Ring opening polymerization of 2,5-dihydro-2,5-dimethoxyfuran by electrochemical initiation

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Summary

2,5-Dihydro-2,5-dimethoxyfuran (DHMF) was polymerized via constant current electrolysis (CCE), in CH_3CN-$NaClO_4$ solvent-electrolyte couple. Poly(DHMF) was obtained from the anolyte. The effect of current density, temperature, monomer and electrolyte concentrations on the polymer yield have been examined. The apparent activation energy for CCE of DHMF was found to be 37.2 kj/mol. The FTIR and ^{1}H-NMR analyses show that DHMF polymerizes by a ring opening. Molecular weight of poly(DHMF) was found by using cryoscopy.

Introduction

The cationic polymerization of furan and derivatives were shown to give complex conjugated polymers (eventually leading from orange to black insoluble products), from the pioneering work carried out by Armour group in 1967 to date[1-12]. Little work has been published on the polymerization of furan and derivatives under the action of added Lewis and Brønsted acids or the electrochemical initiation, than that of corresponding 5 member heterocyclic homologues. It has

been reported that, the polymers obtained from furan and the derivatives had non-linear, irregular enchainments, which was mainly crosslinked structures. The presence of alternating furan and dihydrofuran moieties separated by a methine group have been suggested to be responsible for the black color of the products. Most of the authors also reported, little solubility and the form of insoluble network structure. Various polymerization reaction mechanisms and the products have been suggested such as the absence of furan rings in the polymer structures and the presence of both $-CH=CH-O-$ and $-CH=C(CH_3)-O-$ units and hydroxyl groups.

In this study, we report the ring opening polymerization of 2,5-dihydro-2,5-dimethoxyfuran in AN-NaClO$_4$ solvent-electrolyte couple by CCE at various temperatures. The effect of electrolyte and the monomer concentration on percent conversion was also investigated.

Experimental

Chemicals

2,5-Dihydro-2,5-dimethoxyfuran was obtained from commercial source. It was a mixture cis and trans isomers (Merck- Schuchardt order no: 803509). Acetonitrile (AN), was purified by drying over CaH$_2$ followed by fractional distillation. NaClO$_4$ (Merck) was dried under vacuum before use. All the other reagents were reagent grade and used without further purification.

Electrochemical experiments

The electrochemical examinations and the polymerizations were performed in a two-compartment cell separated with a sintered glass (Por. 2). A DC power supply (Leybold model max output potential 500 V) was used for electrochemical studies. The galvanostatic method was used for the electrochemical polymerization.

Electrochemical polymerization of the monomer was achieved by constant current electrolysis. The supporting electrolyte, NaClO$_4$, was dissolved in freshly distilled acetonitrile and introduced together with monomer solution into H- type glass cell. The solution in the cell was equilibrated and the cell was placed in a constant temperature bath. The solutions were flushed with nitrogen prior to electrolysis (15 min.) and this atmosphere was maintained above the solution throughout the experiment. The working and counter electrodes were platinum plate (1cm^2) which was polished and cleaned before each of the experiment.

At the end of each experiment, the solutions in each of the compartment were taken to beakers followed by the addition of distilled water. The polymeric product was separated by centrifuging the solution 45 min at 3000 rpm. Finally, the dark green to black color solid products were handled after drying under vacuum. Most of the polymeric product was soluble in common organic solvents but the solid became insoluble upon standing. No melting point was observed on a hot stage heated gradually to 300°C.

FTIR spectra of the samples were taken with a Jasco FT/IR-480 Plus FTIR spectrometer. ^{1}H-NMR spectra of the polymers were taken by Bruker Instrument NMR spectrometer (DPX-400) in CDCl$_3$ and d-acetone. Cryoscopic method was used for the determination of molecular weight. Beckmann thermometer was calibrated with sublimed naphthalene in DMSO.

Result and discussion

Synthesis of poly(DHMF)

When the current was turned on, a dark violet product formed in the anode compartment. Dark violet color changed to dark green and finally black during the CCE. Although no polymer film was deposited on the surface of the anode, dark green to black color solid product was isolated from the anolyte solution by precipitating with water.

