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Studies in Cyclocopolymerization. VII. Copolymerization of Chloromaleic Anhydride with Divinyl Ether

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Studies in Cyclocopolymerization. VII. Copolymerization of Chloromaleic Anhydride with Divinyl Ether

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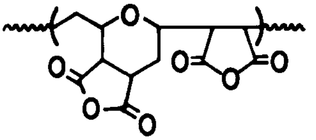
SUMMARY

Chloromaleic anhydride was found to copolymerize with divinyl ether to form soluble copolymers of 1:1 composition, devoid of residual unsaturation. A bicyclic structure is proposed in which the polymer backbone consists only of divinyl ether units. The ease with which the copolymers underwent dehydrohalogenation suggests that the hydrogen and chlorine atoms on the anhydride unit are in a trans configuration as a result of a stepwise cyclization process.

Oxidation of the hydrolyzed, dehydrohalogenated copolymers afforded the corresponding vic-diol copolymers. The absence of a significant decrease in copolymer molecular weight upon periodic acid cleavage of the vic-diol copolymers supported the proposed structure. Functional group analyses and softening points were in accord with the structures of the derived copolymers.

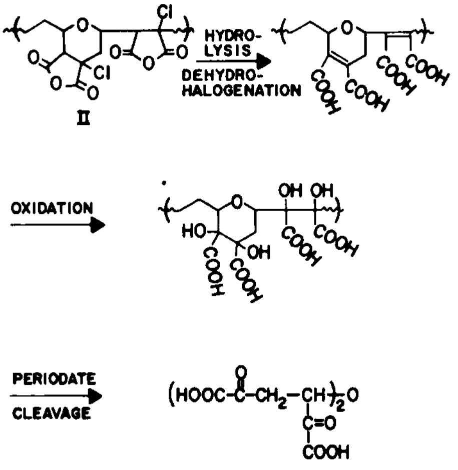
INTRODUCTION

The copolymerization of divinyl ether (DVE) with maleic anhydride (MA) to form regular cyclocopolymers of Structure I has been studied extensively in this laboratory [1]. This structure has been postulated to result from an alternating copolymerization of DVE-MA charge transfer complex with free MA, yielding copolymers of constant 1:2 composition regardless of monomer feed composition. The position of the proposed charge transfer complex on the reaction coordinate has not been determined however.



I

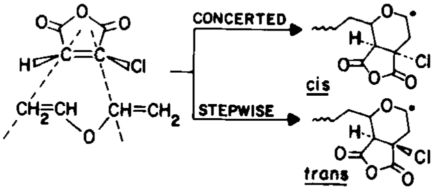
In an extension of these studies, we have investigated the copolymerization of chloromaleic anhydride (CMA) with DVE. Initially assuming that this system would copolymerize like the DVE-MA system, we proposed to apply the reaction scheme shown to obtain strong proof for the copolymer structure. If the copolymer consisted entirely of units of Structure II, then the sole product isolated should be the complex α-keto acid III.



III

The presence of additional products would give an indication of the extent of structural irregularities present. Thus for example, adjacent CMA units in the polymer backbone might be expected to yield glyoxylic acid.

Finally, it was hoped that studies of this system would provide additional information about the mechanism of cyclocopolymerization. Assuming the participation of a charge transfer complex in the polymerization, if σ-bond formation between the donor and acceptor portions occurs via a concerted process, one would expect the hydrogen and chlorine atoms on the CMA unit to be present in a cis configuration. On the other hand, if a stepwise process were involved, a trans structure might be predicted. The ease of dehydrohalogenation of the copolymers would be expected to indicate which structure is present, since trans eliminations are known to proceed much more readily [2].



RESULTS AND DISCUSSION

Spectroscopic studies indicated the presence of a DVE-CMA charge transfer complex in chloroform solution. DVE exhibits an absorption maximum at 220 mμ, $\epsilon = 5300\ M^{-1}cm^{-1}$. CMA exhibits two maxima, at 220 mμ, $\epsilon = 7200\ M^{-1}cm^{-1}$, and at 252 mμ, $\epsilon = 4600\ M^{-1}cm^{-1}$. Mixtures of the two monomers exhibited enhanced absorbance at 252 mμ. By varying the CMA:DVE ratio in mixtures, and by blanking out the inherent CMA absorbance by use of reference solutions of the same concentration, the stoichiometry of the complex was determined to be 1:1. These results are shown in Fig. 1. The complex also appeared to enhance absorption at 220 mμ, since the extinction coefficient of DVE in a 1:1 mixture was increased to $7000\ M^{-1}cm^{-1}$. The equilibrium constant for complex formation in $CHCl_3$ (25°C) was found to be 1.5×10^{-1}; $\epsilon = 5.6 \times 10^{2}$; $\lambda =$ 299 mμ [3]. The concentration of complex, as in the DVE-MA case [1], is therefore low.

