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NOTE

SYNTHESIS AND CHARACTERIZATION OF POLY-(2-METHALLYL-*p*-CRESOL)

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INTRODUCTION

In spite of the low reactivity of allyl monomers, attempts have been made to prepare polymers by polyrecombination of allyl aromatic compounds. We were encouraged by the stability of allyl radicals [1-8]. The literature on the Claisen rearrangement of polyfunctional allyl aryl ethers contains some observations of the formation of tarry masses and resinification of polyfunctional aryl ethers. Details of the polymerization and the possible structures were not studied. We felt it interesting to synthesize this new monomer, 2-methyallyl-*p*-cresol, by the rearrangement, and to study in detail the polymerization and characterization of the polymer.

EXPERIMENTAL

Methallyl chloride (Aldrich) was used as received. *p*-Cresol (BDH) was distilled twice and used. BF_3 etherate was BDH LR and was used as received. All other solvents were purified by standard procedures. IR spectra were recorded with a Shimadzu IR 810 instrument; NMR spectra were recorded with a Bruker F 90 spectrometer while using TMS as the internal standard. Thermogravimetric analyses under N_2 were recorded with a TA 3000 analyzer.

Synthesis of Methallyl-*p*-cresyl Ether

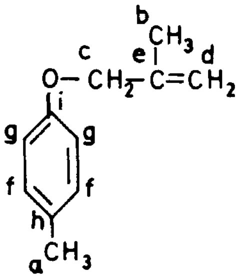
p-Cresol (25 g, 1 mol), 23 g methallyl chloride (1.2 mol), 15 g anhydrous potassium carbonate (1.1 mol), and 50 mL acetone were refluxed for 12 h. The reaction was followed by TLC. The mixture was then cooled and extracted with ether. The ether layer was washed with 10% NaOH several times to remove the unreacted *p*-cresol completely. The ether layer was separated, dried over anhydrous sodium sulfate, and the solvent was evaporated on a water bath. The purity of the monomer was tested by TLC; the yield was 70%. The structure of 2-methallyl-*p*-cresol was confirmed by IR (KBr) and NMR data.

IR (KBr): 3400 cm^{-1} (aromatic OH stretching),
1600 cm^{-1} (C=C stretching),
1245 cm^{-1} (COC asymmetric stretching),
1220 cm^{-1} (COC symmetric stretching).

^1H NMR ($CDCl_3$): δ ppm: 2.2 (S, 3H), 2.8 (S, 3H), 4 (S, 2H), 4.8 (S, 2H), 7.2 (m, 3H). ^{13}C NMR: see Structure 1.

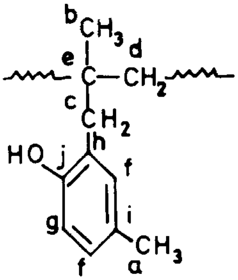
POLYMERIZATION OF 2-METHALLYL-*p*-CRESOL

Pure and dry methallyl-*p*-cresyl ether (5 g) was degassed by passing nitrogen for about 1 h in a polymerization tube. The BF_3 etherate (1-2 mol in solution) was added dropwise, and the mixture was kept for 2 days at room temperature. The resulting dark brown solid was dissolved in a minimum amount of acetone



^{13}C NMR : δ ppm : 1915(a); 20.24(b); 50.52(c); 114.59(d); 115.93(e); 129.90(f); 129.70(g); 140.60(h); 150.57(i)

STRUCTURE 1.



^{13}C NMR : δ ppm : 20.71(a); 21.51(b); 29.59(c); 29.99(d); 37.94(e); 123.3(f); 130.1(g); 133.5(h); 152.3(i); 153(j)

STRUCTURE 2.

and poured into ice-cold water with constant stirring. The brown solid (5 g) obtained was filtered and dried over P_2O_5 in a vacuum desiccator. The structure of the polymer was confirmed by IR (KBr) cm^{-1} : 3400 (aromatic OH stretching), 2900 (aromatic CH stretching). The absence of a sharp band at 1625 cm^{-1} indicates the absence of olefinic bonds in the polymer.

^1H NMR ($CDCl_3$): δ ppm: 2.0 (S, 3H), 2.6 (S, 3H), 3.25 (S, H), 3.0 (S, 2H), 4.8 (S, 2H), 6.3 (m, 3H). ^{13}C NMR: see Structure 2.

RESULTS AND DISCUSSION

The polymer was found to be soluble in liquids like benzene, toluene, CCl_4, $CHCl_3$, and acetone but insoluble in ethanol, methanol, and water, indicating the partial ionic character of the polymer. The intrinsic viscosity of the polymer was found to be 0.082 dL/g in benzene at 25°C, which indicates the formation of a very low molecular weight polymer.

The thermogravimetric data indicate major weight loss in two stages and decomposition starting only beyond 500°C. The polymer showed 75.6% decomposition in the temperature range from 125 to 374°C, and the remaining weight was found to decompose in the range from 375 to 693°C. The first-stage decomposition (weight loss 75%) indicates the possible degradation of the 2-hydroxy-5-methylbenzyl group of the polymer chain. The second stage probably involves the scission of the polymer backbone.

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