The Electropolymerization of Poly(styrene-co-4-carboxyphenyl maleimide) Coatings onto Steel

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SYNOPSIS

Electropolymerization can be used to produce uniform and pin-hole free coatings on surfaces of complex shapes, due to the intrinsic characteristic of the process. In this article, the electrocopolymerization behavior of 4-carboxyphenyl maleimide (4CPMI) with styrene onto a steel surface is reported. The polymerization mechanism is by free radical, as might be expected for an aqueous reaction environment. Experimental results suggest that initially a charge transfer complex forms between styrene and 4CPMI, which is much more reactive than either of the two monomers. Alternating copolymers are always obtained at low conversion, even with significant changes in the monomer feed compositions. Because of the incorporation of rigid imide rings into the copolymer backbone, the coating formed has very good thermal properties and is thus a potential candidate for high-temperature applications. Furthermore, the copolymer dielectric constant is comparable to that of commercial polyimides, making it attractive for use in electrical and electronic insulation applications. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Coatings are widely used on metal surfaces for decorative and/or protective purposes. Electropolymerization is a novel coating method in which polymerization is achieved simply by passing an electrical current through a solution of the monomer, solvent, initiator, and electrolyte, thereby forming a polymeric coating up to 25 μm thick in-situ on the electrode surface.[1-6] This technique has several advantages over conventional methods. The starting monomer solution is of very low viscosity, resulting in improved adhesion because of the good wetting of the surface by the monomer solution. In spite of the insulating nature of the coating formed, resistance at spots where the coating is thin is sufficiently low that polymerization occurs preferentially there. The net result is that uniform and pin-hole free coatings can be obtained on surfaces of complex shape. The process conditions are mild: low potential

(< -2 V half-cell) and current (<10 mA/cm^2) are used under room temperature and atmosphere, and process control is relatively simple. Finally, dominantly aqueous systems can be used, which have advantages of lower pollution, lower cost, and easier process control.

An electropolymerization mechanism can be cationic, anionic, or free radical, depending upon whether the cathode or anode is used as the working electrode, and upon the choice of reaction systems. The polymerization can be initiated by either the monomer itself, if it is electrochemically active, or by added initiators. During the reaction, the electrochemically active species undergoes a heterogeneous surface reaction on the electrode. The species can give up one or more electrons under anodic conditions, or obtain electrons from the electrode under cathodic conditions. Free radical or cationic mechanisms are thus possible for anodic conditions, and free radical or anionic for cathodic conditions. These active centers react with monomer molecules close to the surface and propagate as in a normal polymerization process. The polymer formed will either precipitate onto the

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electrode surface if it is insoluble in the solution, or dissolve if soluble.

Starting in the 1970s, various vinyl monomers in aqueous solutions have been studied using this method. Styrene, acrylic acid, acrylamide, and methyl methacrylate, to name a few, have been polymerized on metal substrates successfully.[9-12] Subramanian et al.[6,13] and Bell et. al.[7,8] applied this technique to provide an interlayer for graphite fiber composites. They were able to improve the interlaminar shear strength of the composite without lowering the impact strength.

However, for most systems studied, the polymers formed have a glass transition temperature, T_g, of only about 100°C, and are thus unsuitable for high temperature applications. Maleimide and its derivatives have been widely used to improve the thermal stability of common vinyl resins due to the rigid imide ring in their structure.[14] In this article, we report the electrocopolymerization behavior of a N-substituted maleimide, 4-carboxyphenyl maleimide (4CPMI), with styrene on a steel surface, with the goal of a high temperature resistant coating.

EXPERIMENTAL

Materials

Styrene was obtained from Fisher Scientific Company, and the inhibitor free styrene was obtained by vacuum distillation. N-Methyl-2-pyrrolidinone (NMP) and sodium nitrate were used as received from Fisher Scientific Company. 4-Carboxyphenyl maleimide (4CPMI) was prepared according to the method of Rao.[15] Monomer purity was confirmed by nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC). The DSC thermogram shows only one sharp melting peak at 241°C. SAE 1010 carbon steel coupons from Q-Panel Company were used as the substrate for the study.

Electrochemical Cell

A three-compartment polypropylene cell was used in the study. A schematic diagram is shown in Figure 1. The cathode and anode compartments are separated by SEPA polypropylene membranes from Osmonics, Inc. Pore size is 0.05 μm. The substrate to be coated was placed in the central cathode compartment, and two stainless steel plates were placed in the two side compartments as anodes. A Princeton Applied Research potentiostat Model 363 was used
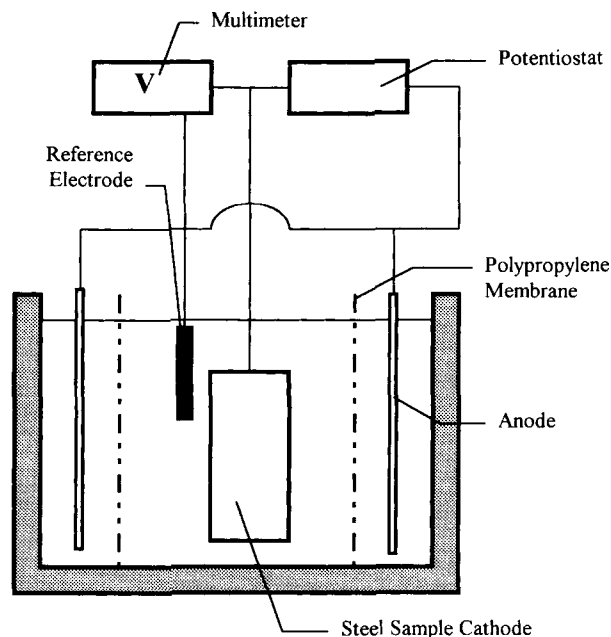

Figure 1 Schematic diagram of the electrochemical cell.

to supply constant potential to the cell. A Keithley digital multimeter Model 160 was used to measure the current flowing through the cell and monitor the cathode potential with respect to a saturated calomel reference electrode (SCE).

