

Ultraviolet Surface-Photopolymerization from Phenol, Cyclohexanol, and Ethylbenzene

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Synopsis

The formation of surface-photopolymerized films from the vapors of phenol, cyclohexanol, and ethylbenzene is described. The structures of the films are discussed in terms of their multiple-reflection infrared spectra.

INTRODUCTION

The formation of thin polymer films on surfaces in contact with an organic vapor in glow discharges, by electron bombardment, and by ultraviolet photolysis, is well established.¹⁻⁶ The latter technique has dealt almost exclusively with readily polymerizable materials containing aliphatic unsaturation, e.g., 1,3-butadiene,^{1,4} C₂F₄,^{4,7} C₄Cl₆,^{4,8} and N-phenylmaleimide.⁵

We now wish to describe the extension of the UV photolytic process to formation⁹ of thin polymer films from phenol, cyclohexanol, and ethylbenzene, starting materials which do not contain aliphatic unsaturation. Polymer formation has been observed previously in the gas-phase photolysis ($\lambda \leq 2537 \text{ \AA}$) of alkyl benzenes including toluene and ethylbenzene.¹⁰

EXPERIMENTAL

The full spectrum of a 700-watt Hanovia, or General Electric H3T7 medium pressure mercury lamp operated at 800 watts, was used to irradiate "monomer" vapor at 0.5 to 1 torr in contact with evaporated aluminum on glass substrates in a vacuum chamber fitted with a quartz window. Liquid monomers, after purification by bulb-to-bulk distillation under vacuum, were maintained in thermostatted baths connected through valves to the reaction chamber; the solid phenol was placed in a covered dish in a shaded part of the reaction chamber. Capacitance and dissipation factor measurements using a mercury drop top electrode were made at 1 kHz with a General Radio Company Type 1650A inductance bridge; multiple-reflection infrared spectra were measured with a Beckman IR12 spectrophotometer.

RESULTS AND DISCUSSION

A typical 20-min deposition from phenol vapor at ~ 1 torr and an average substrate temperature of 100°C produced a yellow-brown film with average capacitance 0.9 nanofarads and dissipation factor 0.006 at room temperature. Assuming a value of 3.5 as reasonable for the dielectric constant of the film (ϵ for thin polymer films varies from 2.5 to 6.0^{8,11,12}), the capacitance indicates an average thickness of 3600 Å.

A 4-hr deposition from cyclohexanol vapor at ~ 1 torr substrate temperature 55°C gave a greenish-yellow film with average capacitance 0.8 nanofarads (thickness 4000 Å for $\epsilon = 3.5$) and dissipation factor 0.008. Similar surface films were also obtained in depositions from toluene, ethylbenzene, and 2,6-xylene. The films were usually slightly soluble in organic solvents.

The growth rate for the film from phenol was ~ 180 Å/min, but otherwise the growth rates were substantially lower than those obtained for monomers such as C_4Cl_6 or unsaturated imides⁸ (100–1000 Å/min).

Figure 1 shows the multiple-reflection infrared spectra (11–13 reflections) of the films from phenol, cyclohexanol, and ethylbenzene vapors.

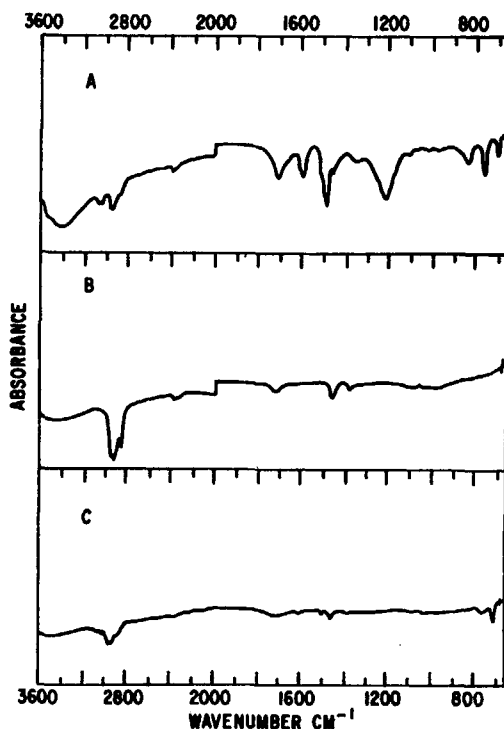


Fig. 1. Multiple-reflection infrared spectra of films from (A) phenol, (B) cyclohexanol, and (C) ethylbenzene.

The retention of aromaticity (bands at 3000–3100, \sim 1500, \sim 1600, and 690–800 cm^{-1}) in the films from phenol and ethylbenzene vapors is not surprising in view of the inherent stability of this grouping, and has been observed in polymer films deposited from aromatic compounds by the more energetic glow discharge technique.⁶

Several workers have shown that β -bond dissociation is the favored primary process in the photolysis of many substituted benzenes,^{10,13,14} e.g., producing phenoxy radicals from phenol and $\text{C}_6\text{H}_5\text{CHCH}_3$ and $\text{C}_6\text{H}_5\text{CH}_2$ radicals from ethylbenzene. Loss of hydrogen to give styrene, $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2$, is also a possibility in the case of ethylbenzene.^{10,14} Thus the presence of CH_2 and CH_3 groups (2800–3000, 1375, 1455 cm^{-1}) in the film from ethylbenzene is readily explained, but their presence in the film from phenol indicates that ring opening and hydrogenation reactions must have taken place. Porter and co-workers have shown that the cyclopentadienyl radical is a transient intermediate in the photolysis of phenol vapor,¹⁵ and the possibility of other transient species cannot be discounted. Roebber has also shown that photolysis of trapped phenoxy radical leads to ring opening and elimination of carbon monoxide.¹⁶

The presence of methyl groups in the film from cyclohexanol indicates that this monomer has also undergone ring opening reactions.

Carbonyl and hydroxyl groups, as observed before in photopolymerized films from nonoxygen-containing monomers,^{4,17} can be seen here in the infrared spectrum of the film from ethylbenzene (bands at 1710–1720, and 3100–3600 cm^{-1}). These groups may be due to reaction with oxygen-containing material on the substrate surface¹⁷ or to reaction with oxygen and water vapor when the film is just exposed to air, as is observed with glow-discharge polymers.⁶

The film from cyclohexanol apparently contains no more hydroxyl than is observed for films from nonoxygen-containing materials, but it does contain carbonyl groups (band at 1720 cm^{-1}). However, the film from phenol contains a large amount of phenolic —OH (bands at 3100–3600 and \sim 1215 cm^{-1}), thus suggesting some retention of the original phenolic C—O—H grouping during the formation of the film.

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