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Donor-Acceptor Complexes in Copolymerization. XXXIX. Alternating Diene-Dienophile Copolymers. 6. Photosensitized Copolymerization of Conjugated Dienes and Maleic Anhydride

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ABSTRACT

Equimolar, alternating copolymers are produced when solutions of conjugated dienes and maleic anhydride are subjected to 2537 Å UV light in the presence of photosensitizers or 3000 Å or higher wavelength light in the absence or presence of sensitizers. The yield of copolymer is highest when the sensitizer has $E_T > 74$ kcal/mole. The copolymers are insoluble in polar organic solvents when the sensitizer has $E_T > 75$.

INTRODUCTION

It is well-known that the uncatalyzed reaction of a conjugated diene and maleic anhydride yields the 1:1 cyclic Diels-Alder adduct [1]. It has recently been shown that equimolar, alternating copolymers were formed under the influence of ionizing radiation [2] or free radical initiators [2-7].

The present paper reports the preparation of alternating conjugated diene-maleic anhydride copolymers under UV irradiation.

EXPERIMENTAL

Materials

Dioxane was refluxed over stannous chloride for 5 hr in order to destroy peroxides and then distilled. The distilled dioxane gave a negative peroxide test with acidified KI. Monomers and sensitizers were freshly distilled before use.

Polymerization

The reactions were carried out in quartz tubes stoppered with a rubber cap. After 30 mmoles of maleic anhydride was dissolved in 3 ml dioxane, the solution was purged with nitrogen for 20 min. The sensitizer was then added and the tube was chilled in ice water. An exothermic reaction occurred upon the addition of 30 mmoles of diene. The tube was warmed to 30°C and then suspended in the center of a "Rayonet" Srinivasan-Griffin Photochemical Reactor, 5 in. from 16 UV bulbs (2537, 3000, or 3500 Å). The solution was irradiated for 45 min while the temperature inside the reactor was maintained at 40°C. The reaction mixture was poured into benzene and the precipitated copolymer was filtered, washed with hot benzene, and dried in vacuo at 45°C. The adduct was isolated as the anhydride by evaporation of filtrates containing low boiling sensitizers. The adduct was isolated as the acid from the filtrates containing high boiling sensitizers by extraction with aqueous alkali, neutralization with HCl, and extraction with ether.

Irradiations under a high-pressure mercury lamp were carried out in Pyrex tubes suspended 5 in. from the light source.

The equimolar, alternating structure of the copolymers was confirmed by elemental and NMR analyses. Intrinsic viscosities were determined in methyl ethyl ketone at 30°C.

RESULTS

Irradiation of a solution of isoprene or butadiene and maleic anhydride in peroxide-free dioxane under 2537 Å UV light in the absence of oxygen or a free radical catalyst yields the cyclic Diels-Alder adduct. However, when the irradiated solution contains a photosensitizer, the adduct is accompanied by the equimolar, alternating copolymer [7]. The Diels-Alder reaction is extremely rapid when the diene and maleic anhydride are present in high concentrations and the adduct is the major product. The copolymer is the predominant product and adduct formation is greatly reduced when the polymerization is carried out in the presence of a free radical catalyst and a solution of the diene and the catalyst is added to a solution of maleic anhydride [5-7].

As shown in Table 1, the equimolar copolymer is formed with photosensitizers having triplet energies ranging from 54 to 78 kcal/mole. However, the maximum yield of copolymer is obtained under 2537-3500 Å irradiation when E_T of the sensitizer is 74-75 kcal/mole. The lower yields when $E_T > 75$ are probably due to the formation of a thin polymer film on the wall of the tube with resultant reduced light transmission.

Similar results are obtained upon irradiation of dioxane solutions containing butadiene or piperylene, maleic anhydride, and various sensitizers (Table 2).

Copolymerization also occurs upon irradiation of solutions containing diene, maleic anhydride, and photosensitizer in the absence of dioxane or other solvent.

Although copolymerization of conjugated dienes and maleic anhydride in peroxide-free dioxane does not occur in the absence of oxygen, a free radical catalyst or a photosensitizer under irradiation with 2537 Å UV light, copolymerization does occur in peroxide-free dioxane in the absence of these additives under irradiation with 3000 and 3500 Å UV light as well as under irradiation from a high-pressure mercury lamp.

Irradiation of a mixture of isoprene, furan, maleic anhydride, and acetophenone under 2537 Å light gives a lower yield of isoprene-maleic anhydride copolymer than is obtained in the absence of furan (Table 3). Under 2537-3500 Å irradiation furan and maleic anhydride fail to yield any copolymer in the presence of acetophenone.

