Donor-Acceptor Complexes in Copolymerization. XLVII. Alternating Diene-Dienophile Copolymers. 8. Preparation of Equimolar Cyclopentadiene-Maleic Anhydride Copolymers through Copolymerization and Retrograde Isomerization of Diels-Alder Adducts

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Donor-Acceptor Complexes in Copolymerization. XLVII. Alternating Diene-Dienophile Copolymers. 8. Preparation of Equimolar Cyclopentadiene-Maleic Anhydride Copolymers through Copolymerization and Retrograde Isomerization of Diels-Alder Adducts

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ABSTRACT

An equimolar cyclopentadiene-maleic anhydride copolymer was formed by the addition of t-butyl hydroperoxide to the molten Diels-Alder adducts at 175 to 285°C. The same co-polymer was formed by the high temperature copolymerization of maleic anhydride, in the presence of the hydroperoxide, with cyclopentadiene per se or as generated in situ from dicyclopentadiene. The copolymer resulted from the homopolymerization of the comonomer complex which underwent excitation under the influence of the catalyst. The copolymer, softening point 290 to 320°C, was saturated and had a proposed norbornane-2,3-dicarboxylic anhydride repeating unit with 5,7 linkage.

INTRODUCTION

The copolymerization of conjugated dienes, such as butadiene, isoprene [1, 2], and piperylene [3], with maleic anhydride (MAn) in the presence of a free radical catalyst yields equimolar, alternating copolymers [4]. Furan-MAn alternating copolymers are produced under analogous conditions [5]. The furan-MAn Diels-Alder adduct undergoes retrograde dissociation in solution above 60°C and, in the presence of a free radical catalyst, yields the identical copolymer as if formed from the monomers [5].

The reaction of cyclopentadiene (CPD) and MAn in dioxane or toluene readily yields the Diels-Alder adduct, endo-cis-5-norbornene-2, 3-dicarboxylic anhydride. When a solution of t-butyl peroxypivalate in CPD is added to a preheated solution of MAn in dioxane or xylene at 80°C, the cyclic adduct is the only isolatable product. Under the same conditions, the reaction of isoprene or furan with MAn yields the corresponding alternating copolymer containing 1, 4 unsaturation.

The present study was undertaken to determine the feasibility of utilizing the retrograde isomerization of the endo-CPD-MAn adduct to the exo adduct as a route to the CPD-MAn equimolar copolymer and ultimately led to the elucidation of conditions for preparing the copolymer through monomer copolymerization.

RESULTS

The dropwise addition of t-butyl peroxypivalate to a solution of the endo-CPD-MAn adduct in dioxane at 80°C failed to yield any copolymer.

The endo adduct, mp 165°C, undergoes isomerization above its melting point to the exo adduct, mp 143°C [6]. Mixtures containing both isomers are produced from heating either isomer. The addition of t-butyl hydroperoxide-70 (tBHP) to the molten endo adduct resulted in the formation of equimolar copolymer. As shown in Table 1, the yield of 25%, obtained when the reaction was carried out at 175 to 225°C, increased to more than 80% at 240°C and then decreased to 20 to 30% at 265 to 285°C. When the molten endo adduct was maintained at 240°C, without the addition of tBHP, the product was a mixture of endo and exo adducts. The addition of tBHP to the molten exo adduct at 240°C resulted in a 35% yield of the same equimolar copolymer, as was formed from the endo adduct. The copolymer as well as a mixture of endo and exo adducts could be recovered when either adduct was subjected to polymerization conditions.

