

## Electroinitiated polymerization of aziridines

James J. Jakubowski and R. V. Subramanian

Department of Materials Science and Engineering, Washington State University, Pullman, WA 99164, USA

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### INTRODUCTION

While electroinitiated polymerization has been applied mostly to vinyl monomers in solution<sup>1</sup>, it has been used only recently, and much less extensively, to form coatings on electrodes<sup>2</sup>. The effect of electroinitiated polymer on the properties of composites prepared from electrolytically-coated graphite fibres has been the subject of recent investigation in our laboratory<sup>3-5</sup>. In the course of this research, the novel electropolymerization of monomers other than vinyl species, such as phenylacetylene<sup>6</sup>, benzonitrile<sup>6,7</sup>, and aziridines has been observed. In this report, the previously unreported electropolymerization of aziridines is described. The monomers studied are *N*-(2-hydroxyethyl) ethyleneimine (HEEI), and 2-(1-aziridinyl)ethyl methacrylate (AEMA). The latter monomer carries both vinyl and aziridinyl functional groups; selective electropolymerization through either one of the two functional groups has been achieved, and evidence for the structure of the polymers obtained by i.r. and n.m.r. spectroscopy.

### EXPERIMENTAL

Monomer grade HEEI, (Cardova Chemical) and AEMA (Polyscience) were used as received. Electroinitiated polymerization was conducted in 0.2 N NaNO<sub>3</sub>/DMF solutions at room temperature, applying a constant voltage of 12 V for 18 h. A three-compartment cell with fritted glass disc separators was used. Monomer was present in the electrolytic solution only in the middle compartment. Hercules AU carbon fibre electrodes were used in the polymerizing solution in the middle chamber, with platinum counter electrodes placed in the end compartments. PolyHEEI was isolated by precipitation with acetone followed by centrifuging. After successive reprecipitation by the addition of acetone, the polymer was dried at 60°C in a vacuum for 24 h. PolyAEMA was isolated by first removing solvent and residual monomer under vacuum, diluting with acetone, filtering-off precipitated NaNO<sub>3</sub> and finally removing acetone under vacuum. The isolated polymer was dried in a vacuum oven at 80°C overnight.

The i.r. spectra were measured on a Perkin-Elmer model 621 i.r. spectrometer; and the n.m.r. spectra in C<sub>6</sub>D<sub>6</sub> solution, with TMS reference, on an EM-360, 60 MHz n.m.r. spectrometer.

### RESULTS AND DISCUSSION

#### *N*-(2-hydroxyethyl)ethyleneimine

The electropolymerization, at the anode, of HEEI at a monomer concentration of 3.4 mol l<sup>-1</sup> gave about 30–40% polymer yield in 18 h. While most of it was present in the anode compartment, a small percentage of the polymer, <5%, was present in the cathode. Typical yields are shown in Table 1. When the monomer was placed in the cathode compartment, the polymer yield was negligible. It is surmised that cathodic polymerization did not occur at all, but that the monomer from the cathode compartment had diffused to the anode where polymerization was initiated. Subsequently, the cationic polymer could have migrated to the cathode compartment as described later.

The polymer formed at the anode was a reddish brown, viscous liquid, contaminated by a small amount of 'gel', probably a crosslinked polymer. The polymer at the cathode was also mainly a reddish liquid, through a brownish white solid, probably an inorganic salt, was also isolated in small amounts. The elemental analysis of the reddish liquid polymer yielded the following results: C = 52.10%, N = 16.01% and H = 10.49%. These values compare well with theoretical values of C = 55.17%, N = 16.09% and H = 10.33% expected for HEEI polymer. The i.r. spectrum of the electroinitiated polymer was identical with that of an acid-catalysed polymerization product prepared in DMF from HEEI.

In the discussion above, the presence of polymer in the cathode compartment was attributed to polymer migration from the anode. To evaluate such a possibility, some

Table 1 Electropolymerization<sup>a</sup> of HEEI

Monomer compartment	% Yield		Conditions
	Cathode	Anode	
Anode <sup>b</sup>	3.0	41.6	Wet
Anode	4.2	32.8	Wet
Cathode	2.3	3.2	Wet
Anode	10.6	52.4	Anhydrous
Anode	9.6	45.7	Anhydrous
Cathode	0.3	0.1	Anhydrous
Anode	2.3	35.1	Anhydrous N <sub>2</sub>

