Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Electroinitiated Cationic Polymerization of Indene

U. Akbulut[a]; S. Eren[a]; L. K. Toppare[a]
[a] Polymer Research Division Department of Chemistry, Middle East Technical University, Ankara, Turkey

To cite this Article Akbulut, U. , Eren, S. and Toppare, L. K.(1984) 'Electroinitiated Cationic Polymerization of Indene', Journal of Macromolecular Science, Part A, 21: 3, 335 — 342

To link to this Article: DOI: 10.1080/00222338408069467

URL: http://dx.doi.org/10.1080/00222338408069467

J. MACROMOL. SCI.–CHEM., A21(3), pp. 335-342 (1984)

Electroinitiated Cationic Polymerization of Indene

U. AKBULUT, S. EREN, and L. K. TOPPARE*

Polymer Research Division
Department of Chemistry
Middle East Technical University
Ankara, Turkey

ABSTRACT

The polymerization of indene by constant potential electrolysis in dichloromethane was achieved at low temperatures. Molecular weights were found to be inversely proportional to polymerization temperature. The oxidation peak potential of indene in the $(C_4H_9)_4$-NBF_4-CH_3CN electrolyte-solvent system was measured by cyclic voltammetry. Polymers which were produced electrochemically by constant potential electrolysis have the same spectral properties with those obtained by chemical methods.

INTRODUCTION

A large number of publications have appeared on electrochemical polymerization of vinyl and cyclic monomers. Detailed work is also available on the polymerization of indene by chemical [1-4] and by constant current electrolysis [5-9]. Polymerization of indene by constant potential electrolysis (CPE), which is based on cyclic voltam-

---

*To whom correspondence should be addressed.

0022-233X/84/2103-0335$3.50/0

metry measurements, has not been reported. It was claimed that the electroinitiated polymerization of indene below +15° was not possible [8]. In the constant current approach, for polymerization temperatures below +15°, it was also claimed that the electric current passing through the reaction mixture could not be maintained constant because the applied voltage increased considerably [8].

In constant potential electrolysis technique, the electroinitiation potential is kept constant at the oxidation peak potential of the monomer while the current varies.

In this work, CPE of indene was carried out at and above the oxidation peak potential of the monomer which was measured by cyclic voltammetry (CV). CPE allowed the cationic polymerization of indene in dichloromethane by direct electron transfer at temperatures below +15°.

EXPERIMENTAL

Materials

Tetrabutylammonium fluoroborate (TBAFB) was prepared and purified as described previously [10].

Dichloromethane was dried over CaH_2 for 12 h and later distilled over fresh CaH_2.

Acetonitrile was dried over CaH_2 for 24 h, then refluxed over fresh CaH_2 under nitrogen for 10 h and fractionally distilled, and stored over molecular sieves.

Indene was washed with 6 M HCl, then with 40% NaOH, stirred on CaH_2 for 12 h, and vacuum distilled over CaH_2 at 24°C at 5 mmHg pressure. The literature value is 114.5°C at 100 mmHg pressure [11].

Procedure

Cyclic Voltammetry

The cyclic voltammetry system has been discussed in a previous publication [12]. CV data were obtained in acetonitrile and in dichloromethane at -10, 0, and 20°C. The controlled potential electrolysis system consisted of an electrolysis cell (Fig. 1), a Tacussell potentiostat type PRT 30-0.1, and a Sefram X-Y recorder. The reference electrode in the three-electrode system was a Ag°/Ag^{+} electrode which contained 0.01 M silver fluoroborate and 0.10 M TBAFB. The cathode and anode were platinum foils with 2.5 cm^2 area, and the voltage scan rate (VSR) was 200 mV/s.