TABLE 1. Preparation of Cyclopentadiene-Maleic Anhydride
Copolymers from Diels-Alder Adduct

Adduct (g)	Catalyst[a]		Reaction		Copolymer[b] (%)
	tBHP (ml)	Addition time (min)	Time (hr)	Temp (°C)	
		endo			
2.0	3 × 0.2	10	0.33	175	25
1.4	1 × 0.3	5	5.75	225	23
15.0	0.8d	30	0.50	230	54
10.0	3 × 0.2	30	1.33	240	83
10.0	4 × 0.2	40	1.40	240	85
1.5	1 × 0.3	5	4.50	265	25
5.9	3 × 0.1	15	5.00	280	30
2.8	1 × 0.3	5	2.00	285	20
7.5	0	0	1.40	240	0
		exo			
2.0	4 × 0.1	30	1.33	240	35

[a]Catalyst added either dropwise (d) or in portions (3 × 0.2 = 3
portions of 0.2 ml each added at equal intervals during indicated
addition time).
[b]Softening point, 290 to 320°C.

The dropwise addition of a solution of t-butyl peroxypivalate
in CPD to a solution of MAn in dioxane at 80°C failed to yield any
copolymer. However, as shown in Table 2, the dropwise addition of
CPD containing tBHP to molten MAn at temperatures above 100°C
resulted in the formation of the equimolar copolymer. The yield
was 20 to 30% when the reaction was carried out at 155 to 205°C.
Since CPD is obtained as a result of the thermal cracking of
the Diels-Alder adduct dicyclopentadiene (DCPD) at elevated tem-
peratures, the latter was utilized in attempted copolymerization
reactions with MAn. As shown in Table 3, the addition of DCPD to
molten MAn at 215°C failed to yield any copolymer. However, when

TABLE 2. Copolymerization of Cyclopentadiene and Maleic
Anhydride[a]

Temp (°C)	Time (min)	Yield [g (%)]
105	25	0.55 (3.4)
155	25	3.7 (22.6)
180	25	5.0 (30.5)
205	25	4.5 (27.4)
205	90	5.0 (30.5)

[a]tBHP (0.18 g, 0.002 mole) in CPD (6.6 g, 0.1 mole) added drop-
wise over 10 min to molten MAn (9.8 g, 0.1 mole).

the DCPD contained tBHP, addition to MAn at 180 and 215°C gave
equimolar CPD-MAn copolymer in yields of 32 and 48%, respectively.

The equimolar CPD-MAn copolymers have softening points in the
range of 290 to 320°C, are soluble in acetone, dioxane, pyridine, and
dimethylformamide; and are insoluble in chloroform, carbon tetra-
chloride, carbon disulfide, hexane, and benzene.

The copolymers obtained from the endo and exo adducts at 240°C
had cyroscopic molecular weights of 3250 and 2500, respectively.

The CPD-MAn copolymer was readily hydrolyzed to the equimolar
CPD-maleic acid copolymer with aqueous sodium hydroxide, followed
by acidification. The CPD-MAn copolymer was esterified with
methanol under reflux, using p-toluenesulfonic acid as catalyst, to
yield a mixture of the equimolar CPD-monomethyl maleate and CPD-
dimethyl maleate copolymers. The mono and diester copolymers
were readily separated by virtue of the solubility of the latter in
benzene, and their identity was confirmed by elemental analyses as
well as IR and NMR analyses. The diester copolymer was also pre-
pared by reaction of the CPD-maleic acid copolymer with diazomethane.

The IR spectrum of the CPD-MAn copolymer (Fig. 1) shows absorp-
tion peaks at 1760 and 1835 cm^{-1}. The ratio of these absorptions are
estimated at about 2.5, a value that has been observed with other MAn
copolymers. A shoulder at 1705 cm^{-1} suggests the presence of
carboxyl groups. However, the nonbroadening of the absorption at
3000 cm^{-1} indicates that the content is low. The absence of absorp-
tion peaks at 1640 and 3050 cm^{-1} indicates the absence of double
bonds. Weak peaks are observed at 1360 and 1440 cm^{-1} and stronger

TABLE 3. Reaction of Dicyclopentadiene and Maleic Anhydride[a]