DVE and CMA were found to copolymerize readily in methylene chloride at 60° in the presence of azobisisobutyronitrile to give soluble copolymers of molecular weight ca. 11,000. A series of low conversion copolymers were prepared in which the total monomer feed concentration was maintained constant and the monomer ratio varied systematically. Copolymer compositions were determined by oscillometric titration and verified by

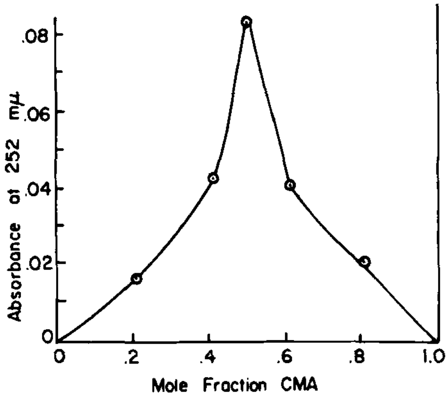


Fig. 1. Absorbance at 252 mμ for DVE-CMA mixtures.

chlorine analysis in some cases. These results are given in Table 1 and Fig. 2. In analyzing the titration data, we assumed that both hydrolysis and dehydrohalogenation occurred upon dissolving the copolymers in base. Chlorine analysis of copolymers isolated after this treatment indicated that approximately 92-98% of the chlorine had been eliminated. Thus it appeared that each CMA unit consumed three equivalents of base. In fact, we found that somewhat less than this was consumed when the copolymers were simply dissolved in dilute base at room temperature. By heating the alkaline copolymer solutions for 15 min at 50° however, an amount of base corresponding to a 1:1 CMA:DVE composition was consumed. The ease with which the copolymers underwent elimination strongly suggests that the hydrogen and chlorine atoms of the CMA unit are in a trans configuration, presumably as a result of a stepwise bond formation process. Kinetic studies on appropriate cis and trans model compounds will be required to verfiy this however.

The infrared spectra of the initial copolymers showed no evidence of residual unsaturation at 1600 or 850 cm^{-1}. The presence of an absorption shoulder at 1600 cm^{-1} in the infrared spectra of DVE cyclocopolymers has often been considered to be evidence for some residual unsaturation [4]. In fact, this shoulder appears to be an artifact of the anhydride unit, since succinic anhydride exhibits an identical absorbance. In examining the infrared spectra of such copolymers for residual unsaturation, it is advisable to also study the region around 850 cm^{-1} where vinyl ether groups on copolymers have been observed to absorb [5].

Table 1. Copolymerization of Chloromaleic Anhydride and Divinyl Ether

Monomer feed composition (mole fraction CMA)	Conversion (mole-%)	Copolymer composition (mole fraction CMA)	
0.200	3.76	0.500	
0.350	4.07	0.496	(0.43)[a]
0.500	3.96	0.511	(0.46)[a]
0.650	2.66	0.513	
0.800	1.59	0.497	

[a] Compositions based on chlorine analysis.

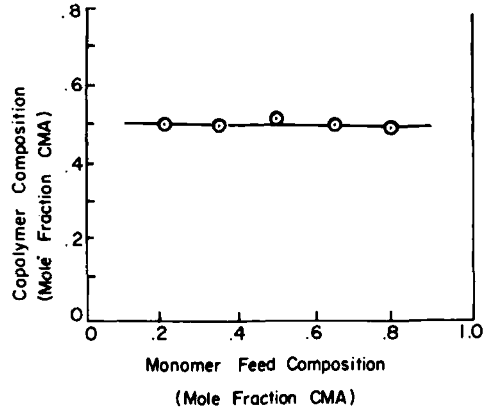
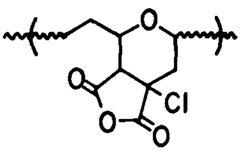


Fig. 2. Feed composition data for DVE-CMA copolymers.

