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Polymer Formation by γ -Irradiation of Dichloromaleic Anhydride (DCIMA) in Benzene Solution

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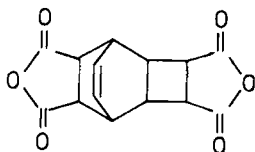
ABSTRACT

In the γ -irradiation of dichloromaleic anhydride (DCIMA) in benzene solution, the first step of the reaction, analogous to photochemistry, is the formation of α -chloro- α -phenylmaleic anhydride (CIPhMA). In contrast to photochemistry, where this intermediate is transformed into a cycloaddition product, a polymer is formed in radiolysis. The polymer consists of CIPhMA units as well as components resulting from benzene radiolysis.

INTRODUCTION

The homopolymerization of maleic anhydride (MA) is well known and described to be initiated by radicals [1, 2], organic bases [3-5], and UV and ionizing radiation in bulk or in inert solvents [6]. The polymerization is accompanied by CO₂ elimination. In the presence of olefinic or aromatic compounds, however, the photolysis of MA

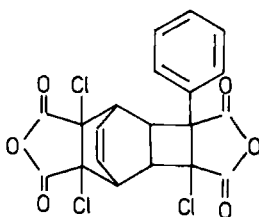
results in a cycloaddition of MA to the double bonds. In the case of benzene, a 1:1 cycloaddition intermediate is formed which immediately undergoes a Diels-Alder reaction to form a 2:1 MA-benzene adduct (I) [7, 8].



I

The radiolysis of MA in benzene solution has been investigated by Raciszewski [9]. He found that the 2:1 adduct (I) is formed in small amounts as well, but the main product is a polymer which consists mainly of MA units.

For disubstituted maleic anhydrides neither homo- nor copolymerization reactions are reported. Nevertheless, photochemical cycloadditions are still possible. Dimethylmaleic anhydride (DMMA) adds to cyclohexene [10] and dichloromaleic anhydride (DCIMA) adds to butadiene [11]. In benzene solution a photochemically induced cycloaddition of these α, α' -disubstituted compounds to the aromate is not observed. While DMMA cyclodimerizes [12], DCIMA undergoes an exotic reaction. In the first step, an α -chloro- α -phenylmaleic anhydride (ClPhMA) is formed. The ClPhMA product then behaves like the unsubstituted MA, which means a second step cycloaddition to benzene takes place, followed by a third step Diels-Alder reaction with a DCIMA molecule to result in the product II [13].



II

Working with DMMA and DCIMA in benzene solution we find that the radiolysis of DMMA-benzene leads mainly to the DMMA cyclodimer,

whereas the main product of the DC1MA-benzene radiolysis is a polymer. In this article we want to report on this polymer.

RESULTS

With benzoyl peroxide as radical initiator and $\text{KOC}(\text{CH}_3)_3$ as ionic initiator for polymerization we proved that DC1MA in benzene solution is not able to undergo polymerization reactions. Also, the photolysis and radiolysis of DC1MA in cyclohexane solutions does not result in polymer formation in the presence or absence of sensitizers like acetophenone or benzophenone. Sensitized photolysis in benzene results in the formation of the product II. No polymer is formed.

Adding pyridine to a benzene-DC1MA solution causes immediate formation of a brown-green precipitate which is unstable. Therefore it was not possible to purify and analyze this compound. During γ -irradiation of a DC1MA-benzene solution DC1MA is consumed. Figure 1 shows the DC1MA conversion for different irradiation conditions. In Fig. 2 the CO_2 and CO formation is plotted.

