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### Donor-Acceptor Complexes in Copolymerization. XXXVI. Alternating Diene-Dienophile Copolymers. 4. Copolymerization of Furan and 2-Methylfuran with Maleic Anhydride

Norman G. Gaylord<sup>a</sup>; Sukumar Maiti<sup>a</sup>; Birendra K. Patnaik<sup>a</sup>; Akio Takahashi<sup>a</sup>

<sup>a</sup> Gaylord Research Institute Inc., Newark, New Jersey

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**Donor-Acceptor Complexes in Copolymerization.  
XXXVI. Alternating Diene-Dienophile  
Copolymers. 4. Copolymerization of Furan  
and 2-Methylfuran with Maleic Anhydride**

NORMAN G. GAYLORD, SUKUMAR MAITI,  
BIRENDRA K. PATNAIK, and AKIO TAKAHASHI

Gaylord Research Institute Inc.  
Newark, New Jersey 07104

**ABSTRACT**

The copolymerization of furan and 2-methylfuran with maleic anhydride in the presence of a radical catalyst yields equimolar, alternating copolymers in which the furan units have a 2,5-linkage (NMR and IR). The copolymerization appears to have a floor temperature of about 40°C. The furan-maleic anhydride Diels-Alder adduct polymerizes in solution in the presence of a radical catalyst at temperatures above 60°C to yield the identical copolymer as is obtained from the monomers. The adduct undergoes a retrograde reaction above 60°C to regenerate the monomers which then copolymerize through excitation of the ground state comonomer charge transfer complex.

## INTRODUCTION

Furan is known to readily undergo the Diels-Alder reaction with maleic anhydride to form the cyclic adduct in almost quantitative yield [1]. It has recently been shown that conjugated dienes and maleic anhydride not only form the cyclic adducts but also copolymerize in the presence of conventional free radical catalysts to form equimolar, alternating copolymers [2-5]. In an extension of our study [6] of the homopolymerization of the comonomer charge transfer complexes which are precursors of both the cyclic adducts and the alternating copolymers, the radical catalyzed copolymerization of furan and 2-methylfuran with maleic anhydride was investigated. Butler et al. [7] have recently demonstrated the existence of the charge transfer complex in the furan-maleic anhydride system and the formation of equimolar, alternating copolymers by azobisisobutyronitrile initiation of benzene solutions of the monomers as well as the cyclic adduct.

## EXPERIMENTAL

### Materials

Maleic anhydride was purified by sublimation. Furan and 2-methylfuran were distilled immediately before use. Azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol. *t*-Butyl peroxyvalate (BPP) as a 75% solution in mineral spirits and 2-methylpentanoyl peroxide (MPP) as a 50% solution in mineral spirits were used as received (Lucidol Division, Pennwalt Corp.). Isoprene was distilled over calcium hydride. Dioxane was refluxed with  $\text{SnCl}_2$  for 6 hr and then distilled to yield a peroxide-free product. All other solvents were purified and dried according to standard procedures.

### Polymerization

In some cases the copolymerization of furan and maleic anhydride was carried out in a tube sealed with a rubber cap under a nitrogen atmosphere. The radical catalyst was added at one time or over a period of time by hypodermic syringe.

Larger scale reactions were carried out in a flask equipped with a mechanical stirrer, condenser, thermometer, and dropping funnel. In the "normal" mode of addition, a solution of furan or 2-methylfuran and catalyst in solvent was added over a period of 10-15 min to a solution of maleic anhydride in the solvent maintained at the desired temperature  $\pm 2^\circ\text{C}$ . In the "reverse" mode of addition, a solution of maleic anhydride and catalyst in solvent was added over 10-15 min to a preheated solution of the furan. In either case, the reaction was continued for a total reaction time of 1-2 hr and the polymer recovered by precipitation into benzene. The polymer was washed with hot benzene and diethyl ether and, where desired, purified by solution in acetone and reprecipitation in benzene. The cyclic adduct was isolated on evaporation of the collected filtrates in vacuo.

The reactions under UV light were conducted under nitrogen in a quartz tube stoppered with a rubber cap. Irradiation was carried out in a circular "Rayonet" Srinivasan-Griffin Photochemical Reactor with the tube suspended in the center 4 in. from 16 UV lamps.

The polymerization of the furan-maleic anhydride adduct, mp  $123-125^\circ\text{C}$ , was carried out in the same manner as the copolymerization of the monomers.

