

# Synthesis and Electrochemistry of Grafted Copolymers of Cellulose with 4-Vinylpyridine, 1-Vinylimidazole, 1-Vinyl-2-pyrrolidinone, and 9-Vinylcarbazole

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## SYNOPSIS

Some new cellulosic materials, suitable for the adsorption of noble metal ions, were synthesized by chemical and electrochemical modification of cellulose. The polymerizable groups were introduced in cellulose with ~ 80% yield of substitution by esterification with acryloyl chloride. The vinyl monomers (4-vinylpyridine, 1-vinylimidazole, 1-vinyl-2-pyrrolidinone, and 9-vinylcarbazole) were readily grafted into cellulose acrylate via radical polymerization in acetonitrile. The grafted copolymers of cellulose with 4-vinylpyridine and 4-vinylimidazole were reacted with methyl iodide and the corresponding 1-methylpyridinium iodide (**6**) and 3-methylimidazolium iodide (**7**) copolymers of cellulose were obtained. Copolymers **6** and **7** were transformed into new polymeric reagents, differing in anions ( $\text{ClO}_4^-$ ,  $\text{CF}_3\text{COO}^-$ ,  $\text{NO}_3^-$ ,  $p\text{-TsO}^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ) by using a supporting electrolyte carrying the desired anions through the ion-exchange-electrochemical oxidation of the released iodide at a controlled anodic potential. © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Chemical modifications are of great interest in polysaccharide applications involving the preparation of selectively permeable membranes,<sup>1</sup> as matrices for drug delivery,<sup>2</sup> as well as in various processes relating to recovery of biological materials.<sup>3</sup>

Cellulose is the most abundant, renewable, natural polymer and a very promising raw material available at low cost for the preparation of various functional polymers. A wide range of sorbents for metal ions based on chemical modifications of cellulose have been developed<sup>4</sup> and some of them have shown outstanding sorptive capacity, high hydrophobicity, and selectivity.<sup>5</sup>

In this article, we describe the optimized procedure for the preparation of cellulose acrylate, grafting of vinyl monomers into cellulose acrylate, methylation of the grafted copolymers of cellulose with

4-vinylpyridine and 1-vinylimidazole, and their electrochemical transformations. Some of the synthesized new materials have shown excellent properties in adsorption and desorption of noble metal ions from dilute solutions.<sup>6</sup>

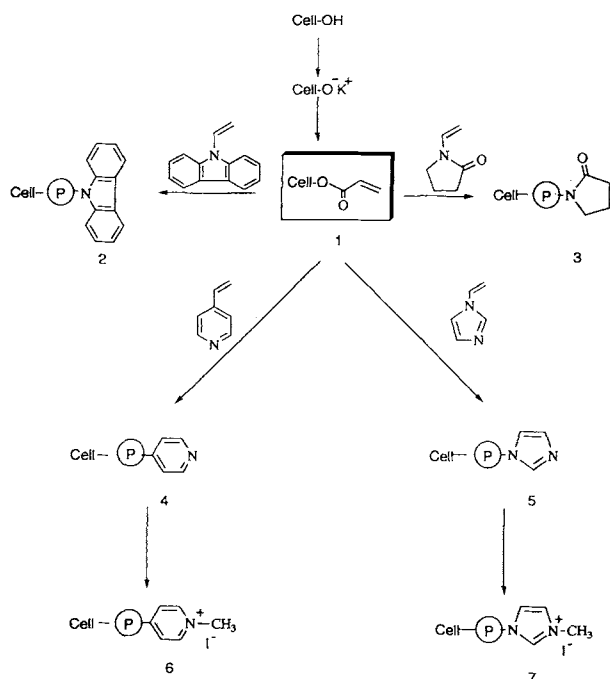
## EXPERIMENTAL

### Materials and Apparatus

Cellulose powder (Whatman Standard Grade) supplied by Aldrich was washed with water, methanol, and acetone and then vacuum-dried to a constant weight at 80°C. Dimethylformamide (DMF), acryloyl chloride, and vinyl monomers (4-vinylpyridine, 1-vinylimidazole, 1-vinyl-2-pyrrolidinone, 9-vinylcarbazole) supplied by Aldrich were used after purification by vacuum-distillation.