DCPD [g (mole)]	MAn [g (mole)]	tBHP [g (mmole)]	Temp (°C)	Time (min)	Yield [g (%)]
13.2 (0.1)	19.6 (0.2)	0	215	20	0
12.2 (0.1)	19.6 (0.2)	0.36 (4)	180	20	10.5 (32.0)
13.2 (0.1)	19.6 (0.2)	0.36 (4)	215	20	15.9 (48.5)
13.2 (0.1)	0.5 (0.005)	0.36 (4)	210	20	Trace

[a]tBHP in DCPD added dropwise over 10 min to molten MAn.

peaks at 1220, 1080, 940, and 900 cm^{-1}. The shape of the peaks at 940 and 900 cm^{-1} is characteristic of that observed with other diene-MAn copolymers. It is apparent that these absorptions are due to the MAn units, since only a weak peak is noted at 920 cm^{-1} when the anhydride copolymer is converted to mono and dimethyl ester copolymers.

The IR spectra of the monoethyl and dimethyl ester copolymers resemble that of the CPD-MAn copolymer except that the anhydride absorption is replaced by the carbonyl absorption at 1720 cm^{-1}, accompanied by the hydroxyl absorption at 3300 cm^{-1}, and the peak at 1080 cm^{-1} is shifted to 1035 cm^{-1}. The absence of unsaturation is evident from the 1600 and 3000 cm^{-1} regions. Strong absorptions at 970 or 730 cm^{-1}, characteristic of the polymers derived from cyclopentene or cyclopentadiene [7, 8], are also absent. The 730 cm^{-1} peak is present in the spectrum of the CPD-MAn adduct.

The NMR spectra of the CPD-MAn copolymer and its derivatives are shown in Fig. 2. The absorption is complex and appears in the 5.7 to 9.1 τ region. There is no absorption below 6.0 τ in the spectra of the monomethyl and dimethyl ester copolymers. The anhydride copolymer has a very low absorption at 4.0 τ, attributed to the presence of double bonds. Integration of the area indicates the double bond content to be less than 3%. Assigning the 5.60 to 6.90 τ region to the maleic anhydride protons leads to a calculated essentially equimolar CPD-MAn composition, in agreement with the elemental analyses. Integration of the methoxy resonance in the monomethyl and dimethyl ester copolymers also confirms the equimolar compositions, in agreement with the elemental analyses.
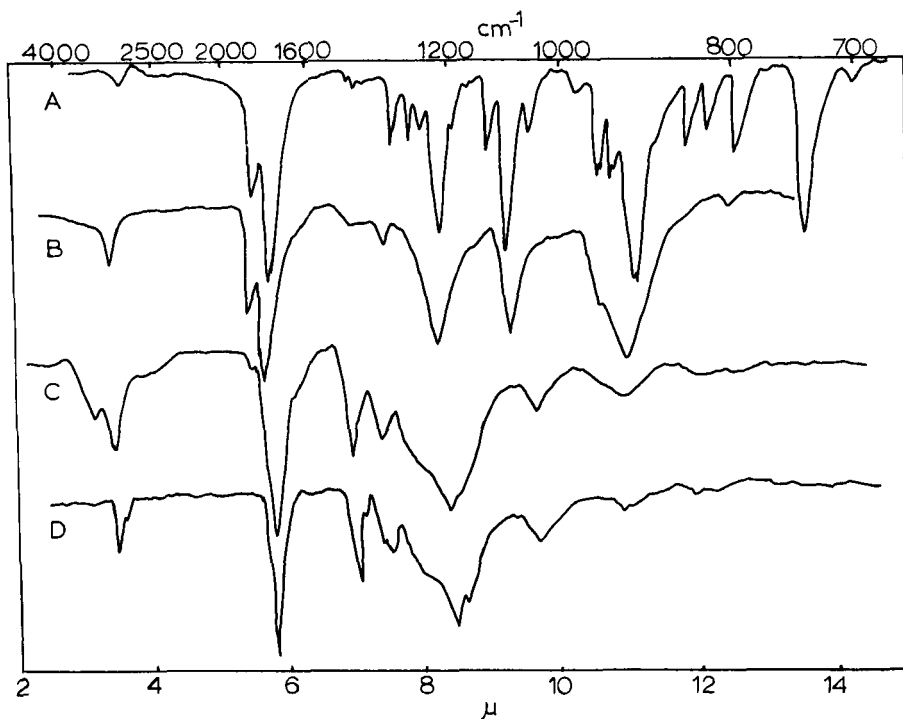
FIG. 1. IR spectra of cyclopentadiene-maleic anhydride (CPD-MAn) reaction products and derivatives. A = Diels-Alder adduct (KBr); B = anhydride copolymer; C = monomethyl ester copolymer; D = dimethyl ester copolymer.