Figure 3 shows a gas chromatogram of the dimeric products of benzene radiolysis. Obviously the benzene radiolysis is completely altered in the presence of 0.1 mole/liter DC1MA. The formation of

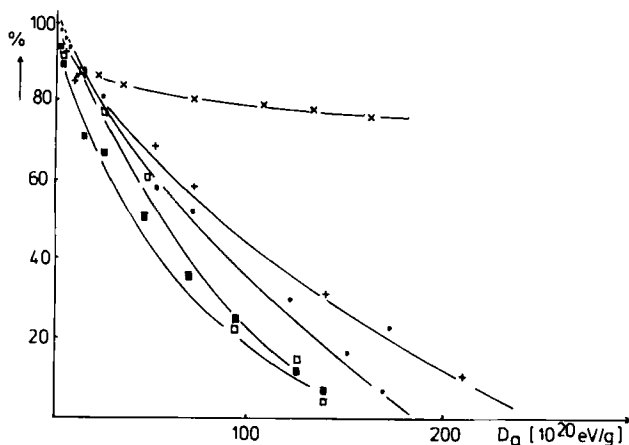


FIG. 1. Radiolytic DC1MA conversion in a 0.1 M solution of DC1MA in benzene: (●) without additive; (□) benzophenone, 0.2 mole/liter; (■) acetophenone, 0.2 mole/liter; (×) $\text{C}(\text{NO}_2)_4$, 0.8 mole/liter; (+) saturated with air.

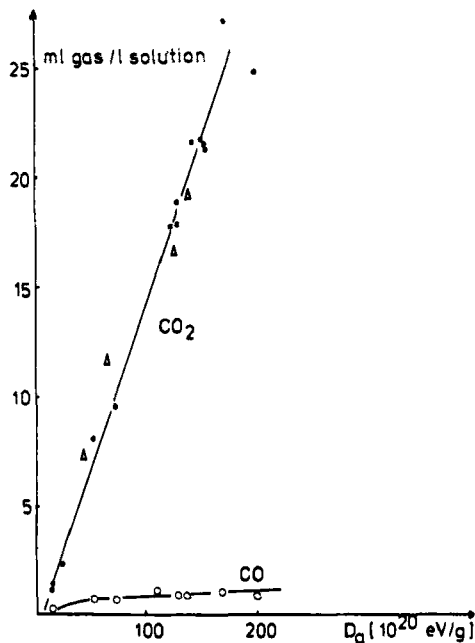
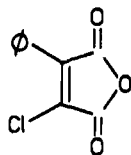


FIG. 2. Radiolytic CO_2 and CO production: (\bullet) 0.1 mole/liter DC1MA in benzene; (Δ) 0.1 mole/liter DC1MA + 0.8 mole/liter $\text{C}(\text{NO}_2)_4$ in benzene.

diphenyl is unchanged, but formation of all other dimeric products is almost completely suppressed.

C1PhMA (III) could be isolated by preparative gas chromatography. It is identical with the first-step substitution product formed in photolysis. Figure 4 shows the concentration of C1PhMA versus radiation dose.



