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SYNTHESIS AND FREE RADICAL POLYMERIZATION OF N-(P-PHENYLENE) ACRYLATE-YL-MALEIMIDE

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ABSTRACT

P-hydroxyaniline was allowed to react with maleic anhydride producing N-(p-hydroxyphenyl)maleamic acid 1 in high yields. When 1 was allowed to react with excess acryloyl chloride in presence of triethylamine N-(p-phenylene) acrylate-yl-maleimide 2 was formed in fair yields. Free radical polymerization of 2 using AIBN as the initiater resulted in the formation of a poly acrylate having residual maleimide vinyls 3. The resulting polymer 3 was further solidified on curing by heat.

INTRODUCTION

Polyimides are well defined commercialized polymers [1]. They are characterized by their thermal and mechanical stabilities [2,3]. In fact the term " Polyimide" means two types of polymers having similar structural repeating units. The first type is prepared by step growth polycondensation of a dianhydride with a diamine [4], while the second type is produced from chain growth polymerization of unsaturated imides such as N-substituted maleimides [5] or N-substituted itaconimides [2] or even citraaconimides [6]. However, molecular weights of the second type of polyimides have been low in most cases.

In the present paper a novel N-substituted maleimide containing acrylate functional group 2 was synthesized and polymerized. The acrylate group was expected to produce high molecular weight chains while the imide vinyls may partially remain since they are of low reactivity compaired to acrylic vinyls. The remaining unsaturation in the polyimide may be cured by heat later to yield thermally stable polymers.

EXPERIMENTAL

NMR spectra were recorded using FT-EX-90 Joel type Spectrometer. IR spectra were recorded as KBr discs on Pye Unicam SP-3-300 Spectrophotometer. Elemental analysis were performed by the Petroleum Discoveries Office, Baghdad, Iraq. Viscosities were measured using Tafesa-Ubbelohde automatic Viscometere.

Preparation of N-(p-hydroxyphenyl)maleamic Acid 1.

Literature procedure [7] was followed in the preparation of the titled compound. The product was purified by dissolving in sodium bicarbonate solution followed by reprecipitation with dilute hydrochloric acid.
IR (in KBr): 3380 cm^{-1} (OH, phenolic); 3310 cm^{-1} (NH); 2900 cm^{-1} (C=O, amide); 1580 cm^{-1} (C=C).
NMR DMSO-d6): δ 9.00 (s,1H,NH); δ 6.40 (two d,2H,H=CH); δ 4.21 (t,1H -CH_2-OH) ; δ 3.50 (t,2H,N-CH_2-CH_2-O) ; δ 2.50 (q,2H,NCH_2CH_2
H
Anal. for $C_{10}H_9NO_4$: C,57.97; H,4.34; N,6.76 Fond: C,57.88; H,4.42; N,6.82.

Reaction of 1 With Excess Acryloyl Chloride.

In a round bottom flask (250 ml) was placed 2.0g (0.009 mole) of 1, 30 ml of acetonitrile and 1.95 ml (0.019 mole) of triethylamine. 0.97 ml (0.009 mole) of acryloyl chloride was placed in a pressure-equalized separatory funnel placed on the mouth of the flask. The acryloyl chloride was added drop wise while stirring and cooling the flask contents. A white precepitate of triethylammonium chloride was formed, and stirring was continued for 6 hours before filtering the precipitate. The filtrate was evaporated under reduced pressure. The residue was added to a 1:1 H_2O : $CHCl_3$ mixture, stirred, and the layers were separated in a separatory funnel. The $CHCl_3$ layer was dried with anhydrous $CaCl_2$ and cooled in liquid nitrogen. White crystals, M.P. 145°C was obtained in 78% yield.

IR (KBr): 1740 cm^{-1} (C=O, ester); 1710 cm_{-1} (C=O, amide); 1635 cm^{-1} (C=C); 1300 cm^{-1} (C-O-C, ester).
NMR (DMSO-d6) : δ 7.35 (two d,4H,aromatic); δ 7.10 (s,2H,$\underline{H}C=C\underline{H}$); δ 6.50 (t,1H,$CH_2=C\underline{H}-C=O$); δ 6.06 (d,2H,$C\underline{H_2}=CHCO$).

Anal. for $C_{13}H_9NO_4$: Calcld. C,64.19; H,3.70; N,5.76. Found: C,63.87; H,3.65; N,5.32.

