

Short communication

Electroinitiated polymerization of 2-chloroethylvinyl ether

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Abstract—The electroinitiated polymerization of 2-chloroethylvinyl ether via controlled potential conditions has been achieved. The kinetics of the polymerization were determined by cyclic voltammetry at different temperatures in dichloromethane (DM) and acetonitrile (AN). The post-polymerization kinetics were followed with a similar technique. It was found that polymerization was twice as fast in DM as in AN. In DM, both the polymerization and the post-polymerization rates increased with decreasing temperature, whereas in AN the reverse behavior was observed.

Keywords: Electroinitiation; cyclic voltammetry.

1. INTRODUCTION

The use of electroinitiated cationic polymerization via the controlled potential method has become widespread in the last decade. In fact, this technique has some significant advantages over other techniques. The most attractive one is the elimination of unnecessary reactions by control of the applied potential [1–4]. In polymer synthesis, the purity of the medium is an important factor. The solution of this problem lies behind the direct initiation of the monomer; that is, the direct oxidation of the monomer onto a propagating radical cation. It has, in fact, been shown that to achieve direct initiation, electrolysis must be carried out at or below the measured anodic peak potentials of the monomers [5, 6]. This method provides direct initiation by transferring an electron from the monomer to the anode directly, i.e. the polymer obtained does not contain any impurities arising from initiation and/or catalysis reactions. This method cannot be applied when activation of the monomer is possible only beyond the discharge potential of the solvent–electrolyte couple. Electroinitiated cationic polymerization is a powerful method when it is used under controlled potential conditions. Selection of the solvent is an essential

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part of electroinitiated cationic polymerization. In a sense, the solvent particularly affects the yield and rate of polymerization. The chain-transfer constants for the solvents determine the rate and yield of polymerization. Small chain-transfer constants to a solvent are preferable in cationic polymerization. The chain-transfer constant is somehow related to the temperature. This relation varies solvent to solvent. For some solvents it decreases with decreasing temperature and for others the reverse is true [7].

In this study we compared the rates of polymerization and post-polymerization of 2-chloroethylvinyl ether in dichloromethane (DM) and in acetonitrile (AN) at different temperatures by cyclic voltammetry. The electroinitiated polymerization of this monomer is of importance to us, since our aim is to study the polymerization of pyrrole on poly(*N*-pyrrolyl)ethylvinyl ether, which can be synthesized by the reaction between poly(2-chloroethylvinyl ether) and pyrrolyl potassium. The significance in synthesizing such polymers lies in the production of conducting polymers with good mechanical properties. Since pure conducting polymers are very brittle, blends [8, 9] and/or several copolymers [10–12] of these have proved to be valuable. Poly(2-chloroethylvinyl ether) produced in DM at -20°C was analyzed via gel permeation chromatography (GPC) and Fourier transform infrared (FTIR) spectroscopic studies.

2. MATERIALS AND METHODS

2.1. Materials

2-Chloroethylvinyl ether (Aldrich) was distilled before use. Dichloromethane (Aldrich) and acetonitrile (Aldrich) were used as received. As the supporting electrolyte, tetrabutylammonium tetrafluoroborate (Merck) was used as received.

2.2. Methods

The kinetics of the polymerization and post-polymerization rates were investigated via cyclic voltammetry (CV) at different temperatures in DM and AN. A Wenking POS 73 Potentiostat was used for the supply of a constant potential.

A four-compartment cell equipped with platinum foils (1.5 cm^2) as the working and the counter-electrodes, a capillary reference electrode, and a CV electrode was utilized. This cell enables one to perform electrolysis and CV runs simultaneously [2].

In the polymerization kinetics, variation of the monomer concentration ($c_0 = 200\ \mu\text{l}/50\text{ ml}$ in DM; $c_0 = 100\ \mu\text{l}/50\text{ ml}$ in AN) was followed by CV after 1 or 2 min electrolysis at several temperatures (-20°C , -10°C , 0°C , and $+20^{\circ}\text{C}$). The post-polymerization kinetics were also studied. After carrying out electrolysis for 10 or 15 min, the decrease in the monomer concentration was again determined by CV runs at either 1 or 2 min time intervals at the same temperatures as those used

in the polymerization kinetics study. All these experiments were performed under a nitrogen atmosphere. Electrolyses in DM and AN were carried out at a constant potential of +2.6 and +2.4 V, respectively.

Preparative electrolyses were carried out in DM at -20°C under the same conditions as those employed in the kinetic studies. Poly(2-chloroethylvinyl ether) was characterized by FTIR (Bomem-MB) and GPC (Waters 590) analyses.