All solvents were dried and distilled before use. IR spectra were recorded on a Perkin-Elmer IRDMI (FTIR 1724X) spectrometer using KBr palets. All elemental microanalyses were carried out in the

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Scheme 1.

usual way using a Perkin-Elmer 240 elemental analyzer.

The equipment and acetonitrile purification for the voltammetric measurement were described previously.<sup>7</sup> A standard, three-electrode electrochemical cell was used for all experiments, with a Pt disc ( $2r = 2$  mm) and gauze ( $3 \times 5$  cm) for analytical experiments and large-scale electrolysis, respectively. The potentials were related to SCE. All electrochemical experiments were carried out at room temperature. All the supporting electrolytes were commercially available.

### Synthesis of Cellulose Acrylate

Cellulose powder (3.24 g) was swollen in acetonitrile (50 mL) at room temperature for 1 h. The solution of potassium-*t*-butoxide (6.72 g) in acetonitrile (50 mL) was added and the reaction mixture was allowed to react at room temperature for 4 h. An excess of acryloyl chloride (18.0 g) in acetonitrile (50 mL) was added dropwise to the stirred reaction mixture at room temperature. Stirring was continued under reflux for another 10 h. The cellulose acrylate **1** was filtered, washed thoroughly with water, ethanol, acetone, and diethyl ether and then dried in vacuum at 50°C. A yield of 4.65 g of product was obtained. IR (KBr) spectra of product **1** showed an absorption at  $1720\text{ cm}^{-1}$  (C=O of ester). The substitution per-

**Table I** Elemental Analysis and Degree of Substitution of Cellulose Derivate

Reaction Time <sup>a</sup> (h)	Substitution of Cellulose, Y (%)	Microanalysis	
		C (%)	H (%)
0	0	42.53	6.40
1	26.2	44.00	6.18
3	44.5	45.02	6.16
5	55.7	45.65	6.08
6	70.9	46.50	6.03
10	80.2	47.02	5.97

<sup>a</sup> Molar ratio: glucose unit/*t*-butoxide/acryloyl chloride = 1 : 3 : 10.

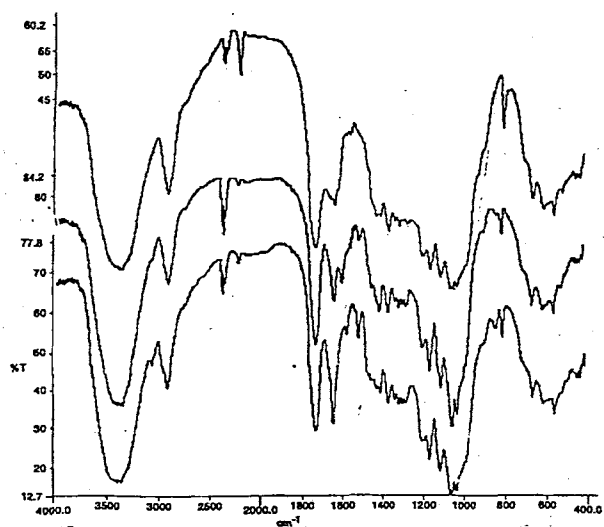
centage of the glucose units in cellulose ( $Y = 80.7\%$ ) was calculated from the expression

$$Y = \frac{A - B}{C - D} \times 100$$

where  $A = \% \text{ carbon found for derivatized cellulose}$ ,  $B = \% \text{ carbon found for starting cellulose}$ ,  $C = \% \text{ carbon calculated for 100\% derivatization}$ , and  $D = \% \text{ carbon calculated for cellulose}$ .

