

Radiation-induced and electroinitiated polymerization of allylbenzene

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Radiation-induced and electroinitiated polymerization of allylbenzene has been investigated. Radiation-induced polymerization at room temperature was found to give mainly dimers and trimers with a maximum yield of 5%. Electroinitiated polymerization of the monomer yielded insoluble polymer films on the surface of the anode together with low molecular weight polymers in the bulk solution. The effects of temperature and monomer concentration on the rate of electroinitiated polymerization were also studied. The decrease in monomer concentration during electroinitiated polymerization was studied by taking cyclic voltammograms of the electrolysis solution. An apparent activation energy of 5.5 kJ mol^{-1} was found for the electroinitiated polymerization. The polymers were characterized by taking infra-red and nuclear magnetic resonance spectra. The polymerization proceeds via double bond addition of monomer together with isomerization of allylbenzene into β -methylstyrene.

(Keywords: allylbenzene; electroinitiation; cyclic voltammetry; activation energy; molecular weight)

INTRODUCTION

Although allyl compounds polymerize with difficulty and give low molecular weight products, some special allyl monomers are used for various purposes. The polymerization of allylbenzene, AB, has been studied by various investigators via classical initiation techniques, i.e. by using catalysts such as aluminium alkyls or of Ziegler-Natta type¹⁻³. Schmidt *et al.*¹ reported the polymerization of AB in 1942. Kennedy² reported the polymerization of AB catalysed by aluminium chloride in dichloromethane that also gave poly(β -methylstyrene) after isomerization. Davidson⁴ reported the polymerization of AB with AlCl_3 through a Friedel-Craft alkylation reaction.

Few reports on radiation-induced and electroinitiated polymerization of allylic monomers have been made. Radiation-induced polymerization of allylurea⁵ and allylthiourea⁶ and electroinitiated polymerization of allylphenol^{7,8} by constant current electrolysis have been reported, but no work has been reported for the polymerization of AB initiated by radiation or electrochemical means.

In the present work polymerization of AB via irradiation and electroinitiation was studied based on cyclic voltammetry (c.v.) measurements.

EXPERIMENTAL

The monomer allylbenzene (Aldrich Chemical Co., 98%) was dried over CaH_2 for 48 h and distilled over fresh CaH_2 under reduced pressure (b.p. $50^\circ\text{C}/12 \text{ mmHg}$ (1.6 kPa)). Tetrabutylammonium tetrafluoroborate (TBAFB) (Aldrich Chemical Co.) was used

without further purification as supporting electrolyte both for c.v. measurements and for controlled potential electrolysis (c.p.e.). Acetonitrile was purified by drying over CaH_2 followed by fractional distillation. It was stored under nitrogen atmosphere over Linde 4 Å (40 nm) molecular sieves.

Radiation-induced polymerization reactions were carried out in irradiation ampoules evacuated at 10^{-4} – 10^{-5} Torr (10^{-2} – 10^{-3} Pa) for 5–6 h. Monomers were irradiated in a ^{60}Co γ -ray source with a dose rate of 0.06 Mrad h^{-1} . The unpolymerized monomer was separated after the desired irradiation time by freeze drying.

Oxidation-reduction behaviour of the monomer was determined by c.v. as described previously⁹. The c.v. measurements were made in acetonitrile at 25°C on a Pt bead *versus* Ag^0/Ag^+ reference electrode. Electroinitiated polymerizations were carried out by c.p.e.

Equal amounts of TBAFB were placed in the two cell compartments. The electrolysis cell was purged with N_2 and then distilled acetonitrile and AB were introduced into the cell. Before the c.p.e. was started, the solutions in the cell compartments were equilibrated and the cell was placed into a constant temperature bath while the solution was blanketed with N_2 .

The kinetics of electrolysis were followed by c.v., by determining the concentration of samples taken at different times from the electrolysis solution. A calibration curve was drawn by plotting peak heights *versus* monomer concentration. Then the monomer concentrations were found by interpolating on the calibration curve using $80 \mu\text{l}$ aliquots from each compartment.

Molecular weights of the polymers were determined cryoscopically using dimethyl sulphoxide (DMSO) as solvent. Infra-red (i.r.) spectra of the monomer and products were recorded on a Philips PV 7900 i.r.

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spectrophotometer. ^1H nuclear magnetic resonance (n.m.r.) spectra were recorded in CCl_3D at room temperature on a Bruker A-80 NMR spectrometer. Tetramethylsilane was used as the internal reference for all the samples.