TABLE 1. Copolymerization of Isoprene with Maleic Anhydride under UV Irradiation[a]

	Sensitizer			Yield (%)	
UV (Å)	Nature	mmoles	E_T (kcal/mole)	Adduct[b]	Copolymer
None	None			78[c]	0
2537	None	0	0	88[c]	0
	Benzil	5	54	61	6.1
	Biacetyl	30	55	nd	3.1
	p-Diacetylbenzene	5	68	nd	2.5
	Benzophenone	20	69	nd	2.0
	Acetophenone	30	74	68	6.5[d]
	Propiophenone	30	75	65	7.8[d]
	Acetone	40	78	78[c]	4.5
	Cyclohexanone	30	78	69	1.1

3000	None	0	0	57[c]	4.6
	2-Acetonaphthone	3	59	71	5.9
	Acetophenone	30	74	61	7.2
	Acetone	30	78	66[c]	2.4
3500	None	0	0	61[c]	8.9
	2-Acetonaphthone	3	59	65	4.5
	Acetophenone	30	74	31	7.6
	Acetone	30	78	72[c]	2.8
HP Hg	None	0	0	64[c]	2.4
	2-Acetonaphthone	3	59	65	11.3
	Acetophenone	30	74	67	2.3
	Acetone	30	78	53[c]	4.7

[a] Temp., 40°C; time, 45 min; 3 ml dioxane; [I] = [MAnh] = 30 mmoles.

[b] Isolated as diacid; nd = not determined.

[c] Isolated as anhydride.

[d] $[\eta]$ = 0.20 dl/g (MEK, 30°C).

TABLE 2. Copolymerization of Butadiene and Piperylene with Maleic Anhydride under UV Irradiation[a]

	Sensitizer			Yield		
					Copolymer	
UV (Å)	Nature	mmoles	E_T (kcal/mole)	Adduct (%)[b]	(%)	[η] (dl/g)[c]
Butadiene						
2537	None	0	0	75	0	
	Benzil	10	54	nd	5.2	
	Acetophenone	30	74	nd	9.2	0.98
	Acetone	40	78	63	5.6	
	Cyclohexanone	30	78	80	0.5	
HP Hg	None	0	0	nd	3.1	1.03
	Acetophenone	30	74	nd	6.6	

2537	Acetophenone	10	74	nd	20.4	0.94
HP Hg	None	0	0	nd	12.7	1.4
	Acetophenone	10	74	nd	8.4	
trans-Piperylene						
2537	Acetophenone	10	74	nd	6.6	0.26
HP Hg	None	0	0	nd	8.1	0.19

[a] Temp., 40°C; time, 45 min; 3 ml dioxane; [D] = [MAnh] = 30 mmoles.
[b] nd = not determined.
[c] MEK, 30°C.

TABLE 3. Copolymer Formation from Isoprene, Furan, and Maleic Anhydride under 2537 Å UV Irradiation[a]

Isoprene (mmoles)	Furan (mmoles)	Maleic anhydride (mmoles)	Acetophenone (ml)	Copolymer (%)
30	0	30	3	3.0
0	30	30	3	0
30	30	30	3	1.6[b]

[a] Temp. 30°C; time, 45 min; no solvent.

[b] Identified as isoprene-maleic anhydride copolymer.

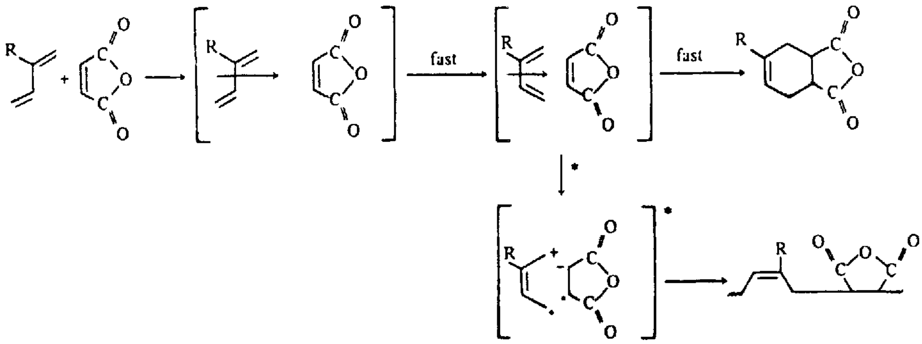
The major portion of the conjugated diene-maleic anhydride copolymer produced in the presence of sensitizers having $E_T < 75$ is soluble in polar solvents such as acetone, methyl ethyl ketone, and dioxane. However, a small amount of insoluble copolymer is formed as a thin film on the walls of the tube. The insoluble copolymer, in the form of a thin film or a granular deposit, is the predominant or exclusive product when the copolymerization is carried out in the presence of a sensitizer having $E_T > 75$.

The insoluble copolymer has an equimolar composition and an IR spectrum which is essentially identical to that of the soluble copolymer. The copolymer is insoluble in acetone, methyl ethyl ketone, dioxane, tetrahydrofuran, diethyl ether, dimethyl formamide, dimethyl sulfoxide, chloroform, carbon tetrachloride, and aliphatic, alicyclic, and aromatic hydrocarbons. The cross-linked nature of the product is indicated by its failure to dissolve in aqueous alkali and the charring, without apparent softening, which occurs when exposed to temperatures above 250°C.

