

Thermoplastic Matrix Composites by Aqueous Electrocopolymerization onto Graphite Fibers

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Synopsis

Electrocopolymerization of 3-carboxyphenyl maleimide and styrene onto Hercules AS-4 graphite fiber surfaces has been successfully carried out from an aqueous solution containing monomers and dilute sulfuric acid. Initiation of copolymerization of the monomers dissolved in a small amount of dimethylacetamide is achieved by constant-current electrolysis in the cathodic chamber of a three-compartment electrolysis cell. Polymerization is initiated at the fiber surfaces; little polymer is formed in the cell solution. Electrocopolymerization is very consistent and rapid. The amount of polymer increases predictably with increasing comonomer concentration and current density. Using a 0.4 M (1 : 1) comonomer concentration, 0.0125 M sulfuric acid solution, and a current density of 20 mA/g, more than 60 wt % of copolymer coating per unit weight of graphite fibers is obtained within thirty minutes. Thermal gravimetric analysis showed the copolymer to be very stable at elevated temperatures and has initial and final decomposition temperatures of 430 and 520°C, respectively. The glass transition temperature measurement of the copolymer coatings was carried out by differential scanning calorimetry. A single glass transition temperature was obtained of about 210°C for most samples. The glass transition temperature of the copolymers did not change significantly with changing comonomer feed composition. Functional group and compositional analysis of the copolymer was done by FTIR spectroscopy. The copolymer composition remained relatively the same for copolymers made from different styrene/3-carboxyphenyl maleimide feed composition, confirming a strong tendency toward alternation for the system.

INTRODUCTION

Electrochemical initiation of polymerization is an established technique and has been used to direct the formation of polymers onto electrode surfaces.¹⁻⁵ Polymerizations have generally been from nonaqueous solutions, by ionic or mixed ionic-radical mechanisms. Molecular weights of the electropolymers from these solutions have generally been low. Prior workers such as Funt and Toppare et al.⁶⁻¹³ have contributed greatly to the understanding of the nature and mechanism of electropolymerization. Advanced composites reinforced with stiff, light weight, and strong reinforcements, such as graphite fibers, have added a new dimension to the application of electroinitiated polymerization. Graphite fibers are very good electrical conductors and have been variously used as the working electrode onto which polymer coatings are applied during electrosynthesis.¹³⁻¹⁵

In a recent work, Bell et al.^{16,17} and earlier Subramanian and Jakubowski^{18,19} used aqueous solution electropolymerization to apply thin polymeric coatings onto graphite fibers. High molecular weight polymers were obtained.²⁰ MacCallum and MacKerron have also studied the kinetics of aqueous electropolymerization of methyl methacrylate onto graphite fiber surfaces. They suggested a radical-ion mechanism.^{1a} The electrocoated fiber-reinforced epoxy

composites showed improved impact and interlaminar shear properties over commercially surface-treated graphite fiber reinforced epoxy composites.

Bulk copolymerization of maleimides with electron donor monomers such as styrene is well documented.²¹⁻²⁷ Such copolymerizations have been clearly shown to follow an alternating mechanism. The extent of alternation, however, is dependent on such factors as the nature of solvent used, comonomer concentration, and copolymerization temperature. No information has been found in the area of electroinitiated copolymerization of maleimides with vinyl monomers. Previous attempts at the electrolysis of *N*-phenyl maleimide alone in a monomer-electrolyte solution of varying pH have resulted in the formation of monomeric *N*-phenylsuccinimide (mp $\sim 152^\circ\text{C}$) and succinilide (mp $\sim 148^\circ\text{C}$).²⁸⁻³¹ There is still much controversy surrounding the mechanism of electrochemical reduction of maleimides. In our present work we report the successful aqueous electrocopolymerization of 3-carboxyphenyl maleimide and styrene onto AS-4 graphite fibers.

EXPERIMENTAL

Materials

Monomeric styrene (99.9%), purchased from Aldrich Chemical Company, was extracted twice in 10% sodium hydroxide solution to remove inhibitor and washed twice in distilled water. 3-Carboxyphenyl maleimide (3-CMI) was purchased from Mitsui Toatsu Chemicals Inc. (Japan) and was used as received. Laboratory grade sulfuric acid, 96%, from May and Baker Ltd., was diluted to 0.0125 *M* by adding distilled water and was then used as the supporting electrolyte. High-purity dimethylacetamide (99.9%) was used as purchased from Aldrich Chemical Company. Unsized AS-4 graphite fibers (7.2 μm diameter, 3000 filament bundle) from Hercules Inc., wound onto an H-shaped 6 \times 6 in. aluminum frame (Fig. 1) was used as the working electrode.

Electrocopolymerization

Electrocopolymerization of 3-carboxyphenyl maleimide and styrene was carried out in the middle compartment of a three-chamber polypropylene cell described earlier by Chang.²⁰ A schematic representation of the cell is shown in Figure 2. The central compartment contains the monomer-electrolyte solution, composed of 3-carboxyphenyl maleimide (0.5 *M*), styrene (0.5 *M*), DMAc, and sulfuric acid (0.0125 *M*) in the volume ratio 50 : 50 : 20 : 100. It is separated from the two side compartments by a polypropylene membrane (0.04 μm pore diameter), glued to perforated polypropylene sheets. The side chambers contain the supporting electrolyte and two rectangular stainless steel (8 \times 8 \times $\frac{1}{16}$ in.) counter electrodes. Initiation of copolymerization was achieved by constant-current polymerization. The current density applied ranged from 2 to 35 mA, and the electrocopolymerization time was varied to give the thickness of coating desired. Electrocopolymerized materials precipitated onto the surfaces of the graphite fiber cathode and were removed by withdrawing the frames from the cell. The coated fibers were rinsed in distilled water, dried at 100°C for 12 h at vacuum and weighed to determine the amount of copolymer formed.

