

Preparation and Characterization of Electropolymerized Poly(*N*-Substituted Maleimide-co-Styrene) Coatings on Copper Substrates

JENG-LI LIANG,¹ JAMES P. BELL,^{1,*} J. O. IROH,¹ and ASHIT MEHTA²

¹Polymer Science Program, Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269 and

²Endicott Research Laboratories, IBM, Endicott, New York 13760

SYNOPSIS

Poly(*N*-substituted maleimide-co-styrene) copolymer films were electropolymerized onto copper substrates as possible candidates for electronic applications. The *N*-substituted moieties that were investigated include phenyl, 3-carboxyphenyl, and 4-carboxyphenyl. Uniform coatings of 25 μm or more thickness were successfully applied using each of the three *N*-substituted maleimides. The thickness was controlled by manipulating the monomer concentration, current density, and reaction time. Not only did the 3- and 4-carboxyphenylmaleimide (CMI)/styrene copolymers have high glass transition temperatures (220°C) and fairly good thermal stability ($\sim 430^\circ\text{C}$), but they also have rather low dielectric constants (2.55 for 4-CMI/styrene), comparable to those of polyimides. Polymerization of the coatings was observed by *in-situ* Fourier transform infrared spectroscopy (FTIRS), using a special cell that made the observation of the polymer structure development possible. It was found by FTIRS that all three monomers, when used with styrene, produced alternating copolymers. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyimides are very important materials in the electronics industry, particularly in the manufacture of flexible printed circuit boards and semiconductor chip devices. A reason for this is that polyimides exhibit superior resistance to chemical and thermal attack and thus withstand the degradative effects of wet-etching and hot-soldering processes.¹ Conventional methods of applying polymer films, such as spraying, spin-coating, and laminating can be used for polyimides, but these methods are most suitable for applying the films to essentially planar substrates. Electropolymerization is a low current, room temperature, low solvent process that can uniformly coat both planar and complex shapes inexpensively.

The polymers produced by electropolymerization increase the cell resistivity, and thus additional

polymer tends to be formed in any "thin" areas; the result is a rather uniform coating.² Another important advantage of electropolymerization is its ability to obtain even film thickness over irregular surfaces. The starting monomer solutions are of very low viscosity and can easily wet the metal substrates; and polymerization occurs in the proximity of the metal surface. The resulting adhesion to the metal may be improved due to excellent wetting. It was these considerations that provided the initiative for the work reported in this paper. Adaptation of this method to polyimides could increase their effectiveness significantly.

Teng and Mahalingam,³ and Garg, Raff, and Subramanian,⁴ have investigated the use of electropolymerization to coat metal electrode surfaces with acrylate polymers. These polymers have relatively low glass-transition temperature and their thermal stability appears too low for many electronic applications, however.

Iroh, Bell, and Scola⁵ have electropolymerized poly(3-carboxyphenyl maleimide-co-styrene) onto AS-4 graphite fibers from aqueous monomer-dilute

* To whom correspondence should be addressed.

sulfuric acid solutions. The resulting thermoplastic matrices appear ideal for composite technology because of their high thermal stability, decomposition temperature, $\sim 430^\circ\text{C}$, and glass-transition temperature, $\sim 220^\circ\text{C}$. The copolymer matrices are also easily and reversibly processable. We describe here the preparation and characterization of poly(*N*-substituted maleimide-*co*-styrene) coatings onto copper sheets that have had different surface treatments.

EXPERIMENTAL

Materials

3-Carboxyphenylmaleimide (3-CMI) and 4-carboxyphenylmaleimide (4-CMI) were prepared according to the method of Sauers⁶ using reagent-grade ingredients. *n*-Phenylmaleimide (NPMI) (from Mitsui Toatsu Chemical Inc., Japan) was used as received. Monomer purity was confirmed by IR spectroscopy and differential scanning calorimetry. Styrene (99.9%, Aldrich Chemical Company) was extracted twice with 10% sodium hydroxide solution and washed several times with distilled water to remove inhibitors. The structures of these monomers are shown in Figure 1.

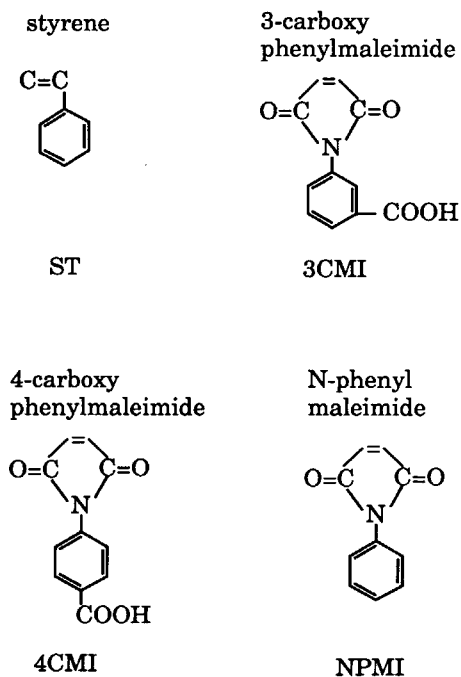


Figure 1 Chemical structures of monomers.

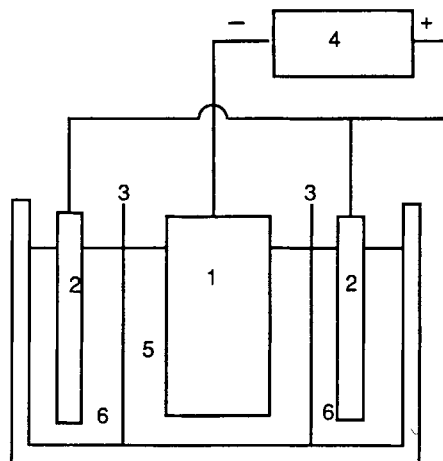


Figure 2 Schematic description of the electrochemical cell. (1) copper cathode sample; (2) anode; (3) polypropylene membrane; (4) potentiostat; (5) monomer solution; (6) diluted sulfuric acid solution.