DISCUSSION

It has been reported that certain Diels-Alder reactions are subject to photochemical as well as thermal catalysis, e.g., anthracene-maleic anhydride [8] and butadiene—α-acetoxyacrylonitrile [9, 10]. In the presence of photosensitizers, the relative amounts and the structures of the reaction products depend upon the excitation energies of the triplet states of the sensitizers, e.g., dimerization of conjugated dienes [11, 12] and diene-p-benzoquinone [13].

It has been proposed [6, 7] that the formation of alternating copolymer in lieu of cyclic adduct, when the reaction of a conjugated diene and maleic anhydride is carried out in the presence of a free radical precursor at a temperature where the latter has a short half-life, is due to the generation of electronically excited states which promote photochemical reactions. It is presumed that the cyclic adduct and the alternating copolymer arise from a common intermediate, i.e., the charge transfer complex, but that the adduct arises from the ground state complex while the alternating copolymer arises from the excited complex. The excitation of the complex is the result of the transfer of energy from the chemically generated excited states.



The formation of alternating copolymers from the reactions of conjugated dienes with maleic anhydride under UV irradiation, reported herein, is undoubtedly due to the homopolymerization of diene-maleic anhydride exciplexes. However, the formation of the exciplexes and the initiation of their homopolymerization apparently depend upon the wavelength of light, the triplet energy of the photosensitizer, and donor monomer-acceptor monomer as well as monomer-solvent interactions.

The excitation of the ground state diene-maleic anhydride complexes may occur through one or more of the following paths:

1. direct excitation of the comonomer complex under irradiation,
2. excitation of the photosensitizer under irradiation followed by energy transfer to
    a. the comonomer complex
    b. maleic anhydride followed by energy transfer from excited maleic anhydride to the comonomer complex.

The initiation of the homopolymerization of comonomer exciplexes [14] may occur

3. spontaneously when the exciplex concentration is high,
4. through hydrogen abstraction by
    a. excited photosensitizer
    b. excited maleic anhydride
    c. free radicals generated
        i. by maleic anhydride-dioxane interaction under irradiation
        ii. from dioxane as a result of hydrogen abstraction by
            a excited photosensitizer
            b excited maleic anhydride.

The failure to obtain copolymer in the absence of a photosensitizer under 2537 Å irradiation indicates that direct excitation of the ground state comonomer complex (Path 1) does not occur under these conditions. However, direct excitation apparently occurs at higher wavelengths and polymerization is initiated either spontaneously (Path 3) or through hydrogen abstraction by free radicals generated by maleic anhydride-dioxane interaction (Path 4.c.i).

The formation of alternating copolymer in the presence of a photosensitizer, particularly under 2537 Å irradiation, indicates that energy transfer from the excited sensitizer is responsible for the formation of the exciplexes (Path 2) and also possibly for the polymerization (Paths 3, 4.a, or 4.c.ii.a). However, the maximum yield of copolymer under 2537-3500 Å irradiation when the triplet energy of the sensitizer is 74-75 kcal/mole suggests that excitation of maleic anhydride which has a triplet energy of 72 kcal/mole plays an important role in polymer formation. It is not possible, from the available data, to determine whether excited maleic anhydride is responsible for the generation of exciplexes (Path 2.b) and/or the initiation of the polymerization (Paths 4.b or 4.c.ii.b).

Since copolymers are formed in the presence of photosensitizer in the absence of dioxane, the participation of the latter (Path 4.c) is probably not a major factor in the polymerization reaction.

The diketone photosensitizers such as benzil and biacetyl, which undergo cleavage to radical species under irradiation, may function as the source of excitation energy in the formation of exciplexes and as hydrogen abstracting radicals in polymerization initiation.

Furan and maleic anhydride do not copolymerize under 2537-3500 Å light in the presence of photosensitizers at 30 or 65°C [15]. This has been attributed to the apparent quenching action of furan. However, the failure to copolymerize furan and maleic anhydride may be due to the low concentration of complexes. The reduction in the yield of isoprene-maleic anhydride copolymer in the presence of furan may be a dilution effect, i.e., a reduction in the concentration of isoprene-maleic anhydride complexes, rather than quenching by furan.

The formation of insoluble, cross-linked diene-maleic anhydride copolymers when photosensitizers, such as acetone or cyclohexanone with E_T of 78 kcal/mole, are present suggests that the excited species or the radicals generated under these conditions are effective in hydrogen abstraction from the allylic methylene groups in the copolymer. The resultant radicals on the polymer backbone can couple to generate cross-links. It is of interest to note that insoluble polymers are also formed in the presence of excited species which are chemically generated from free radical precursors when benzene and other aromatic hydrocarbons [2, 3, 6] as well as methyl isobutyl ketone [16] ($E_T > 75$) are used as reaction media. These species can apparently transfer their excitation energy to the aromatic hydrocarbons and methyl isobutyl ketone, in the presence of the conjugated dienes and/or maleic anhydride, but not to acetone since the latter yields soluble copolymers in the presence of the free radical precursors [5, 6].

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