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**Donor-Acceptor Complexes in Copolymerization.
LIX. Alternating Diene-Dienophile Copolymers.
13. Copolymerization of Dicyclopentadiene
and Maleic Anhydride**

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ABSTRACT

The solution and bulk copolymerization of dicyclopentadiene (DCP) and maleic anhydride (MAH) occurs over the temperature range 80-240°C, upon the addition of a free-radical catalyst which has a short half-life at the reaction temperature. An unsaturated 1/1 MAH/DCP copolymer, derived from the copolymerization of MAH with the norbornene double bond, followed by a Wagner-Meerwein rearrangement, is obtained in the presence of a large excess of DCP at 80°C, while a saturated 2/1 MAH/DCP copolymer, derived from the cyclocopolymerization of the residual cyclopentene unsaturation, is obtained at higher temperatures or in the presence of excess MAH. The copolymers prepared under other conditions with intermediate MAH/DCP mole ratios contain both 1/1 and 2/1 repeating units. The copolymer obtained from bulk copolymerization above 170°C contains units derived from cyclopentadiene-MAH cyclocopolymerization as well as DCP-MAH copolymerization.

INTRODUCTION

Cyclic conjugated dienes such as cyclopentadiene (CPD) undergo uncatalyzed dimerization to yield the tricyclic Diels-Alder adduct containing nonconjugated diolefinic unsaturation. The dimer dicyclopentadiene (DCP) distills under reduced pressure without decomposition. However, CPD is obtained by the retrograde dissociation of the dimer DCP at its boiling point of 170°C or higher.

The reaction between CPD and maleic anhydride (MAH) yields the cyclic Diels-Alder adduct, endo-cis-5-norbornene-2,3-dicarboxylic anhydride. Copolymerization of CPD and MAH occurs when the reaction is carried out in the presence of a free-radical catalyst which has a short half-life at the reaction temperature. The copolymer is obtained over the temperature range 80-205°C and has a 1/2 CPD/MAH composition [1].

The reaction between DCP and MAH at temperatures at which DCP dissociates to CPD, e.g., 170°C or higher, yields the CPD-MAH Diels-Alder adduct. It has now been found that copolymers of DCP and MAH are formed in the presence of a free-radical catalyst at temperatures below the DCP dissociation temperature and complex terpolymers of CPD, DCP, and MAH are formed above the dissociation temperature.

EXPERIMENTAL

Materials

Maleic anhydride (MAH) and dicyclopentadiene (DCP) were purified by sublimation and distillation at 50°C/2 Torr, respectively. Tert-butyl peroxyvalate (BPP), tert-butyl peracetate (BPA), tert-butyl hydroperoxide-70 (P-70), and tert-butyl hydroperoxide-90 (P-90) were used as received. Solvents were dried and purified by distillation in the usual manner.

Copolymerization

A solution of the catalyst in freshly distilled DCP was added in four portions over a period of 10 min to molten MAH or to a solution of MAH in cyclohexanone or dioxane in a flask immersed in a constant temperature bath. After the catalyst addition was completed, the reaction mixture was maintained at temperature for an additional 20

min and then cooled to room temperature. Acetone was added to dissolve the uncrosslinked polymer. The mixture was filtered to separate the acetone-insoluble polymer, if any. The acetone-soluble polymer was isolated by precipitation with hexane. The polymer was purified by reprecipitation with hexane from acetone solution and dried in vacuo at 45°C.

Characterization

The composition of the copolymers was determined by elemental and NMR analyses. MAH content was determined by potentiometric titration, and unsaturation was determined by reaction with iodine monochloride [2]. The 60 MHz spectra were recorded in acetone- d_6 with tetramethylsilane as internal standard at ambient temperature. Infrared spectra of thin films cast from acetone were recorded using a Perkin-Elmer 137 NaCl spectrophotometer. Molecular weights were determined by cryoscopy in dioxane.