Electropolymerization

The monomer-electrolyte solution was prepared by dissolving the desired amounts *N*-substituted maleimide and styrene in dimethylacetamide. The resulting solution and aqueous sulfuric acid (0.025 *M*) were then mixed in a 50 : 50 volume ratio. The mixture was introduced into the central chamber of the electrochemical cell. A copper sheet (5 cm \times 15 cm) of 25 μm thickness was acetone-degreased for 24 h by immersion at room temperature and was then centrally positioned in this chamber. Sulfuric acid solution (0.0125 *M*) was placed in the two outer counter electrode chambers. The anodes were tantalum substrates coated with magnesium oxide. A schematic sketch of the three-compartment polypropylene cell is shown in Figure 2. Additional information about the cell has been given previously.⁵

Electropolymerization was done at a current density of 0.3–0.6 mA/cm² sheet area. After a given time, the coated copper sheet was withdrawn from the cell, dried at room temperature overnight, and vacuum dried at 250°C to remove any residual dimethylacetamide.

Characterization

Copper substrates were characterized in terms of surface morphology and composition. Surface morphology was examined by scanning electron microscopy (SEM). Elemental analysis of the surface region was done simultaneously with SEM and energy dispersive X-ray analysis (EDAX). Information

concerning surface roughness was provided by the Endicott Laboratories of IBM, from Talysurf-S-120 profilometer measurements.

The thickness of dried polymer was determined by dividing the weight gain by the polymer density. Gel permeation chromatography (GPC) with Ultrastayragel columns (pore size of 10^4 , 10^3 , 500, and 100 angstroms) was carried out in tetrahydrofuran at 30°C, and number and weight-average molecular weights ($\overline{M}_{n\text{GPC}}$ and $\overline{M}_{w\text{GPC}}$) were calibrated with standard narrow distribution polystyrene samples.

The electroactivities of the monomer, solvent, and electrolyte were monitored by cyclic voltammetry. A BAS-100 electrochemical analyzer manufactured by Bioanalytical Systems, Inc. was used. Copper sheets were used as the working electrode. A platinum electrode and an electrode fabricated by mixing silver chloride and Kel-F800 resin (3M Co.) were used as the counter and reference electrodes, respectively. A potential sweep with reversal between -3.0 V and 0.0 V was applied at a cathodic sweep rate of 100–250 mV/s.

The dielectric constants of *N*-substituted maleimide/styrene alternating copolymers, electropolymerized on smooth copper sheets, were measured with the aid of a dielectric thermal analyzer (DETA) from Polymer Laboratories (Loughborough, UK). The test samples, with a diameter of 33 mm, were cut from a strip that was coated on only one side. A thin layer of gold was then sputtered onto the polymer side of these samples to obtain uniform contact with the electrode plate of the DETA.

FTIR *in situ* multiple internal reflection Fourier transform infrared spectra (FTIRS) were recorded on a Nicolet 60SX Fourier transform spectrometer. A spectroelectrochemical cell (Fig. 3) was designed according to the description of Pham, Adami, and Dubois.⁷ A germanium crystal with or without a thin

layer of copper deposited by sputtering was used as both reflection element and working electrode. The reference electrode was made from AgCl/Kel-F800 and the counterelectrode was a platinum plate. *In situ* FTIRS spectra at an indicated potential (Si) of adsorbed species on the electrode surface are reported here as absorbance difference spectra; for each spectrum of a series, the absorbance spectrum of the electrode/electrolyte solution before polarization was subtracted from that of the reacting system at an indicated voltage. The correction factors are the same for all spectra of a series. The polymerization was performed by cathodic polarization between 0.0 and -3.0 V in a 0.02M tetrabutylammonium perchlorate and DMAC/water solution containing 0.4M of monomers (maleimide/styrene monomer molar feed ratio of 40/60 and 60/40).

The glass-transition temperatures of the polymer were obtained using a DuPont 9900 DSC, under nitrogen environment at a heating rate of 10°C/min. Thermal stability was characterized by a Perkin-Elmer thermogravimetric analyzer (TGA) at a heating rate of 30°C/min under nitrogen environment.

RESULTS AND DISCUSSION

Copper Morphology

Six different copper-based substrates were examined and are illustrated in SEM micrographs (Figs. 4 and 5). It was found that the copper A [Fig. 4(A1)] is actually a fabricated sandwich structure, which consists of two copper foils bonded by an adhesive prepreg. A cross section of the foils with the lighter prepreg in the center is shown [Fig. 4(A2)]. Copper B was made of zinc-coated copper [Fig. 4(B)]. The existence of zinc was proven by the EDAX data. The surface texture of this copper is rough, indicating that it had probably been through an etching process. On the contrary, the surface texture of copper sample C coated with Cr/Cu/Ni/Fe alloy is smooth [Fig. 4(C)]. The presence of Cr/Cu/Ni/Fe elements was also proven by the EDAX data. It was found that copper D is rather smooth and is purely copper substrate [Fig. 5(D)]. Conversely, copper E has a pink color, is rough, and has a rather uniform peak-to-valley ratio of 5 microns [Fig. 5(E)]. Another interesting copper F, with a brown color, also has a rough surface and higher peak-to-valley ratio of 10 microns [Fig. 5(F)]. There are both copper and magnesium signals in the EDAX data for copper F.