DISCUSSION

The reaction between a conjugated diene and maleic anhydride is presumed to proceed through the formation of a ground state comonomer charge transfer complex which undergoes ring closure to the cyclic Diels-Alder adduct. When the reaction is carried out under UV light or in the presence of a free radical precursor under conditions where it is undergoing rapid decomposition, e.g., at a temperature where the half-life is less than 1 hr, the ground state complex
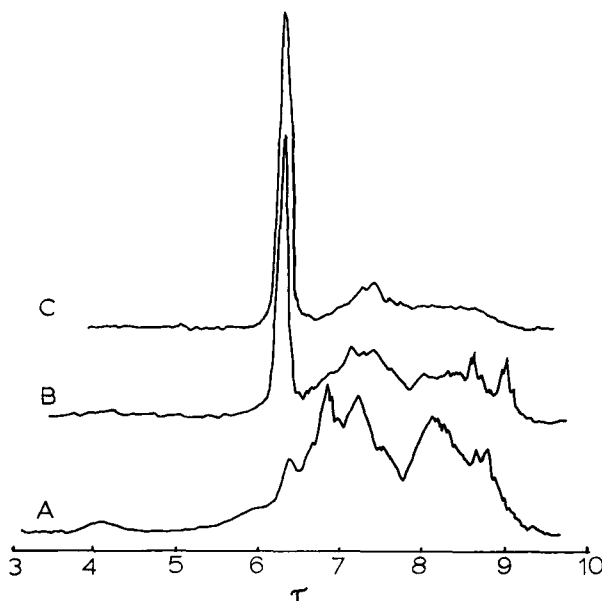
FIG. 2. NMR spectra of CPD-MAn copolymers and derivatives. A = anhydride copolymer; B = monomethyl ester copolymer; C = dimethyl ester copolymer.

undergoes excitation and the resultant exciplex homopolymerizes to yield the equimolar, alternating copolymer [1].

$$D + A \rightleftharpoons [D \rightarrow A] \rightleftharpoons \overset{\frown}{D \cup A} \qquad (1)$$

$$\searrow [\overset{+}{D} \cdot \overset{-}{A}] \rightarrow -(DA)_{\overline{x}} \qquad (2)$$

The retrograde Diels-Alder reaction to regenerate the addends from the parent adduct presumably involves a reversal which proceeds through the ground state complex. The latter also plays a role in the retrograde isomerization of the endo-CPD-MAn adduct to the exo adduct. The mechanism of the endo-exo isomerization has been considered to involve a dissociation of the adduct to the addends which then recombine to give the other isomer and/or a direct conversion not involving dissociation into kinetically free fragments [9, 10]. The

former path is presently considered as the more acceptable repre-
sentation [11, 12].

The formation of equimolar copolymers from the reaction between
CPD and MAn at temperatures above 155°C and from the adducts at
similar temperatures, in the presence of t-butyl hydroperoxide-70
(half-life 1 min at 175°C), suggests that both reactions proceed
through a common intermediate, i.e., the excited complex. Although
the ground state complex is formed at much lower temperatures, the
quenching action of CPD presumably inhibits excitation. However,
this quenching capability is apparently diminished at elevated temper-
atures. Since the adduct only polymerizes at temperatures at which
the ground state complex is generated, the formation of the adduct does
not appear to play a role in the monomer copolymerization.