### Synthesis of Grafted Copolymers 2, 3, 4, and 5

A mixture of cellulose acrylate **1** (1.0 g), acetonitrile (50 mL), the respective vinyl monomer (5.0 mL), and AIBN (0.05 g) was refluxed for 5 h under nitrogen. The products obtained (**2–5**) were filtered and



**Figure 1** IR spectra of polymers: top: **1**; middle: **4**; bottom: **6**.

thoroughly washed with water, ethanol, acetonitrile, acetone, and diethyl ether to eliminate oligomers and homopolymers formed in the reaction as by-products. The products were then dried at 50°C in vacuum. IR (KBr) spectra showed characteristic absorption bands at 1580, 1310, 1210, 740, and 720  $\text{cm}^{-1}$  for product **2**; at 1650, 1340, and 890  $\text{cm}^{-1}$  for product **3**; at 1620 and 820  $\text{cm}^{-1}$  for product **4**; and at 1620, 1480, 910, 820, and 740  $\text{cm}^{-1}$  for product **5**. The levels of grafting achieved with **2**, **3**, **4**, and **5**, expressed as the weight fraction of the corresponding vinyl monomer,  $x$ , in each grafted product, was calculated using the relationship<sup>8</sup>

$$E = (1 - x)A + ax$$

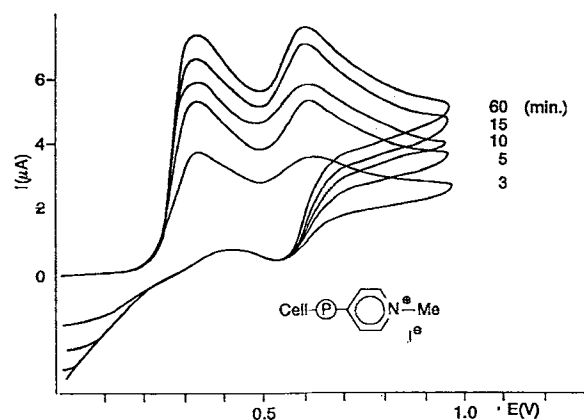
where  $A$  = % carbon found for derivated cellulose,  $B$  = % carbon found for grafted derivative, and  $a$  = % carbon calculated for the corresponding vinyl monomer.

### Synthesis of Grafted Copolymers 6 and 7

A mixture of grafted copolymers, **4** or **5** (2.0 g), methyl iodide (5 mL), and DMF (50 mL) was stirred for 5 h at 110°C. The methylated products (**6** or **7**) formed were filtered, washed with water, methanol, acetone, and diethyl ether, and then dried at 50°C under vacuum. IR (KBr) spectra of products **6** and **7** showed an absorption band at 1642  $\text{cm}^{-1}$  which can be attributed to the  $\text{C}=\text{N}^+$  group of the quaternized nitrogen atom in the pyridine and imidazole ring.

### Electrochemical Transformation of Grafted Copolymers 6 and 7

To the anodic compartment of the divided cell with a Pt-gauze anode (3 × 5 mm) and a Ni cathode,



**Figure 2** Cyclic voltammograms of **6** at a Pt electrode ( $2r = 1$  mm) with a scan rate of 0.1 V/s in  $\text{CH}_3\text{CN}$ -0.1M  $\text{Et}_4\text{NClO}_4$  at different time intervals.

filled with a 0.1M solution (80 mL) in the appropriate solvent (see Table III), 0.2–0.4 g of the polymer **6** and **7** was added and the mixture was stirred for 1 h. The potential was maintained at a fixed value (see Table III) with an initial current generally of 80–150 mA. The electrolysis was discontinued generally when the current dropped to 5–10 mA. The polymeric product was filtered and washed thoroughly with water, methanol, and acetonitrile.