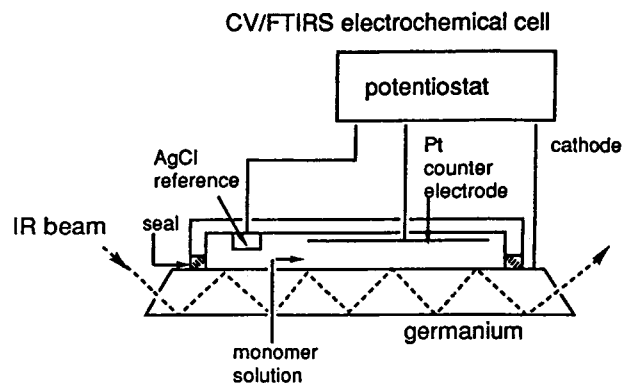


Figure 3 Schematic description of the CV/FTIRS electrochemical cell.⁷

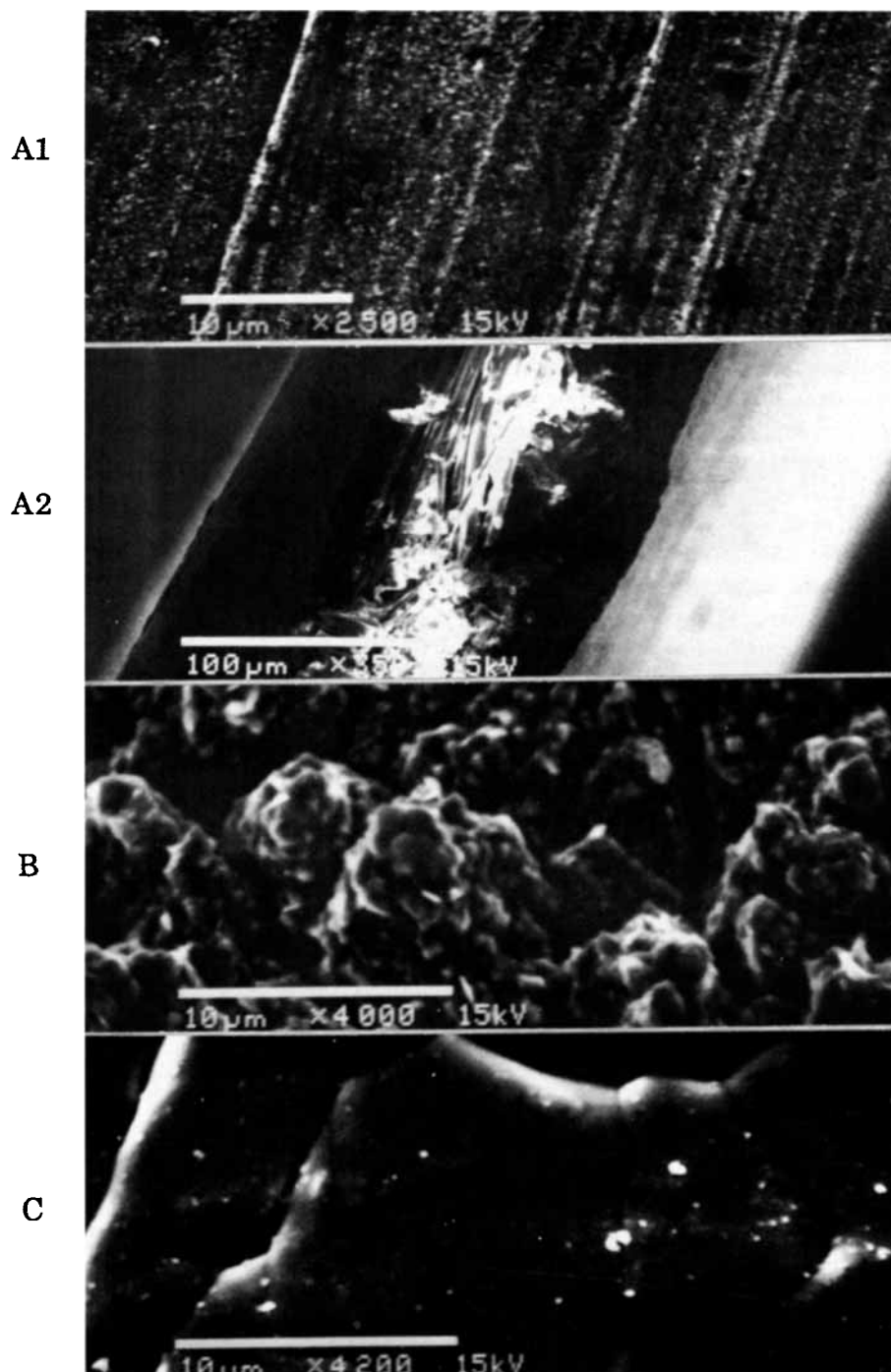


Figure 4 SEM micrograph of copper surface A1, copper sandwich structure A2, copper surface B, and copper surface C.

Cyclic Voltammetry

Each of the copper substrates was used as a working electrode and each electropolymerization was run at current density of 0.5 mA/cm^2 of nominal coatable area for 2 h. The sample weight gain due to 4CMI/

styrene polymer after drying was essentially negligible for copper A, B, and C, but was 45% for copper D, 40% for copper E, and 30% for copper F. After removing the interior adhesive layer, copper A exhibited 30% polymer weight gain. This unusual result for copper surfaces A, B, and C is likely attrib-

