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# Electroinitiated polymerization of 2-allylphenol

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## Summary

Redox behaviour of 2-allylphenol (2APhOH) was studied by using cyclic voltammetry (CV) and electroinitiated polymerization was conducted at the measured peak potentials. Constant potential electrolysis (CPE) of the monomer was carried out in acetonitrile-sodium perchlorate, solvent-electrolyte couple, at room temperature. Polymerization of the monomer yielded insoluble polymer films on the surface of the electrode together with the low molecular weight polymers in the bulk of the solution. The structural analysis of the polymers were carried by $^1$H-NMR and FTIR spectroscopy. Molecular weight of the soluble polymer was determined by GPC. Thermal properties of the polymer film and soluble polymer were studied by DSC. The course of electroinitiated polymerization was monitored by in-situ UV-VIS spectroscopy.

## Introduction

Polymerization of allyl monomers have received much less attention than corresponding vinyl polymerization, since they are not easily polymerized and usually yield low molecular weight product. The polymerization of some allyl monomers, using cationic initiators, has been reported (1-6). It is interesting to note that monomers like allylbenzene and allylphenylether undergo intermolecular isomerization reaction during the polymerization. We have reported electroinitiated and radiation induced polymerization of allylthiourea (7) and allylbenzene (8), and electroinitiated polymerization of allylphenylether (9) previously. We have also observed such isomerizations taking place during the electrochemical polymerization of allylbenzene and allylphenylether (8,9). In the case of allylphenylether we found that monomer undergoes isomerization and forms 2APhOH prior to polymerization. Similar isomerization was also proposed by Hui and Yip (10), and Otsu (11) during the polyme-

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rization of allylphenylether using borontrifluoride etherate. The present study is concerned with the electroinitiated polymerization of 2APhOH based on CV measurements.

## Experiments

### *Materials*

The monomer 2APhOH (Aldrich Chemical Co., 98%) was dried over $CaH_2$ for 48 hours and distilled over fresh $CaH_2$ under reduced pressure. Sodium perchlorate (Aldrich Chemical Co., 99%) was used without further purification as supporting electrolyte for CV measurements and for CPE. Acetonitrile was purified by drying over $CaH_2$ followed by fractional distillation.

### *Cyclic Voltammetry*

The oxidation-reduction behaviour of the monomer was determined by CV. The system consisted of a potentiostat (Bank Pos 73), an X-Y recorder (Lloyd PL-3), and a CV cell containing a Pt-wire working electrode, a Pt-wire counter electrode, and a SCE reference electrode. Measurements were made under $N_2$ atmosphere in acetonitrile at room temperature.

### *Polymer Synthesis*

Electrochemical polymerization of 2APhOH was carried out by CPE using H-type cell in acetonitrile. At the end of the electrolysis, the solution from the anode compartment was concentrated by removing solvent under vacuum. The electrolyte from the remaining mixture was removed by extraction with dichloromethane and water. The black polymer film was separated by peeling off from the electrode surface.

The course of electrolysis was followed in-situ with a UV-VIS spectrophotometer. The constant current electrolysis (CCE) was achieved in a quartz UV cell and UV spectrum of the electrolysis solution was taken at different time intervals. Hewlett Packard 8452A Diode Array Spectrophotometer was used for this process. The electroylsis cell used for in-situ CCE was described elsewhere (12).

### *Polymer Characterization*

$^1$H-NMR spectra of the polymers were taken by a Bruker Instrument-NMR Spectrometer (DPX-400) in $CDCl_3$. FTIR spectra of the polymers were obtained on a Nicolet 510 FTIR Spectrometer using KBr pellets. The thermograms were taken on TA Instruments DSC 910S.