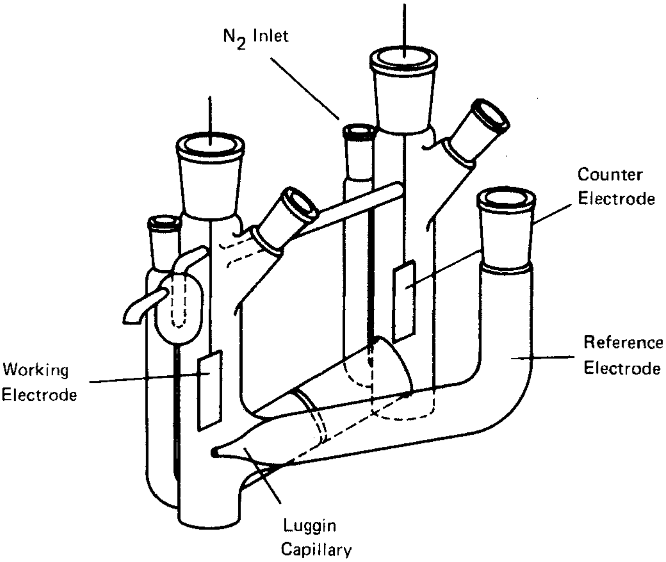

FIG. 1. Constant potential electrolysis cell.

Polymerization

Equal amounts of recrystallized and freshly dried TBAFB were placed in both cell compartments. The cell was purged with nitrogen, and then distilled dichloromethane and indene were introduced into the cell. Before the controlled potential electrolysis was started, the solutions in each compartment of the cell were equilibrated and then the cell was placed into a constant temperature bath. The solution was blanked with nitrogen, and 40 μL aliquots were transferred by microsyringes from each compartment into 1 mL of methanol containing 10 μL α-methylstyrene which was used as the internal standard. During electrolysis at definite time intervals, 40 μL samples from each compartment, for analysis of monomer concentration, were transferred into 1 mL methanol. Unreacted monomer concentrations were determined by gas chromatography. A column of 2.80 m packed with 1.5% Apiezon L on 80-100 mesh size chromosorb was used.

The anode potential was +2.00 V versus Ag°/Ag^{+} and the current was measured as a function of time (Fig. 2). The polymerization was carried out at three different temperatures. The polymer was precipitated at the end of each run by adding the anolyte to 0.5 L of methanol. The molecular weights were determined by viscosity measurements using the literature parameters for polyindene [13].

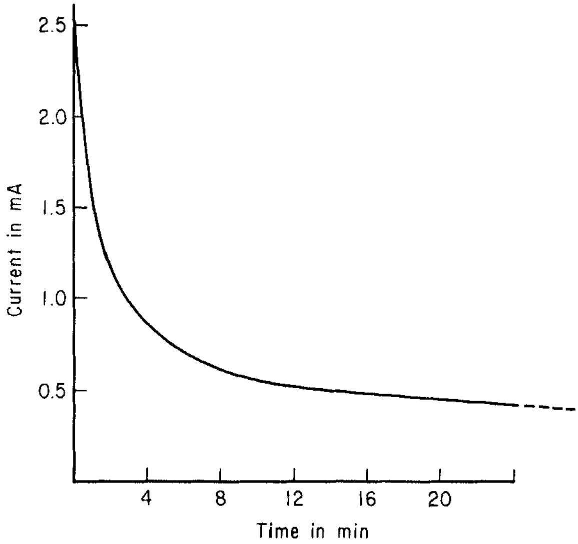

FIG. 2. Current versus time plot for electroinitiated cationic polymerization of indene.