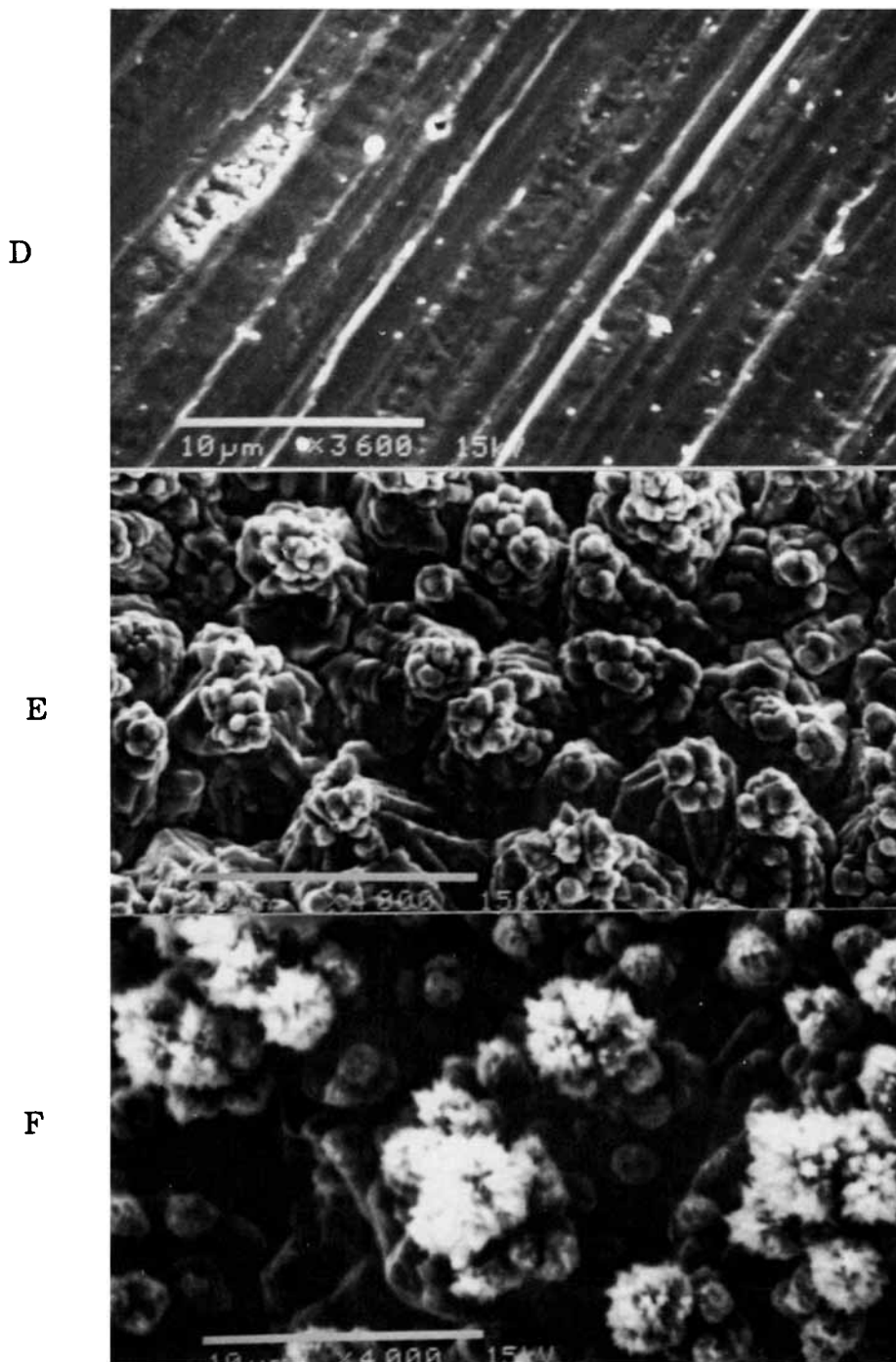
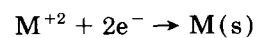
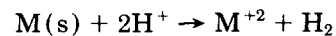


Figure 5 SEM micrograph of copper surfaces D, E, and F.

utable to the interference to electroinitiation either by the adhesive inside the copper sandwich (surface A) or to the presence of other metals on the surfaces. Based on the standard reduction potentials for half-reaction of Cu, H^+ , Zn, Ni, and Fe, there are two possible reactions that could interfere with the electroinitiation:



where $M(s) = Zn, Cr, Ni, Fe$.

Table I indicates the reduction potential of reactive species and metals. In order for the electroin-

Table I Reduction Potential of Reactive Species

Reactive Species	Reduction Potential (V) ^a	Comment
H ₂ O	> 3.0	Solvent
DMAc	> 3.0	Solvent
H ₂ SO ₄	-1.65	Electrolyte
Styrene	> 3.0	—
<i>N</i> -phenylmaleimide	-1.30, -1.70	—
3-Carboxyphenylmaleimide	-1.75	Shifts to -1.30 V w/styrene
4-Carboxyphenylmaleimide	-1.60	Shifts to -1.30 V w/styrene
Copper	+0.34	—
Nickel	-0.25	—
Iron	-0.44	—
Chromium	-0.74	—
Zinc	-0.76	—
Magnesium	-2.36	—

^a Referred to an AgCl reference electrode.

initiation and electropolymerization to occur, the reduction potential of the substrate electrode must be larger than the reduction potential of monomeric

species. Those metals (Zn, Cr, Ni, Fe) with less than -1.0 V reduction potential will be preferentially reduced before the monomers or electrolyte and will

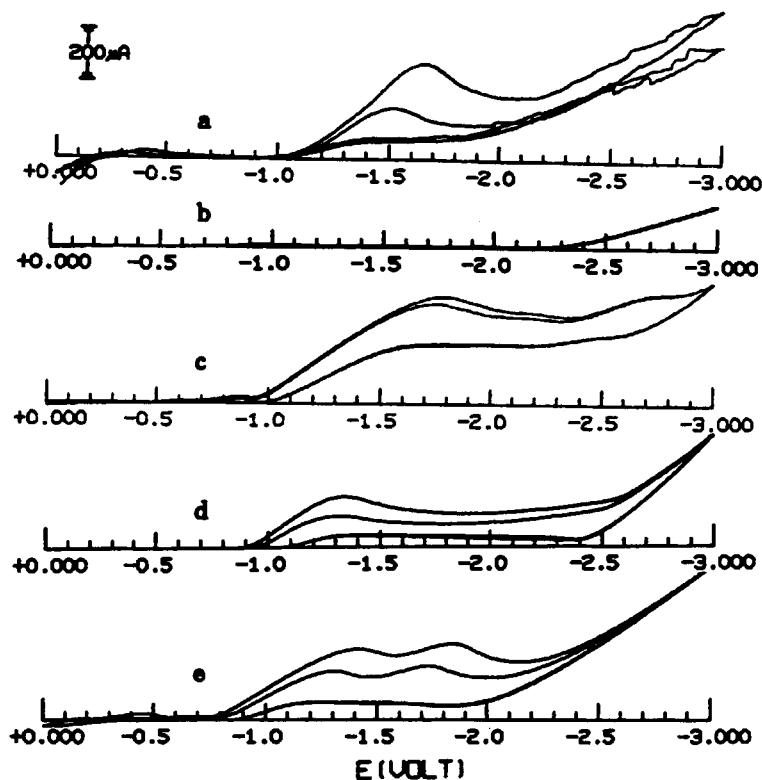
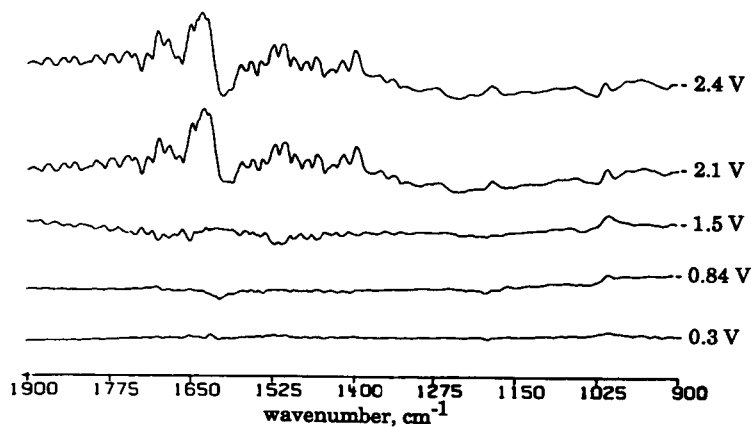
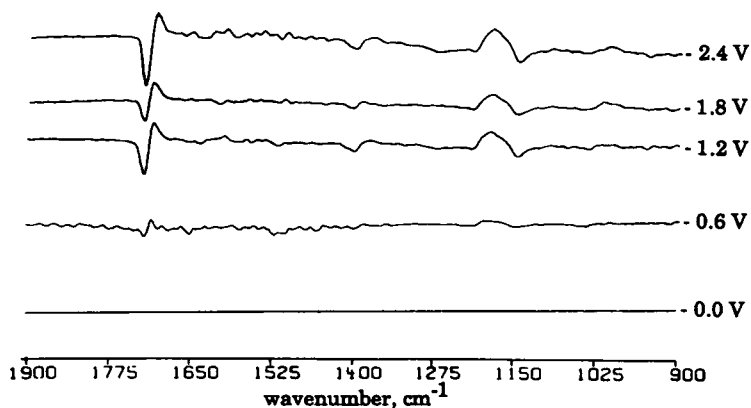