RESULTS AND DISCUSSION

A plot of polymer percentage conversion against irradiation time is given in Figure 1. The polymerization curve is S-shaped, with auto-acceleration at about 1500 h and reaching a limiting value after 2500 h. Further irradiation up to 5500 h did not change the polymer yield. The long irradiation time is mostly due to the low dose rate of the source. The unpolymerized fraction, analysed by i.r. and n.m.r. spectra, was unchanged monomer. The reason for the limited conversion is most probably self-inhibition by stable radicals formed upon irradiation. At the limiting conversion, the system reaches an equilibrium condition when sufficient resonance-stabilized alkyl radicals, which cannot be polymerized and inhibit the polymerization, are formed.

Molecular weights of the products obtained cryoscopically were in the range $350\text{--}500\text{ g mol}^{-1}$. The low average molecular weights are probably due to degradative chain transfer and isomerization of monomer.

Before c.p.e., the oxidation-reduction behaviour of the monomer was studied by using c.v. The solvent-electrolyte system (acetonitrile-TBAFB) used in c.v. measurements was found to be totally inert towards electroreduction and oxidation in a potential difference of 7 V. AB has no reduction peak up to -3.5 V versus Ag^0/Ag^+ , and solvent discharge occurs thereafter, but has one oxidation peak at $+2.8\text{ V}$ versus Ag^0/Ag^+ , representing an irreversible electron transfer. Scanning in either direction does not cause any change in the position of the anodic peak. A voltammogram of AB is given in Figure 2.

The anodic peak potential did not change appreciably when the scan rate was increased to about twice its initial value. However, with further increase of scan rate (e.g. to four times its initial value), the shift of peak potential was significant (e.g. 350 mV). Peak current, I , was changed on changing the scan rate. A positive slope was obtained when current function ($I/CV^{1/2}$) was plotted versus $\log V$, where V is the voltage scan rate and C is the concentration. This is shown in Figure 3.

The positive slope in Figure 3 indicates a reversible one-electron transfer. Although one could conclude an

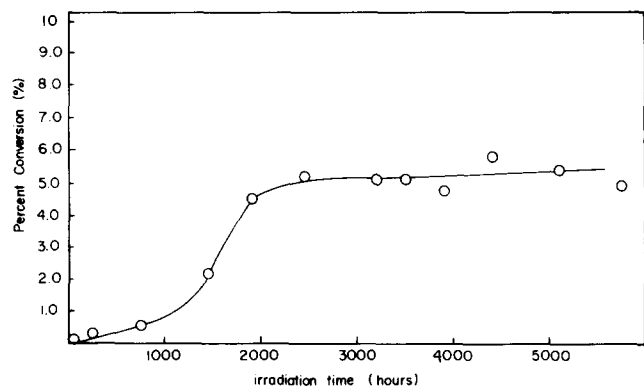


Figure 1 Polymer percentage conversion versus time for allylbenzene irradiated at 20°C under vacuum

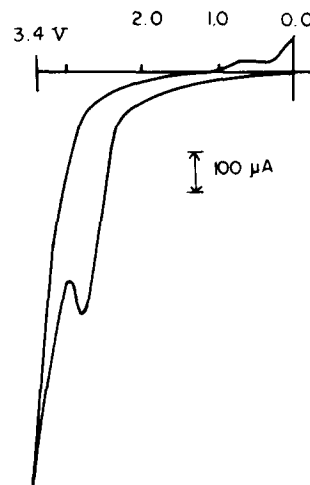
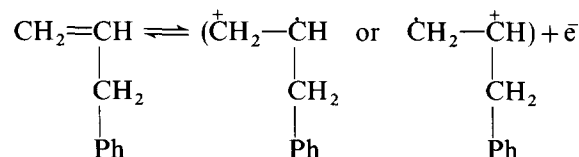


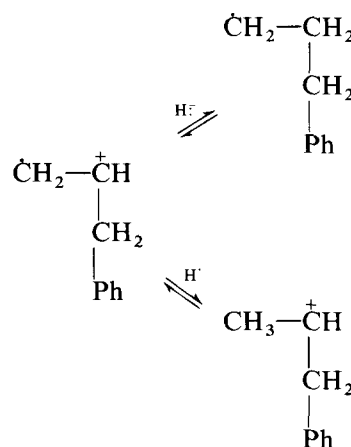
Figure 2 Cyclic voltammogram of allylbenzene measured in acetonitrile at room temperature versus Ag^0/Ag^+

irreversible oxidation from the c.v. of AB (Figure 2), Nicholson-Shain¹⁰ criteria suggest a reversible electron transfer followed by a chemical reaction. The absence of a reversible peak can be explained if the rate of chemical reaction following the electrochemical oxidation is very much greater than the voltage scan rate.

The most probable electrochemical oxidation reaction is



The subsequent chemical reaction might be that the radical cation produced adds hydrogen as follows:



The effect of monomer concentration on the electroinitiated polymerization of AB at room temperature and under N_2 atmosphere is shown in Figure 4. The working electrode potential was $+3.5\text{ V}$ versus Ag^0/Ag^+ .