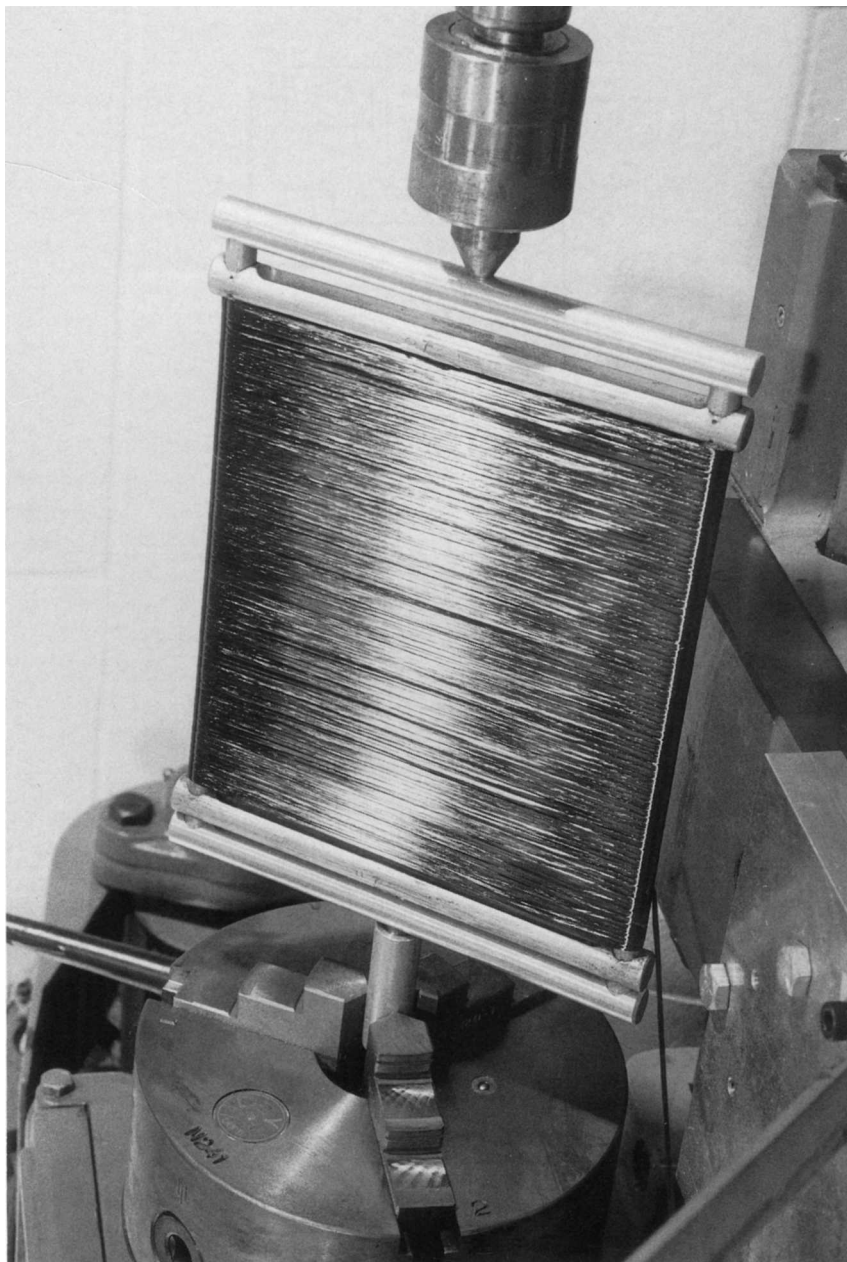


Fig. 1. Graphite fiber working electrode.

It was found that 12 h at 100°C at vacuum was sufficient to bring the prepregs to constant weight. The molecular weight distribution of the copolymer synthesized from a 0.5 *M* (1 : 1) comonomer feed solution was determined by Waters gel permeation chromatograph. Tetrahydrofuran (THF) and mono-dispersed polystyrene were the solvent and calibration standards, respectively.

ELECTROCHEMICAL CELL

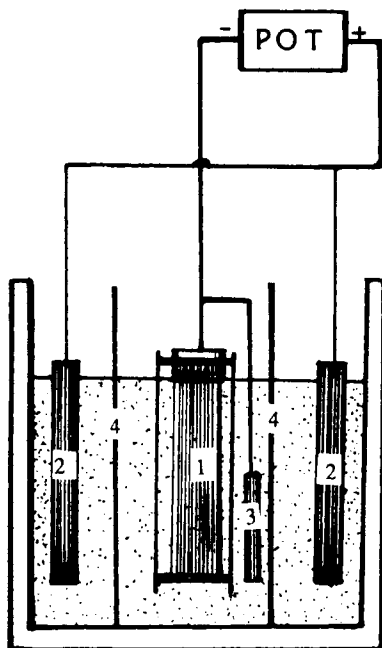


Fig. 2. Schematic representation of the electrochemical cell.

Cyclic Voltammetry

Cyclic voltammetry was used to measure the reduction potential of the comonomers. The use of this technique in electropolymerization is well established.¹⁰⁻¹³ The comonomers (0.5 M) and carrier electrolyte, tetraethylammo-

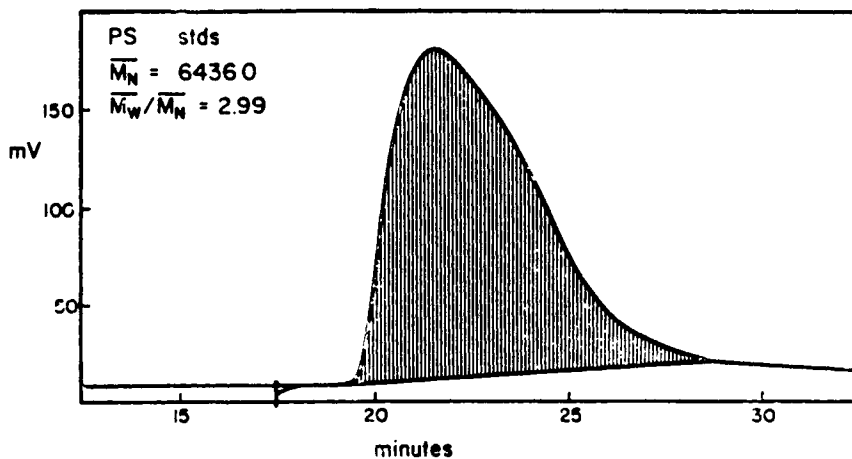


Fig. 3. Molecular weight distribution of poly(3-CMI-co-styrene) electrocopolymerized from a 0.5 M (1:1) comonomer solution.