RESULTS

The copolymerization of DCP and MAH occurs readily at temperatures below 170°C in the presence of a radical catalyst which has a short half-life at the polymerization temperature. When the reaction is carried out in a solvent for the copolymer, e.g., dioxane or cyclohexanone, at a solvent concentration of at least 25%, the copolymer is generally completely soluble in acetone and other polar solvents (Table 1). When the reaction is carried out at a lower solvent concentration, in a hydrocarbon solvent or in the absence of a solvent (Table 2), the product is predominantly a crosslinked copolymer, accompanied by an acetone-soluble copolymer which is the same as the soluble copolymer produced in solution.

The soluble copolymers contain MAH and DCP in a 1/1 to 2/1 mole ratio. A 1/1 MAH/DCP copolymer is obtained in the presence of a large excess of DCP at 80°C. A 2/1 MAH/DCP copolymer is obtained at higher temperatures and/or in the presence of excess MAH. The compositions of the copolymers prepared under conditions other than these are between these extremes.

The 2/1 MAH/DCP copolymer is essentially saturated while copolymers having lower MAH contents are unsaturated, as determined by reaction with ICl and IR and NMR spectra (Fig. 1). The copolymers have molecular weights below 2000 and softening points above 250°C.

TABLE 1. Solution Copolymerization of Dicyclopentadiene (DCP) and Maleic Anhydride (MAH)^a

DCP No. (mmole)	MAH (mmole)	Solvent (ml) ^b	Catalyst (mmole) ^c	Temperature (°C)	Conversion (%)	Copolymer		
						Acetone-soluble		Acetone- insoluble
						MAH/DCP (molar)	MW ^d	
1	100	C, 7.3	BPP, 10	80	72.8	8		92
2	100	C, 12.1	BPP, 10	80	79.9	100 ^e	1.28	1890
3	100	C, 24.2	BPP, 10	80	84.8	100 ^f	1.19	
4	200	C, 12.1	BPP, 15	80	71.0	100	1.24	820
5	500	C, 24.2	BPP, 30	80	30.3	100	0.94	812
6	100	D, 12.0	BPP, 10	80	77.6	100		
7	100	T, 12.0	BPP, 10	80	92.5	25		75
8	100	C, 7.3	BPA, 10	155	65.7	9	1.82	91 1.37
9	200	C, 12.1	BPA, 15	155	45.3	100 ^f	1.79	886

^a Catalyst in DCP added in four portions over 10 min to MAH in solvent at temperature, followed by 20 min at temperature.

^b Solvents: C = cyclohexanone; D = dioxane; T = toluene.

^c Catalysts: BPP = tert-butyl peroxyvalerate; BPA = tert-butyl peracetate.

^d Cryoscopic in dioxane.

^e Softening point 305-310°C.

^f Softening point 260-265°C.

TABLE 2. Bulk Copolymerization of DCP and MAH Below 170°C^a

No.	DCP (mmole)	MAH (mmole)	Catalyst (mmole)	Temperature (°C)	Conversion (%)	Copolymer			
						Acetone- soluble %	MAH/DCP (molar) %	Acetone- insoluble %	MAH/DCP (molar) %
10	100	100	BPP 0.5	80	24.3	36 ^b			
11	100	100	BPP 2	80	67.9	15 ^c	1.78	85	
12	200	100	BPP 15	80	61.3	3	1.99	97	1.21
13	500	100	BPP 30	80	33.0	48	0.88	52	
14	200	100	BPP 15	105	24.7	41		59	1.20
15	100	100	BPA 10	155	53.3	9	1.86	91	1.52
16	200	100	BPA 15	155	79.0	12 ^d	1.89	88	0.92
17	100	200	BPA 15	155	88.5	14	2.13	86	

^aCatalyst in DCP added in four portions over 10 min to MAH in solvent at temperature, followed by 20 min at temperature.

^bMolecular weight 339 (cryoscopic in dioxane).