III

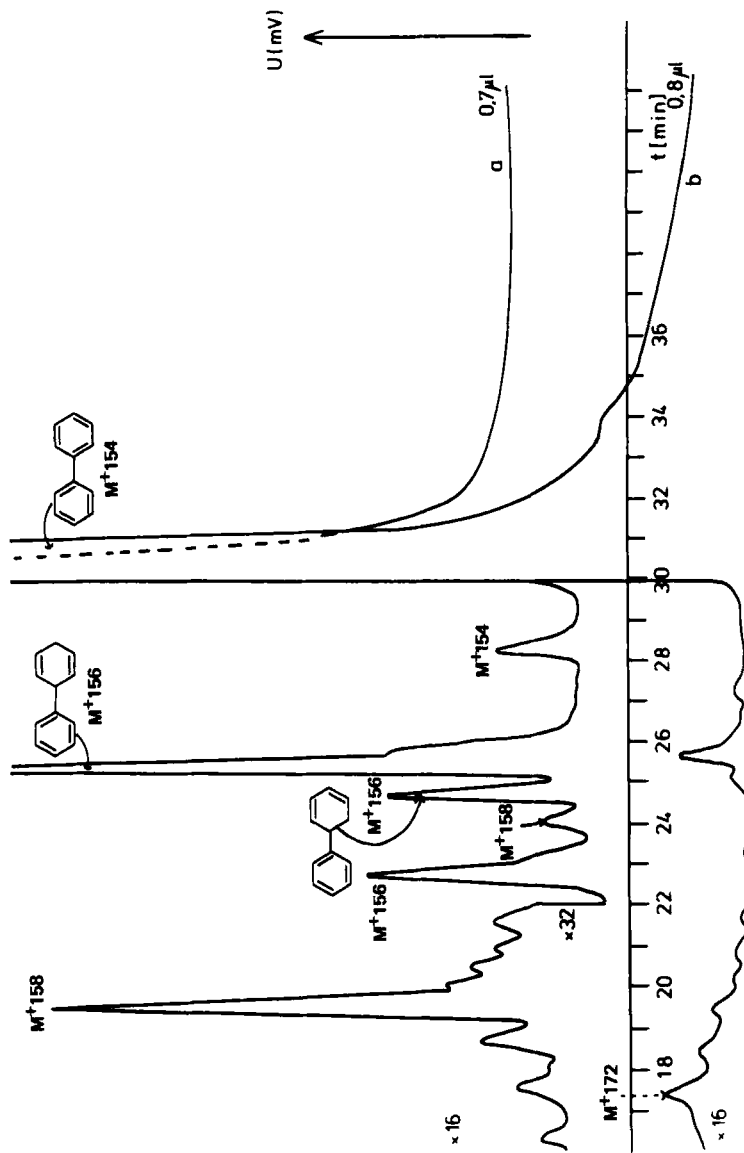


FIG. 3. Gas chromatogram of the dimeric products of benzene radiolysis (radiation dose = 75×10^{20} eV/g): (a) pure benzene; (b) 0.1 mole/liter DCIMA in benzene.

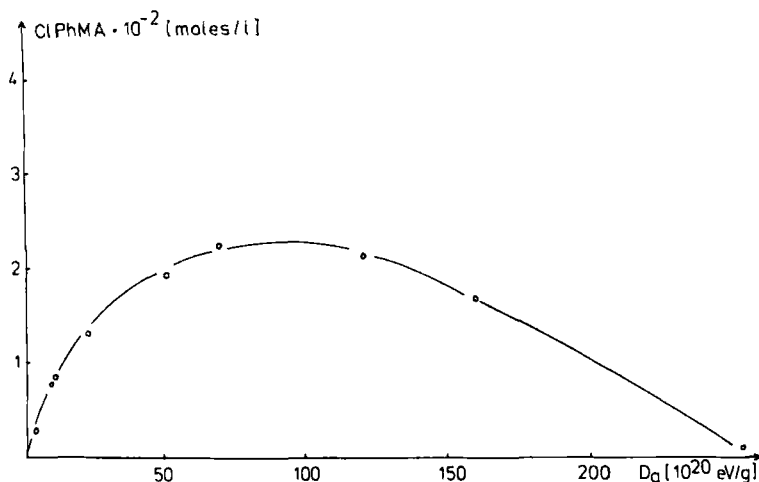


FIG. 4. Concentration of α -chloro- α' -phenylmaleic anhydride (ClPhMA) vs. radiation dose; 0.1 mole/liter DCIMA in benzene.

The main product in radiolysis, however, is a polymer. The yield of this polymer and its molecular weight as functions of radiation dose are shown in Figs. 5 and 6, respectively.

Table 1 gives the results of elemental analysis of various polymer samples. Whereas the polymers are insoluble in water, boiling in KOH results in a completely water-soluble product. This means that any polymer molecule must contain at least one hydrolyzable group. The number of these groups per 100 g polymer were obtained by titration of the excess KOH after hydrolysis. For comparison the photoadduct II was treated under the same conditions (boiling 5 hr in 0.1 M KOH). It could be shown that the anhydride as well as the Cl groups are hydrolyzed quantitatively (Table 1).