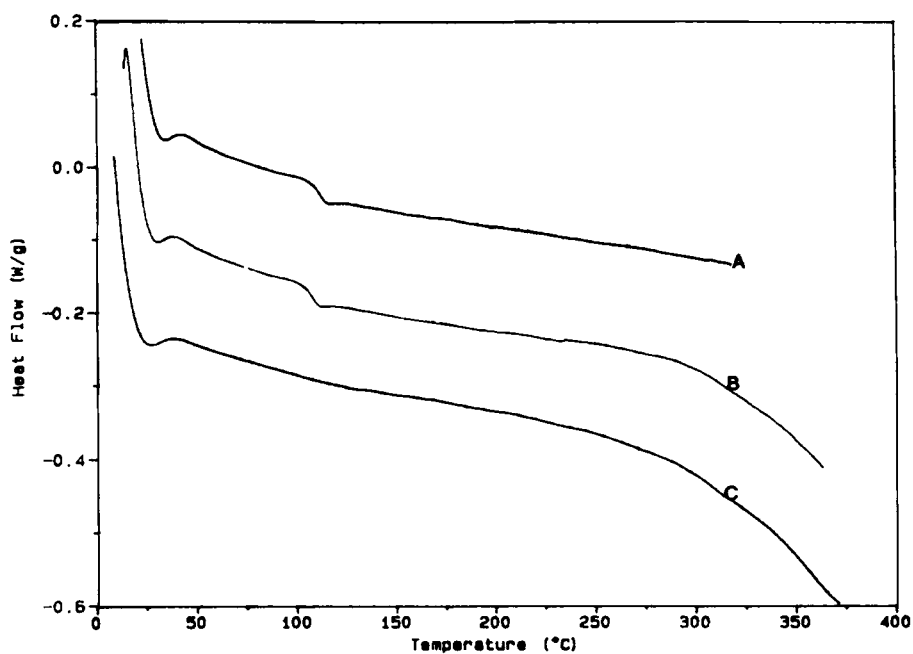
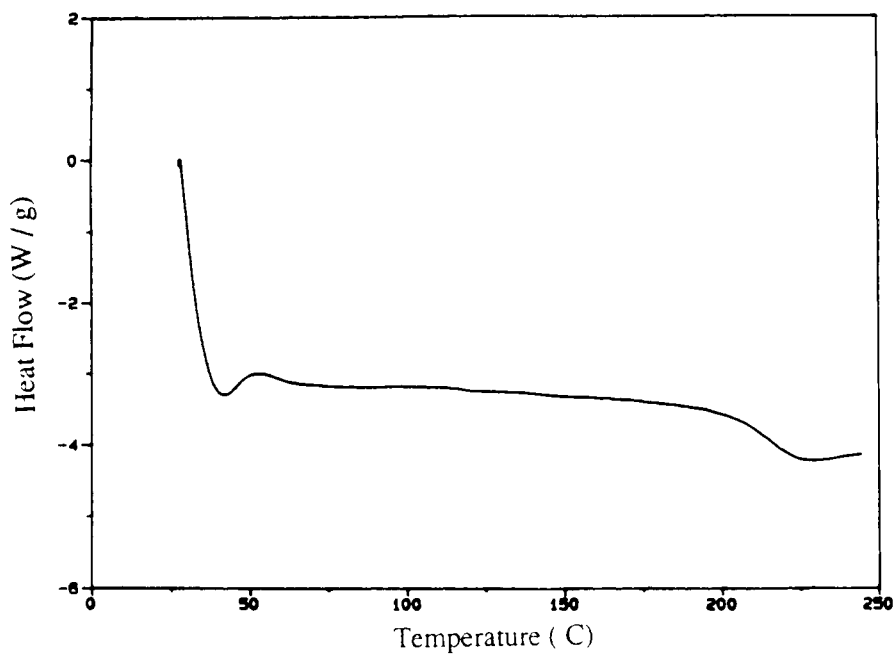


Fig. 4. (a) A DSC thermogram of electropolymerized (1 : 1) copolymer. (b) DSC thermograms of (A) bulk polymerized polystyrene, (B) bulk polymerized poly(3-CMI)-blend-polystyrene, (C) bulk polymerized poly(3-CMI).

TABLE I
Glass Transition Temperature (T_g) of Styrene 3-CMI (SMAB) Copolymers

Sample	Feed (mol % styrene)	T_g (°C)
SMAB-1	40	216
SMAB-2	50	210
SMAB-3	60	223
SMAB-4	67	222
SMAB-5	70	195
SMAB-6	82	206
SMAB-7	94	196

nium perchlorate (TEAP), in pure dimethylacetamide (DMAc) and in sulfuric acid solution (0.0125 M) were studied. A cathodic sweep rate of 250 mV/s was used between +1.0 and -3.0 V. All potentials were measured against SCE electrodes. Changes in current between a microelectrode of carbon black and a platinum counter electrode were measured and plotted against the voltage.

Characterization

Thermal analysis of the copolymer was accomplished on a DuPont 9900 series differential scanning calorimeter and thermogravimetric analyzer operated at 10°C/min under a nitrogen atmosphere. Functional group and copolymer compositional analysis was done by use of a Nicolet FTIR spectrophotometer.

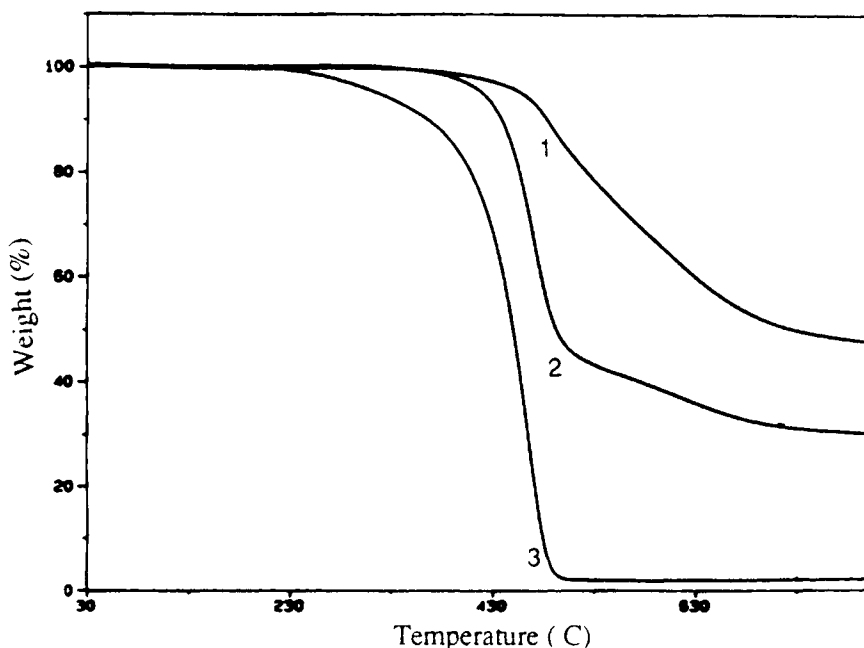


Fig. 5. TGA traces of (1) poly(3-CMI), (2) electropolymerized (1 : 1) poly(3-CMI-co-styrene), (3) polystyrene.