The equimolar, alternating copolymer produced in the reaction
between MAn and acyclic conjugated dienes, such as butadiene [1, 2,
4], isoprene [1, 2, 4], and piperylene [3, 4], in the presence of a
radical precursor, has a repeating unit containing 1,4 unsaturation
(I). The equimolar, alternating copolymer produced in the reaction
between MAn and furan, as well as from the retrograde dissociation
of the furan-MAn adduct, in the presence of a radical precursor,
contains 1,4 unsaturation and the repeating unit has 2,5 linkage (II) [5].

I   II
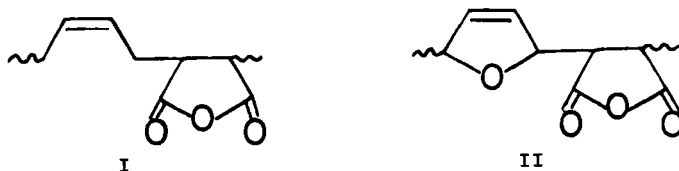
However, IR and NMR analyses of the equimolar copolymers from
CPD and MAn and from the CPD-MAn cyclic adducts, as well as
analyses of their esterified derivatives, indicate that the copolymers
contain little or no unsaturation. This eliminates from consideration
a structure (III) analogous to those obtained with the acyclic dienes
and furan.

Although plausible mechanisms can be proposed to account for
cyclobutane-containing Structure IV and V, they are excluded by the
absence of absorption bands characteristic of such structures in the
IR spectra of the anhydride copolymer as well as the mono- and
dimethyl ester copolymers. The absence of characteristic absorp-
tion bands in the IR and NMR spectra, as well as the inability to pro-
pose reasonable routes for their formation, also exclude nortricyclene
structures.

III   IV   V

VI   VII
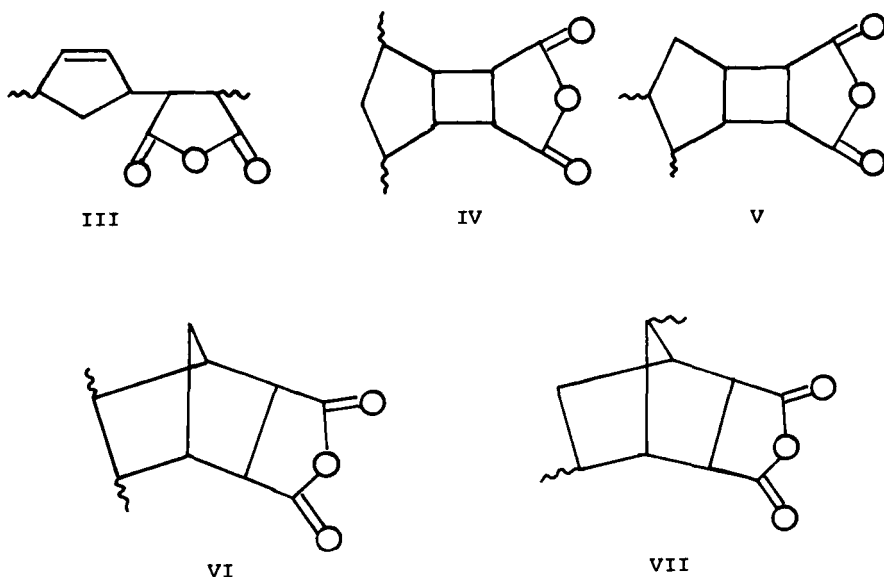
The IR and NMR spectra contain no features which can be used to distinguish between Structures VI and VII.

The failure to polymerize the adduct at temperatures below those at which retrograde isomerization occurs would exclude Structure VI. Although 2-norbornene has been polymerized with free radical catalysts, e.g., at 130°C in the presence of di-t-butyl peroxide under 6000 atm pressure [13], no structure determinations have been reported.

The preferred Structure VII, with a norbornane-2,3-dicarboxylic anhydride repeating unit with 5,7 linkage, may arise from the sequence shown in Eq. 3.