The polymerization rate and the limiting value of the polymer yield decrease with increasing monomer concentration. This is probably due to the decrease of current with increasing monomer concentration.

The effect of temperature was studied at -40 , -10 , $+20$ and $+40^\circ\text{C}$. Plots of percentage conversion versus electrolysis time for each temperature are given in Figure 5. The percentage and the initial rate of reaction increase with increasing temperature. The apparent activation

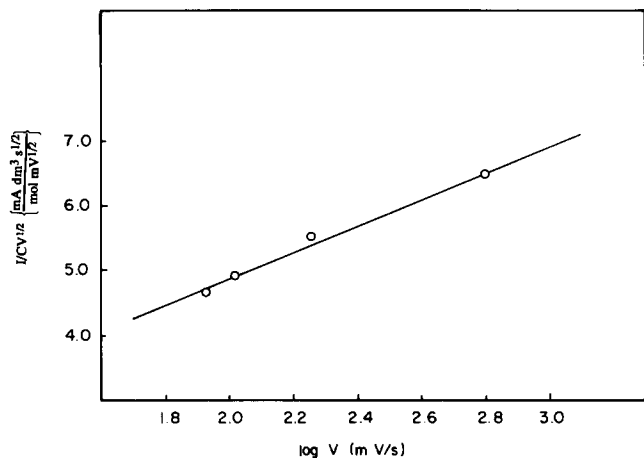


Figure 3 Variation of current function with respect to voltage scan rate

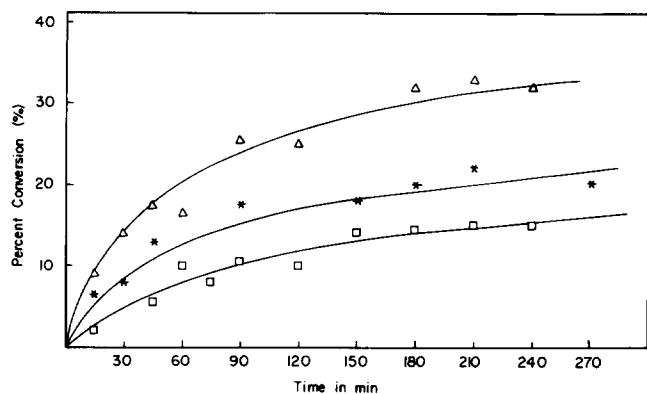


Figure 4 Percentage conversion versus time plot in the electroinitiated polymerization of allylbenzene at +20°C: □, 0.1512 M; *, 0.0755 M; △, 0.0378 M allylbenzene

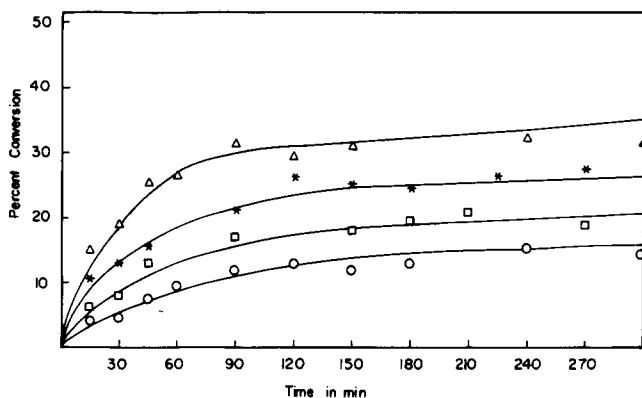


Figure 5 Percentage conversion versus time plot in the electroinitiated polymerization of 0.0755 M allylbenzene: ○, -40°C; □, -10°C; *, +20°C; and △, +40°C

energy for the electroinitiated polymerization of AB was calculated from the initial rates as +5.5 kJ mol⁻¹.

The electroinitiated polymerization of AB yielded two different products. One was an insoluble polymer film on the working electrode surface and the other was obtained from the bulk of the anolyte after removal of unreacted monomer, solvent and electrolyte.

The molecular weights of the polymers from the anolyte at the end of electrolysis under different conditions were determined cryoscopically using DMSO as

solvent. The molecular weights were in the range 300–1000 g mol⁻¹. Molecular weights of the surface coating polymers could not be obtained because of their insolubility in any common solvents.