Figure 6 Cyclic voltammogram of reactive species on copper sheet (a) 0.0125 M diluted sulfuric acid solution; (b) 0.25 M styrene/0.02 M TBAP; (c) 0.25 M 4-CMI/0.02 M TBAP; (d) 0.125 M 4-CMI/0.125 M styrene/0.02 M TBAP; (e) 0.125 M 4-CMI/0.125 M styrene/0.0125 M sulfuric acid solution.



(a)



(b)

Figure 7 CV/FTIRS spectra of reactive species on a germanium electrode at different potentials (a) 0.25 *M* styrene/0.0125 *M* sulfuric acid solution; (b) 0.25 *M* 4-CMI/0.0125 *M* sulfuric acid solution.

therefore cause difficulty in generating polymer coatings. On the other hand, pure copper and magnesium show no interference to electroinitiation.

Therefore, a thick layer of polymer coating generated on the copper D, E, and F substrates is expected.

The reduction potentials of 3-CMI and 4-CMI

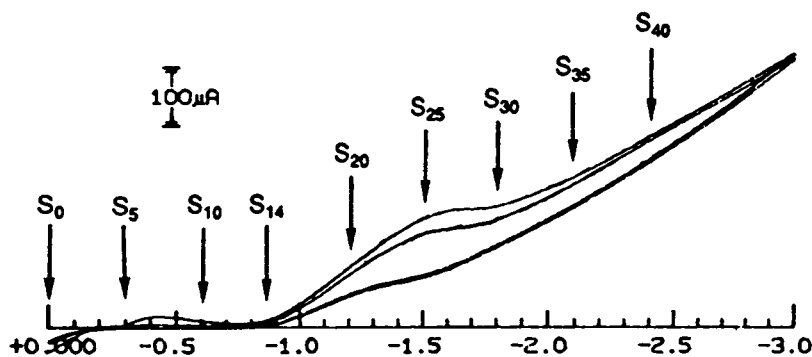


Figure 8 Cyclic voltammetry of 4-CMI/styrene/TBAP on a germanium electrode.

are both changed from -1.7 V to -1.3 V when they are mixed with styrene [Fig. 6(C,D)]. The decrease in reduction potentials is probably due to the formation of a reactive complex species. It was shown by Barrales-Rienda, De La Campa, and Ramos,⁸ and Iroh⁹ that *N*-substituted maleimide and styrene form a complex upon mixing in solution because of the intrinsic properties of electron donating (styrene) and electron withdrawing (maleimide). The initiation step of polymerization may also occur for the 4CMI/styrene/sulfuric acid system through the reduction of hydrogen ions to hydrogen radicals¹⁰ with peak potential at -1.65 V [Fig. 6(A)]. These hydrogen radicals react with the double bond of the monomer to produce monomer radicals that grow into macroradicals. Nevertheless, the 4CMI/styrene system with tetraethyl ammonium perchlorate as an electrolyte still was reduced at a peak potential of -1.3 V. A thick polymer coating was generated on the copper substrate. This result shows that the initiation mechanism is dominated by the reduction of 4CMI/styrene monomer complex rather than by the reduction of hydrogen ions. In the later stages of electropolymerization at constant current, the voltage tends to rise because of the coating resistivity. It is possible that reduction of hydrogen ions could become significant at that time.

FTIRS Study of Electropolymerization

To provide deeper insight into the electropolymerization of *N*-substituted maleimide/styrene comonomers, that is, to obtain information about the initiation mechanism and the polymer composition formed in the reaction, we have applied *in situ* internal FTIRS. FTIRS spectra [Fig. 7(a)] recorded during the cyclic voltammetry of styrene alone are complex and show no sign of polystyrene presence. FTIRS spectra recorded during the cyclic voltammetry of 4-CMI are presented in Figure 7(b). No characteristic absorbance peaks for polymaleimide formation at 1770 cm^{-1} and 1710 cm^{-1} were detected and no polymer film was found on the electrode surface. However, in the presence of a radical initiator, *N*-substituted maleimides polymerize readily to give a high molecular weight.¹¹ The band at 1710 cm^{-1} has a negative sign, which may correspond to less adsorption of 4-CMI or to noise.