RESULTS AND DISCUSSION

The cyclic voltammogram of indene obtained in acetonitrile at room temperature was reported [12] to have one oxidation peak at +1.40 V and one reduction peak at -2.90 V versus Ag°/Ag⁺. We have found that the oxidation peak potential ($E_{p,a}$) measured in dichloromethane tends to shift to more anodic values as the temperature decreases. $E_{p,a}$ is +1.40 V at +20°C which shifts to +3.20 V at -40°C (Fig. 3). Such a large shift in $E_{p,a}$ due to a temperature change in this range is not acceptable. We have observed that the shift was due to the quick coating of the electrode surface by a polymer film at low temperatures. When the surface was cleaned and flamed before each CV measurement, the effect of temperature on $E_{p,a}$ was not easily detectable. Even at room temperature after a few cycles, the working electrode was still coated by a film, which caused the $E_{p,a}$ to shift to more anodic potentials than +1.40 V. During polymerization the thin polymer film coating the anode caused the current to drop very quickly. Because of this property of indene, the polymerizations were carried out at potentials slightly above the $E_{p,a}$ of the monomer measured on freshly cleaned electrodes.

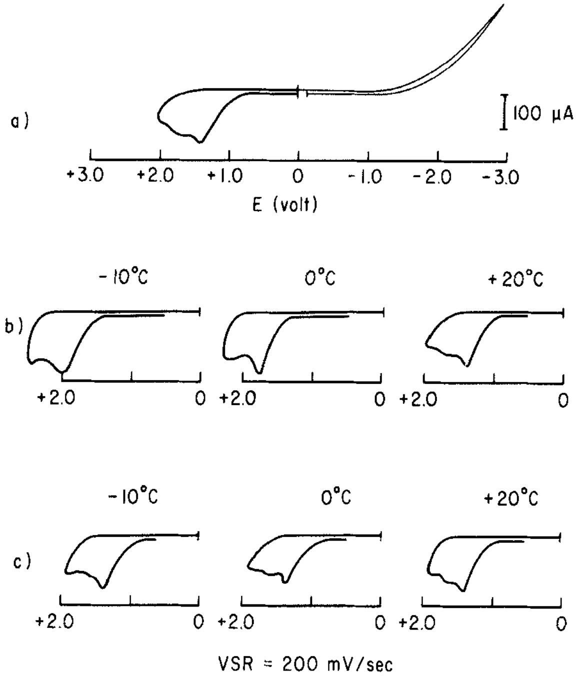

FIG. 3. Cyclic voltammograms of indene (10^{-3} M) obtained on platinum wire versus Ag°/Ag^+. a) Cyclic voltammogram of indene measured in acetonitrile. Electrolyte was 0.10 M TBAFB. b) Cyclic voltammogram measurements in dichloromethane obtained successively without clearing the anode surface. c) Cyclic voltammogram measurements obtained by flaming the electrode surface before each run.

The potential chosen for polymerization was +2.00 V versus Ag°/Ag^+. Since the chain transfer constants are negligible for dichloromethane [14] in cationic polymerization, it was preferred over acetonitrile.

During constant potential electrolyses at +1.40 V versus Ag°/Ag^+, a polymer film, which lowered the current passing through the system coated the anode, and the polymerization rate dropped very quickly. At +2.00 V the large IR drop due to coating was overcome and the polymerization rate was enhanced. Electrolyses carried out at -10, 0, and +20°C produced polyindene with different yields and molecular weights (Table 1).

For analysis of the reacted monomer, 40 μL aliquots were taken from both compartments. Samples which were taken only from one compartment (anolyte) gave misleading results in gas chromatography

TABLE 1. Electroinitiated Cationic Polymerization of Indene at Constant Potential

T (°C)	Yield[a] (%)	Molecular weight × 10^{-3}	Initial rate × 10^5 (mol/L·s)	$E_{p,a}$[b] (V)	E_p[c] (V)
20	4.7	3.0	20.30	+1.4	+2.0
0	3.2	4.8	8.25	+1.4	+2.0
-10	2.6	4.9	4.98	+1.4	+2.0

[a] Isolated by precipitation.

[b] Measured in acetonitrile-tetrabutylammonium fluoroborate system versus Ag°/Ag$^+$ reference electrode.

[c] Minimum electrolysis potential for the formation of the polymer in the solution.