<sup>a</sup> At room temperature, 12 V d.c., 18 h, [HEEI] = 3.44 M

<sup>b</sup> Platinum anodes used

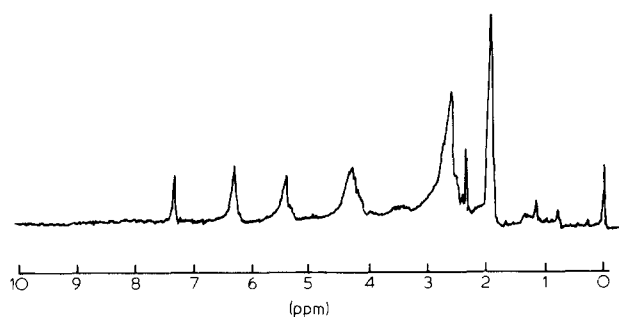


Figure 1  $^1\text{H}$  n.m.r. spectrum of poly{2-(1-aziridinyl)ethyl methacrylate} electroinitiated at the anode

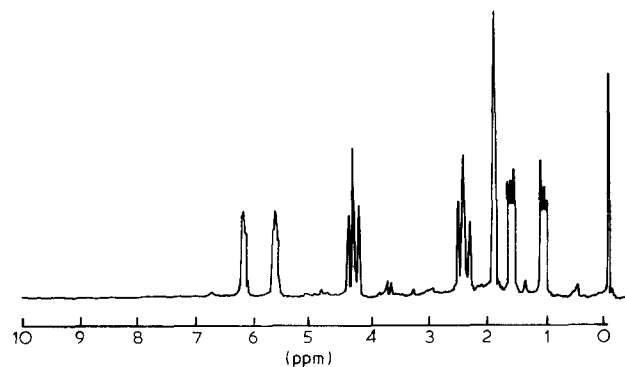
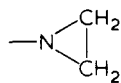


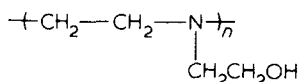
Figure 2  $^1\text{H}$  n.m.r. spectrum of 2-(1-aziridinyl)ethyl methacrylate monomer

polyHEEI, prepared from an earlier experiment, was placed in the anode compartment of the three compartment cell, and 12 V d.c. applied for 18 h. It was found that 3.5% of the polymer initially placed in the anode could be isolated from the cathode; the weight of the cathodic fibre had also increased by 390%. In comparison, the fibre anode had picked up only 13% increase in weight. These experiments supported the inference that the polyHEEI migrated to the cathode from the anode compartment.

The results discussed above show that the electropolymerization of HEEI is initiated by an anode reaction, and that a portion of the polymer can, and probably does, migrate into the cathode compartment. Initiation of polymerization at the anode would be consistent with the chemistry of the aziridinyl ring<sup>8</sup>



which, being electron rich, would be subject to electrophilic, rather than nucleophilic attack. The cationic polymerization of HEEI can be initiated by acid catalysts<sup>8</sup>, and, as pointed out earlier, the i.r. spectrum of the acid catalysed polymer was identical to that of the electroinitiated polymer. The following structure could therefore be written for the polymer, consistent with the chemistry of cationic polymerizations through the aziridine ring<sup>9</sup>:



The proposed structure would also account for the migration of polymer from the anode to the cathode. The protonated or cationic polyamine would be repelled by the anode and would be attracted to the cathode.

### 2-(1-Aziridinyl)ethyl methacrylate

This difunctional monomer (AEMA), containing both an aziridinyl and a vinyl group, was polymerized at the cathode and at the anode in separate experiments. The structures of the polymers prepared by the two methods were determined by i.r. and n.m.r. spectroscopy.

The anodic polymer of AEMA showed a vinyl absorption band at  $1650\text{---}1$  as did the acid catalysed polymer. This indicated that the double bond is retained, and that anodic polymerization occurs through the aziridinyl group. In the i.r. spectrum of the cathodic polymer on the other hand, the vinyl absorption had completely disappeared as in polyAEMA prepared through free radical initiation by benzoyl peroxide. Clearly, cathodic polymerization occurs through the double bond.

Further evidence is found in the n.m.r. spectra of the monomer and the different polymers shown in Figures 1–3 and summarized in Table 2. For the anode polymer, the spectrum shows: (1) the complete disappearance of the AA'BB' multiplets for the protons of the aziridinyl ring; (2) an increase in the absorption of linear  $\text{---N---CH}_2\text{---}$  type protons at  $2.60\delta$ ; and (3) the presence of two vinyl absorptions at  $6.63\delta$  and  $5.43\delta$ . In the spectrum of the cathode polymer, the salient features are: (1) the complete disappearance of the two vinyl absorptions and (2) retention of the aziridinyl ring protons as AA'BB' multiplets.