The reaction of isoprene with the furan-maleic anhydride adduct was carried out in a sealed tube under nitrogen or in a flask by adding an isoprene solution over 10 min to a preheated solution of the adduct. The reaction mixture was carefully evaporated to dryness on a flash evaporator at a temperature below the reaction temperature. The residue was extracted with cold diethyl ether. The residue, if any, was the furan-maleic anhydride adduct. The ether extract was carefully evaporated to dryness and the solid residue was repeatedly leached with warm water to remove maleic anhydride. The residue was the adduct of isoprene and maleic anhydride, identified by elemental analysis and mixed mp with an authentic sample.

### Characterization

The equimolar composition of the copolymers was confirmed by elemental analysis. The softening range of the furan-maleic anhydride copolymer is  $185-210^\circ\text{C}$  and that of the 2-methylfuran-maleic anhydride copolymer is  $265-275^\circ\text{C}$ .

Intrinsic viscosities of the copolymers were determined in methyl ethyl ketone at 30°C with a Ubbelohde viscometer.

The IR spectra of the adducts and the copolymers were run as either KBr pellets, nujol mulls, or films from acetone in a Perkin-Elmer Model 21 IR spectrophotometer.

The NMR spectra of the copolymers were run as 10% solutions in acetone- $d_6$  using tetramethylsilane as the internal standard at 100 MHz at 72°C.

## RESULTS

### Copolymerization of Furan and Maleic Anhydride

As shown in Table 1, the cyclic Diels-Alder adduct is the major product when furan, maleic anhydride, and catalyst are mixed at one time and the temperature is below 60°C. However, when the catalyst is used at a temperature where it has a shorter half-life and particularly when the catalyst is added with the furan to the maleic anhydride solution over a slightly extended period, the yield of equimolar, alternating copolymer is higher (Table 2). Negligible yields of copolymer are obtained when the reaction temperature is below 40°C.

The order of addition, i.e., the addition of catalyst and furan to maleic anhydride vs the addition of catalyst and maleic anhydride to furan, and the total reaction time are apparently less significant than the temperature and the time of addition of the catalyst (Table 3).

UV irradiation of a mixture of furan and maleic anhydride at 30 and 60°C in the presence of photosensitizers at 2537 and 3000 Å fails to yield any copolymer (Table 4).

### Polymerization of Furan-Maleic Anhydride Adduct

The alternating furan-maleic anhydride copolymer is produced when the Diels-Alder adduct is heated in solution at 60-78°C in the presence of a radical catalyst (Table 5). No copolymer is formed when the reaction temperature is below 60°C.

When a benzene solution of the furan-maleic anhydride adduct is heated under the reflux at 78°C for 2 hr, no benzene-insoluble copolymer is formed. However, when the benzene solution is

TABLE 1. Copolymerization of Furan and Maleic Anhydride: One-Shot Catalyst Addition<sup>a</sup>

Furan (mole)	MAnh (mole)	Catalyst (mmole)	Solvent <sup>b</sup> (ml)	Temp. (°C)/ Time (hr)	Yield (%)	
					Adduct	Copolymer
0.1	0.1	MPP (2)	D (10)	35/2	90.5	1.0
0.2	0.2	AIBN (2)	T (10)	55/2.5	80.5	2.5
0.1	0.1	MPP (3)	D (10)	60/2.5		50.2
0.2	0.2	AIBN (2)	T (10)	70/2		14.5
0.2	0.2	AIBN (6)	B (65)	70/3		16.7

<sup>a</sup> Reaction carried out in sealed tube under nitrogen; catalyst added in one shot at beginning of reaction period.

<sup>b</sup> B = benzene; D = dioxane; T = tetrahydrofuran.

TABLE 2. Copolymerization of Furan and Maleic Anhydride: Extended Catalyst Addition<sup>a</sup>

Furan (mole)	MANh (mole)	BPP (mmole)	Solvents <sup>b</sup> (ml)	Temp. (°C)/ Time (hr)	Copolymer yield (%)
0.01	0.01	2	A (5)	30/1	trace
0.01	0.01	1	A (5)	40/1	22.9
0.01	0.01	1	A (5)	50/1	64.5
0.01	0.01	1	M (5)	50/1	37.4
0.01	0.01	1	D (5)	50/1	35.0
0.01	0.01	1	T (5)	50/1	36.2

<sup>a</sup> Reaction carried out in sealed tube under a nitrogen atmosphere in ambient light. Catalyst mixed with furan and added to preheated MANh solution over 10 min. Reaction continued for additional 50 min.

<sup>b</sup> A = acetone; M = methyl ethyl ketone.