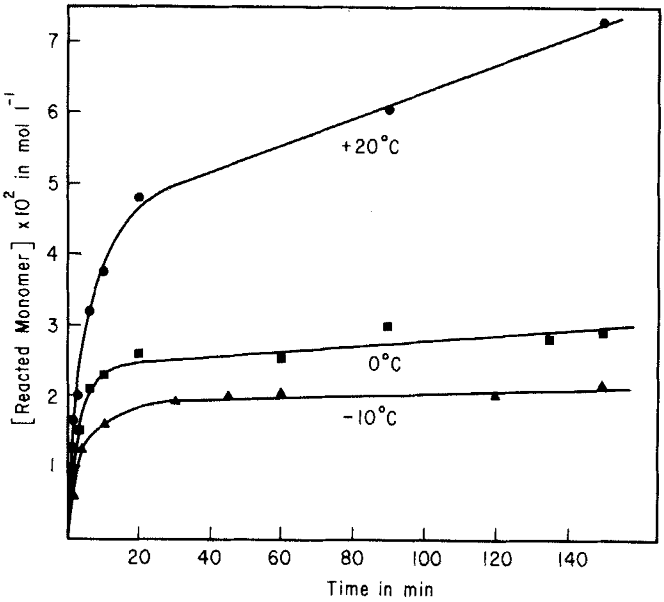

FIG. 4. Polymerization of indene carried out in dichloromethane by constant potential electrolysis at three different temperatures.

due to the diffusion of the monomer through the sintered disk. Whenever a certain amount of monomer was consumed by polymerization, equilibrium was immediately established in both compartments by means of diffusion due to the concentration gradient. This was eliminated by taking aliquots from both compartments at certain time intervals. Monomer consumption in the cathode compartment by electrolytic decomposition was neglected since it is very small. The reacted monomer concentration during polymerization was plotted as a function of time (Fig. 4). From the slope of these plots, the initial rates were found for three different temperatures (Table 1). The apparent activation energy of the electroinitiated polymerization was found, from initial rates, to be 29.73 kJ/mol.

In the present work it is shown that the electroinitiated polymerization of indene at temperatures below room temperature can be achieved by CPE. The molecular weight increases as the polymerization temperature decreases.

ACKNOWLEDGMENT

We are grateful to the British Council and TUBITAK for the supply of the chemicals used in this work.

REFERENCES

[1] I. Sakurado, N. Ise, V. Hayashi, and M. Nakao, Makromolecules, 1(3), 265 (1968).
[2] A. D. Eckard, A. Ledwith, and D. C. Sherrington, Polymers, 12, 444 (1971).
[3] H. J. Prosser and R. N. Young, Eur. Polym. J., 11, 403 (1975).
[4] P. Sigwalt, J. Polym. Sci., 52, 15 (1961).
[5] Y. Kikuchi and H. Fukuda, J. Polym. Sci., Polym. Chem. Ed., 11, 2709 (1973).
[6] S. N. Bhadani and P. P. Baranwal, Makromol. Chem., 178, 1049 (1977).
[7] S. N. Bhadani and P. P. Baranwal, Ibid., 178, 2637 (1977).
[8] S. N. Bhadani, P. P. Baranwal, and Y. K. Prasad, Ibid., 179, 1623 (1978).
[9] E. B. Mano and B. A. L. Calafate, J. Polym. Sci., Polym. Chem. Ed., 19, 3325 (1981).
[10] U. Akbulut, R. L. Birke, and J. E. Fernandez, Makromol. Chem., 179, 2507 (1978).
[11] D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, Purification of Laboratory Chemicals, Pergamon, Oxford, 1966.
[12] U. Akbulut, J. E. Fernandez, and R. L. Birke, J. Polym. Sci., Polym. Chem. Ed., 13, 133 (1975).

[13] A. Mizote, T. Tanaka, and T. Higashimura, Kobunshi Kagaku, 23, 78 (1966).

[14] B. L. Funt and T. J. Blain, J. Polym. Sci., Part A-1, 9, 115 (1971).

Accepted by editor July 5, 1983
Received for publication August 2, 1983