TABLE II
Thermal Stability of Copolymers from Thermogravimetric Analysis in Nitrogen

Feed (mol % styrene)	Initial decomp. temp. (°C)	Final decomp. temp. (°C)
20	432	511
30	435	519
50	431	519
60	432	525
70	409	526
80	426	521

KBr pellets were used. For calculation of the copolymer composition, a calibration curve for imide and styrene peak area absorption ratio against the imide-styrene mole composition was constructed using blends of bulk polymerized polystyrene and poly(3-carboxyphenyl maleimide). Copolymer reactivity ratios were obtained by use of the Fineman-Ross method.³²

RESULTS AND DISCUSSION

Aspects of Electrocopolymerization

Neither of the individual comonomers would homopolymerize without current flow under the experimental conditions adopted. Also copolymerization did not

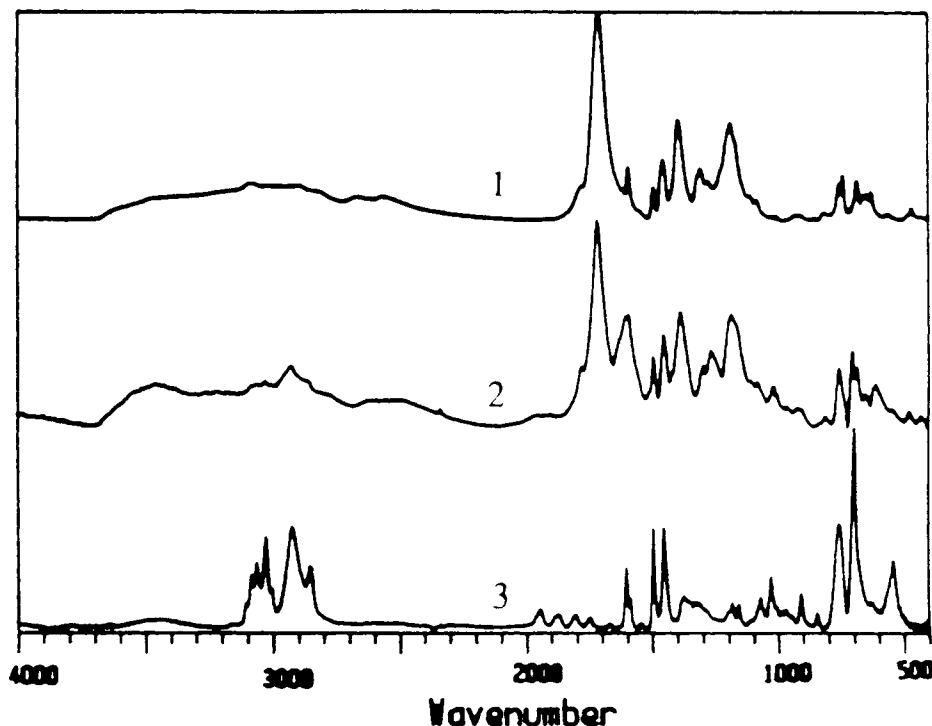


Fig. 6. FTIR spectra of (1) bulk polymerized poly(3-CMI), (2) electropolymerized poly(3-CMI-co-Styrene), (3) solution cast polystyrene.

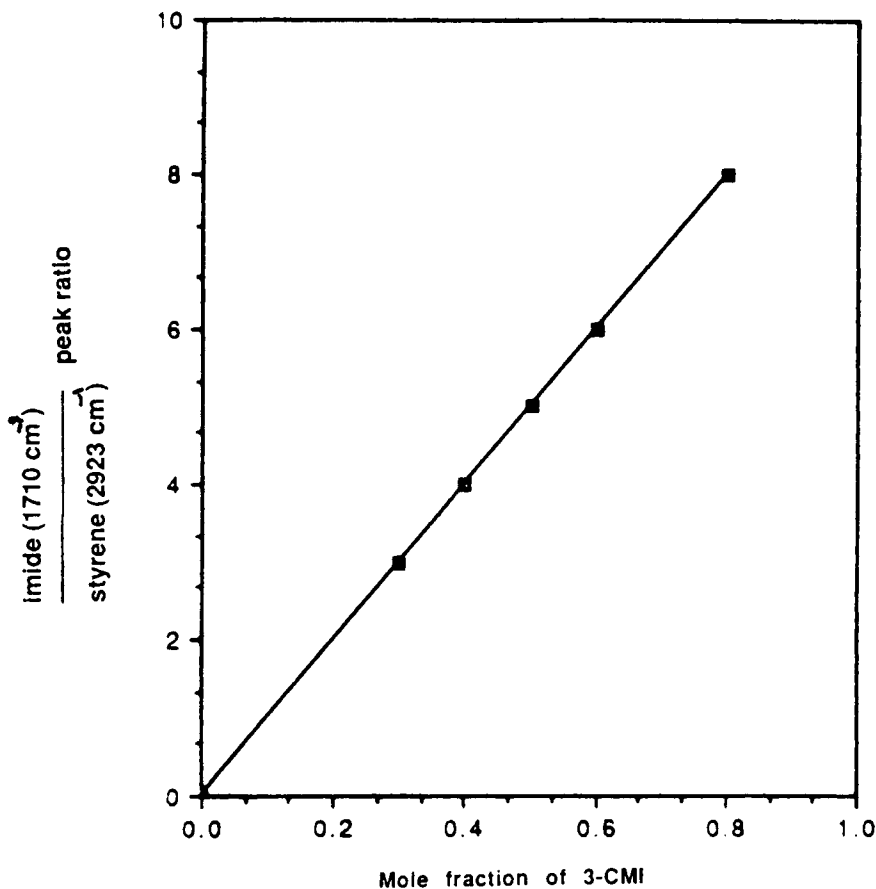


Fig. 7. Calibration curve for compositional analysis.

take place without current. However, when a current density of about 10 mA per gram of fiber was passed through a solution of styrene (0.5 *M*), 3-CMI (0.5 *M*), DMAc, and sulfuric acid (0.0125 *M*), present in the volume ratio 50 : 50 : 20 : 100, respectively, copolymer coatings on the graphite fiber cathode surface occurred almost immediately. A preliminary molecular weight estimate (Fig. 3) indicates a wide polydispersity index $\bar{M}_w/\bar{M}_n = 3$, and a moderately high number average molecular weight, $\bar{M}_n = 64,000$, consistent with radical copolymerization. The molecular weight is an estimate only since it was assumed that the same calibration was applicable for the copolymer as for a series of known polystyrene calibration standards.