## Results and Discussion

Electrochemical polymerization of 2APhOH was studied in acetonitrile on Pt-electrodes. Prior to CPE, the oxidation-reduction behaviour of 2APhOH was studied by CV in acetonitrile-sodium perchlorate, solvent-electrolyte couple, at room temperature under $N_2$ atmosphere. A voltammogram of 2APhOH is given Figure 1. 2APhOH have three oxidation peaks at +1.25, +1.6, and +2,55 V versus SCE, and all peaks represent an irreversible electron transfer.

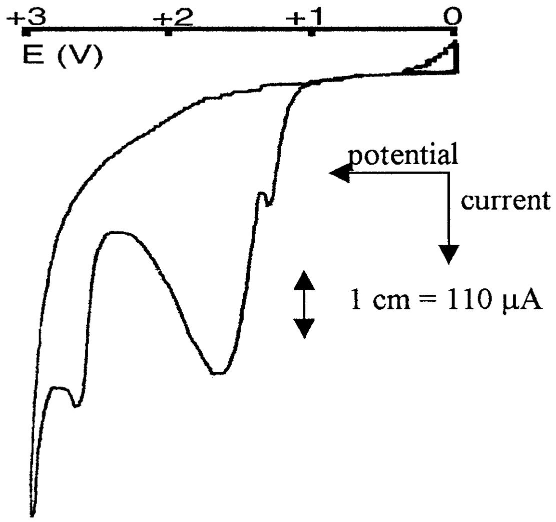


**Figure 1.** Cyclic voltammogram of 1.6*10$^{-3}$ M 2APhOH measured in 0.1 M $NaClO_4$-acetonitrile solution at room temperature, (voltage scan rate: 100 mV/sec).

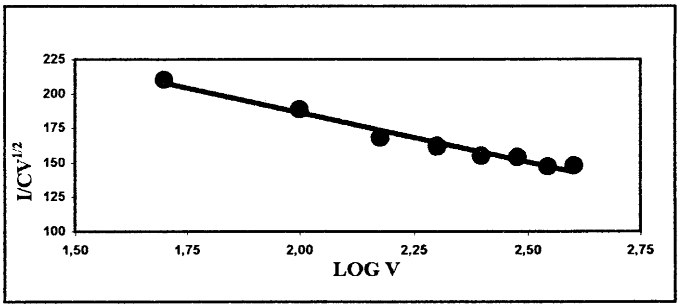


**Figure 2.** Variation of current function (I/CV$^{1/2}$) with voltage scan rate, where I is current in mA, C is concentration in mol/L , and V is scan rate in mV/s.

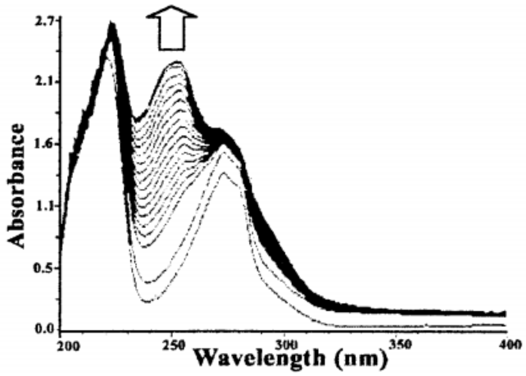


**Figure 3.** UV spectrum of $3.4{\bullet}10^{-4}$ M 2APhOH in $1.6{\bullet}10^{-2}$ M $NaClO_4$-acetonitrile solution by using 100 μA constant current (There are 10 min. time intervals between two scans).

Although the anodic peak potential didn't change appreciably with increasing voltage scan rate, the peak current was changed on changing the voltage scan rate. A negative slope was obtained when current function ($I/CV^{1/2}$) for second oxidation peak was plotted against log V, where I is the peak current, V is the voltage scan rate and C is the concentration (Figure 2). The negative slope in Figure 2 indicates a reversible one-electron transfer, at +1.6 V versus SCE, followed by a chemical reaction according to Nicholson-Shain criteria (13). Appearance of an irreversible peak in the voltammogram of 2APhOH instead of a reversible one can be explained due to higher rate of chemical reaction following the electrochemical oxidation.

