major structural differences between **3** and **4** are that the former has two less carbons in the repeat unit and has two rather than four carboxylate groups per pyran unit. From a synthetic perspective, cyclopolymerization of a single monomer (i.e., **1**) offers several advantages over copolymerization involving three monomer units in each propagation step. Specifically, material balance is inherent, and the probability of obtaining well-defined molecular weight fractions with structural uniformity along the polymer backbone is greater. Further interest in polymer **3** centers on evaluating biological activity and synthesizing appropriate model compounds for confirmation of polymer repeat unit structure.

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References and Notes

(1) Permanent address: Department of Chemistry, Bogazici University, Istanbul, Turkey.
(2) Mathias, L. J.; Kusefoglu, S. H. *Macromolecules* **1987**, *20*, 2039.
(3) Mathias, L. J.; Kusefoglu, S. H. *J. Polym. Sci., Polym. Lett.* **1987**, *25*, 451.
(4) While we have postulated the six-membered ring repeat unit, it is also possible that five-membered rings are formed competatively or completely; this possibility will be examined spectroscopically with appropriate model compounds.
(5) Butler, G. B. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1982**, *C22*, 89.
(6) Shultz, R. M.; Altom, M. G. *J. Immunopharmacol.* **1983**, *5*, 277.
(7) Zaharko, S. D.; Covey, J. M. *Cancer Treat. Rep.* **1984**, *68*, 1255.

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