In Figure 6 the i.r. spectra of AB monomer and the products obtained by irradiation and electroinitiation are given. The absorption bands at 1640, 990 and 910 cm⁻¹ of monomer become weaker upon polymerization due

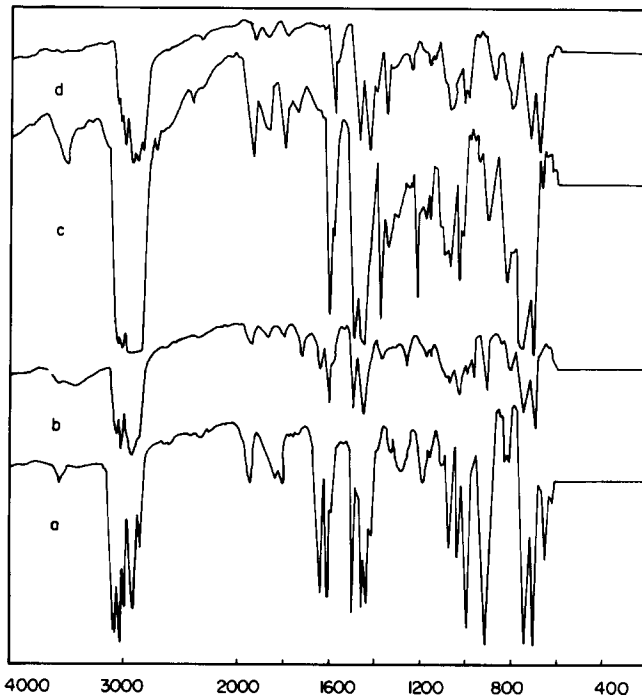


Figure 6 I.r. spectra of (a) AB monomer, (b) poly(AB) obtained by irradiation, (c) poly(AB) obtained by c.p.e. electrolysis-surface coating and (d) poly(AB) obtained by c.p.e. electrolysis from anolyte

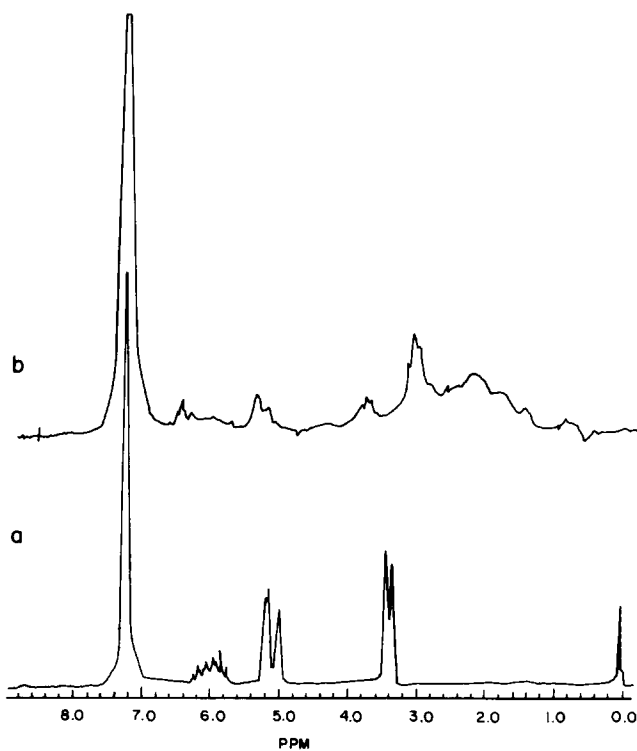


Figure 7 ¹H n.m.r. spectra of (a) AB monomer and (b) poly(AB) obtained by irradiation

to the disappearance of double bonds present in the monomer. These bands disappear completely in the i.r. spectra of both the electroinitiated products (Figure 6c and d). Further comparison of the i.r. spectra of the polymers obtained with the i.r. spectrum of the monomer shows that three new absorption bands appear in the i.r. spectra of products: at 2960, 2870 and 1373 cm^{-1} . These peaks indicate the presence of methyl groups in the products. This can be explained by isomerization of monomer to β -methylstyrene during irradiation or electrolysis. Similar isomerization was reported by Kennedy² in the polymerization of AB using chemical catalyst.

In Figure 7 ¹H n.m.r. spectra of AB and polymer obtained by irradiation are given. The assignments of various protons in AB are as follows: singlet appearing at $\delta=7.3$ corresponds to aromatic protons; doublet at $\delta=5.1$ corresponds to vinylic protons; doublet at $\delta=3.4$ corresponds to benzylic protons; and a complicated signal at $\delta=6.0$ is due to secondary vinylic protons.

A comparison of the n.m.r. spectra of the monomer with the spectrum of the polymer (Figure 7b) shows the appearance of new broad signals at $\delta=0.9$, 1.3 and 1.6 and a signal at $\delta=2.8$ in addition to the original signals of monomer. The new signals correspond to primary, secondary, tertiary and benzylic protons, respectively. The presence of primary protons, shown by the peak at $\delta=0.9$ in the n.m.r. spectrum of polymer, indicates isomerization of allylbenzene to β -methylstyrene during irradiation.

The i.r. and n.m.r. results indicate that the electroinitiated and radiation-induced polymerizations of AB proceed through opening of the aliphatic double bonds, together with isomerization to β -methylstyrene, which also takes part in the polymerization, giving either a mixture of homopolymers of allylbenzene and β -methylstyrene or a copolymer of both monomers.

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