

Electron spin resonance (ESR) studies upon iodine initiated polymerisation of alkyl vinyl ethers

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Summary: Electron spin resonance technique was used for detecting the role of radical intermediates in the iodine initiated polymerisation of alkyl vinyl ethers. DPPH was used as a radical scavenger. The reaction was carried out in the presence of DPPH to find a clue to the presence of a free radical in the system. The results clearly indicated the presence of a radical intermediate in the reaction.

Introduction

Hossein et. al¹ reported the polymerisation of isoprene with iodine at high temperature. A radical mechanism was proposed. A free radical mechanism has also been reported by Okamura's^{2,3} group in the iodine initiated polymerisations. The solid state polymerisation of trioxane⁴ with iodine by simultaneous sublimation of monomer and catalyst has been studied and the presence of free radical was confirmed. The presence of a free-radical propagating centre was reported in the styrene-iodine system⁵.

Materials and Methods

Alkylvinyl ethers (Koch Light Laboratory Grade) were further purified by the Schildknecht method⁶. The purity was checked by vapour phase chromatography which showed no impurities.

1.1 Diphenyl picryl hydrazyl (Koch Light Laboratory Grade) was used without further purification.

Iodine (B.D.H. Laboratory Grade) Was resublimed in the presence of potassium iodine through a sintered glass crucible under nitrogen atmosphere⁷.

Dichloromethane (May and Baker, Laboratory Grade) was further purified by the Weissberger method⁸. The purity was checked by vapour phase chromatography which showed no impurities.

The esr (V. 4500) measurements were carried out

at room temperature with DPPH in dichloromethane containing molecular iodine. It exhibited its typical spectrum (Fig I (a)). At 25° the iodine appears to quench the signal but only at a very slow rate. On adding alkylvinyl ethers to the system, the signal instantaneously quenched (Fig I (b)) which indicated, that it is radical intermediate which removed the DPPH during polymerisation.

UV (Unicam SP 800 A) studies showed the following results. A solution of molecular iodine and DPPH in methylene dichloride at 25°C gave broad absorptions at λ max 525 nm and λ max 326 nm. Both these absorptions disappeared instantaneously on the addition of alkylvinyl ethers.

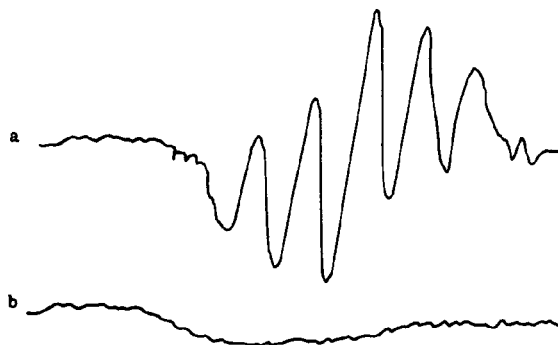


Fig. 1: (a) ESR Spectrum of DPPH in dichloromethane in presence of iodine. (b) On addition of alkylvinylethers.

Discussion

The addition of DPPH as a radical scavenger is a standard method for detecting free radical intermediates in a reaction. Different techniques have been utilised for confirming the presence of the radical reaction in the iodine initiated polymerisation of vinyl monomers.

The results of reactions carried out in the presence of DPPH provide evidence of the presence of a free radical in the system.

The disappearance of the characteristic radical (Fig I (b)) signals of DPPH from the iodine/DPPH solution on the addition of the alkylvinyl ethers confirms the role of the free radical reaction in the system. Conductometric studies⁽⁹⁻¹⁰⁾ of the polymerisation reaction in the presence of DPPH showed a probational period before the actual initiation of polymerisation reaction.

The formation of vicinal diiodide has been confirmed⁷ in the iodine initiated polymerisation of alkylvinyl ethers. ESR studies favour the idea of the formation of vicinal diiodide through radical mechanism as an initiation step in iodine initiated polymerisations. UV spectra showed the immediate disappearance of iodine and the DPPH characteristic absorptions on the addition of alkylvinyl ethers. These results clearly indicate the presence of radical intermediates in these polymerisations.

References

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