## RESULTS AND DISCUSSION

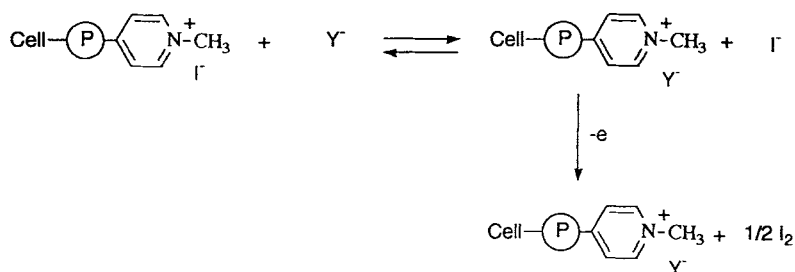
### Synthesis of Grafted Copolymers

Grafting reactions provide a potential route for altering the physical and mechanical properties of a substrate polymer to specific end uses. Graft copolymerization of vinyl monomers on cellulose by either ionic or free-radical initiation has been extensively investigated in recent years.<sup>9</sup> Akelah and Sherrington showed an alternative approach in the

**Table II** Elemental Analysis and Weight Fraction of Vinyl Monomers

Copolymer	Weight Fraction of Vinyl Monomer ( $x$ )	Microanalysis			
		C (%)	H (%)	N (%)	I <sup>-</sup> (%) <sup>a</sup>
2	0.76	77.74	5.20	6.46	—
3	0.16	49.93	6.28	2.25	—
4	0.16	52.43	6.05	4.77	—
5	0.05	47.90	5.91	5.76	—
6	—	45.11	5.31	2.93	20.12
7	—	42.63	5.39	5.25	14.12

<sup>a</sup> Analyzed by coulometry at a controlled potential (see text).

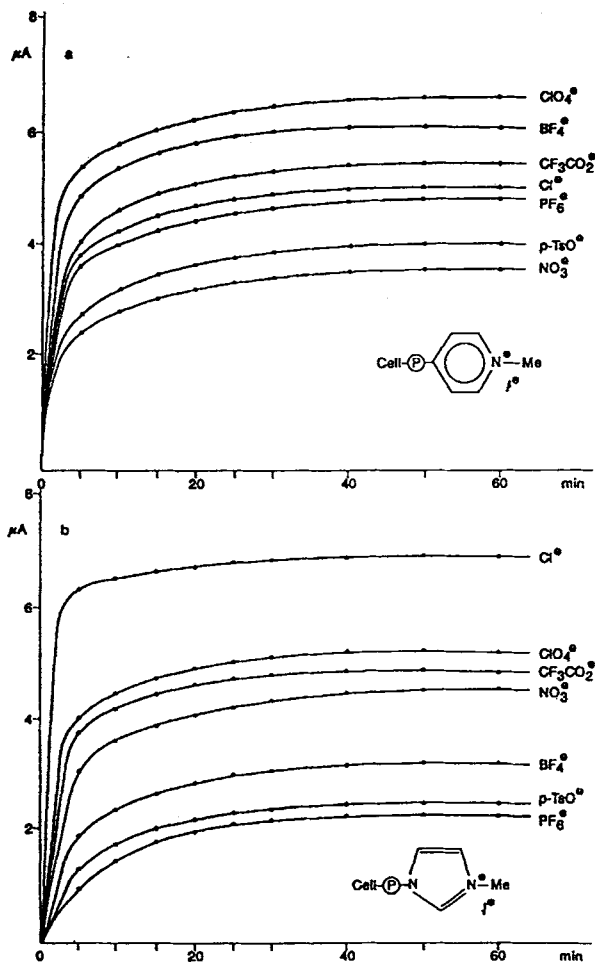


Scheme 2.