The effect of current density on the percent conversion of the polymerization of DHMF was studied by using NaClO$_4$-AN electrolyte-solvent couple at 20°C. As shown in Fig.1, the polymer yield tends to increase with increasing current density as a function of time. The maximum yield was observed when 5 mA current density was used.

The effect of temperature on the rate of polymerization of DHMF was studied gravimetrically. From the blank experiments, it was confirmed that no thermal polymerization occurs in the range of 0°C to 40°C. An increase in polymerization temperature enhances the rate of polymerization and the percent conversion as shown in Fig.2. In particular, increasing the temperature seems not to agree with the trend frequently observed for cationic polymerizations. An opposite temperature dependence in the ionic polymerization, although rare, was reported earlier [13-15]. Initial rate constants for the electrochemical polymerization of DHMF were found from the initial slopes and the apparent activation energy of 37.2 kJ/mol was obtained from the Arrhenius plot.
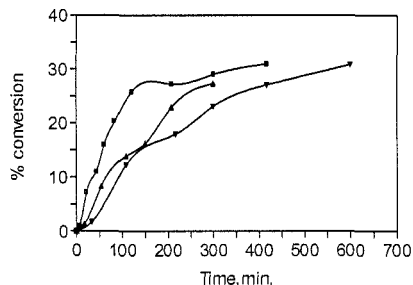
Figure 1. Percent conversion versus time plot at different current strength NaClO$_4$ = 0.1 M, DHMF = 0.33 M, 20°C (♦) 5 mA, (▲) 2 mA, (▼) 1 mA
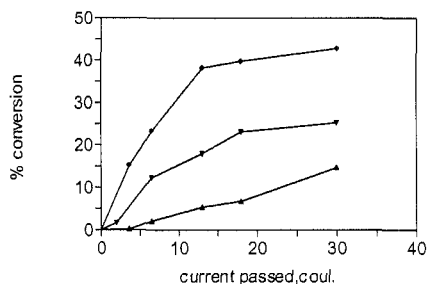
Figure 2. Percent conversion versus time plot at different temperatures NaClO$_4$=0.1M DHMF = 0.33 M, I = 1 mA (♦) 40°C, (▼) 20°C, (▲) 0°C

The presence of postpolymerization gave the opportunity to check the mechanism of polymerization. Since polymeric product was obtained from the anolyte only, the electrochemical reaction is an oxidation reaction. Thus, the active species responsible for polymerization could be a cation or a radical cation. Therefore, in order to check the mechanism, quinone and pyridine solutions were used as a radical and cationic inhibitor, respectively. The concentrations of the inhibitors were 3.0×10^{-3} M. Polymerization was performed for 108 minutes, (NaClO$_4$= 0.1 M DHMF= 0.33 M, 20°C, total electricity passed from the solution was 6.5 coul) then the inhibitors were added one at a time while the electrolyses stopped. It was found that quinone has no effect on the percent conversion of polymerization whereas pyridine inhibits further polymerization. So, the mechanism of polymerization of DHMF in AN by CCE is most probably cationic in character.

The effect of electrolyte concentration on the percent conversion was studied at four different NaClO$_4$ concentrations an is given in Fig 3.

As seen from Fig.3, the percent conversion first increases by increasing supporting electrolyte concentration, then it decreases slightly by further increase in electrolyte concentration. This behavior was also reported by Pistola, who suggested that an increase in ClO$_4^-$ concentration enhances the ion pair formation thus making the propagation slower, which was the rate determining step in HClO$_4$ catalyzed polymerizations [16]. In our experimental conditions the results seemed to suggest that the polymerization may be initiated by the anodically

formed $HClO_4$. Moreover, we have also found that DHMF polymerization can be initiated chemically by $HClO_4$ in AN and the results show in a good agreement with those CCE results.