EXPERIMENTAL

Materials

t-Butyl peroxypivalate (tBPP) and t-butyl hydroperoxide-70 (tBHP) were used as received.

Cyclopentadiene was prepared by the thermal cracking of commercial dicyclopentadiene and was freshly distilled before use. Maleic anhydride was purified by sublimation.

(3)

VII
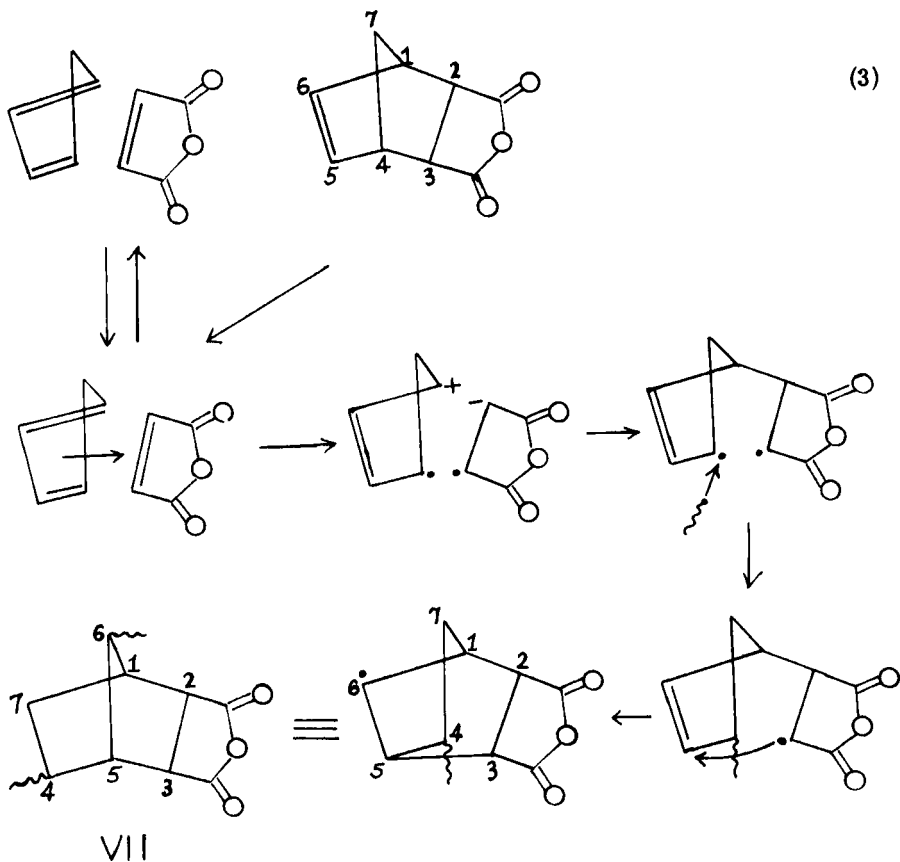
The Diels-Alder adduct, endo-cis-5-norbornene-2,3-dicarboxylic anhydride, mp 165°C, was purified by recrystallization of practical grade material. The exo isomer was prepared by maintaining the endo isomer at 220°C for 4 hr. The crude reaction product, mp 101°C, was a mixture of endo and exo anhydrides. The crude product was recrystallized 3 times from benzene to isolate the exo isomer, mp 141°C, in 25% yield.

Polymerization of Adducts

The catalyst was added dropwise or in portions, by means of a hypodermic syringe, to the molten adduct which was either in a long

test tube containing a magnetic stirrer and sealed with a rubber serum cap or in a 3-necked flask equipped with a mechanical stirrer, long air condenser, and gas inlet tube capped with a rubber serum cap. The reaction vessel was heated in an oil bath. The reaction was exothermic and was accompanied by the refluxing of cyclopentadiene which gradually lowered the temperature of the reaction mixture. The reaction could be terminated by cooling within a few minutes after the catalyst addition was completed. Maintaining the mixture for several hours at the reaction temperature did not increase the yield of copolymer. The mixture was diluted with acetone and the copolymer was precipitated with chloroform. After solution in acetone, reprecipitation in chloroform, and drying in vacuo at 45°C, the copolymer analyzed as an equimolar product. In some cases the copolymer was partially hydrolyzed on exposure to the atmosphere and required azeotropic distillation with xylene to reconvert the acid groups to the anhydride form.

