Polymer Bulletin 4, 629-633 (1981)

Polymer Bulletin

Synthesis and Oligomerization of Carbomethoxymaleic Anhydride

A New Trisubstituted Electrophilic Vinyl Monomer

H.K. Hall, Jr., James W. Rhoades, Pierre Nogues and G.K.C. Wai

Chemistry Department, University of Arizona, Tucson, Arizona 85721, USA

Abstract

Carbomethoxymaleic anhydride has been prepared from the reaction of tricarbomethoxyethylene and phosphoric anhydride. It oligomerized under free radical conditions, the first trisubstituted ethylene to do so under usual laboratory conditions.

Introduction

Trisubstituted olefins do not homopolymerize under usual laboratory conditions (HALL and DALY 1975). Steric crowding is generally accepted as the explanation for this reluctance. Propagation will be slow and the resulting homopolymer will be sterically congested, causing low ceiling temperatures.

These steric strains can be overcome at extremely high pressure (ANDERSON, HOOVER and VOGL 1979). Under ordinary laboratory conditions, steric effects might be minimized by confining two of the substituents into a ring. This is known to be effective among the 1,2-disubstituted olefins, where maleic anhydride and maleimide are much more reactive monomers than other 1,2-disubstituted monomers. The propagation rate should also be increased because the growing radical or anion can enjoy more extensive delocalization than in acyclic cases.

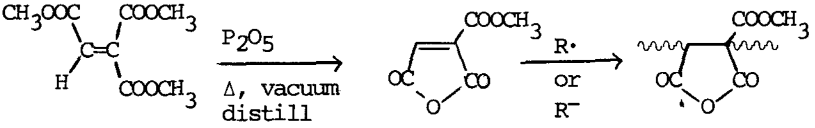
The literature did not provide an example of a maleic anhydride derivative carrying a single electron-attracting carbon function at the α-position. We have examined the synthesis and homopolymerization of α-carbomethoxymaleic anhydride, CMA.

Results

A variety of conventional synthesis methods failed to yield CMA. After CMA had been obtained and examined, it became evident that its high reactivity had caused it to react or oligomerize under conventional conditions.

0170-0839/81/0004/0629/$01.00

Successful synthesis was achieved by using phosphoric anhydride to demethoxylate - cyclize trimethyl ethylenetricarboxylate:



CMA poly-CMA

This procedure had been used (BOWMAN, CLOSIER and ISLIP, 1964) to make α-(trichloromethyl)maleic anhydride from dimethyl α-hydroxy-α-(trichloromethyl)succinate. The structure of CMA was fully confirmed by microanalysis, and by infrared, NMR, and mass spectrometry.

CMA oligomerized slowly but completely under free radical polymerization conditions. Molecular weights, determined by both vapor pressure osmometry and elemental analysis, were in the range 800 to 1200. This corresponds to an average of ca. five monomer units per molecule of initiator. Results are summarized in Table 1.

TABLE 1

Oligomerization of Carbomethoxymaleic Anhydride[a]

			Molecular Weight	
Weight CMA	Weight AIBN	η_{inh}[b]	by Vapor Pressure Osmometry	by End Group Analysis
0.3	0.061	--	990	--
0.3	0.025	--	1170	--
0.5	0.125	0.16	1010	820 ± 50[c]

[a] 70°C in 0.75 ml C_6D_6

[b] 50 mg in 10 ml of CH_3CN at 25°C

[c] Calcd. for $NC(CH_3)_2C-(C_6H_4O_5)_5$; C, 48.1; H, 3.1; N, 1.7. Found: C, 46.1; H, 2.6; N, 1.7.

The polymerizations were extremely slow and required high initiator concentrations. Varying the reactant concentrations showed the reaction is first order in monomer (Figure 1) and half order in initiator (Figure 2) as expected for free radical polymerization. The classic strategy of using less initiator to increase molecular weight fails here; halving the initiator concentration added exactly one monomer unit (entries 1 and 2, Table 1) to the average chain!

Anionic polymerization of CMA was accomplished by anhydrous potassium cyanide in dry tetrahydrofuran. The polymer, obtained in almost quantitative yield, possessed low molecular weight comparable to the free radical-initiated polymer.

Discussion

Carbomethoxymaleic anhyride, CMA, oligomerizes using either free radical or anionic initiators, the first trisubstituted vinyl monomer to do so under normal laboratory conditions. The strategy of confining two of the substituents into a ring reduced steric hindrance sufficiently to permit oligomerization. The rather slow free radical polymerization rate permits termination to compete with propagation. This slow propagation may be caused by the requirement for a very electrophilic radical to react with a very electrophilic monomer. This effect was observed in the free radical-initiated polymerization of methyl α-cyanoacrylate (BEVINGTON, JEMMETT and ONYON, 1976, 1977). In keeping with this thought, CMA proved to be highly reactive toward electron-rich vinyl monomers in cycloaddition and copolymerization reactions. These results will be reported separately.