TABLE 3. Copolymerization of Furan and Maleic Anhydride: Effect of Order of Addition

Furan (mole)	MAnh (mole)	Catalyst (mmole)	Solvent (ml)	Addition		Temp. (°C)/ Time (hr)	Adduct (%)	Copolymer	
				Order <sup>a</sup>	Time (min)			%	[ $\eta$ ] (dl/g)
0.25	0.25	BPP (6)	D (45)	N	15	60/2	69.2	5.0	
0.25	0.25	BPP (6)	D (35)	R	15	60/2	3.5	37.4	0.09
0.006	0.006	BPP (0.3)	A (3) + M (3)	N	10	60/1	5.0	66.0	
0.006	0.006	BPP (0.3)	A (3) + M (3)	N	10	70/1	1.0	97.0	
0.25	0.25	AIBN (10)	D (35)	R	15	55/2	6.5	31.4	0.12
0.25	0.25	AIBN (10)	D (15)	N	15	70/2	18.0	25.3	0.04
0.25	0.25	AIBN (10)	D (35)	R	15	70/2	8.0	52.8	0.04

<sup>a</sup>N = solution of catalyst and furan added to preheated solution of MAnh; R = solution of catalyst and MAnh added to preheated solution of furan.



TABLE 4. UV Irradiation of Furan and Maleic Anhydride in Presence of Sensitizer<sup>a</sup>

Sensitizer	E <sub>T</sub> (kcal/mole)	λ (Å)	Adduct (%)	Copolymer (%)
Acetone	78.0	2537	24.2	0
Acetophenone	73.6	2537	31.0	0
Acetonaphthone	56.4	2537	40.1	0
Acetone		3000	16.4	0
Acetophenone		3000	42.0	0
Acetonaphthone		3000	47.5	0
Acetone <sup>b</sup>		2537	nd	0
Acetophenone		Dark	38.3	0

<sup>a</sup>[Furan] = 0.03 mole; [MAh] = 0.03 mole; sensitizer, 3 ml; temperature, 30°C; time, 45 min. Irradiation of reactants in sealed quartz tube carried out under nitrogen.

<sup>b</sup>Irradiation at 65°C for 70 min.

evaporated on a steam bath, maleic anhydride is recovered essentially quantitatively.

When the furan-maleic anhydride adduct is heated in solution in the presence of isoprene at 60-78°C, the product is the isoprene-maleic anhydride adduct (Table 6).

#### Copolymerization of 2-Methylfuran and Maleic Anhydride

The reaction of 2-methylfuran with maleic anhydride to form the cyclic adduct in the absence of a radical catalyst and the equimolar, alternating copolymer in the presence of a radical catalyst occurs more readily than the corresponding reaction with furan (Table 7). The greatly increased yield of copolymer on increasing the temperature from 50 to 60°C demonstrates the effect of using the catalyst at a temperature where it has a shorter half-life and decomposes at a faster rate.

TABLE 5. Polymerization of Furan-Maleic Anhydride Adduct

Adduct (mole)	Catalyst (mmole)	Solvent (ml)	Method <sup>a</sup>	Temp. (°C)/ Time (hr)	Copolymer (%)
0.017	AIBN (1)	B (10)	ST	78/2	25.0 <sup>b</sup>
0.025	AIBN (1)	T (10)	ST	70/2	51.2
0.025	AIBN (1)	D (10)	CA	70/2	60.3
0.006	BPP (0.3)	A (3) + M (3)	CA	70/1	25.0
0.01	BPP (1)	M (10)	CA	70/1	32.5
0.006	BPP (0.3)	A (3) + M (3)	CA	60/1	9.0
0.01	BPP (2)	M (10)	CA	60/1	Trace
0.01	BPP (1)	A (10)	CA	56/2	0
0.01	BPP (2)	M (10)	CA	50/1	0
0.01	BPP (3)	A (10)	CA	50/1	0

<sup>a</sup>ST = reaction carried out in sealed tube under nitrogen; CA = catalyst in solvent added over 15 min to preheated solution of adduct.

<sup>b</sup>Insoluble in acetone.

TABLE 6. Reaction of Furan-Maleic Anhydride Adduct with Isoprene

F-MAnh adduct (mole)	Isoprene (mole)	Solvent (ml)	Method <sup>a</sup>	Temp. (°C)/ Time (hr)	I-MAnh adduct <sup>b</sup> (%)
0.006	0.01	A (3) + M (3)	A	24/1	0
0.006	0.01	A (3) + M (3)	A	60/1	76
0.006	0.01	A (3) + M (3)	A	70/1	85
0.005	0.005	T (10)	ST	70/3	95
0.01	0.01	B (10)	ST	78/3	60

<sup>a</sup>A = solution of isoprene added over 10 min to preheated solution of F-MAnh adduct; ST = reaction carried out in sealed tube under nitrogen.