The IR spectra of the polymers are in good agreement with these results and only depend to a small extent on radiation dose. The bands at 1860, 1780, 1300, and 960 cm^{-1} due to C=O and =C-O-C stretching vibrations of anhydrides in five-membered rings are replaced completely after hydrolysis of the polymer by bands at 1590 and 1390 cm^{-1} due to carboxyl groups. The former Cl groups are transformed during hydrolysis into secondary or tertiary alcohols with bands at 1100-1050 cm^{-1} . Furthermore, characteristic absorption bands of mono- and disubstituted benzene as well as for olefinic

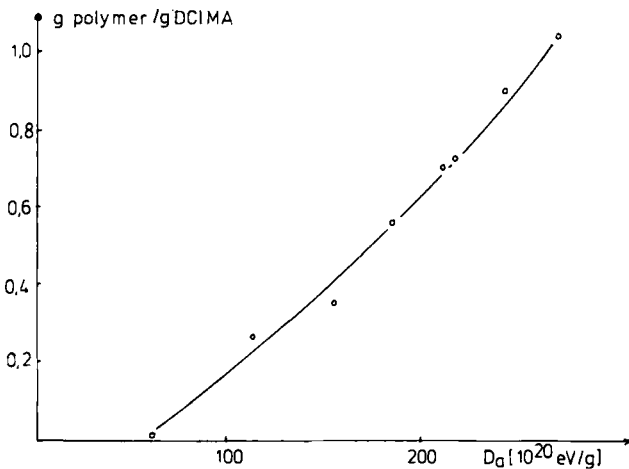


FIG. 5. Yield of polymer (g polymer formed/g DC1MA originally present) in radiolysis of a 0.1 M solution of DC1MA in benzene.

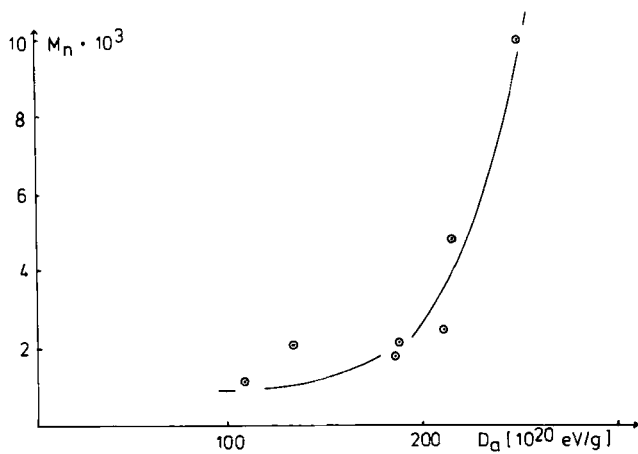


FIG. 6. Molecular weight dependence of DC1MA-benzene polymer on radiation dose.

TABLE 1. Analysis of DCIMA-Benzene Polymer

Radiation polymer	Dose (eV/g)	C (%)	H (%)	O		Cl mole/100 g	Number of hydrolyz- able groups			
				%	mole/100 g		Per mole	Per 100 g (calcd) ^a	Per 100 g (exptl)	
										%
	110×10^{20}	60.0	3.7	21.6	1.35	14.7	0.41	1.30	1.3	
	187×10^{20}	58.7	4.1	20.6	1.29	16.6	0.48	1.33	1.3	
	206×10^{20}	58.6	4.0	19.6	1.22	17.8	0.50	1.31	-	
Photoadduct (II)	-	53.0	2.4	21.2	1.32	23.5	0.63	7	1.55	1.6

^a Calculated from elemental analysis data on the assumptions that all oxygen is present in anhydride groups, and all Cl groups can be hydrolyzed.

and aliphatic groups are present in the IR spectra of the polymer. The NMR spectrum (Fig. 7) shows that the polymer contains aromatic ($\delta = 7.36$ ppm) and olefinic ($\delta = 5.75$ ppm) protons.