^cMolecular weight 475 (cryoscopic in dioxane).

^dSoftening point 250-255°C.

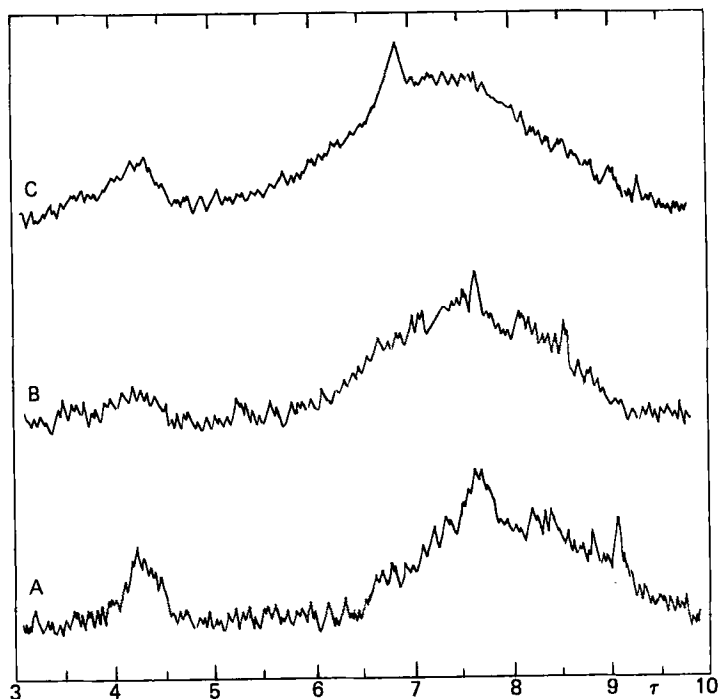


FIG. 1. NMR spectra of copolymers from copolymerization of dicyclopentadiene (DCP) and maleic anhydride (MAH) at various copolymer MAH/DCP mole ratios and temperatures: (A) 0.94/1, 80°C (Table 1, No. 5); (B) 1.82/1, 155°C (Table 1, No. 8); (C) 1.80/1, 205°C (Table 3, No. 20).

The soluble and insoluble copolymers obtained in bulk copolymerization also contain MAH and DCP in 1/1 to 2/1 mole ratio. The molecular weights of the soluble fractions produced in bulk copolymerization are considerably lower than those of the copolymers produced in solution (Table 2).

In some cases, the presence of poly(maleic anhydride) (PMAH) as a by-product in bulk copolymerization is indicated by the elemental analysis. This was confirmed by treatment of the insoluble gel fraction with alkali at 25°C, followed by filtration to separate the alkali-soluble fraction. The polyacid was isolated by acidification with HCl, dried in vacuo, and reconverted to the anhydride form by refluxing in

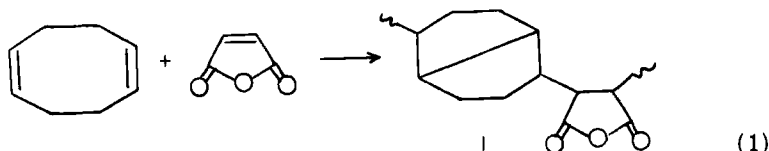
xylene. Elemental analyses and NMR spectra confirmed the identity of the alkali-soluble fraction as PMAH. Elemental analyses also confirmed the identity of the alkali-insoluble fraction as the MAH/DCP copolymer.

When the bulk copolymerization of DCP and MAH is carried out under conditions where cracking of DCP occurs, i.e., above 170°C, the major portion of the product is an acetone-insoluble gel (Table 3). The NMR spectrum (Fig. 1) of the acetone-soluble fraction shows the presence of unsaturation and absorption peaks found in the spectra of CPD-MAH copolymers [1] and not found in the spectra of the DCP-MAH copolymers obtained at lower temperatures. The copolymer presumably contains units derived from the copolymerization of CPD and MAH as well as DCP and MAH.

