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POLYMERIZATION OF MALEIC ANHYDRIDE INITIATED BY IMIDAZOLE

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ABSTRACT

Imidazole was employed as an anionic initiator for the homopolymerization of maleic anhydride in various solvents.Polymerization was very rapid and the obtained products have different colours varying from white to dark brown. The colour of the product was found to depend on the quantity of imidazole added, and the solvent of polymerization. Darkness of polymers are thought to be due to cross-conjugation displaying paramagnetic character. The ESR signals of dark brown polymers were more intense than the lighter ones whereas the white products had no ESR signal.

INTRODUCTION

It is known since nineteen sixtees that maleic anhydride can be homopolymerized by various techniques [1-3]. Initiation of homopolymerization by organic bases [4] such as triethylamine and pyridine is among these techniques. The polymers obtained by those organic bases were reported to have dark brown or almost black colour. They were found to have paramagnetic and semiconductor character. The researchers have explained these properties by the existence of cross-conjugation in the polymer chain.

Poly(maleic anhydride) can have different structural units,depending upon the type of initiator

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employed. Polymers obtained by the triphenyl phosphine initiation contain succinic anhydride units and cyclopentanone derivatives whereas tributyl phosphine initiation yields mostly cross-conjugated ketoolefinic units [5]. Polymers obtained by the former initiator had no ESR signal while the latter initiator yielded polymers displaying paramagnetic character.

On the other hand, it was reported that some polar vinyl monomers such as acrolein can be polymerized in the presence of imidazole [6]. The mechanism of polymerization was proposed as anionic.

In this work, homopolymerization of maleic anhydride initiated by imidazole was performed. The effect of solvent and initiator concentration were investigated.

MATERIALS

Maleic anhydride was purified by sublimation before use.All the solvents were purified by standard methods prior to polymerization reactions. Imidazole was reagent grade (Aldrich Chem. Co.) and it was used as obtained.

POLYMERIZATION

Definite amounts of monomer and the initiator were dissolved in the chosen solvent seperately and after being equilibrated at the required temperature, they were mixed.Insoluble product was seperated after filtering the solution and the soluble polymer was precipitated in toluene to find the yields gravimetrically.

FTIR spectra of polymers were taken as KBr pellets using a Perkin-Elmer 1710 Model FTIR combined with PE 7500 Data Station.

RESULTS AND DISCUSSION

Homopolymerization of maleic anhydride was achieved by using imidazole as initiator. Various solvents were used in order to examine their effect on polymerization. At high initiator concentrations, the reactions are very rapid and

TABLE 1
Experimental details of the polymerization of maleic anhydride by imidazole at 25°C.Polymerization time was one hour.

Expt. No.	[MAH]/[IM] mol/l mol/l	Solvent	%Sol. Polym.	%Insol. Polym.	Colour of Products
1	1.5/0.15	Dioxane	9.8	16.8	dark brown
2	1.5/0.015	Dioxane	1.8	-	brown
3	1.0/0.1	Dioxane	7.1	21.4	brown
4	1.0/0.01	Dioxane	1.1	0.5	light brown
5	0.5/0.05	Dioxane	7.1	18.6	light brown
6	0.5/0.005	Dioxane	2.6	3.6	light brown
7	1.5/0.15	Diox./Tol.	0.3	28.5	brown
8	1.5/0.015	Diox./Tol.	0.1	4.1	white
9	1.0/0.016	Diox./Tol.	-	16.0[a]	white
10	0.5/0.016	Diox./Tol.	-	27.8	white
11	1.5/0.15	Acetone	31.2	25.6[b]	dark brown
12	1.5/0.015	Acetone	5.1	3.7	light brown
13	0.5/0.05	Acetone	33.6	25.2	light brown
14	0.5/0.005	Acetone	0.2	-	light brov
15	1.5/0.15	DMF	31.5	-	brown
16	1.5/0.015	DMF	3.2	-	brown
17	1.5/0.0015	DMF	0.4	-	light brown

a : $[\eta]$=0.008 dl/g in DMF at 25°C.

b : $[\eta]$=0.03 dl/g in DMF at 25°C.

polymers precipitate out from the polymerization solution immediately after the initiator addition. The yields were found to be the same in the presence or absence of air.In most of the cases ,there are two types of products where one of them is soluble in the polymerization solvent and the other is not.

Colour of the products were dependent on the type of solvent and amount of initiator. Polymerizations conducted in dimethylformamide which is a solvent for both monomer and polymer yield brown oily polymers whatever the concentration of imidazole was. On the other hand, white or brown products may be obtained in toluene-dioxane mixture (40% dioxane) by changing the amount of initiator.The results are presented in Table 1 .