The mechanism of electroinitiated polymerization was investigated by monitoring the changes in the UV-VIS absorption spectra during the CCE and the results are shown in Figure 3. The bands at 226 nm, 274 run and 286 nm (B band) are characteristic bands in the spectrum of the monomer. During CCE the band at 274 nm and 286 nm undergo a blue shift and a new band at 254 nm intensifies. This band is characteristic K-band for $\pi \rightarrow \pi^*$ transition which appears when a chromophore is attached to the aromatic ring (14). Appearance of the new band could be most probably due to isomerization of 2APhOH to 2-propenylphenol during the CCE.

### *Polymer Characterization*

The polymers obtained at +1.25 V and at +1.6 V electrode potential were in very small quantity and could not be used for polymer characterization. Therefore, only the polymer products obtained at +2.55 V versus SCE were used. In this case, the electrochemical polymerization of 2APhOH yielded two different products in the anode compartment. (i) an insoluble polymer film on the electrode surface, and (ii) a soluble polymer from the anolyte. No polymer was obtained in the cathode compartment. This observation suggests that no active species were produced by reduction, or, if they were, inhibitors were produced along with them.

Figure 4 compares the IR spectra of 2APhOH and its products obtained by electrochemical polymerization. For the polymer obtained from the bulk of anolyte in acetonitrile by CPE, absorptions peaks at 2969 (asymmetry), 2868 (symmetry), and 1378 $cm^{-1}$ (bend) in the spectrum (Fig. 4b) present strong unmistakeable evidence with the presence of $CH_3$-C groups, i.e, methyl groups in the backbone of the polymer, but not in the monomer spectrum (Fig.4a). However, the peaks at 2928 and 1450 $cm^{-1}$ indicate methylene, -$CH_2$-, groups in this spectrum. Also, noteworthy points are appearance of an OH peak at 3372 $cm^{-1}$, appearance of a C-O-C peak at 1236 and 1037 $cm^{-1}$, slightly appearance of the C=C peak at 911 and 998 $cm^{-1}$, appearance of a prominent peak at 754 $cm^{-1}$ assigned to the 1,2-disubstituted benzene ring and a peak at 821 $cm^{-1}$ assigned to the 1,2,4-trisubstituted benzene ring. If the monomer were polymerized by allyl double bond addition, this peak would not be observed. For the polymer film, the characteristic peaks of the groups $CH_3$-C at 2967, 2869, and 1382 $cm^{-1}$ also appear (Fig. 4c) together with peaks at 2929 and 1435 $cm^{-1}$ indicating the presence of methylene groups. Also, in the spectrum the absorption peaks at 917 and 999 $cm^{-1}$ due to allylic double bond appear with a reduced intensity than the peaks in the monomer spectrum. In addition, IR spectra show the presence of the phenolic OH group (3404 $cm^{-1}$), di and trisubstituted aromatic ring (757 and 825 $cm^{-1}$, respectively) and C-O-C etheric peak (1241 $cm^{-1}$). Strong absorptions at 1090 and 625 $cm^{-1}$ in the spectrum are due to the presence of $ClO_4^-$ ion. When the spectra of the polymers were compared with that of poly ( oxy( 2-allylphenylene)) (755, 915, 1020, 1270, 1430, 1455, 1600 $cm^{-1}$) they were found to have the same principal absorption peaks.