DISCUSSION

The radical copolymerization of MAH with various nonconjugated cyclic dienes has been reported to yield saturated products whose composition is essentially independent of the initial MAH/diene mole ratio.

The copolymerization of the monocyclic diene *cis,cis*-1,5-cyclo-octadiene and MAH yields a saturated 1/1 MAH/diene copolymer (I) as a result of transannular cyclocopolymerization [3].



Dicyclic dienes such as bicyclopentene undergo cyclocopolymerization with MAH to yield fused ring structures having a saturated 2/1 MAH/diene copolymer composition (II) [4].

The fused-ring bicyclic diene bicyclo[2.2.1]-2,5-heptadiene undergoes copolymerization with MAH to yield a saturated copolymer containing nortricyclene units (III) [5]. Although it is suggested [5] that there may be sequences of MAH in the copolymer, the reported data show that the MAH/diene mole ratio varies from essentially 1/1 to 1/1.5, the former at a 2/1 feed ratio. It is reasonable to presume that the copolymer contains alternating nortricyclene and MAH units (III) and nortricyclene sequences, in view of the ease of homopolymerizability of norbornadiene but not MAH under the indicated conditions.

TABLE 3. Bulk Copolymerization of DCP and MAH Above 170° Ca

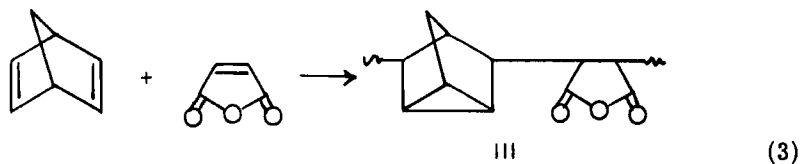
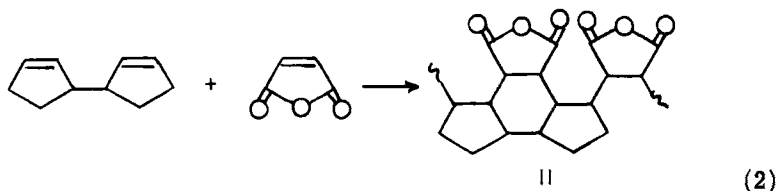
No.	DCP (mmole)	MAH (mmole)	Catalyst (mmole) ^b	Temperature (°C)	Conversion (%)	Copolymer		
						Acetone-soluble %	MAH/DCP (molar)	MAH/DCP (molar)
18	100	200	-	215	0 ^c			
19	200	100	P-70 15	205	77.9	7	93	1.12
20	50	100	P-70 2	205	47.8		1.80	
21	200	100	P-90 15	240	26.6	31	69	1.24
22	100	100	P-90 10	240	74.0	16	2.05	1.54
23	50	100	P-90 2	240	50.0		1.66	
24	100	200	P-90 15	240	93.4	14 ^d	86	

^aCatalyst in DCP added in four portions over 10 min to MAH in solvent at temperature, followed by 20 min at temperature.

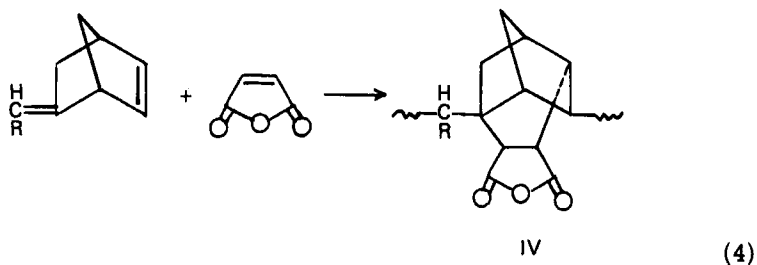
^bCatalysts: P-70 = tert-butyl hydroperoxide (70%); P-90 = tert-butyl hydroperoxide (90%).