<sup>b</sup>Identified as I-MAnh adduct by elemental analysis and mixed mp with authentic adduct, mp 62-65°C.

TABLE 7. Copolymerization of 2-Methylfuran and Maleic Anhydride<sup>a</sup>

Catalyst (mmole)	Dioxane (ml)	Method <sup>b</sup>	Temp. (°C)/ Time (hr)	Copolymer	
				Yield (%)	$[\eta]$ (dl/g)
BPP (4)	15	N	50/2	25.6	0.06
BPP (4)	15	R	50/2	27.1	0.09
AIBN (4)	15	N	60/2	21.3	0.06
BPP (2)	15	N	60/2	46.7	0.12
BPP (2)	15	R	60/2	69.3	0.15
BPP (4)	15 + 30	N	60/2	93.5	0.33

<sup>a</sup>[MF] = 0.25 mole; [MAnh] = 0.25 mole.

<sup>b</sup>N = solution of catalyst and MF added over 15 min to preheated solution of MAnh; R = solution of catalyst and MAnh added over 15 min to preheated solution of MF.

UV irradiation of a mixture of 2-methylfuran and maleic anhydride at 30°C in the presence of acetone, acetophenone, or acetophenone at 2537 and 3000 Å fails to yield any copolymer, analogous to the results with furan and maleic anhydride.

### Copolymer Structure

The IR spectra of the furan-maleic anhydride adduct and copolymer are shown in Fig. 1. The carbonyl groups in the anhydride unit appear as two peaks at 1850 and 1770  $\text{cm}^{-1}$ , corresponding to the symmetrical and asymmetrical stretching, respectively. The ratios of the optical densities for the asymmetric and symmetric bands are low (2-3), indicating that the carbonyl groups are far from colinear, which would be anticipated from their structure. In the copolymer a low peak is observed at 1725  $\text{cm}^{-1}$  due to the presence of some  $-\text{COOH}$  groups formed by partial hydrolysis of the anhydride group during handling. The isolated double bond is observed at 1590 and 1650  $\text{cm}^{-1}$  in the adduct and at 1620  $\text{cm}^{-1}$  in the copolymer which is assigned to the  $\text{C}=\text{C}$  stretching of the cis double bond present in the ring. It should be noted that this  $\text{C}=\text{C}$  stretching is not observed in the IR spectra of copolymers of maleic anhydride with butadiene or isoprene. This might be due to the symmetrical structure of the compound. The other strong peaks observed at 1230, 1080, and 930  $\text{cm}^{-1}$  and a medium peak at 730  $\text{cm}^{-1}$  in the copolymer are attributed to the presence of the maleic anhydride unit. Some of the peaks due to the furan ring are also overlapped in this region. Such strong peaks are also observed in the IR spectra of copolymers of maleic anhydride with various other monomers such as butadiene, isoprene, and vinyl methyl ether.

The IR spectra of the adduct and copolymer obtained from 2-methylfuran and maleic anhydride are shown in Fig. 2. In general, these spectra resemble the corresponding materials obtained from furan. In the adduct the double bond is evident from the  $=\text{C}-\text{H}$  stretching at 3070  $\text{cm}^{-1}$  and the  $\text{C}=\text{C}$  stretching at 1620 and 1585  $\text{cm}^{-1}$ . In the copolymer the unsaturation is observed at 1625  $\text{cm}^{-1}$ . The other peaks are the same as those observed in the furan-maleic anhydride compounds. These results suggest the similarity of the structures of the copolymers from furan and 2-methylfuran.