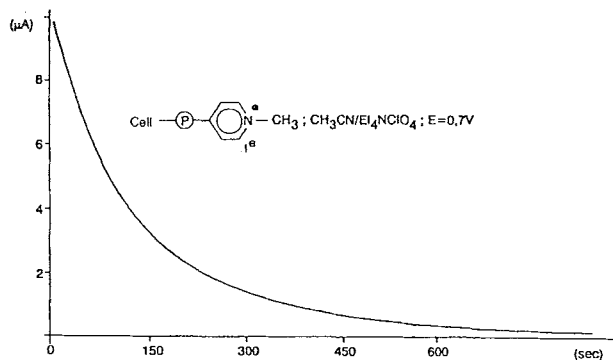
grafting reactions involving the introduction of carbon-carbon double bonds onto cellulose by esterification with acryloyl chloride.<sup>8</sup> Their approach seemed rational for our synthetic plan although they obtained cellulose acrylate, **1**, with a low level of substitution ( $Y = 27\%$ ) and we decided to optimize the process of esterification as the first reaction step.

Cellulose was esterified and grafted with the vinyl monomer according to Scheme 1. In an attempt to increase the yield of the esterification reaction of cellulose, the effects of the reactants on the degree of substitution was investigated. It was found that the content of acrylic groups in **1** increases with increase of the acryloyl chloride concentration and by maintaining a molar ratio between the glucose unit in cellulose and potassium *t*-butoxide in a 1 : 3 ratio. The content of acrylic groups reached a maximum value when acryloyl chloride was used in more than a 10 molar excess under constant reaction conditions, i.e., the time (3 h) and ratio of the glucose unit and potassium *t*-butoxide (1 : 3). It appeared that the reaction time was important in obtaining a high yield of cellulose acrylate. In Table I are presented results of the elemental microanalysis and the substitution percentage of glucose units determined after different time periods at optimal molar ratio of the reactants.

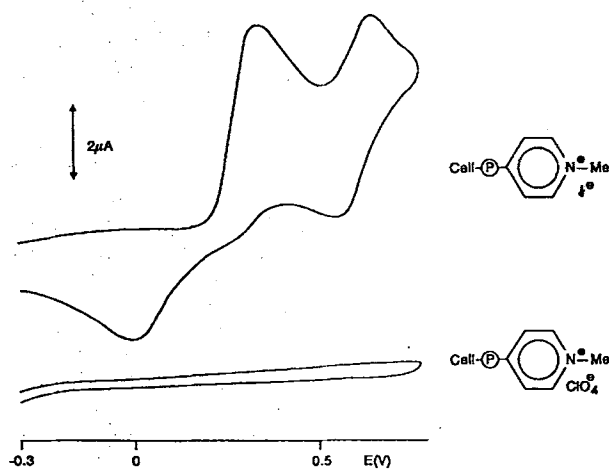
The results presented in Table I show that the carbon content and degree of substitution increase with a longer reaction time, and after 10 h, product **1** exhibited about a threefold higher level of substitution ( $Y = 80.2\%$ ) than that of the product obtained by the Akelah and Scherington procedure ( $Y$



**Figure 3** Effects of time on the rate of anion-exchange reaction with the corresponding support electrolyte (0.1M) except for  $\text{NH}_4\text{NO}_3$  ( $c = 0.025M$ ): (a) **6** (14.5 mg); (b) **7** (14.5 mg).



**Figure 4** The current-time curve during the coulometry at a controlled potential (0.7 V vs. SCE) at the Pt-gauze electrode ( $2 \times 3$  mm) for **6** (14.5 mg).



**Figure 5** Cyclic voltammograms at the Pt electrode ( $2r = 1$  mm) with scan rate of 0.1 V/s in  $\text{CH}_3\text{CN}$ -0.1M  $\text{Et}_4\text{NClO}_4$ ; top: **6** (14.5 mg) with iodide as a counterion; bottom: **6** (14.5 mg) with perchlorate as a counterion.

= 27%). IR spectra of cellulose acrylate **1** showed a strong absorption band at  $1720\text{ cm}^{-1}$  for the carbonyl group (Fig. 1). Similar levels of substitution, which were in accordance with elemental analysis, were obtained by IR analysis of the ratio of absorption intensities at  $1720$  and  $1410\text{ cm}^{-1}$ , respectively.