The constant 1:1 composition of the soluble copolymers, and the absence of residual unsaturation leads us to propose Structure IV for the copolymers.



IV

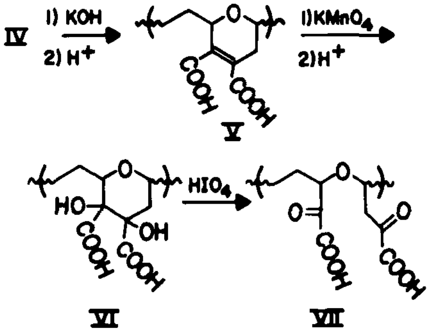
It appears that, unlike the DVE-MA case, the cyclized radical prefers to attack the exo-methylene carbon of a charge transfer complex, rather than a free anhydride molecule, apparently due to the steric and polar influences of the chlorine substituent. A similar effect has been observed in the formation of 1:1 copolymers of divinylsulfone and t-butyl N-vinyl carbamate [6], where the donor-acceptor roles are reversed. In both cases, it appears that homopolymerization of the charge transfer complex occurs.

Since CMA units are apparently absent from the copolymer backbone, results obtainable from the reaction scheme proposed earlier must be interpreted differently. Applied to the present case, we would expect to observe no catastrophic decrease in molecular weight upon periodic acid cleavage if CMA units are present only in bicyclic units as IV.

Thus the following series of reactions were conducted on DVE-CMA copolymer samples, and the molecular weight after each transformation determined. Reaction conditions were chosen to insure near quantitative reaction at each step, while being mild enough to minimize copolymer degradation. Copolymer samples were simultaneously hydrolyzed and dehydrohalogenated as described earlier and then oxidized with cold, dilute potassium permanganate. Elemental analysis of the resulting vic-diol copolymer was in good agreement with the proposed Structure VI, verifying that the initial copolymer (IV) was indeed 1:1 composition and that the hydrolysis, dehydrohalogenation, and oxidation steps were essentially quantitative.

Analysis calculated for $(C_8H_{10}O_7)_x$: C, 44.10; H, 4.58; O, 51.30. Found: C, 43.88; H, 4.58; O, 50.94.

Cleavage of VI was effected by treatment with aqueous periodic acid at room temperature [7]. α-Hydroxy acids are not cleaved under the conditions



employed. The vic-diol cleavage occurred to ca. 90%, based on the consumption of periodic acid. Unfortunately, the infrared spectra of vic-diol copolymer (VI) and the cleaved copolymer (VII) were too broad to distinguish the differences in their structures. Conventional functional group analyses [8] however, verified that the cleavage reaction had occurred. Thus, the vic-diol copolymer reacted immediately with phenyl isocyanate in the presence of pyridine in acetone solution to form the insoluble polymeric carbamate derivative, while the cleaved copolymer reacted only very slowly, presumably via the carboxyl group. Alternatively, the cleaved copolymer reacted with dinitrophenylhydrazine reagent to form the insoluble hydrazone derivative, while the vic-diol copolymer failed to react.

The molecular weights of the derived copolymers are given in Table 2. One notes a gradual decrease in molecular weight after each reaction step, amounting to approximately one scission per chain, indicating that a small amount of random degradation occurred under the reaction conditions employed. Of primary significance however, is the absence of catastrophic decrease in molecular weight upon periodic acid cleavage of the vic-diol copolymer. From these results one must conclude that virtually all the CMA units are present in a bicyclic structure as IV.

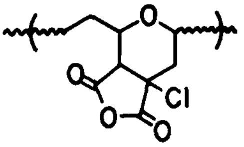
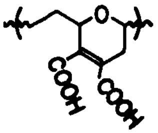
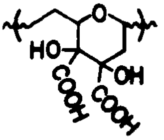
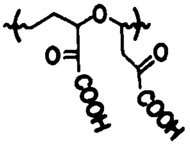
Finally, one would expect to observe a significant decrease in copolymer softening point in proceeding from the cyclic vic-diol copolymer (VI) to the linear cleaved copolymer (VII). In one experiment, a sample of VI (M_n = 1085) was found to soften at 215°, while after cleavage to VII (M_n = 1050), a softening point of 125° was obtained.