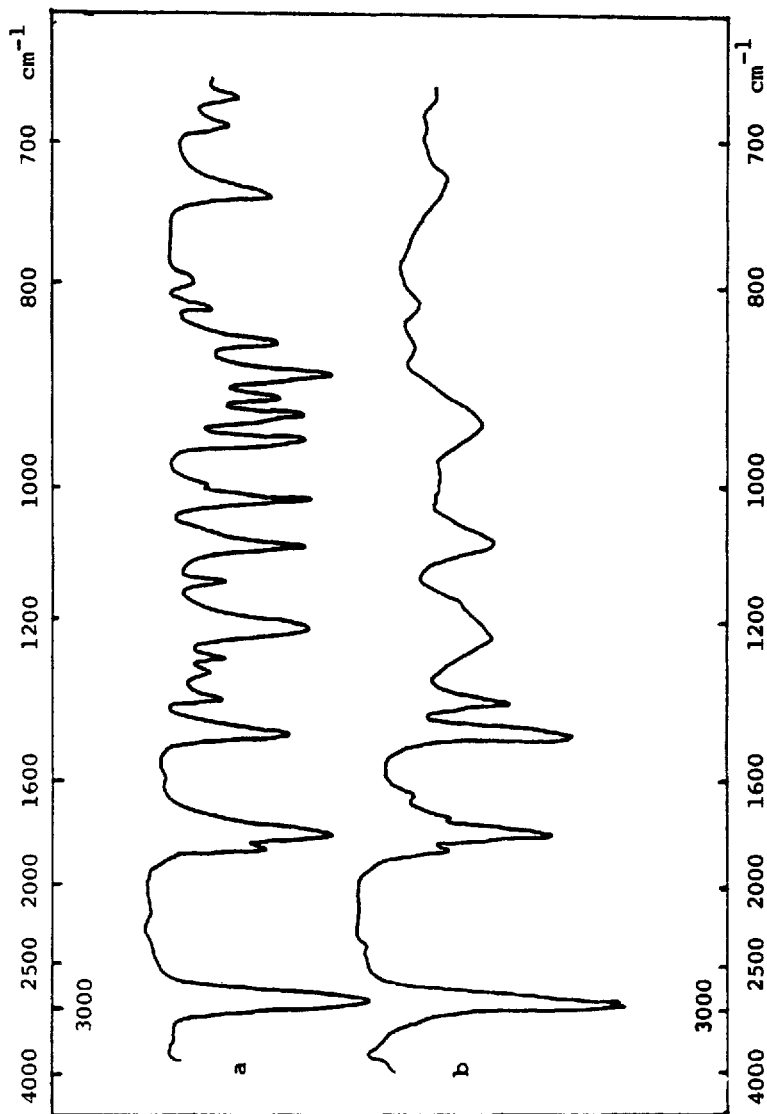


FIG. 1. IR spectra of (a) furan-maleic anhydride adduct and (b) furan-maleic anhydride copolymer (nujol mulls).

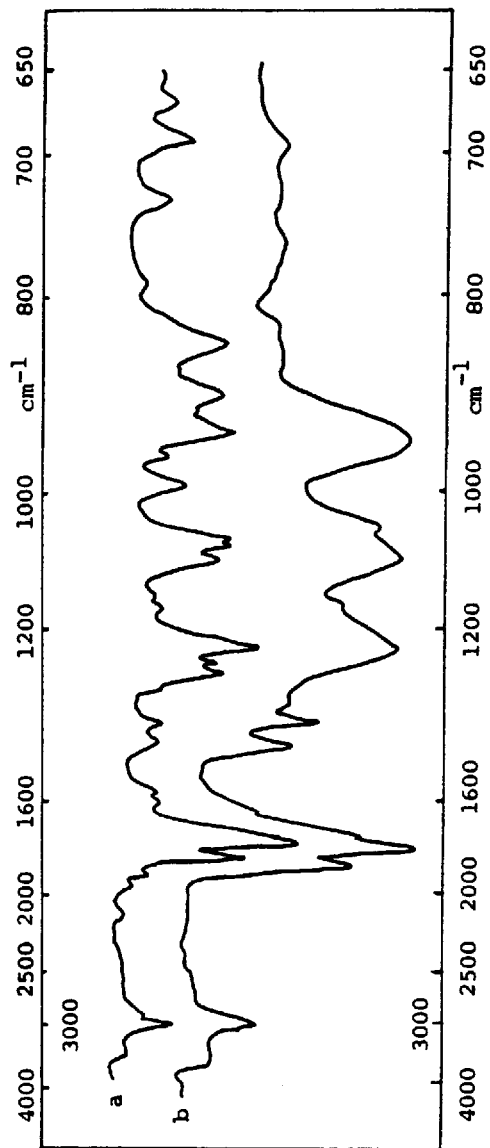
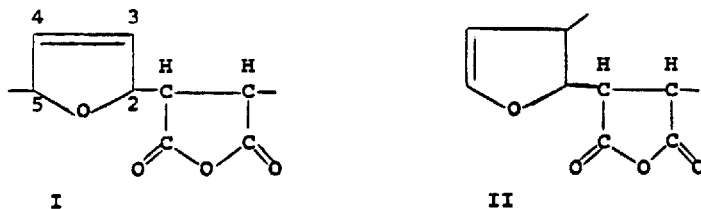


FIG. 2. IR spectra of (a) 2-methylfuran-maleic anhydride adduct (KBr) and (b) 2-methylfuran-maleic anhydride copolymer (film from acetone).