The effect of monomer concentration on the percent conversion was studied at 1 mA current density at 20°C and given in Fig.4. As seen from the figure, the polymer formation depends on the monomer concentration.
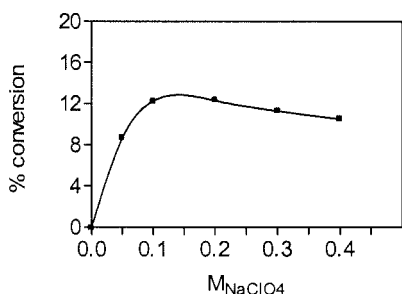

Figure 3. Polymer formation as a function electrolyte concentration, DHMF = 0.33 M Total electricity passed = 6.5 coul, 20°C
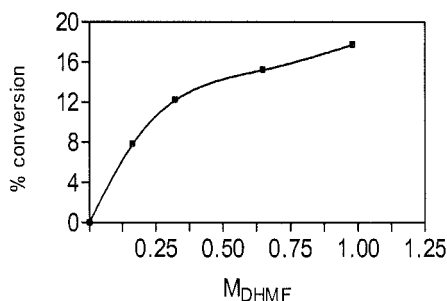
Figure 4. Polymer formation as a function of monomer concentration, $NaClO_4$ = 0.1 M, total electricity passed = 6.5 coul, 20°C

Polymer Characterization

Fig. 5 shows the infrared spectra of monomer (A) and the soluble (B) and insoluble part (C) of the polymer. The infrared spectrum of DHMF exhibits several characteristic vibrational modes (2932, 2832, 1631, 1450, 1372, 1335, 1280, 1195, 1120, 1091, 1024, 804, 723, 620 cm^{-1}). Some of the bands are retained in the spectra of the polymer. The i.r. absorption spectrum of the soluble part of the polymer (B) reveal the presence of aliphatic vibrations at about 2930 and 2840 cm^{-1}. The presence of ring vibrations at about 1630 cm^{-1} and 1450 cm^{-1} associated with $-C=C$, CH out-of-plane bending mode below 800 cm^{-1}, and the peak at about 1200 cm^{-1} corresponding to the $(-C-O-C-)$ vibration, provides an indication of the methoxy group of the polymer. On the other hand peaks at 675-630 and 970-960 cm^{-1} are assigned to cis and trans double bonds, respectively. The presence of CH stretching vibrations indicates that some of the furan rings may have been hydrogenated. Furthermore, the presence of $-OH$ and $-C=O$ bands at about 3500 cm^{-1} and 1750 cm^{-1} respectively, reveals the ring opening with the

consequent generation of non-conjugated structure. Although, the i.r. spectrum of the undissolved part of the polymer (C) shows the same characteristic vibrational modes, the intensity of –C=O vibration increases and –C=C vibration diminishes. This may be explained by the crosslinking of polymer from the double bond between C(3) and C(4) position.
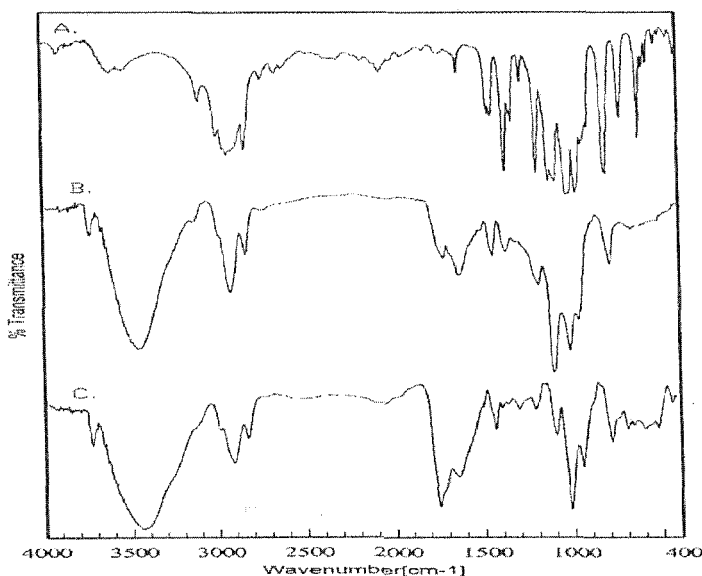

Figure 5. FTIR spectra of monomer (A) and poly(DHMF). Soluble part (B), insoluble part(C)