Experimental

NMR Spectra were recorded on a Varian T60. IR spectra were obtained with a Perkin-Elmer 337 grating spectrophotometer. Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona. Vapor pressure osmometry measurements were made on a Hewlett Packard 302B vapor pressure osmometer at 37°C with acetonitrile. The double Diels-Alder adduct of CMA and 4-methoxystyrene was used as the standard.

Carbomethoxymaleic Anhydride. Tricarbomethoxyethylene (HALL, DALY, 1975), 10.1 g (0.05 mole) was mixed with 14.2 g (0.1 mole) P_2O_5 and heated at 160°C for 5 hours. The product was then distilled from the black mass (120° at 0.2 mm Hg), as a liquid which solidified upon cooling. Redistillation gave b.p. 80° (0.1 mm Hg). Recrystallization from diethyl ether gave pure anhydride in 60% yield. M.p. 37-38°. NMR ($CDCl_3$) δ3.85 (s, 3H), 7.35 (s, 1H). IR (NaCl, neat) 1840 and 1770 (anhydride), 1725 (ester) and 1640 (double bond). Mass spectrum (70 ev) 156 ($M\cdot^+$). Anal. Calcd. for $C_6H_4O_5$:C, 46.16; H, 2.59. Found: C, 46.09; H, 2.81.

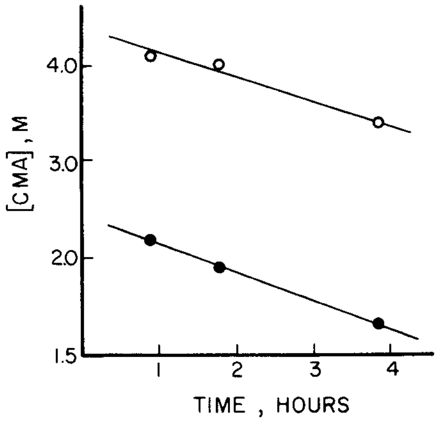


Fig. 1. Polymerization is First Order in CMA Concentration in Deuterobenzene at 70°C;

○ $(CMA)_o$ = 4.3M, $(AIBN)_o$ = 0.50

● $(CMA)_o$ = 2.15M, $(AIBN)_o$ = 0.50

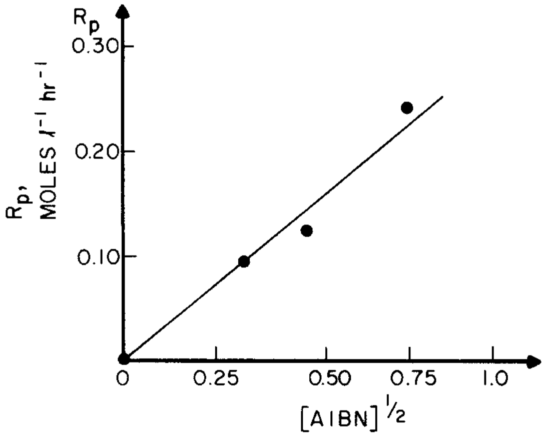


Fig. 2. Polymerization is One-Half Order in AIBN Concentration in Deuterobenzene at 70°C; $(CMA)_o$ = 4.3M.

CMA is hygroscopic; on standing in air it becomes a semi-solid insoluble gel. Initial reaction is the opening of the anhydride ring, with a second equivalent of water adding across the double bond.

CMA is soluble in chloroform, acetone, and benzene.

Polymerizations. In a typical reaction, AIBN and freshly distilled CMA were placed in an NMR tube purged with nitrogen. Benzene-d_6 (0.75 ml) was added by syringe and the tube sealed. Reactions were run at 70°C and were monitored by NMR. After five hours all vinyl protons had disappeared.

The polymer was precipitated in diethyl ether, and dried. Viscosity measurements were taken on 50 mg in acetonitrile using an Ubbelhohde viscosimeter at 25°.

Acknowledgement

The authors are indebted to the National Science Foundation, Polymers Program, Division of Materials Research, Grant No. DMR-78-09290 and to the U. S. Army Research Office, Grant No. DAAG 29-77-G-0231 for support. We also thank Crowder College, Neosho, MO for granting J. W. R. a sabbatical leave, Mr. R. C. Sentman for help with the manuscript, and Dr. W. Fischer for pointing out to us the work of Bowman et al.

References

ANDERSON, B. C., HOOVER, C. and VOGL, O.: Macromolecules 12, 222 (1976)

BEVINGTON, J.C., JEMMETT, J. A. L. and ONYON, P.F.: Europ. Polym. J. 255 (1976); Polymer 18, 73 (1977)

BOWMAN, R. E., CLOSIER, M. D. and ISLIP, P. J.: J. Chem. Soc. 3841 (1964)

HALL, H. K., JR. and DALY, R. C.: Macromolecules 8, 22 (1975)

Received May 15, 1981