The graft copolymerizations were performed under heterogeneous conditions using an excess of vinyl monomers (1-vinylcarbazole, 1-vinyl-2-pyrrolidinone, 4-vinylpyridine, and 1-vinylimidazole) in the presence of AIBN as a free-radical initiator and products **2** and **5** were obtained. Copolymers **4** and **5** were methylated, yielding their quaternary iodide salts **6** and **7** (Scheme 1). The products obtained, **2**–**7**, were analyzed by elemental microanalysis and by IR spectroscopy. The results of elemental analysis

and weight fraction of vinyl monomers are presented in Table II.

From Table II it can be seen that under similar reaction conditions the weight fraction of 1-vinylimidazole grafted is the lowest ( $x = 0.05$ ), and of 9-vinylcarbazole, the highest ( $x = 0.76$ ), implying that the relative reactivity of vinyl monomers toward cellulose acrylate **1** lie in the following order: 9-vinylcarbazole > 1-vinyl-2-pyrrolidinone = 4-vinylpyridine > 1-vinylimidazole. We did not make any attempt to optimize the grafting processes, but we believe that the grafting process can be improved and it is certainly worthy of further consideration and further experimentation. The changes of the structure in the reaction sequences  $1 \rightarrow 4 \rightarrow 6$  can be illustrated by IR spectra as shown in Figure 1.

The IR spectra of cellulose acrylate showed a strong carbonyl band absorption at  $1720\text{ cm}^{-1}$ . The grafted copolymer **4** showed new absorption at  $1620$  and  $810\text{ cm}^{-1}$ , which clearly indicates the presence of the pyridine ring. The grafted copolymer **6** exhibited a new absorption band at  $1642\text{ cm}^{-1}$ , which can be attributed to the quaternized pyridine ring.

#### Electrochemistry of Grafted Copolymers **6** and **7**

Recently, we developed a simple and versatile electrochemical synthesis of new polymeric reagents by using controlled potential electrolysis for transformation of crosslinked poly[styrene-4-vinyl(*N*-methylpyridinium iodide)] to new polymeric reagents differing in anions by merely using a supporting electrolyte carrying the desired anion.<sup>10</sup> We hoped that by using the same method in the case of copolymers **6** and **5** would give a specific feature to new polymeric materials. We found<sup>6</sup> that the elec-

**Table III** The Electrochemical Transformation of Copolymers **6** and **5**

Y <sup>-</sup> in Product	Solvent/Support Electrolyte (0.1M)	Applied Potential (V vs. SCE)	Characteristic IR Bands for Y <sup>-</sup> (KBr) cm <sup>-1</sup>
$\text{ClO}_4^-$	$\text{CH}_3\text{CN}/\text{Et}_4\text{NClO}_4$	0.7	1095, 650
$\text{CF}_3\text{COO}^-$	$\text{CH}_3\text{CN}/\text{CF}_3\text{COONa}$	0.7	1683, 1204, 834
$\text{NO}_3^-$	$\text{CH}_3\text{CN}/\text{H}_2\text{O}(9 : 1)/\text{NH}_4\text{NO}_3$	1	1380
$p\text{-TsO}^-$	$\text{CH}_3\text{CN}/\text{Et}_4\text{NTsO}$	0.7	1191, 811
$\text{BF}_4^-$	$\text{CH}_3\text{CN}/\text{Bu}_4\text{NBF}_4$	0.7	1120, 1080
$\text{PF}_6^-$	$\text{CH}_3\text{CN}/\text{Bu}_4\text{NPF}_6$	0.7	841, 558

In summary, we developed a useful synthesis of cellulose acrylate grafting with 4-vinylpyridine, 1-vinylimidazole, 1-vinyl-2-pyrrolidinone, and 9-vinylcarbazole. Copolymers **4** and **5** were methylated to **6** and **7**, which were transformed through an ion-exchange-electrochemical oxidation to new polymeric materials suitable as sorbents for noble metal ions from their dilute solutions.

trochemical exchange of iodide in **6** and **5** with other anions improved the capacity of a new material as ion exchangers for the separation of noble metals from dilute solutions.