Figure 8 shows a cyclic voltammogram of a germanium electrode in a 0.02 M TBAP solution containing 0.4 M 4-CMI/styrene. The reduction peak potential of the 4-CMI/styrene is observed at -1.6 V vs. AgCl/Kel-F800 reference electrode. In Figure 8, the numbers of the spectra (S_0 to $> S_{40}$) recorded

during cyclic voltammetry of 4-CMI/styrene are indicated at the potential at the end of the sampling of 10 interferograms. These spectra are presented in Figures 9 and 10. Beginning with spectrum number 14 (S_{14}), formation of polymer on the electrode surface results in an absorption band from the ($-\text{CH}_2-$) groups of polystyrene. These bands are observed at 2876 cm^{-1} for C—H symmetric stretching. The intensity of these bands increases from S_{14} to S_{35} and remains constant afterwards (Fig. 9). From spectrum S_{14} corresponding to a potential of ca. -0.84 V, different bands begin to appear at frequencies 1770 , 1706 , 1395 , and 1188 cm^{-1} . The characteristic imide C = O vibrations are seen at 1770 cm^{-1} and 1706 cm^{-1} (Fig. 10). The FTIRS spectrum of the electropolymerized film is identical to the transmission spectrum of the poly(4-CMI-co-styrene). The intensity evolution of different bands observed during the electropolymerization of 4-CMI/styrene is presented in Table II. The characteristics for C—H stretching of polystyrene and for carbonyl C = O stretching of polymaleimide are seen at 2876 cm^{-1} and 1706 cm^{-1} , respectively. Each

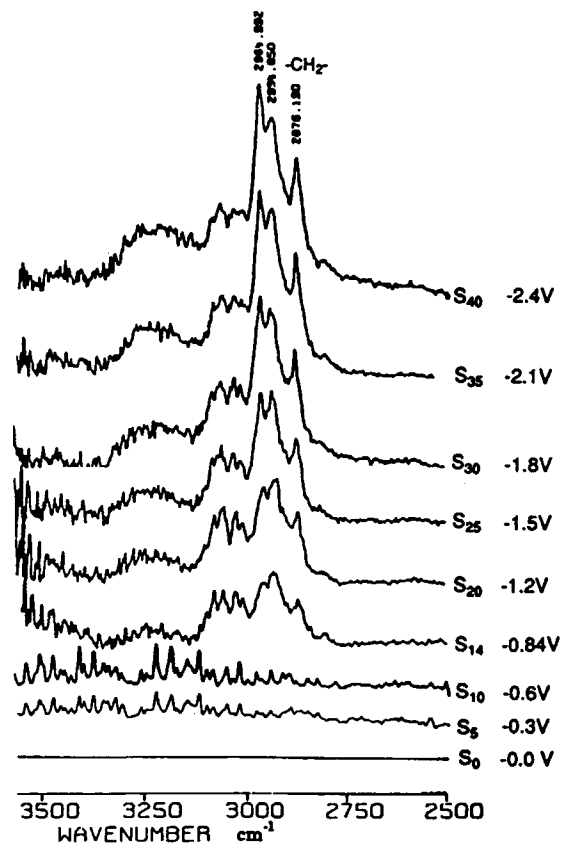


Figure 9 CV/FTIRS spectra of 4-CMI/styrene/TBAP at different reduction potentials.

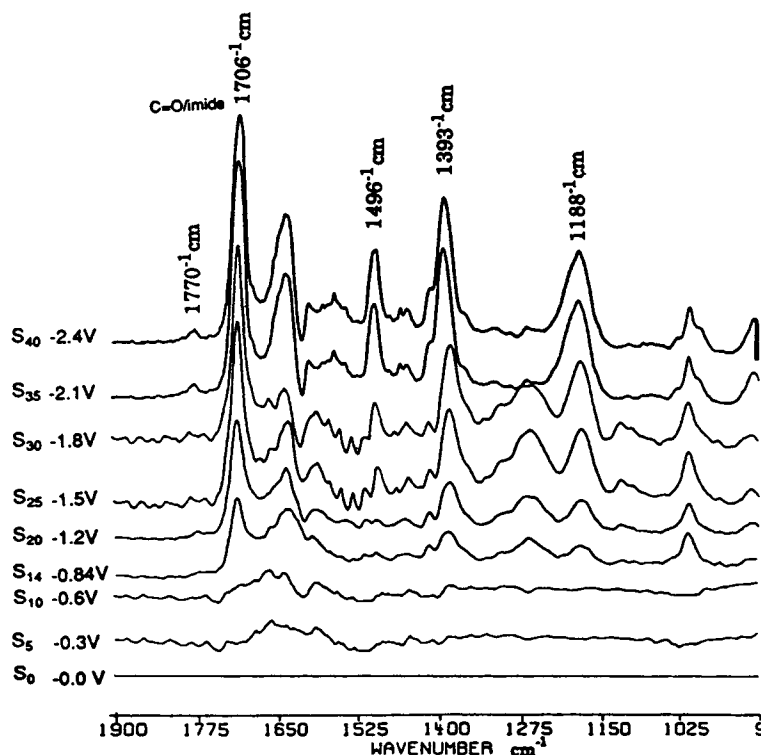


Figure 10 CV/FTIRS spectra of 4-CMI/styrene/TBAP at different reduction potentials.

spectrum was collected for 2 s of every period of 10 s. The intensity of the 1706 cm^{-1} and 2876 cm^{-1} absorptions increases from spectrum no. 14 (-0.84 V) to no. 35 for both of the two different monomer feed ratios and then remains constant during reverse scans.

The copolymer composition in terms of imide/styrene intensity ratio is tabulated as a function of

spectrum number (related to reaction time or film thickness) in Table II. This result indicates that the copolymer composition remains constant during the electropolymerization for various applied polarization potentials. The same 1 : 1 composition was also observed for constant potential polarization at -1.5 V for a given time, represented in Table III. From these spectroscopic results, the electroinitiation

Table II Intensity^a Variation of CV/FTIRS Spectra During Cyclic Voltammetry

Spectrum No.	4-CMI/Styrene Ratio				Band Intensity Ratio	
	40/60		60/40		40/60	60/40
	1706	2876	1706	2876	1706/2876	1706/2876
14	5.60	1.10	5.52	1.10	5.09	4.98
15	6.71	1.30	6.60	1.32	5.15	5.01
17	7.11	1.39	7.22	1.42	5.07	5.10
20	8.59	1.69	8.51	1.74	5.06	5.09
25	9.10	1.91	9.05	1.88	4.79	4.90
30	8.90	1.71	8.85	1.84	4.90	4.82
35	9.01	1.89	8.92	1.82	4.75	4.92
40	8.81	1.80	8.85	1.85	4.89	4.79
50	8.72	1.71	8.81	1.78	5.11	4.95

^a Peak intensity of 9.0 equals an absorbance of 0.5.