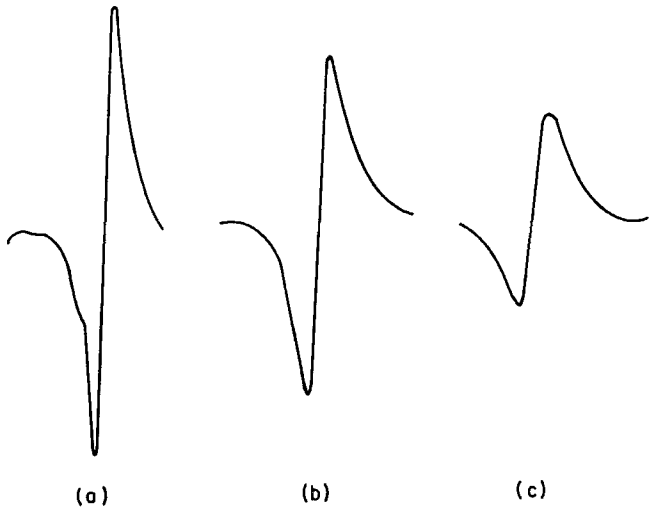

Figure 1. ESR spectra of polymers obtained from (a) exp.1, (b) exp.12, (c) exp.9 after pyrolysis at 220°C.

Some of the polymers show paramagnetic character in solid form.The ESR signal was a singlet and all the colored polymers were found to be paramagnetic. On the other hand, white products did not have any paramagnetic character. Pyrolysis of white products at 220°C caused them to be dark coloured and be paramagnetic. In addition, it was found that the intensity of the ESR signal increased as the colour of the polymer became darker. Paramagnetic character was reported elsewhere [5] for maleic anhydride polymers and it was explained by the cross-conjugation in the system after the evolution of carbon dioxide from the polymer. The same argument seems to be valid also in the present case for coloured polymers.

FTIR spectra of brown polymers (both soluble and insoluble fractions) are similar to those obtained in other studies [2,4] whereas the FTIR spectra of the white products show completely different absorption characteristics (Figures 2 and 3). Thus,

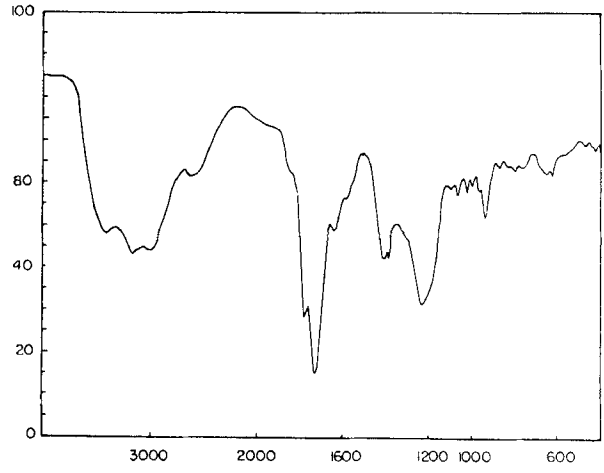

Figure 2.FTIR spectrum of brown polymer.

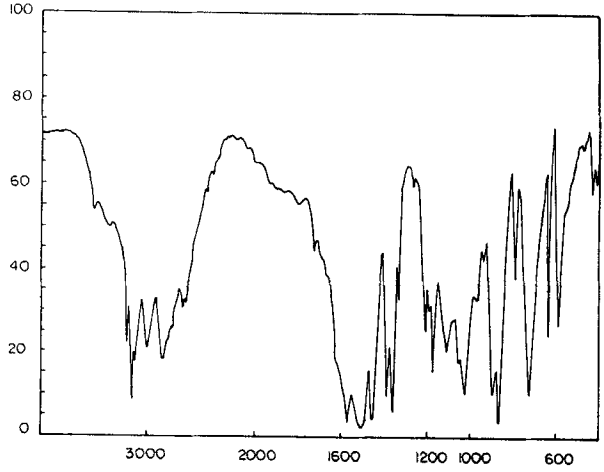

Figure 3.FTIR spectrum of white polymer.

FTIR and ESR analysis showed that the brown polymer is poly(maleic anhydride) having mostly ketoolefinic structure.

Addition of hydroquinone to polymerization solution had no effect on the yields indicating that polymerization was not radical.

Studies for further characterization of the white product and detailed analysis are in progress in our laboratories.

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