The furan-maleic anhydride copolymer might have the structure of I or II. Structure I has a 2,5-linkage whereas structure II has a



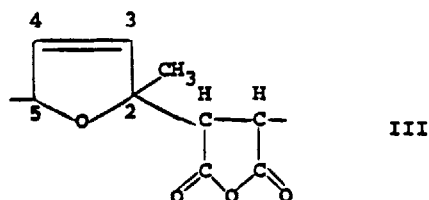
2,3-linkage. In the polymerization of furan by cationic catalysts, it has been observed that the 2,5-dihydro-2,5-furylene units do not occur to any significant extent [8]. Similarly, in the polymerization of 2-methylfuran, the polymer is reported to have a 2,3-furylene linkage [9, 10].

The NMR spectrum of the alternating furan-maleic anhydride copolymer is presented in Fig. 3. The resonance is observed in three principal regions: (A) 3.40-4.30  $\tau$ , (B) 4.30-5.50  $\tau$ , (C) 6.10-6.95  $\tau$ .

Structure is not supported by the NMR spectrum since no proton absorption takes place at a higher field ( $\sim 7.0$   $\tau$ ) which would be expected from the proton at Position 3 of the furan ring in Structure II. On the basis of relative peak area measurements (A:B:C = 1:1:1) and the chemical shifts of variously substituted furans or furan derivatives (Table 8), the copolymer is assigned Structure I. Thus the peaks A, B, and C are assigned to the olefinic protons (3 and 4H), protons at 2,5 positions of the furan ring, and the protons of the maleic anhydride unit, respectively. The relative downfield shift of the protons in the furan unit compared to that in 2,5-dihydrofuran is due to the presence of the neighboring maleic anhydride units.

The NMR spectrum of the 2-methyl furan-maleic anhydride copolymer is shown in Fig. 4. On the basis of relative peak area measurements and the substituents, the assigned structure of the copolymer is III. The peak centered at 3.82  $\tau$  is assigned to the olefinic proton 4. The partly overlapping peak at 4.72  $\tau$  is assigned to the olefinic proton 3 which has shifted upfield due to the methyl

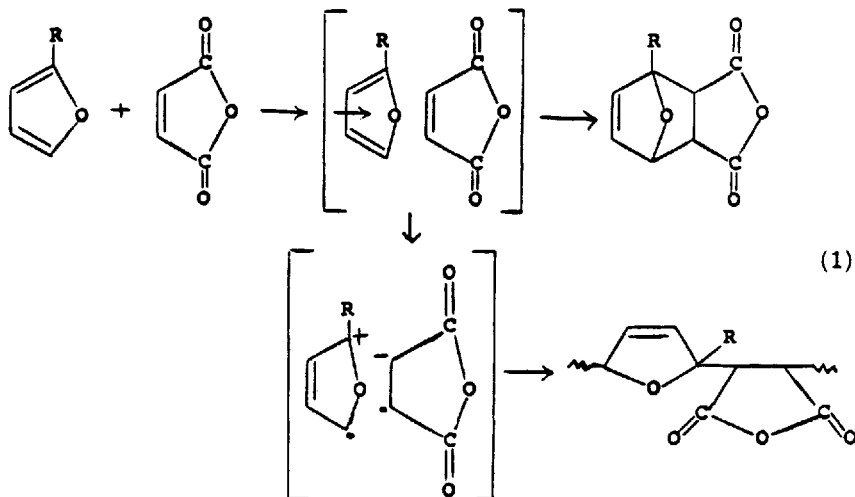




group at the 2 position of the furan ring. The peak at 5.23  $\tau$  is attributed to the proton at the 5 position which has shifted down-field because of the neighboring maleic anhydride units. The protons of the maleic anhydride units are centered at 6.63  $\tau$  and the methyl group appears as a doublet centered at 8.37  $\tau$ . The relative assignments in both the copolymers are tabulated in Table 9.

### DISCUSSION

It has been proposed [4] that a cyclic adduct is formed from a diene-dienophile charge transfer complex in the ground state and an alternating copolymer from the complex in the excited state. This is illustrated in Eq. (1) for the furan-maleic anhydride system.