The ^{1}H-NMR spectra of monomer and the polymer in CDCl$_3$ and d-acetone solution are shown in Fig.6 and Fig.7, respectively. In the ^{1}H-NMR spectrum of monomer (Fig.6), the peaks are assigned as follows: -OCH$_3$ at 3.24 ppm, cis H2-H5 at 5.52 ppm, trans H2-H5 at 5.75 ppm and the H3-H4 protons at 5.93 ppm. Here, the integration of the signals at 5.52 ppm to 5.75 ppm shows, the mixture is 54:46 cis to trans isomer. A comparison of the ^{1}H-NMR spectrum of DHMF with that of polymer shows the appearance of broad signals at around 6.3 ppm and 5.0 ppm and a singlet at 3.5 ppm in addition to the original signals of monomer. The broad peak at 6.3 ppm is assigned to –CH= and the broad peak at 5.0 ppm is due to =CH$_2$. The singlet at 3.5 ppm is due to –CH$_2$-. The signal in the polymer spectrum at 7.3 ppm shows the solvent CDCl$_3$ and the signal at 2.0 ppm is solvent

d-acetone and the signal at 1.55 ppm is water. Although, some small peaks indicate that some side reactions took place, all the major peaks could be assigned.
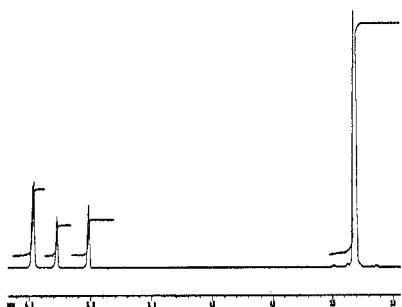

Figure 6. ^{1}H-NMR spectrum of DHMF
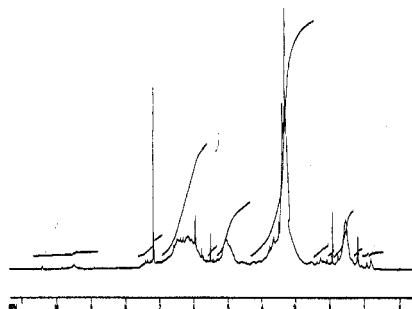
Figure7. ^{1}H-NMR spectrum of polymer

The FTIR and ^{1}H-NMR results indicate that the polymerization proceeds via the ring opening. In literature, the ring opening mechanism of DHMF is not given. Since the product obtained is soluble initially than becomes insoluble on standing, this is due to the crosslinking that might progressed on the aliphatic double bond between H3-H4 and ionic ending of given polymer segment in the mechanism suggested below. The mass spectroscopic work is under progress to elucidate the final structure of crosslinked polymer: This will be published in a following paper.
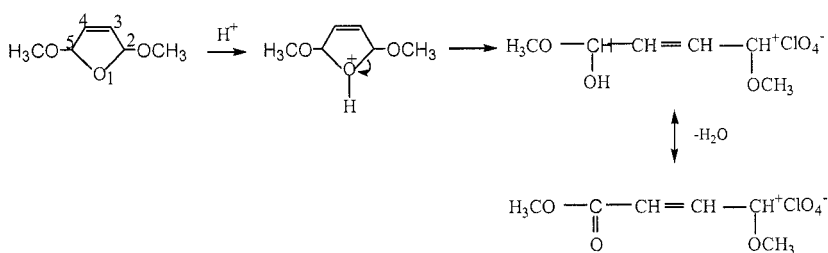
Conclusion

The electrochemical polymerization of DHMF was carried out in AN-NaClO$_4$ solvent-electrolyte couple by CCE. The result of postpolymerization reactions in the presence of cation and radical scavengers revealed that the active specie responsible for the polymerization is a cation.

Conversions as high as 40 % were obtained by changing the polymerization temperature. Changing the initial monomer concentration has a positive effect on the percent conversion whereas the electrolyte concentration not. The polymerization proceeds by the action of electrochemically produced HClO$_4$. FTIR and ^{1}H-NMR spectra of Poly(DHMF) indicates the furan ring opening during CCE.

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