EXPERIMENTAL

Materials and Equipment

Chloromaleic anhydride (K&K Laboratories, Inc.) was freshly distilled prior to use, bp 95° at 25 mm Hg. Divinyl ether (Merck, Sharpe and Dohme) was freshly distilled prior to use, bp 28°. Infrared spectra were recorded using a Beckman IR-8 Infrared Spectrophotometer. Ultraviolet spectra were recorded using a Beckman DK-2A Ratio Recording Spectrophotometer. Oscillometric titrations were conducted utilizing a Sargent Chemical Oscillometer, Model V. Molecular weights were obtained by means of a Mecrolab Vapor Pressure Osmometer, Model 302 (solvent = acetone). Copolymer softening points were determined in capillary melting point tubes.

Table 2. Molecular Weight Data for Derived Copolymers.

Copolymer	Structure	M_n[a]
IV		11,000
V		5,240
VI		2,270
VII		1,500

[a] Vapor pressure osmometry, acetone solutions.

Copolymerizations

Solutions of CMA and DVE (1.82 M) in methylene chloride were combined in various volume ratios in thick-walled polymerization tubes and 0.5 mole-% AIBN added. Following a conventional high vacuum freeze-thaw treatment, the tubes were sealed and placed in a stirred oil bath at 60° for 15 min. The solutions clouded within 5 min and copolymer precipitated as formed. After cooling the tubes in a Dry Ice-isopropanol bath, the contents were dissolved by addition of acetone. The copolymers were isolated as white fluffy solids and purified by repeated precipitation of their acetone solutions into hexane, followed by drying in vacuo at room temperature. The infrared spectra of the copolymers were quite broad, and similar to those of

DVE-MA copolymers in many respects. The anhydride units hydrolyzed slowly in contact with air, as evidenced by a gradual decrease in the anhydride absorbances at 1780 and 1860 cm^{-1}, and an increase in the absorbance at 1730 cm^{-1}.

Copolymer compositions were determined by oscillometric titration. The copolymers were dissolved in an excess of aqueous sodium hydroxide and heated for 15 min at 50°. Excess base present was then back-titrated with HCl and the composition calculated from the titration data, assuming that three equivalents of base were consumed per CMA unit present.

Chemical Reactions on the Copolymers

Hydrolysis and Dehydrohalogenation. Copolymer (2.818 g) was dissolved in 125 ml of water containing 2.62 g KOH (10 w-% excess) in a 200-ml flask and heated at 40° for 1 hr. After cooling, the solution was neutralized with HCl and evaporated to dryness on a rotary solvent evaporator at 45-50°. The resulting solids were dissolved in 30 ml of water and acidified with HCl, followed by evaporation to dryness. The acidified copolymer was dissolved in dioxane, filtered to remove KCl, and precipitated into hexane. Reprecipitation of an acetone solution of the copolymer into hexane, followed by drying in vacuo at room temperature, yielded copolymer V (2.50 g) as an off-white fiberous powder.

Oxidation [9]. Copolymer V (2.69 g) was dissolved in 100 ml of water in a 250-ml flask, yielding a bright yellow solution. Aqueous KOH was added until basic, at which point the solution turned bright orange. After cooling to 0-5°, a cold solution of 1.34 g $KMnO_4$ in 100 ml water (based on an oxidation equivalent of 0.67 mole $KMnO_4$ per mole of double bond) was slowly added. The $KMnO_4$ was consumed as added, the purple color disappearing within 30 min. After storage overnight in a refrigerator, the contents were filtered to remove MnO_2, yielding an amber filtrate which was evaporated to dryness. The resulting solids were dissolved in 75 ml of water, acidified with HCl, and evaporated to dryness. The resulting residue was stirred in acetone for several hours to dissolve the copolymer, followed by filtration to remove KCl. The vic-diol copolymer (VI) was isolated and purified by repeated precipitation of its acetone solution into hexane, followed by drying in vacuo at room temperature to give 1.98 g of light tan powder.

Periodic Acid Cleavage [7]. To a solution of 1.68 g of copolymer VI in 50 ml of water was added a solution of 1.86 g of periodic acid hydrate, $HIO_4 \cdot 2H_2O$, in 50 ml of water. The acidic solution was stirred at room temperature for 24 hr, during which it became bright yellow. Following evaporation to dryness, the solids were stirred in acetone for several hours and filtered to remove the unreacted periodic acid (0.209 g, identified by IR). The cleaved copolymer (VII) was isolated and purified by repeated precipitation of its acetone solution into hexane, followed by drying in vacuo at room temperature to give 1.47 g of light yellow powder.

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