Table III Intensity^a Variation of CV/FTIRS Spectra During Constant Potential Electrolysis

Time (s)	4-CMI/Styrene Ratio				Band Intensity Ratio 1706/2876	
	40/60		60/40		40/60	60/40
	1706	2876	1706	2876		
35	4.11	0.80	3.91	0.79	5.11	4.90
60	4.90	1.00	4.79	0.97	4.89	4.95
84	5.60	1.10	5.81	1.21	5.10	4.81
108	7.32	1.52	7.02	1.40	4.81	5.01
132	8.22	1.64	8.09	1.59	5.01	5.09
156	8.71	1.76	8.54	1.75	4.95	4.85
180	9.05	1.76	9.05	1.81	5.10	5.01
204	8.96	1.85	8.98	1.83	4.85	4.91
228	8.75	1.78	9.02	1.75	4.92	5.15

^a Peak intensity of 9.0 equals an absorbance of 0.45.

probably proceeds through a 1 : 1 intermediate and the polymer composition is independent of comonomers feed ratio, reaction time, and film growth. A similar mechanism has been proposed for the standard-initiator, free-radical polymerization of *N*-substituted maleimide/styrene copolymer.⁸

Properties of Polymer Coatings

The *N*-phenylmaleimide (*N*-PMI) and the 3- or 4-carboxyphenylmaleimide were successfully copolymerized with styrene onto copper surfaces D, E, and F. The coating thickness on copper D vs. reaction time at a current density of 0.5 mA/cm² is tabulated in Table IV. The thickness was estimated from the weight gain of the copper, the polymer density, and

the nominal surface area of the copper. Polymerization of 3- or 4-CMI/styrene results in a thicker coating than for *N*-phenylmaleimide/styrene. The \overline{M}_n of 4-CMI/styrene is approximately 138,000 Da, which is almost three times higher than 47,600 Da of the *N*-PMI/styrene copolymer. The number average molecular weight and dispersity data obtained from GPC experiments on these copolymers are compared in Table IV. The number average molecular weight values were consistently high and polydispersity index values of about 3.0 were observed.

From Table IV, the amount of 4-CMI/styrene copolymer formed during electropolymerization is strongly dependent on the initial monomer concentration. At a constant current density -0.5 mA/cm², more copolymer coating was formed as the initial

Table IV Experimental Conditions for the Electropolymerization of Monomers

Polymer	Monomer Concentration (M/L)	Current Density (mA/cm ²)	Thickness (μm) at Time (h)					R_p^a ($\mu\text{m}/\text{h}$)	$\overline{M}_n^b \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
			0.5	1.0	1.5	2.0	4.0			
NPMI/ST	0.5	0.5	1.5	3.1	—	5.0	10.1	—	0.47	3.4
3-CMI/ST	0.5	0.5	5.2	9.5	—	20.3	33.8	—	1.51	2.9
4-CMI/ST	0.5	0.5	5.0	10.1	—	22.1	35.1	10.4	1.38	2.7
4-CMI/ST	0.6	0.5	6.0	12.8	—	28.1	47.0	12.0	1.44	3.0
4-CMI/ST	0.8	0.5	9.0	18.1	—	35.1	54.9	18.2	1.56	2.9
4-CMI/ST	0.5	0.3	3.7	8.0	12.0	15.1	—	8.31	1.35	3.0
4-CMI/ST	0.5	0.5	5.2	11.1	16.1	21.0	—	10.7	1.23	2.8
4-CMI/ST	0.5	0.6	6.5	13.3	19.0	24.5	—	12.4	1.10	2.9

^a Initial slope from a plot of thickness vs. reaction time.

^b At 2 h reaction time.

comonomer concentration increased, and a linear dependence of the rate of electropolymerization (R_p) on initial comonomer concentration is found in Table IV. The exponent on the monomer concentration when used in a standard free-radical type of rate expression is approximately 1.2. Table IV shows a tabulation of coating thickness of 4CMI/styrene copolymer as a function of time, for reactions performed at different current densities. While the amount of copolymer coatings formed increased with increasing current density, the \overline{M}_n decreased with increasing current density (Table IV). A plot of the natural log of initial rate of electropolymerization against that of the natural log of the current density (Table IV) resulted in a slope of 0.56. These kinetic data are similar to previous results from the electropolymerization of 3-CMI/styrene onto graphite fibers⁹; changing the substrate to copper has had little effect. It is possible to reach a desired thickness and \overline{M}_n under proper conditions (monomer concentration, current density, and time) as indicated in Table IV.

The use of a protic solvent such as a mixture of H₂O and DMAc in this study would have an inhibiting effect on an anionic process. Indeed, the very high \overline{M}_n values and their decrease as a function of the current density (Table IV) are typical of free-

radical processes. A similar free-radical process has been found from the electropolymerization of 3-CMI/styrene onto graphite fibers.⁹

Glass-transition temperatures of 220°C for 4-CMI/styrene copolymer and 210°C for NPMI/styrene copolymer were found. The thermostability of the two copolymers, as measured by Perkin-Elmer TGA7, is shown in Figure 11. The 4-CMI/styrene copolymer has somewhat better thermostability and slower weight loss than the *N*-PMI/styrene copolymer, perhaps because of the existence of the carboxy group and the possible crosslinking through the carboxy group at high temperature.

Dielectric constants of 4-CMI/styrene, 3-CMI/styrene, and commercial DuPont Pyralin 5811® polyimide are tabulated as a function of frequency in Table V. A dielectric constant of 3.1 for this polyimide was reported by the manufacturer. It seems that the dielectric constant of 4CMI/styrene copolymer is lower than that of the commercial polyimide from the biphenyldianhydride/paraphenyldiamine. The dielectric constant of 4CMI/styrene is very close to that of polystyrene¹²; the low value may be due to having a structure similar to polystyrene. The dielectric constant is also similar to the typical values of 2.5–3.1 for polyimide as reported by Stoakley and St. Clair.¹³