3. RESULTS AND DISCUSSION

The cyclic voltammograms of 2-chloroethylvinyl ether are given in Figs 1a (run in DM) and 1b (run in AN). The monomer is electroactive within the solvent-electrolyte discharge range. The oxidation potentials are +2.6 V and +2.4 V vs. Ag/Ag^+ (10^{-2} M) reference electrode in DM and AN, respectively. There is no reduction peak of the monomer in either solvent.

The FTIR spectrum of the polymer contains an aliphatic C-H stretching band at 2940 cm^{-1} , asymmetrical C-O-C stretching at 1121 cm^{-1} , and $\text{CH}_2\text{-Cl}$ bands at 751 and 1257 cm^{-1} . GPC studies gave $M_n = 2.3 \times 10^3$ and $M_w = 16.3 \times 10^3$.

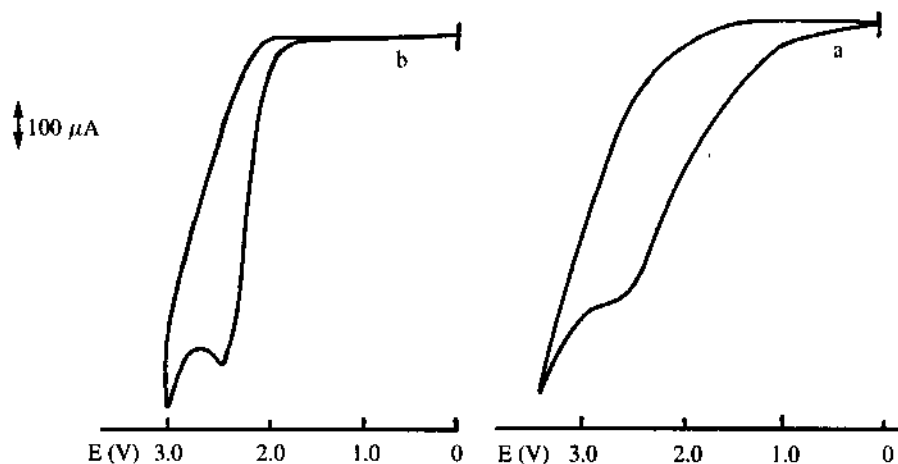
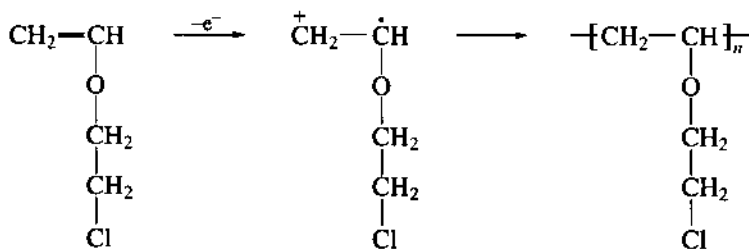


Figure 1. Cyclic voltammograms of 2-chloroethylvinyl ether in (a) DM and (b) AN.



Scheme 1.

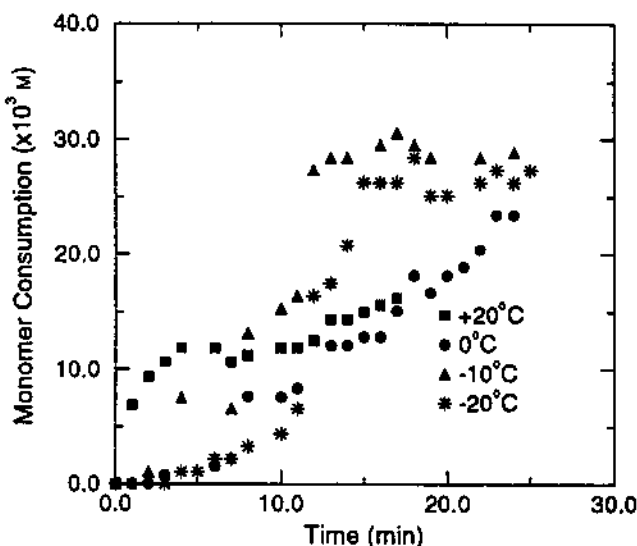


Figure 2. Polymerization kinetics in DM.