In accordance with the IR spectra, in polymers the presence of methyl groups was confirmed by $^1$H-NMR. spectroscopy. A comparison of the $^1$H-NMR spectrum of 2APhOH with that of polymer shows the appearance of new signals in addition to the original signals of monomer (Figure 5). The peaks at 1.1, 3.2 and 3.3 ppm can be assigned, respectively, to $CH_3$, $CH_2$ and CH in structure **I**, and the peaks at 0.9, 2.0 and 3.8 ppm are also assigned to $CH_3$, $CH_2$ and CH in structure **II**, respectively. The peaks at 1.5 and 2.3 ppm are due to structure **III**. Also, the monomer isomerization to 2-propenylphenol was observed in the polymerization of 2APhOH, so that the peaks at 1.2, 1.7, and 2.8 ppm are due to structure **IV** (8,9,11). The peaks at 3.4, 5.0, and 5.9

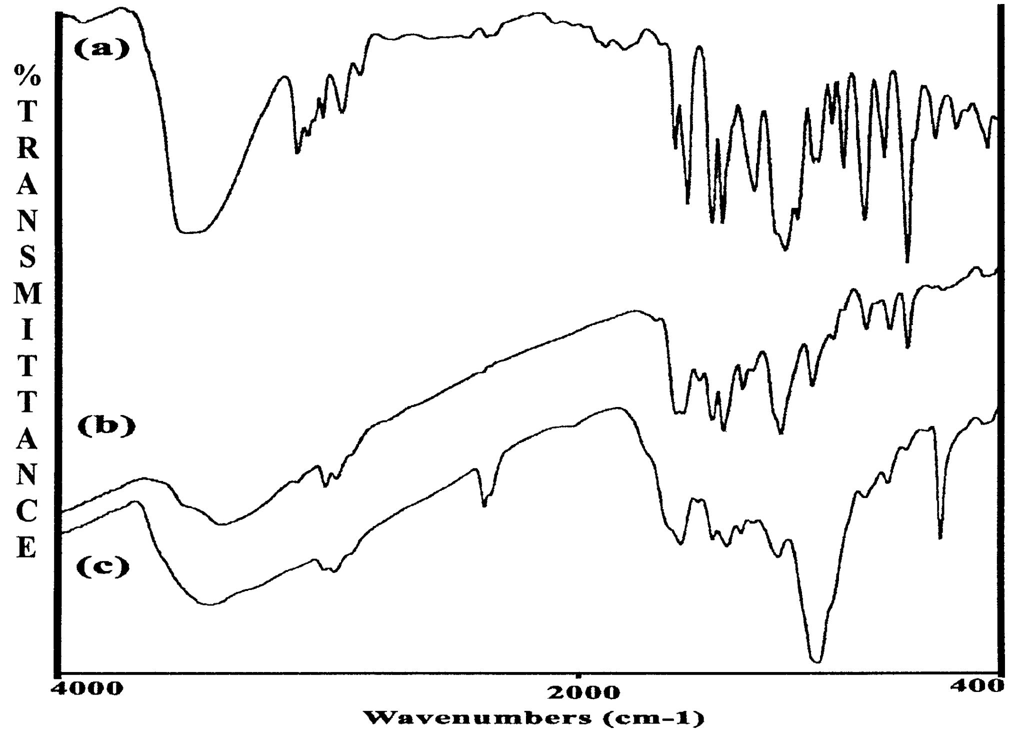


Figure 4. FTIR spectra of (a) 2APhOH, (b) polymer from bulk of the anolyte and (c) polymer film.