Thermal Analysis

Figure 4 (a) shows a typical DSC thermogram of the copolymer synthesized from a 0.5 *M* (1 : 1) comonomer feed solution. Variation of the glass transition temperature of copolymers made using different styrene comonomer feed compositions is shown in Table I. The electrocopolymerized samples show only one

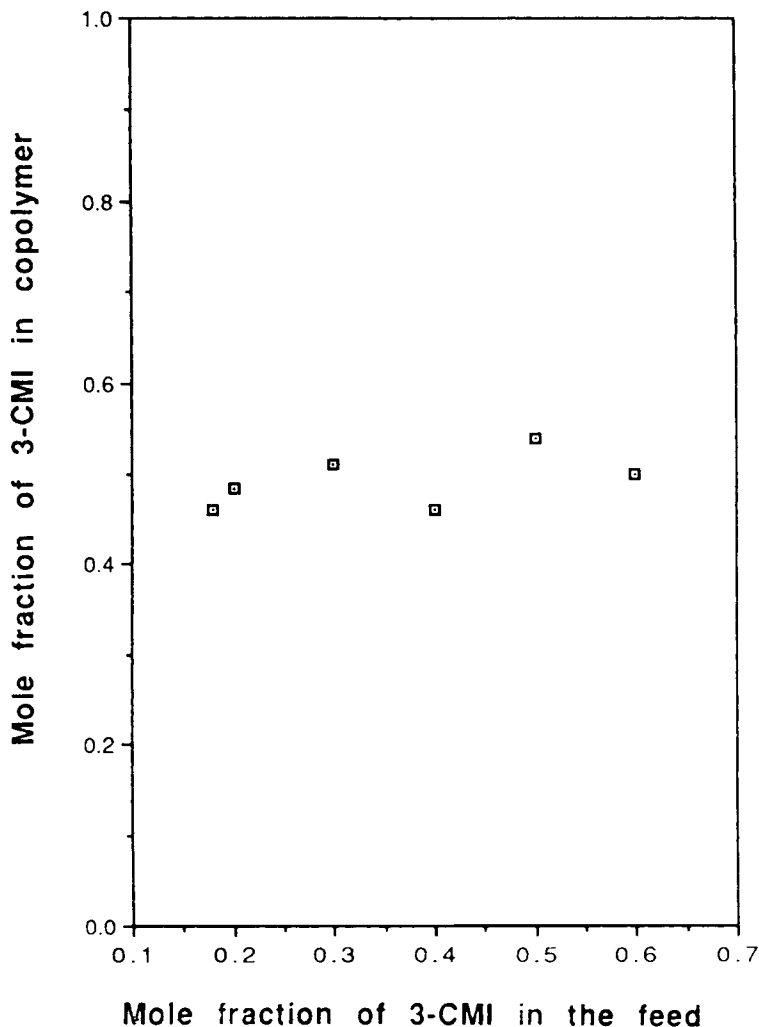
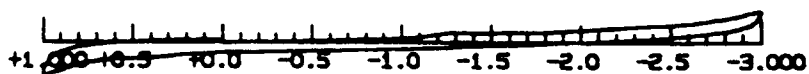


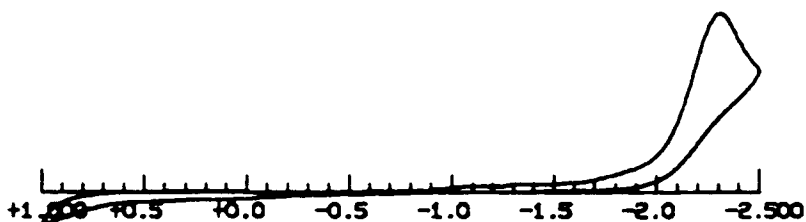
Fig. 8. Copolymer composition at different comonomer feed composition.

glass transition temperature, which remained relatively unchanged for samples synthesized from different comonomer feed composition. The DSC thermograms for free radical bulk polymerized polystyrene, poly(3-CMI), and a 1 : 1 poly(styrene-blend-3-CMI) are shown on Figure 4(b).

Thermogravimetric analysis thermograms of solution cast polystyrene, bulk polymerized 3-CMI, and the electropolymerized (1 : 1) copolymer are shown on Figure 5. These thermograms show the electrocopolymers as having thermal stability intermediate between bulk homopolymerized poly-3-CMI and polystyrene. As expected, the data further shows that the thermal stability of the copolymers does not vary appreciably with changing monomer feed composition (Table II). The electrocopolymerized samples demonstrate excellent thermal stability over a wide range of temperature. They are therefore suitable for moderate- to high-temperature applications.


 A vertical scale bar with a central horizontal line and two short vertical lines extending upwards and downwards from the center. The text "50 μA" is written vertically along the central line.


E (VOLT)


 A vertical scale bar with a central horizontal line and two short vertical lines extending upwards and downwards from the center. The text "50 μA" is written vertically along the central line.


E (VOLT)

Fig. 9. (a) Cyclic voltammogram of tetraethylammonium perchlorate 0.29 *M* in DMAc. (b) Cyclic voltammogram of sulfuric acid 0.0125 *M* in DMAc. (c) Cyclic voltammogram of 3-CMI 0.25 *M* in DMAc and sulfuric acid 0.0125 *M*. (d) Cyclic voltammogram of (1 : 1) 3-CMI 0.5 *M*, styrene 0.5 *M*, in DMAc and sulfuric acid 0.0125 *M*.