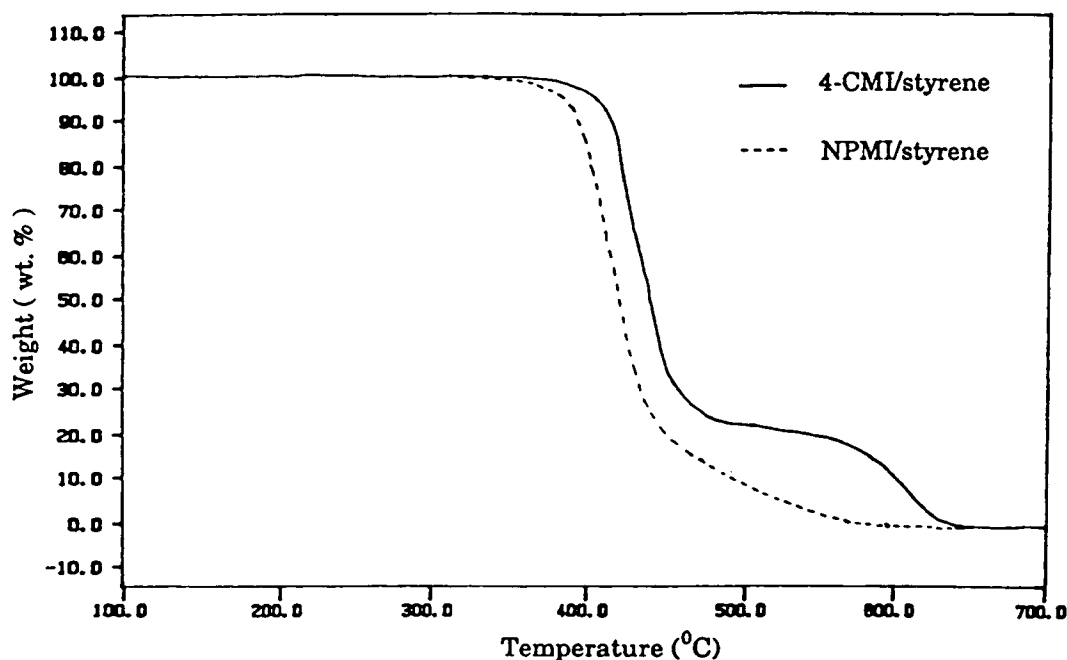


Figure 11 TGA thermogram of 4-CMI/styrene and NPMI/styrene copolymers under nitrogen environment.

Table V Dielectric Constant of Polymers at Various Frequencies

Frequency (kHz)	3-CMI/ST	4-CMI/ST	Polyimide ^a
0.03	2.93	2.55	2.81
0.10	2.89	2.54	2.80
0.30	2.85	2.53	2.79
1.00	2.82	2.52	2.78
3.00	2.78	2.52	2.78
10.0	2.73	2.51	2.77
33.3	2.64	2.51	2.76

^a DuPont Pyralin® 5811.

CONCLUSIONS

Preparation of electrocopolymerized poly(*N*-substituted maleimide-*co*-styrene) copolymer films onto copper substrates was successfully demonstrated. The *N*-substituted maleimides, which include *N*-phenylmaleimide, 3-carboxyphenylmaleimide, and 4-carboxyphenylmaleimide were electropolymerized with styrene to form a rather thick ($\sim 25 \mu\text{m}$) coating on copper. Because Zn, Cr, Ni, and Fe metals have low reduction potential (less than -0.8 V), their reduction tends to override the electrochemical initiation of monomer and to interfere with the electropolymerization process. Pretreatment with these metals before electropolymerization is therefore not desirable, although certain other metals such as magnesium may be used.

The 4-CMI/styrene copolymer films are generated from cathode surfaces with a 1 : 1 copolymer composition, associated with an alternating monomer sequence in the polymer chain, and consistent with prior electropolymerization of 4-CMI/styrene onto graphite fibers. The composition was demonstrated by using *in situ* FTIRS.

Evidence was obtained about the free-radical nature of polymerization. The use of a protic solvent such as a mixture of water and DMAc would have an inhibiting effect on an anionic process. Indeed, the very high number average molecular weights and their decrease as a function of the current density are typical of free-radical processes.

4-CMI/styrene copolymers have not only high glass-transition temperature ($\sim 220^\circ\text{C}$) and fairly good thermal stability (decomposition temperature $\sim 430^\circ\text{C}$), but also have rather low dielectric constant (~ 2.55), comparable to that of polyimides.

The authors wish to acknowledge the support of this research by the Endicott Laboratories, IBM Co., and especially the provision of sample materials by Dr. C. R. Davis.

REFERENCES

1. L. B. Gilman, A. N. Hamilton, J. A. Kreuz, and J. D. Middaugh, *Design Advantages of Kapton Polyimide Film in Flexible Circuitry*, Polyimide Conference, New York, 1980.
2. J. Chang, J. P. Bell, and J. Shkolnik, *J. Appl. Polym. Sci.*, **34**, 2105-2124 (1987).
3. F. S. Teng and R. Mahalingam, *J. Appl. Polym. Sci.*, **23**, 101-113 (1979).
4. B. K. Garg, R. A. Raff, and R. V. Subramanian, *J. Appl. Polym. Sci.*, **22**, 65-87 (1978).
5. J. O. Iroh, J. P. Bell, and D. A. Scola, *J. Appl. Polym. Sci.*, **41**, 735-749 (1990).
6. C. K. Sauers, *J. Organic Chem.*, **34**, 2275 (1969).
7. M. C. Pham, F. Adami, and J. E. Dubois, *J. Electrochem. Soc.*, **134**, 2166 (1987).
8. J. M. Barrales-Rienda, J. I. Gonzalez De La Campa, and J. Gonzalez Ramos, *J. Macromol. Sci.-Chem.*, **A11**, 257-286 (1977).
9. J. O. Iroh, Ph.D. thesis, University of Connecticut, 1990.
10. J. R. MacCallum and D. A. Mackerron, *Eur. Polym. J.*, **18**, 717-724 (1982).
11. T. Otsu, A. Matsumoto, T. Kubota, and S. Mori, *Polym. Bull.*, **23**, 51-56 (1990).
12. R. H. Boundy, R. F. Boyer, eds. *Styrene, Its Polymers, Copolymers and Derivatives*, Reinhold Publishing Corp., New York, 1952.
13. D. M. Stoakley and A. K. St. Clair, *Polym. Mater. Sci. Eng.*, **59**, 33-36 (1988).

Received January 29, 1992

Accepted July 25, 1992