^cNo polymer; product mixture of endo and exo CPD-MAH adducts.

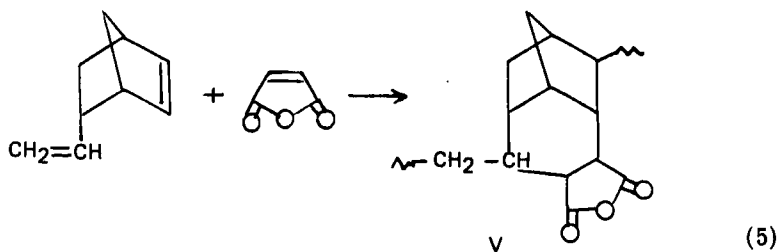
^dMolecular weight 560 (cryoscopic in dioxane); softening point 263-265° C.



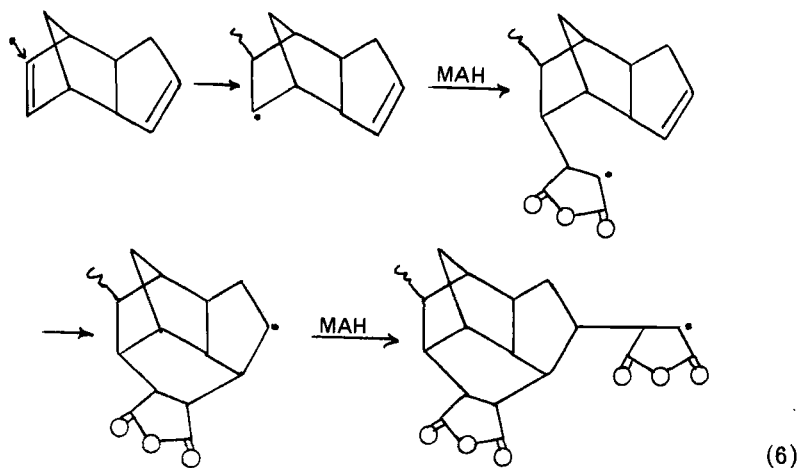
The copolymerization of 5-methylene- and 5-ethylidenebicyclo[2.2.1]-2-heptene, bicyclic dienes containing one exocyclic double bond, with MAH yields saturated 1/1 MAH/diene copolymers having the proposed structure IV [5, 6].



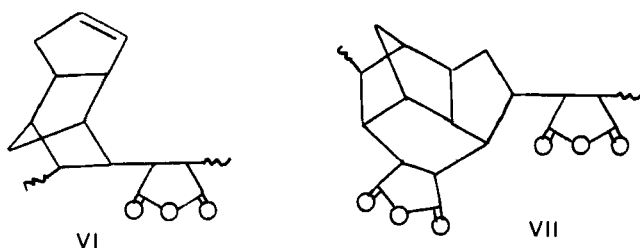
The copolymerization of 5-vinylbicyclo[2.2.1]-2-heptene with MAH yields an analogous saturated 1/1 MAH/diene copolymer (V) [6].