Analysis for 1:1 anhydride copolymer $(C_9H_8O_3)_n$: Calculated: C, 65.85; H, 4.88; O, 29.27. Found: C, 65.68; H, 5.15; O (by difference), 29.13.

A mixture of endo and exo adducts could be recovered by evaporation of the solvent from the chloroform filtrates.

Copolymerizations

A solution of the catalyst in cyclopentadiene or dicyclopentadiene was added dropwise over a 10-min period to molten maleic anhydride. The reaction mixture was maintained at temperature for 10 min after the addition was completed and the copolymer was isolated and purified as above.

Hydrolysis of Anhydride Copolymer

A solution of 2.0 g of the cyclopentadiene-maleic anhydride copolymer in acetone was mixed with aqueous 5% sodium hydroxide. After the mixture was stirred at 50°C for 1 hr, the acetone was removed by evaporation. On acidification with dilute HCl the copolymer precipitated. After filtration, drying, and purification by solution in acetone and precipitation in benzene, the product yield was 1.9 g.

Analysis for diacid copolymer $(C_9H_{10}O_4)_n$: Calculated: C, 59.34; H, 5.50; O, 35.16. Found: C, 58.51; H, 6.18; O (by difference), 35.14.

The IR spectrum indicated that the conversion of the anhydride to the acid copolymer was complete.

Esterification of Anhydride Copolymer

A mixture of 4.4 g of the cyclopentadiene-maleic anhydride copolymer and 0.1 g of p-toluenesulfonic acid in 100 ml of methanol was refluxed for 48 hr. The solvent was removed in vacuo and the residual brown solid was extracted with benzene. The benzene-soluble fraction was washed with an aqueous sodium bicarbonate solution and the benzene-insoluble fraction was extracted with an aqueous sodium hydroxide solution. The combined aqueous extracts were acidified with dilute HCl to precipitate 2.62 g of the half ester copolymer.

Analysis for monomethyl ester copolymer $(C_{10}H_{12}O_4)_n$: Calculated: C, 61.20; H, 6.15; O, 32.65. Found: C, 61.64; H, 6.34; O (by difference), 32.00.

The benzene-soluble fraction, when precipitated in hexane, yielded 2.47 g of the corresponding dimethyl ester copolymer, characterized from elemental analysis and IR and NMR spectra.

Esterification of Acid Copolymer

A suspension of 2.0 g of the cyclopentadiene-maleic acid copolymer, prepared by hydrolysis of the anhydride copolymer, in 20 ml of benzene was treated with 1.5 g of diazomethane in 150 ml of diethyl ether at 5°C for 22 hr. After removal of the ether in vacuo, the resultant clear benzene solution was treated with hexane to precipitate 2.38 g of the diester copolymer.

Analysis for diester copolymer $(C_{11}H_{14}O_4)_n$: Calculated: C, 62.86; H, 6.66; O, 30.48. Found: C, 62.97; H, 6.51; O (by difference), 30.46.

The IR and NMR spectra confirmed that the conversion of the acid to the diester copolymer was complete.

Characterization

Molecular weights were determined cryoscopically in dioxane.

IR spectra were recorded from films cast on NaCl plates from acetone solution using a Perkin Elmer Model 21 spectrophotometer.

NMR spectra were obtained at 60 MHz using tetramethylsilane as internal standard at 60°C. Acetone-d_6 was used as solvent for the anhydride and half-ester copolymers, and $CDCl_3$ was used as solvent for the diester copolymer.

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