DISCUSSION

Analogous to sensitized photolysis, a substitution product C1PhMA is formed in radiolysis, but the mechanism of its formation apparently is not identical. From Fig. 1 one can see that C1PhMA formation in radiolysis can be enhanced by sensitizers (acetophenone and benzophenone) to some extent, but is almost completely inhibited by the presence of $C(NO_2)_4$. $C(NO_2)_4$ is known to be very efficient in scavenging electrons ($K = 6 \times 10^{10}$ liter/mole-sec [14]) whereas benzene is rather inefficient ($K < 7 \times 10^6$ liter/mole-sec [15]). Therefore the inhibition of C1PhMA formation by $C(NO_2)_4$ should be due to a competition between $C(NO_2)_4$ and DC1MA in scavenging electrons; this means that the first step in C1PhMA formation is an electron attachment to DC1MA, whereas the excitation of DC1MA is of lesser importance. Photochemical excitation of DC1MA-benzene leads to the formation of C1PhMA and HCl; in radiolysis no HCl could be detected. According to Fig. 4 C1PhMA is completely consumed in polymer formation. The photochemical addition product II is not obtained.

Homopolymerization of MA is accompanied by CO_2 elimination [1-5]. In the radiolysis of DC1MA in benzene, CO_2 as well as CO formation takes place, but approximately 200 molecules of DC1MA are consumed for each molecule of CO_2 formed (Fig. 2). In addition, $C(NO_2)_4$, which inhibits DC1MA conversion almost completely, has no influence on CO_2 and CO formation. Therefore CO_2 formation must be independent of polymer formation. Taking into account that the molar ratio of benzene/DC1MA (0.1 M solution) is approximately 110/1, CO_2 /CO production should be due to the energy absorbed in DC1MA directly, which is proportional to the electron fraction of DC1MA in the solution. Mass spectra of DC1MA, which we have taken, reveal that elimination of CO_2 from the parent ion is very effective. This fragmentation is followed by a competitive CO and Cl elimination. The constancy of the CO_2 formation up to very high doses (Fig. 2), suggests that direct ionization of the polymer results in CO_2 elimination also. This is in good agreement with the elemental analysis data (Table 1). Here, with increasing dose, the oxygen content of the polymer decreases gradually.

The relatively long induction period and the increase of molecular weight with increasing dose indicates that an intermediate is responsible for polymerization.