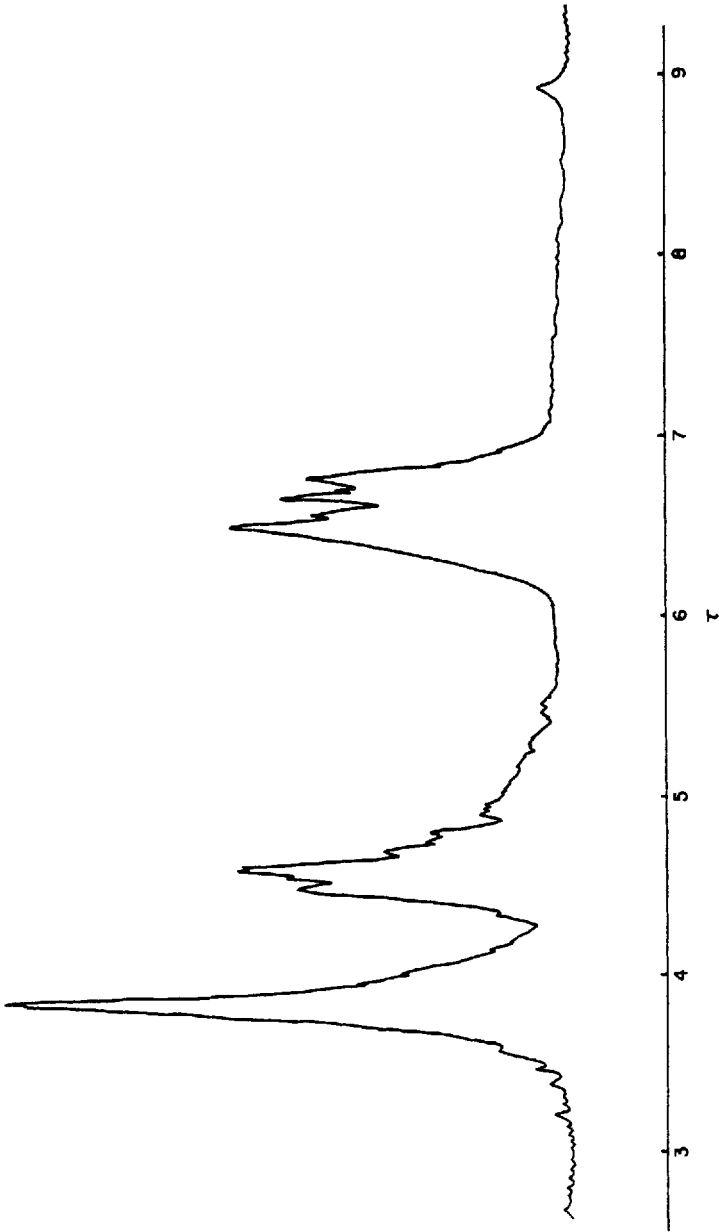

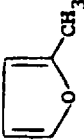


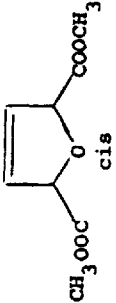


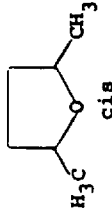
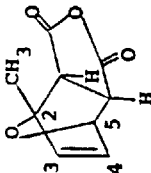


FIG. 3. NMR spectrum of furan-maleic anhydride copolymer.

TABLE 8. Assignments in NMR Spectra of Furan Derivatives

Compound	Chemical shifts ( $\tau$ )				Refs.
	2H	3H	4H	5H	
	2.40	3.40	3.40	2.40	11
	-	3.8	3.5	2.5	11
	-	4.3	4.3	-	11
	5.57	4.22	4.22	5.57	12
	4.69	3.80	3.80	4.69	13

										
	5.80	7.47	5.18	3.78	12					
	5.85	7.53	5.14	3.76	14					
	6.40	8.30	8.30	6.40	15					
	6.14	8.32	8.32	6.14	13					
	-	3.68	3.48	4.74	16					