FTIR Spectroscopy

FTIR spectra for polystyrene, poly(3-CMI), and electropolymerized poly(3-CMI-co-styrene) are shown on Figure 6. Characteristic imide absorption peaks occur at 1771 cm^{-1} , 1710 cm^{-1} while typical polystyrene absorption peaks are shown at 2923 cm^{-1} , 756 cm^{-1} , and 695 cm^{-1} . The FTIR spectra obtained for bulk polymerized poly(3-CMI)-blend-polystyrene samples were used to derive calibration curves of peak absorption as a function of composition (Fig. 7). The poly(3-CMI) imide carbonyl peak absorption and a polystyrene absorption peak, occurring at 1710 cm^{-1} and 2923 cm^{-1} , respectively, were used for this purpose. Copolymer compositions and the respective comonomer feed mole ratios are shown in Figure 8. The constancy of the copolymer composition for

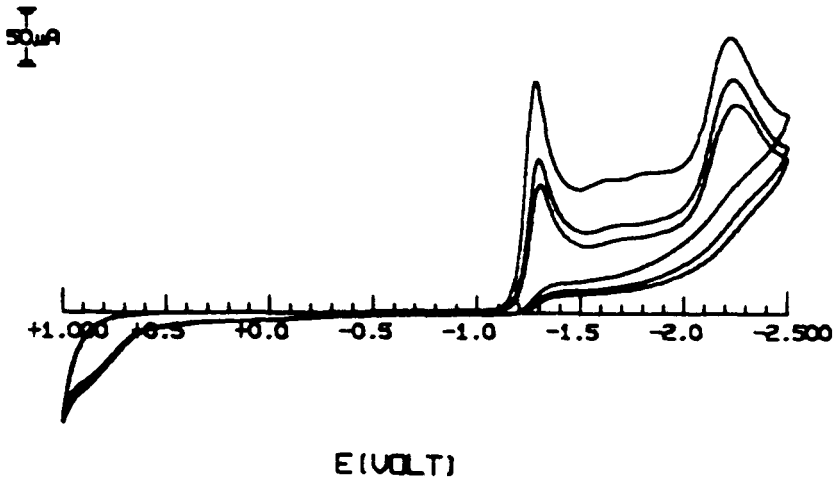
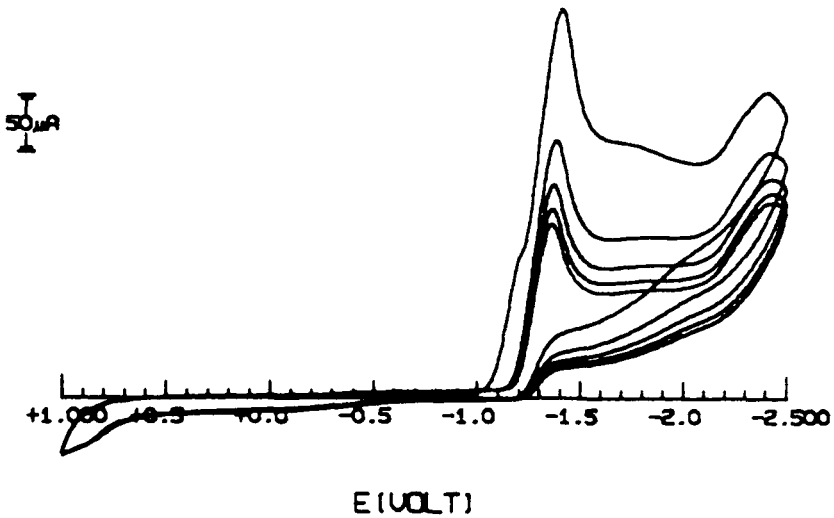


Fig. 9. (Continued from the previous page.)

samples electrocopolymerized from different comonomer feed composition confirms a very strong tendency toward alternation for the system, in agreement with previous findings on bulk copolymerized *N*-phenyl maleimide and its derivatives with electron donor monomers.²¹⁻²⁷ Reactivity ratios of 0.043 and -0.014 were calculated³² for 3-CMI and styrene, respectively.

Cyclic Voltammetry

Cyclic voltammograms of the comonomers and supporting electrolyte in DMAc are shown in Figure 9(a-d). The reduction of hydrogen ions occurs at -2.3 V [Fig. 9(b)]. Monomeric styrene shows no intense reduction peak over the potential range covered. However, 3-CMI has a distinctive reduction peak

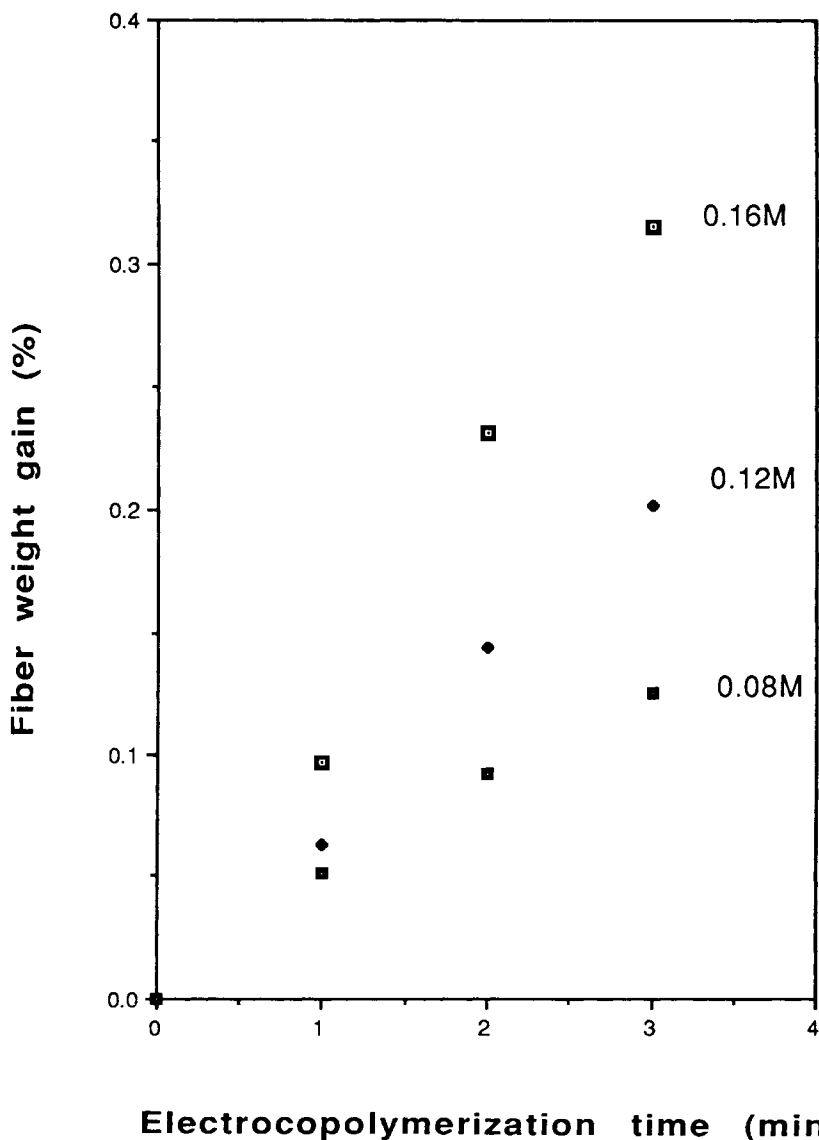


Fig. 10. Weight gain of copolymer per gram of fiber at different comonomer concentrations.