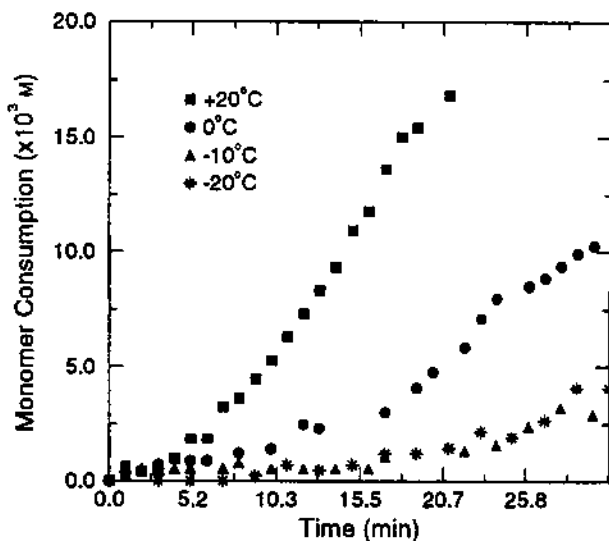


Figure 3. Polymerization kinetics in AN.

The polymerization kinetics of 2-chloroethylvinyl ether were determined in DM and AN at several temperatures. In fact, DM and AN have very different chain-transfer constants [13].

Figure 2 illustrates the monomer consumption upon continuous electropolymerization of 2-chloroethylvinyl ether at several temperatures in DM. It can be seen that as the temperature decreases, the monomer consumption, namely the polymerization rate, rises substantially. However, in Fig. 3, which represents a similar study

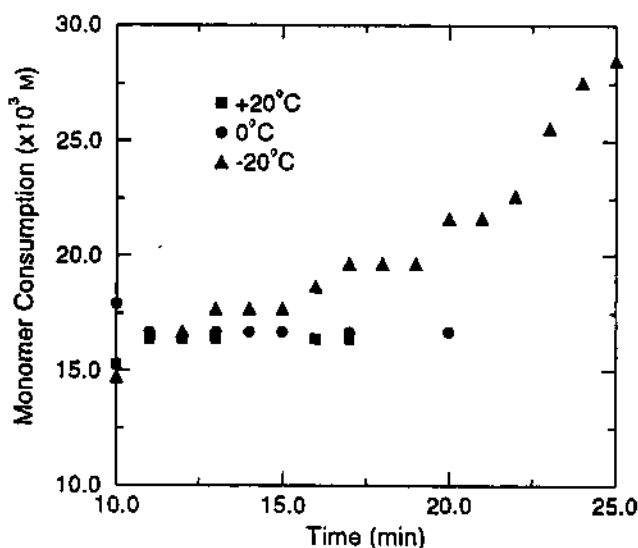


Figure 4. Post-polymerization kinetics in dichloromethane.

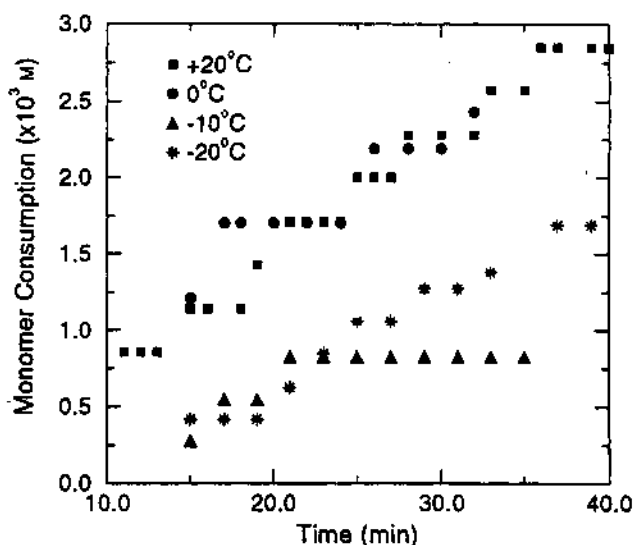


Figure 5. Post-polymerization kinetics in acetonitrile.

in AN, the temperature–monomer consumption relation is clearly the opposite, i.e. the lower the temperature, the lower the monomer consumption. One important feature that can be interpreted from these two figures is that polymerization was almost twice as fast in DM as in AN. Comparing the monomer consumptions for the solvents, the fastest polymerization (at +20°C) in AN can only reach the value of the slowest polymerization rate (at +20°C) in DM. Polymerizations performed in DM at lower temperatures yield higher conversions.

The post-polymerization rates of 2-chloroethylvinyl ether were also studied in DM and AN in the same manner. As can be seen in Fig. 4, it seems that no post-polymerization occurs in DM at high temperatures, whereas at lower temperatures post-polymerization is observed. Actually, the post-polymerization rate and temperature relationship in DM is the same as the relationship between the polymerization rate and temperature. The post-polymerization rate in AN also gives nearly the same relationship with temperature as does the polymerization rate (Fig. 5).

4. CONCLUSION

2-Chloroethylvinyl ether is polymerized electrochemically with a high conversion and high polymerization rate in DM at temperatures below 0°C. This is attributed to the small chain-transfer constant of DM.

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