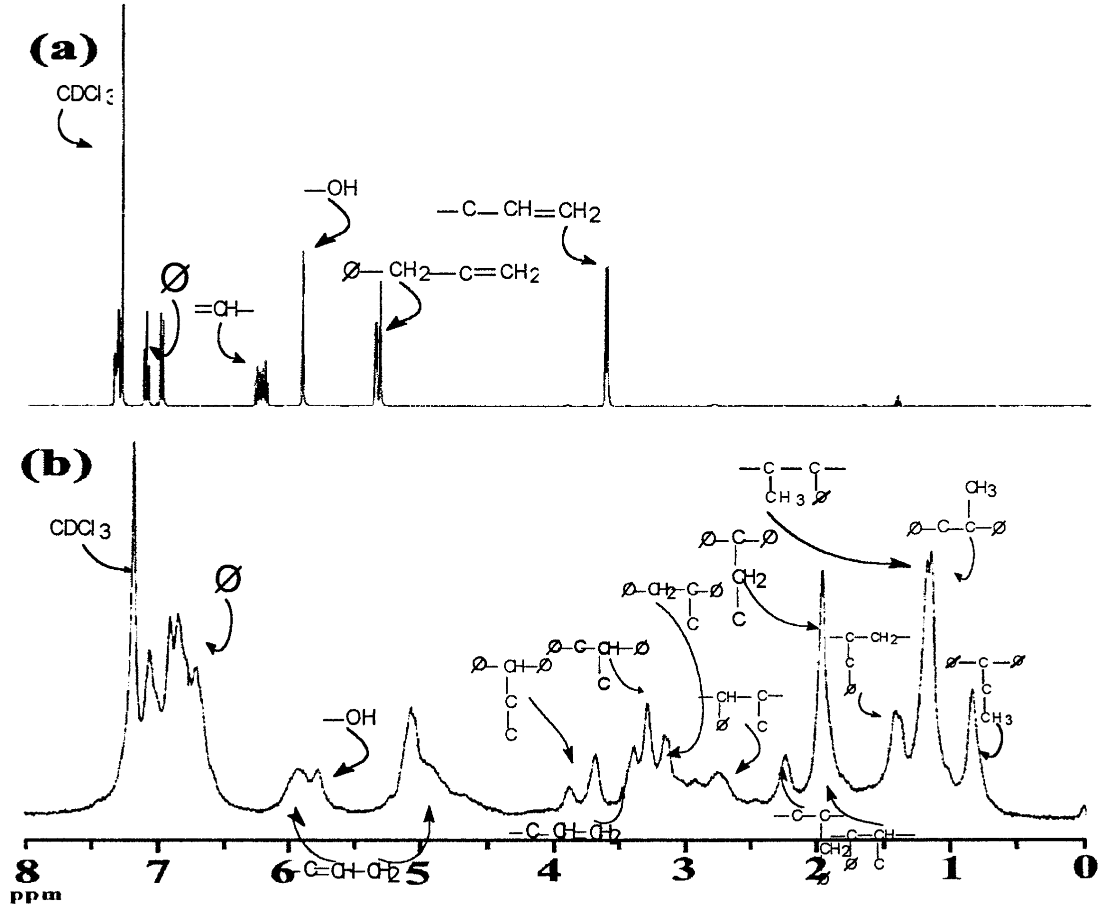
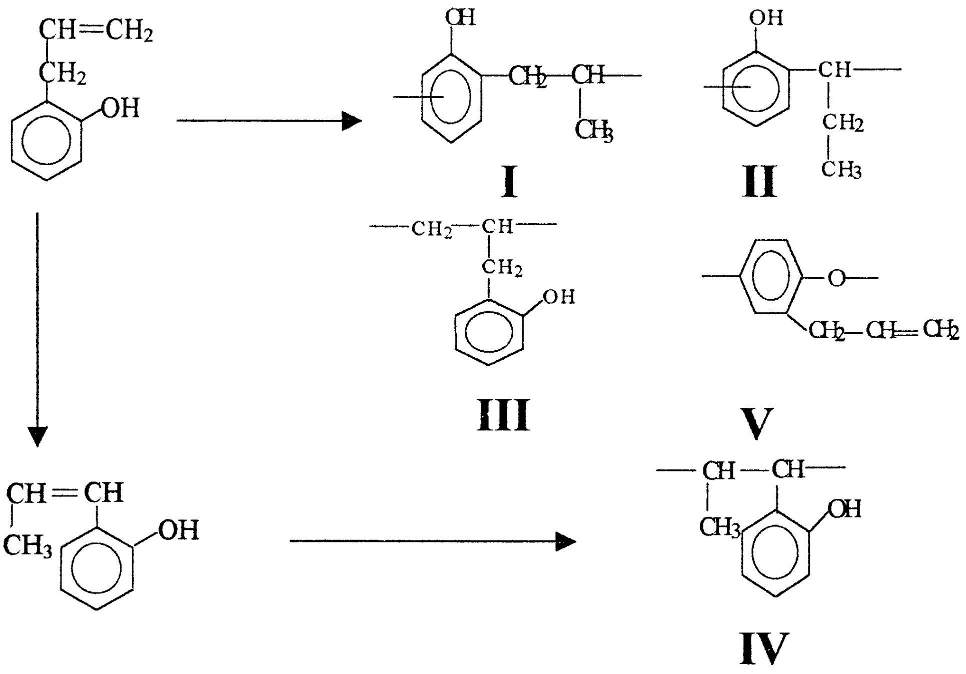