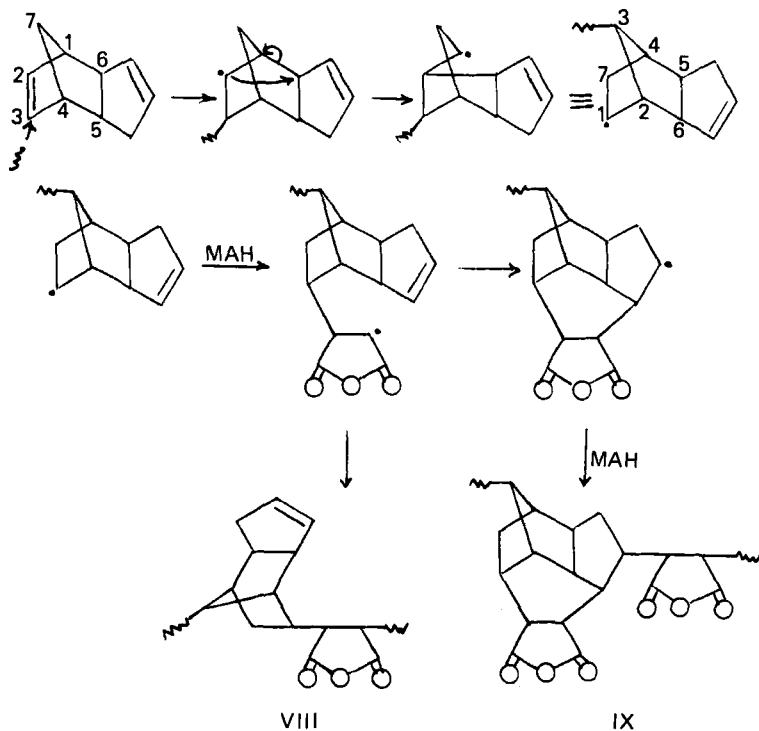
The copolymers of the present study contain MAH and DCP in a 1/1 to 2/1 mole ratio. Since the 1/1 copolymer is unsaturated and the 2/1 copolymer is saturated, the former may be presumed to be an intermediate in the formation of the latter.



The repeating units in the 1/1 and 2/1 MAH/DCP copolymers would have the polycyclic structures VI and VII, respectively.



The radical-catalyzed homopolymerizations of bicyclo[2.2.1]-2-heptene [7] and the CPD-MAH Diels-Alder adduct [8] as well as the copolymerizations of MAH with CPD [1, 8] and with the CPD-MAH adduct [8] have been shown to involve a free-radical Wagner-Meerwein rearrangement. When applied to the DCP-MAH copolymerization, the mechanism may be represented as shown in Eqs. (7).



Scheme 1

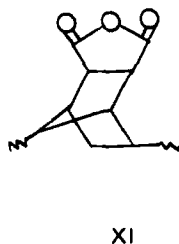
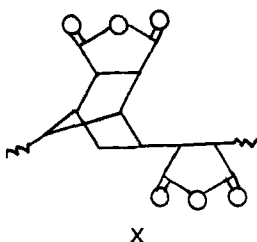
(7)

Copolymers having MAH/DCP mole ratios between 1/1 and 2/1 presumably contain VIII and IX in varying amounts.

The complex NMR spectra do not permit interpretation distinguishing between structure VI and VIII and VII and IX. However, the earlier interpretations of the NMR spectra of the polymers produced from CPD and MAH and from the CPD adducts lend support to VIII and IX.

The crosslinked polymers produced in bulk polymerization arise from the copolymerizability of both the cyclopentene and norbornene unsaturation with MAH.

The polymers produced from DCP and MAH above the cracking temperature of DCP also presumably contain 2/1 MAH/CPD units derived from the copolymerization of MAH and CPD (X) [1, 8] and possibly units from the homopolymerization of the CPD-MAH adduct (XI) and the copolymerization of the CPD-MAH adduct and MAH (X) [8].



It is noteworthy that when the mechanism involving initial attack on the norbornene unsaturation followed by rearrangement is applied to the copolymerizations of MAH with 5-methylene-, 5-ethylidene-, and 5-vinylnorbornene, the final cyclization step involves seven- and eight-membered rings. Since this is less likely than the proposed six-membered rings and since the copolymers have been identified as saturated 1/1 MAH/diene copolymers, the mechanism proposed by Pledger et al. [5, 6] involving initial addition to the exo double bond appears reasonable in these cases.

Analogous to the formation of the saturated 2/1 MAH/DCP copolymer, the radical initiated copolymerization of DCP and SO_2 in liquid SO_2 yields a saturated 2/1 SO_2 /DCP copolymer [9]. Although the proposed structure is similar to VII, it is reasonable to postulate that the actual structure is analogous to IX.

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