at -1.30 V [Fig. 9(c)]. In a typical reaction solution containing 3-CMI (50 parts), styrene (50 parts), sulfuric acid (100 parts), DMAc (20 parts), the 3-CMI-H reduction peak height ratio decreases sharply [Fig. 9(d)]. The solvent DMAc is quite stable and does not decompose over the range of voltage covered. It does not therefore interfere with the electrocopolymerization.

Effect of Reaction Conditions

The amount of the copolymer coating was studied as a function of current density, time, comonomer concentration, and comonomer feed composition. A

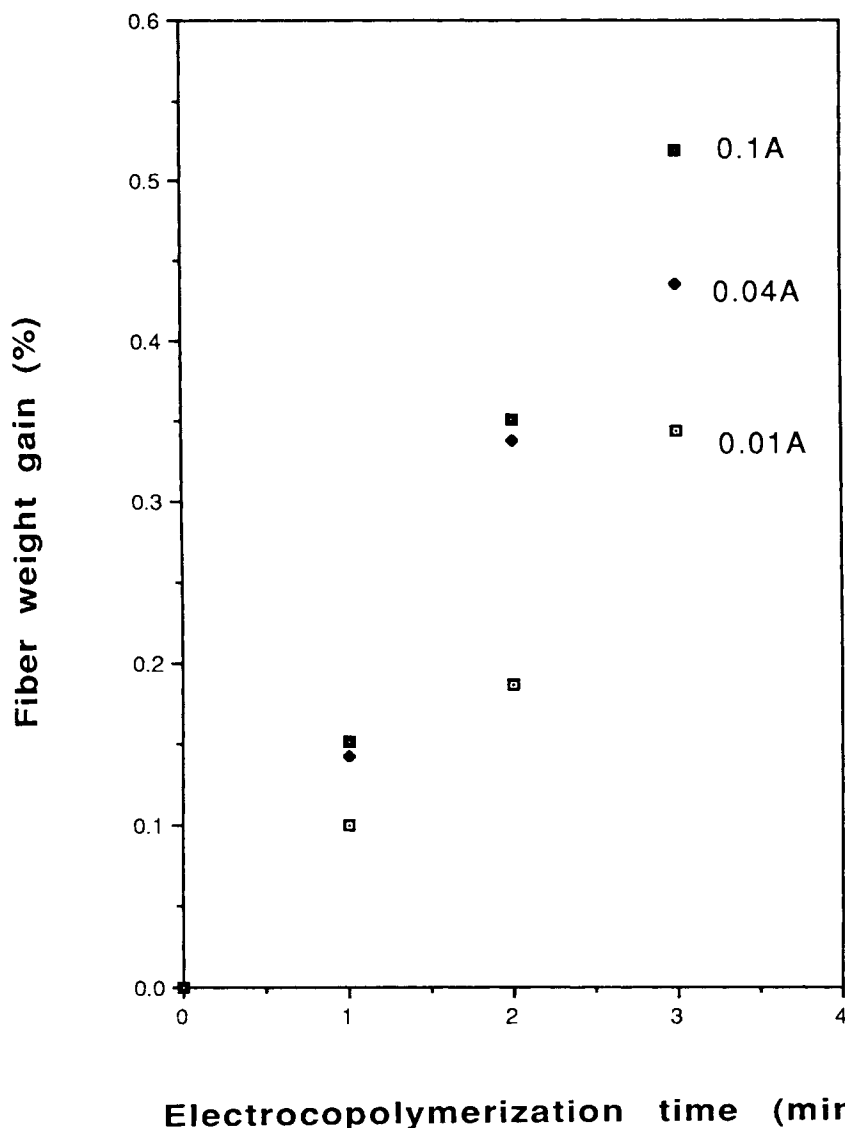


Fig. 11. Weight gain of copolymer per gram of fiber at different current densities and fixed initial concentrations of each comonomer ($0.15 M$) in the cell.

strong dependence of the amount of copolymer formed on the initial comonomer concentration as a function of time is shown in Figure 10. In the same manner, the quantity of copolymer coatings formed on the fiber as a function of time at fixed initial concentration of each comonomer in the cell ($0.15 M$) increases with increasing current density (Fig. 11).

Variations of comonomer feed composition have no significant effect upon the rate of copolymer formation, especially for the comonomer feed ratios covered in this study (Fig. 12). More detailed studies of aqueous electrocopolymerization kinetics and mechanisms are in progress.