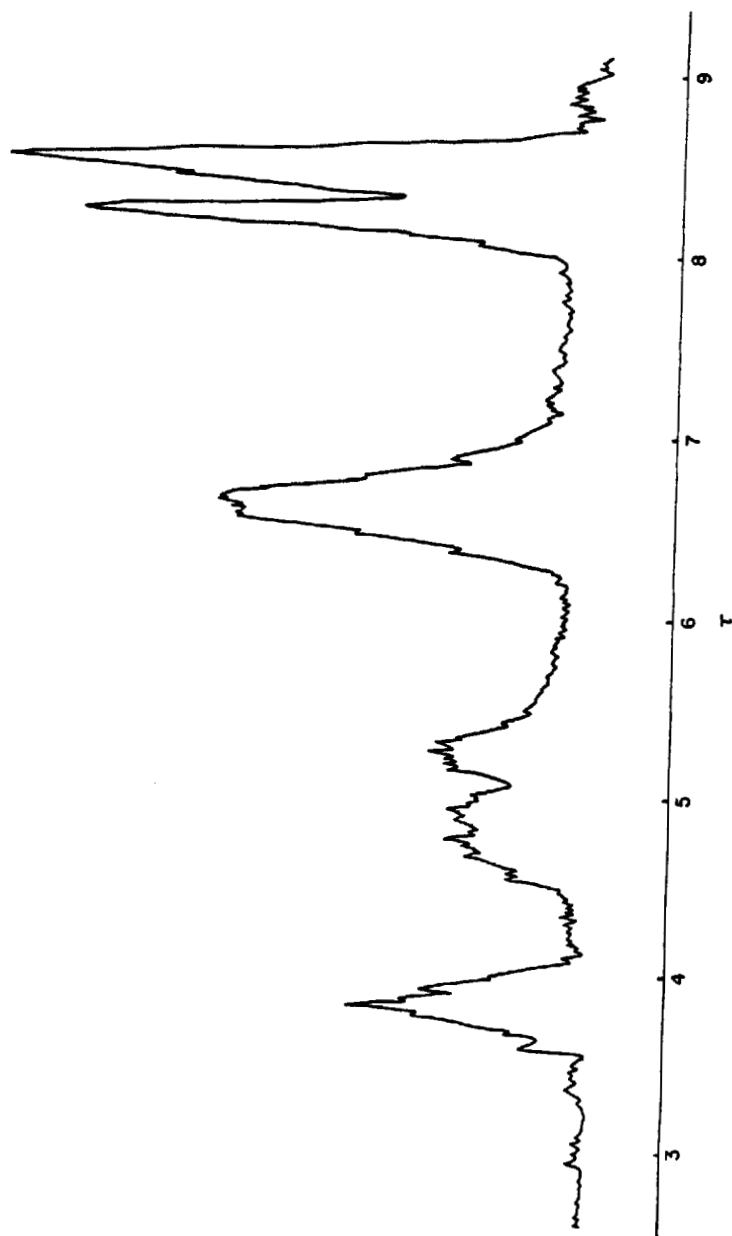


FIG. 4. NMR spectrum of 2-methylfuran-maleic anhydride copolymer.

TABLE 9. Assignments in NMR Spectra of Copolymers

	Chemical shift, $\tau$	
	Furan-maleic anhydride copolymer	2-Methylfuran—maleic anhydride copolymer
2H	4.7	-
3H	3.82	4.72
4H	3.82	3.82
5H	4.7	5.23
MAnh	6.50	6.63
CH <sub>3</sub>	-	8.37

The effect of the rate of catalyst addition and decomposition, i.e., catalyst half-life at the reaction temperature, on the copolymerization of maleic anhydride with furan and with 2-methylfuran is similar to that noted with acyclic conjugated dienes [4, 5]. However, in contrast to the photosensitized copolymerization of the acyclic dienes with maleic anhydride [5], the furan compositions do not respond to irradiation in the presence of a photosensitizer.

It has been suggested that the species which excites the ground state complex is excited maleic anhydride which is, in turn, excited by the excited products from the decomposition of the radical precursors or by the excited photosensitizer. The failure of the furan compositions to respond to photosensitization may be the result of the quenching action of the furans.

The formation of the alternating furan-maleic anhydride copolymer from the polymerization of the Diels-Alder adduct in the presence of a radical catalyst suggests a retrograde reaction in which the comonomers are regenerated and undergo polymerization. The retrograde reaction apparently occurs at 60°C or higher since no copolymer is obtained below 60°C although the polymerization of the comonomers can be carried out above 40°C.

This is confirmed by the formation of the isoprene-maleic anhydride adduct when the furan-maleic anhydride adduct is heated

above 60°C in the presence of isoprene. It has been reported [17] that the menthofuran-maleic anhydride adduct decomposes on refluxing in benzene in the presence of 3-methyl-1,3-pentadiene or  $\alpha$ -phellandrene and the diene-maleic anhydride adduct is formed. The high yield of isoprene-maleic anhydride adduct obtained in the presence of furan indicates that only negligible concentrations of the furan-maleic anhydride ground state complex exist in the presence of isoprene.

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