Free Radical Polymerization of N-(P-phenylene) Acrylate-yl-maleimide 2.

In a polymerization bottle was placed 3.0g (0.01 mole) of the titled monomer with 7 ml of dry THF and 0.054g (3.83 X 10^{-4} mole) of AIBN as the initiater. The solution was purged with dry nitrogen before closing the bottle. The mixture was heated at 65°C on water bath for 1.5 hours and the solution became cloudy. The mixture was poured onto 50 ml of cold methanol and a white precipitate was formed which was filtered, washed, dried and characterized. The product did not melt at 300°C, and dissolved only in DMF and DMSO.
IR(KBr): 1755 cm^{-1} (C=O, imide shoulder); 1724 cm^{-1} (C=O, ester); 1710 cm^{-1} (C=O, imide); 1290 cm^{-1} (C-O-C, ester); 1650 cm^{-1} (C=C); very weak.
NMR(DMSO-d6): δ 7.30 (m,4H,aromatic);δ 3.25 (s,2H,$\underline{H}-C-C-\underline{H}$); δ 2.50 (t,2H,$-CO-C\underline{H}-CH_2$); δ 2.0 (t,2H,$-CO-CHC\underline{H_2}$).

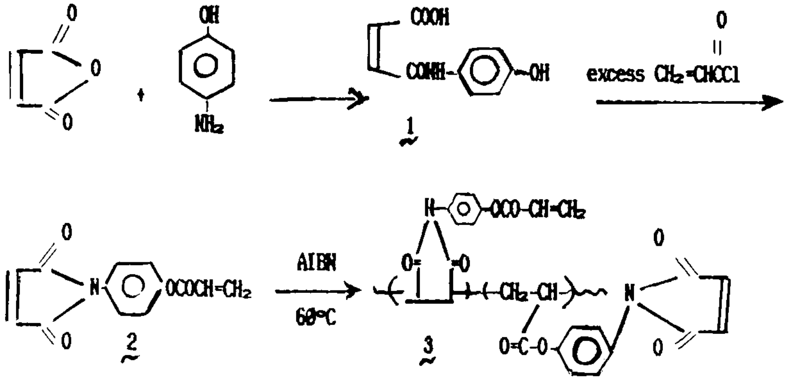
Curing The Prepared Polymer 3 By Heat.

The resulting polymer 3 was cured by heating a thin film of the polymer at 290°C for one hour. The material gained toughness and became less soluble in organic solvents.

RESULTS AND DISCUSSION

The monomer 2 was prepared from the corresponding amic acid 1 using excess acryloyl chloride in presence of triethylamine as shown in Scheme (1) .

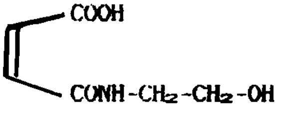
It seems that reaction of the amic acid 1 with acryloyl chloride not only esterified the phenolic hydroxyl but also caused the dehydration of the amic acid 1 to the corresponding cyclic imide 2 [9]. Structures of 1 and 2 were confirmed by IR and NMR spectra (see experimental). The IR spectrum of 2 showed no Absorptions for NH or OH groups indicating cyclization. NMR spectra and elemental analysis also confirmed the structure of 2. Free radical



Scheme (1)

polymerization of 2 using AIBN as the initiater resulted in 95% conversion to polymer 3. 3 was sparingly soluble in chloroform, acetone and benzene, but was soluble in DMF and DMSO. Softening point of 3 was above 300°C, and its IR spectrum showed weak residual vinyl absorption at 1650 cm^{-1} which indicates that some of the unsaturation was still present in the polymer 3.

The fact that polymer 3 in DMF showed intrinsic viscosity of 0.15 dl/g indicates fairly good molecular weight chains. The presence of two vinylic bonds in monomer 2 was also confirmed by measuring the amount of bromine-CCl_4 required to saturate the compound. This was compaired with the amount of bromine/CCl_4 required to saturate another proper amic acid such as N-(2-ethanol)maleamic acid (4).



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Compound 4 was prepared for other purpose [7]. 0.01 mole of 2 required 20 drops of 1% Br_2-CCl_4 solution, while 0.01 mole of compound 4 consumed only 9 drops of the bromine solution.

Thermal curing of polymer 3 resulted in a tough insoluble and infusible which was hard to characterize.

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