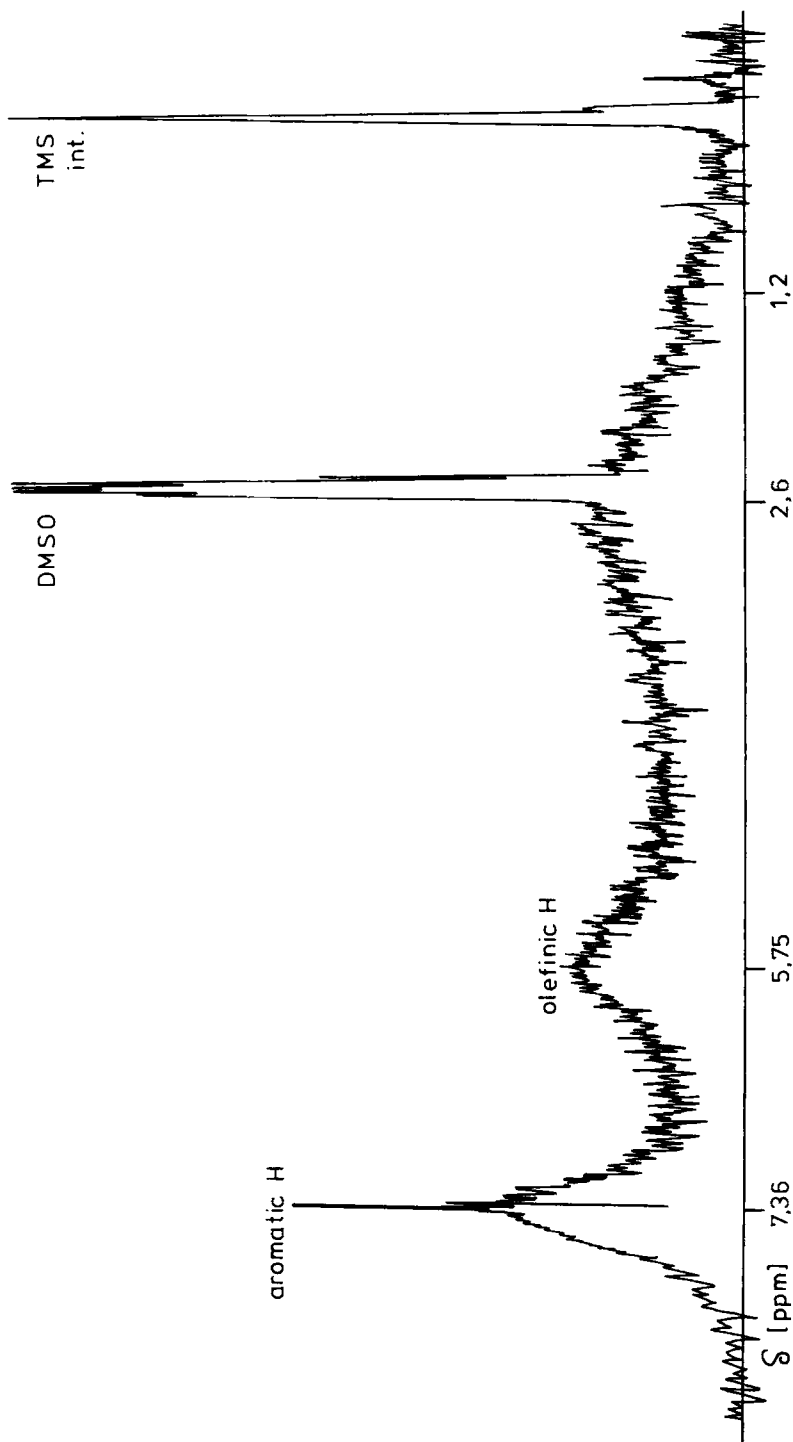


FIG. 7. $^1\text{H-NMR}$ spectrum of the DCIMA-benzene polymer in dimethyl sulfoxide.

Elemental analysis of the polymer formed at low dose yields a ratio of O:Cl \approx 3:1, which is the same as with ClPhMA. The IR spectrum corroborates the existence of anhydride groups in the polymer. If it is assumed that all of the oxygen of the polymer exists in the form of anhydride groups, the O and Cl portion of the polymer should result in 1.3 hydrolyzable groups per 100 g polymer (Table 1). This is in fact the value found by hydrolysis of the polymer. The complete hydrolysis of all anhydride and Cl groups could be proven by the hydrolysis of the photoadduct II. Because of the anhydride groups in the polymer as well as the formation of tertiary alcohol groups following hydrolysis of Cl groups, the polymerization of ClPhMA should proceed via the C=C double bonds. The increase in molecular weight at doses where all DCIMA and nearly all ClPhMA is consumed must be due to crosslinking reactions. Here the decrease of the O portion of the polymer by CO₂ elimination may play a role.

Nevertheless, a polymer consisting only of ClPhMA units should contain 1.5 hydrolyzable groups/100 g. From this difference and from the fact that the benzene radiolysis is completely changed in the presence of DCIMA it must be concluded that at least a second component is included in the polymer. Figure 3 shows that in the radiolysis of benzene the production of diphenyl is not influenced by DCIMA addition, whereas unsaturated products such as phenylcyclohexadiene are suppressed. They should be incorporated in the polymer by copolymerization with ClPhMA or by scavenging of their radical precursors by ClPhMA. This assumption is supported by the NMR data, which show that, besides aromatic hydrogens, olefinic hydrogens are present which should originate in polymerization of cyclic dienes.

EXPERIMENTAL

Reagents

DCIMA was purified by double sublimation in vacuum (Fp 117-119°C).

Sample Preparation and Irradiation

The solutions were filled into glass ampoules degassed several times and sealed under vacuum. Irradiation was performed with γ -radiation from a Co-60 source, at a dose rate of 0.2 - 2.0×10^{20} eV/g-hr.

Gas Chromatography

The preparative collection of ClPhMA was done with a column with 5% Apiezon M on Chromosorb G 45/60 mesh at 180°C.

A stainless steel 1/8-in. packed column was used for the separation of the benzene dimers. The liquid phase was 5% SE30 on Chromosorb T, 40-60 mesh.

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