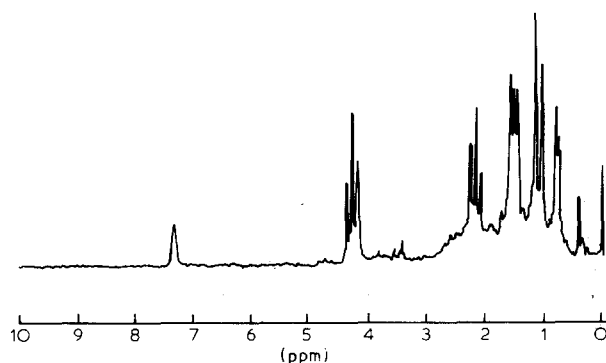
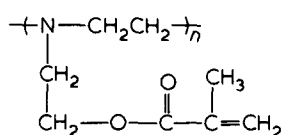


Figure 3  $^1\text{H}$  n.m.r. spectrum of poly{2-(1-aziridinyl)ethyl methacrylate} electroinitiated at the cathode

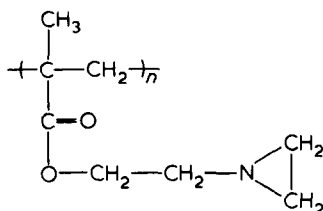
Table 2  $^1\text{H}$  n.m.r. spectra of AEMA and its polymers

Chemical shift, $\delta$	Multiplicity	Assignment
<b>2-(1-Aziridinyl)ethyl methacrylate</b>		
6.23	Broad singlet	Vinyl
5.70	Unresolved quartet	Vinyl
4.37	Triplet ( $J=6$ Hz)	$\text{---CH}_2\text{---O}$
2.47	Triplet ( $J=6$ Hz)	$\text{>N---CH}_2\text{---}$
1.97	Singlet	Methyl
1.63	Multiplet	Aziridinyl AA'
1.10	Multiplet	Aziridinyl BB'
<b>Anode polymer</b>		
6.63	Broad	Vinyl
5.43	Broad	Vinyl
4.30	Broad	$\text{---CO}_2\text{---O}$
2.60	Broad	$\text{---N---CH}_2\text{---}$
1.93	Singlet	Methyl
<b>Cathode polymer</b>		
4.30	Triplet ( $J=6$ Hz)	$\text{---CH}_2\text{---O}$
2.17	Triplet ( $J=6$ Hz)	$\text{>N---CH}_2\text{---}$
1.53	Multiplet	Aziridinyl AA' + C-CH <sub>2</sub> -C
1.15, 1.07	Singlets	Methyl
0.77	Multiplet	Aziridinyl BB'

From these results it can be concluded that anodic polymerization of AEMA occurs through the aziridinyl group to yield a polymer of the structure:



The cathodic polymerization takes place by the opening of the double bond to give a polymer of the following structure:



Selective polymerization through either of the two functional groups of AEMA can thus be achieved by electroinitiation.

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## Preparation and characterization of spin-labelled polystyrene

C. Friedrich and C. Noël

Laboratoire de Physicochimie Structurale et Macromoléculaire, ESPCI, 10, rue Vauquelin, 75231 Paris Cédex 05, France

and R. Ramasseul and A. Rassat

Laboratoire de Chimie Organique et Physique, Centre d'Etudes Nucléaires de Grenoble, 85x, F38041 Grenoble, France

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The dynamic properties of polystyrene in dilute solutions constitute a problem of considerable interest. In recent years, many investigations have been carried out using techniques well-adapted to the study of fast movements such as fluorescence polarization<sup>1</sup>, <sup>13</sup>C and <sup>1</sup>H nuclear magnetic relaxation<sup>2-7</sup>, ultrasonic relaxation<sup>8-11</sup> and Raman line shape analysis<sup>12</sup> to find a description of the molecular motions under a variety of conditions. The spin labelling technique has recently been used to study polystyrenes labelled either at chain ends<sup>13</sup> or at the *para*-<sup>14</sup> or at the *meta*-<sup>15</sup> position of the aromatic ring. The present work is concerned with the preparation and characterization of a polystyrene with a nitroxide group inserted in the main chain.

Basically, the method consists of adding a bifunctional deactivating reagent to the monofunctional 'living' polymer prepared by anionic polymerization, using butyllithium as the initiator and 2,5-di-*t*-butyl-3,4-diethoxycarbonyl pyrrol-2-yloxy as the deactivating agent (shown in the reaction scheme).

Benzene was dried over calcium chloride and freed from moisture by refluxing over sodium wire. It was then twice

distilled over sodium wire and stored over sodium.

Styrene was three times distilled over sodium wire under reduced pressure.

Butyllithium in benzene was freshly prepared before each polymerization by reaction of butyl chloride and lithium metal.

2,5-di-*t*-butyl-3,4-diethoxycarbonyl pyrrol-1-yloxy was prepared as described in ref 16.