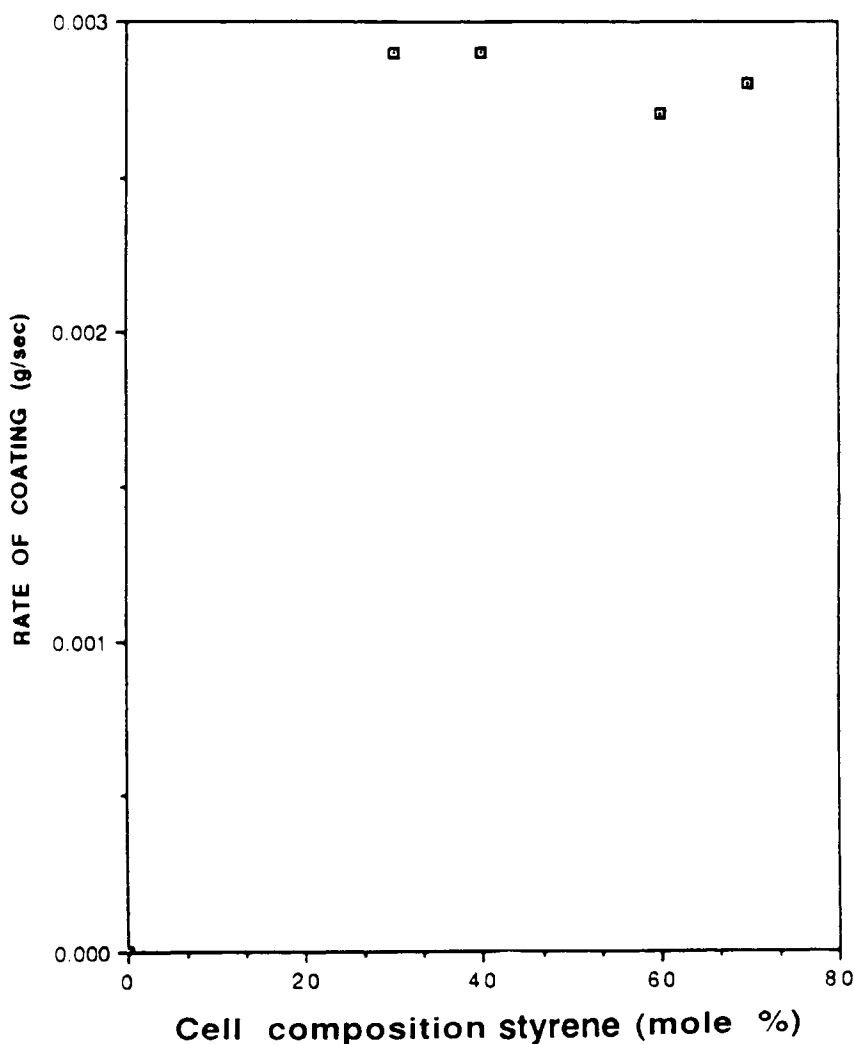


Fig. 12. Weight gain of copolymer per gram of fiber at different comonomer feed composition.

The authors acknowledge the support of a High Technology grant by The Connecticut Department of Higher Education for this research.

References

- 1a. J. R. MacCallum and D. H. MacKerron, *Brit. Polym. J.*, **14**, 14-18 (1982).
- 1b. J. R. MacCallum and D. H. MacKerron, *Eur. Polym. J.*, **18**, 717-724 (1982).
2. L. G. Kolzunova, N. Ya. Kovarskii, and L. M. Novichkova, *J. Polym. Sci. USSR*, **27**, 2662-2668 (1985).
3. L. G. Kolzunova, N. Ya. Kovarskii, and L. M. Novichkova, *J. Polym. Sci. USSR*, **28**, 245-250 (1986).
4. U. Akbulut, J. E. Fernandez, and R. L. Birke, *J. Polym. Sci. Polym. Chem. Ed.*, **13**, 133-149 (1975).
5. B. L. Funt and K. C. Yu, *J. Polym. Sci.*, **62**, 359 (1962).

6. B. L. Funt and S. N. Bhdani, *Can. J. Chem.*, **42**, 2733 (1964).
7. B. L. Funt and O. G. Gray, *J. Macromol. Chem.*, **1**, 625 (1966).
8. B. L. Funt, I. McGregor, and J. Tanner, *J. Polym. Sci. Polym. Lett.*, **8**, 695-699 (1970).
9. B. L. Funt and J. Rybicky, *J. Polym. Sci.*, **A1**, 1441 (1971).
10. L. Toppare, L. Turker, and U. Akbulut, *Makromol. Chem.*, **184**, 1661 (1983).
11. L. Toppare, S. Eren, O. Ozel, and U. Akbulut, *J. Macromol. Sci. Chem.*, **A21**(10), 1281 (1984).
12. L. Toppare, S. Eren, and U. Akbulut, *J. Polym. Sci. Polym. Chem. Ed.*, **23**, 303 (1985).
13. L. Toppare, S. Eren, and U. Akbulut, *Brit. Polym. J.*, **17**, 257 (1985).
14. J. Chang, J. P. Bell, and R. Joseph, *SAMPE Q*, **18**, 39 (1987).
15. R. V. Subramanian, *Pure Appl. Chem.*, **52**, 1929-1937 (1980).
16. J. P. Bell, J. Chang, H. W. Rhee, and R. Joseph, *Polym. Composites*, **8**, 46 (1987).
17. J. P. Bell and H. W. Rhee, *SPE/ANTECH '88, Trans.*, 1590 (1988).
18. R. V. Subramanian and J. J. Jakubowski, *Polym. Eng. Sci.*, **18**, 590 (1978).
19. R. V. Subramanian and J. J. Jakubowski, *Org. Coat. Plast. Chem.*, **40**, 688 (1979).
20. J. Chang, Ph.D. Thesis, University of Connecticut, 1986.
21. A. A. Mohammed, F. H. Jebrael, and M. Z. Elsabee, *Macromolecules*, **19**, 32-37 (1986).
22. J. M. Barrales-Rienda and J. Gonzalez-Ramos, *J. Macromol. Sci. Chem.*, **A11**(2), 267-286 (1977).
23. B. D. Dean, *J. Appl. Polym. Sci.*, **34**, 887-890 (1987).
24. O. Sosanwo, J. Lokaj, and F. Hrabak, *Eur. Polym. J.*, **18**, 341-345 (1982).
25. M. Z. Elsabee, M. W. Sabaa, and S. Mokhtar, *Polym. J.*, **15**(6), 429-434 (1983).
26. M. Yoshimura, H. Mikawa, and Y. Shirota, *Macromolecules*, **11**, 1089-1091 (1978).
27. M. Z. Elsabee and S. Mokhtar, *Eur. Polym. J.*, **19**(5), 451-456 (1983).
28. L. E. Colman and J. A. Conrady, *J. Polym. Sci.*, **38**, 241-245 (1959).
29. H. Lund, *J. Electrochem.*, **202**, 299-302 (1986).
30. R. G. Barrantas, S. Fletcher, and J. D. Porter, *J. Electroanal. Chem.*, **75**, 533-543 (1977).
31. H. M. Fahmy, B. Nashed, F. A. Khalifa, and M. A. Abdel, *J. Electroanal. Chem.*, **184**, 147-160 (1985).
32. M. Fineman and S. D. Ross, *J. Polym. Sci.*, **5**, 259 (1950).

Received March 31, 1989

Accepted October 2, 1989