Figure 5. $^1$HNMR spectra of (a) 2APhOH, (b) polymer from bulk of the anolyte.

ppm are assigned to allylic group attached to the aromatic ring which indicates structure **V** (5).

From the evidence gathered, it is apparent that the polymerization proceeds mainly via polyalkylation to the aromatic ring, and a conventional double bond opening also takes place. Consequently, the electrochemical polymerization of 2APhOH gives a mixture of following different repeating units instead of a simple polymer structure.



Melting point $T_m$ and glass transition temperature $T_g$ were determined from DSC thermogram. The $T_g$ and $T_m$ values appeared around 77 and 247°C, respectively, for the soluble polymer obtained from the anolyte and for the polymer film $T_m$ value is found to be 241°C. The $T_g$ value for poly(2APhOH) obtained using borontrifluoride etherate was reported to be about 70-74°C (11).

Molecular weight of the polymer obtained from the anolyte was determined by GPC in THF and it was found about 900. The average degree of polymerization was reported to be 6.7 monomers units per chain.

## Conclusion

The polymerization of 2APhOH was carried out at room temperature in acetonitrile-sodium perchlorate, solvent-electrolyte couple, by CPE. It was shown that the electrochemical polymerization of 2APhOH gives a mixture of different polymers instead of a single polymer product. FTIR and $^1$H-NMR spectral investigation showed trisubstituted benzene to be predominant in polymer chain as well as disubstituted form. This was also observed by Endo and Otsu for the polymerization by using borontrifluoride etherate as catalyst (11). Although, Endo and Otsu reported that 2APhOH does not undergo isomerization to 2-propenylphenol, our NMR and UV-VIS data suggest that isomerization to 2-propenylphenol is also taking place during the CPE. The molecular weight of the soluble polymer as determined by GPC is not far from the reported values (11).

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## References

1. Schimidt AW, Schoelle V (1942) Brennstoff Chem 23:247
2. Kennedy JP (1964) J Polym Sci A 2:5171
3. Seefried CG, Kolesk JV (1976) J Polym Sci Polym. Phys Ed 14:663
4. Davidson EE (1966) Polym Lett 4:175
5. Mengoli G, Bianco P, Daolio S, Munari MT (1981) J Electrochem Soc 128(11):2276
6. Mengoli G, Musiani MM (1986) Electrochim Acta 31(2):201
7. Usanmaz A, Yilmaz E (1987) J Macromol Sci Chem A24(5):179
8. Sousy K, Usanmaz A, Önal AM (1990) Polymer 31:1564
9. Şen Ş, Usanmaz A, Önal AM (1995) J Polym. Sci A 33:1817
10. Hui KM, Yip LC (1971) J Chem Soc Chem Comm 825
11. Endo K, Otsu T (1991) Polymer 32(15):2856
12. Pulat M, Önal AM, Kisakürek D (1994) New Polymeric Mater 4(2):111
13. Nicholson RS, Shain I (1964) Anal Chem 36:706
14. Silverstein RM, Bassler GG, Morrill TC (1974) Spectrometric Identification of Organic Compounds, Wiley Inst. Ed. New York