The electrochemical behavior of insoluble copolymer **6**, added in acetonitrile containing tetraethylammonium perchlorate as a supporting electrolyte, was studied in some detail. A single-compartment cell containing a saturated calomel electrode (SCE) was employed. The counterelectrode was a platinum sheet and the working electrode was a polished disc of platinum ( $2r = 1$  mm). Typical cyclic voltammograms of copolymer **6**, run after different time intervals of mixing (500 rpm) in acetonitrile-tetramethylammonium perchlorate solution, are shown in Figure 2.

The cyclic voltammogram shows two anodic waves with the peak potentials at 0.35 and 0.65 V vs. SCE. It is known<sup>7</sup> that the iodide ion displays two anodic waves in acetonitrile at the Pt electrode within the potential range examined. The increase of both waves as a function of time can be attributed to the ion exchange given in Scheme 2. A number of micromoles of iodide were generated as a function of time. The quantity of iodide generated was measured as the peak current of the first wave and the resulting curves obtained in acetonitrile by using different supporting electrolyte are shown in Figure 3. Similar experiments were done with copolymer **7** and the results are also shown in Figure 3.

These curves show that the system approaches equilibrium at different time intervals depending on the anion used. It is important to note that the rate exchange reaction, or mobility of anions, is quite different for two copolymers studied (**6** and **7**) and it is difficult to explain this kind of behavior at the present time. We have shown<sup>10</sup> that a sterically hindered polymer has a negative influence on the anion-exchange reaction, but other factors, such as the rate of diffusion of the anion into the polymer matrix and the ion-pairing effect, may play an equally important role on the rate of the anion-exchange reaction.

The equilibrium shown in Scheme 2 can be shifted toward product formation by the electrochemical oxidation of the released iodide. The global stoichiometry of the process seems to be  $2I^- \rightarrow I_2 + 2e^-$ . The concept, ion-exchange-electrochemical oxidation, can be used in the analysis of iodide content in an insoluble polymer as well as in the preparation of the new polymers differing in the anion.

Coulometry at a controlled potential corresponding to the second wave ( $E = 0.7$  V vs. SCE) of the cyclic voltammogram was carried out in a divided

cell at the Pt-gauze anode ( $2 \times 3$  cm) after mixing (60 min) 14.5 mg of copolymer **6** in  $CH_3CN-0.1M$   $Et_4NClO_4$  solution and the current time curve was recorded and the quantity of electricity passed was measured during the electrolysis by means of an electronic integrator. The electrolysis proceeded smoothly and after 10 min the current dropped to the residual current (Fig. 4). This reaction proceeds with 100% efficiency and the coulometry at a controlled potential appears to be a useful analytical technique for the determination of the oxidizable anions present in the cationic polymers. Knowing the amount of the insoluble starting polymer and the amount of electricity passed, the amount of the iodide can be easily obtained from the Faraday equation.

The cyclic voltammograms of starting copolymer **6** and the new polymer formed through the ion-exchange-electrochemical oxidation reactions are shown in Figure 5. The new product containing perchlorate as a counterion exhibited on IR spectra characteristic absorption bands at  $1720\text{ cm}^{-1}$  (ester  $C=O$ ) and  $1642\text{ cm}^{-1}$  ( $C=N^+$ ) and a strong absorption at  $1095$  and  $650\text{ cm}^{-1}$ , corresponding to the perchlorate ion. The cyclic voltammogram of the new product did not indicate the presence of the iodide ion, even in traces.

The preparative transformations of copolymers **6** and **7** were performed by anodic oxidation at a controlled potential in the corresponding solvent-supporting electrolyte system (see Table III). After isolation (see Experimental), all new products exhibited the characteristic IR bands for the anions present (Table III).

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