Polymerization

The substrate surface was cleaned by detergent washing, and then etching in a citric acid solution for 5 min; the etching solution temperature was maintained at 70°C and the pH was adjusted to 4.0 using ammonium hydroxide. The coupons were then washed with an ample amount of distilled water and dried in an oven at 90°C for immediate use.

A monomer solution was prepared by first dissolving appropriate amounts of styrene and 4CPMI in N-methyl-2-pyrrolidinone, then mixing with 0.025M aqueous NaNO$_3$ electrolyte solution. The monomer solution was poured into the central compartment while the two side compartments were filled with 0.025M aqueous NaNO$_3$ solution. Electropolymerization was started by the application of a defined reduction potential to the cathode. Simultaneous polymerization of the monomers and deposition of the formed polymers occurred at the electrode surface. After the reaction, the coupon was withdrawn from the cell, thoroughly rinsed with distilled water, and dried in an oven at 150°C for 3

h. Further drying was carried out at 250°C under vacuum to remove any trapped solvent.

Characterization

A CV-100W cyclic voltammeter from Bioanalytical Systems Inc. was used to study the electrochemical activity of the monomers, solvent, and electrolyte. A glassy carbon electrode was used as the working electrode, a platinum electrode as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. A TOSHIBA R-1200 NMR spectrometer was used for the determination of the equilibrium constant of complex formation. A Nicolet 60SX Fourier transform infrared spectrometer (FT–IR) was used to characterize the composition of the obtained polymer, with resolution of 4 cm^{-1}. A differential scanning calorimeter (DSC) model 2920 and thermogravimetric analyzer (TGA) model 2950 from TA Instruments were used for the thermal analysis. The heating rate was 10°C/min for the DSC and 20°C/min for the TGA. The molecular weight of the polymer was obtained on a Waters 150C gel permeation chromatography (GPC) using polystyrene standards. The measurement was conducted at 35°C using tetrahydrofuran as the solvent. The morphology of the substrate and coating was examined using an Olympus optical microscope. The dielectric constant measurement of the coating was conducted on a Time Domain Dielectric Spectrometer (TDDS) from IMASS, Inc.

RESULTS AND DISCUSSION

There have been quite a few reports in the literature concerning the copolymerization of monomers with strong electron accepting group, such as maleic anhydride, and those with an electron donating group, such as styrene or vinyl acetate.[16-19,31,32] Alternating copolymers are usually obtained in strong donor-acceptor systems regardless of the monomer feed composition. Many theories have been proposed to explain this phenomenon, and they are generally grouped into two categories. The first group of theories attributes alternation to a combination of steric, polar, or possibly coordination factors working against random cross-propagation. Such factors may include, for example, electrostatic interaction between monomer and radical at the chain end, or formation of a monomer-radical complex at the chain end. Alfrey and Price's "Q-e" scheme[16] is an attempt to systematically quantify the influence of

both polar and resonance stabilization factors affecting cross-propagation reactions. Another group[24] argues that a 1 : 1 charge transfer complex forms between the monomers, and the reaction proceeds as a homopolymerization of the complex. The complex has been found experimentally in several systems, such as maleic anhydride/styrene.[26] Its strength is characterized by the equilibrium constant of complex formation. Iwatsuki and Yamashita[33] correlated the equilibrium constant with the polymerization behavior of charge transfer complex. Such behavior ranges from random copolymerization with radical initiator, alternating copolymerization with initiator, spontaneous alternating copolymerization, to ionic spontaneous homopolymerization as the strength of the donor and acceptor strength of the olefins increase. Worth mentioning is the bond formation mechanism[31] proposed by H. Hall, et al. to explain the spontaneous initiation of a strong donor monomer and strong acceptor monomer system. It suggests that a bond is formed between the donor monomer and acceptor monomer to generate a tetramethylene intermediate, which is the true initiation species. This mechanism explains satisfactorily the formation of cyclic by-product during spontaneous polymerization in many systems. Hall's kinetic study on p-methoxystyrene/dimethyl cyanofumarate system[34] indicates that such spontaneous polymerization proceeds via free monomer after initiation by the tetramethylene intermediate.

The techniques usually used to determine the equilibrium constant of charge transfer complex formation are UV spectroscopy[20] and NMR.[21] In our case, there is no distinct absorption peak appearing in the UV/VIS range upon mixing of the two monomers; thus, the Benesi–Hildebrand method is inapplicable.[20] The equilibrium constant K for charge transfer complex formation between styrene and 4CPMI is defined as in eq. (1),

$$4CPMI + St \rightleftharpoons C$$

$$K = \frac{[C]}{[St][4CPMI]} \qquad (1)$$

where C refers to the charge transfer complex. K was then evaluated by ^1H NMR, according to the method of Hanna et al.[21] Assuming rapid exchange between complexed and free states of styrene molecules, the measured chemical shift of styrene protons is a weighted average of that of the free and complexed molecules.

$$\delta_{obsd}^{St} = \delta_{free}^{St} \frac{[St]}{[St] + [C]} + \delta_c^{St} \frac{[C]}{[St] + [C]} \quad (2)$$

δ_{obsd}^{St}, δ_{free}^{St}, and δ_C^{St} are the shifts of styrene protons in a specific observation, in free form, and in complex, respectively. If $[St] \ll [4CPMI]$, eq. (2) can be simplified to[21]
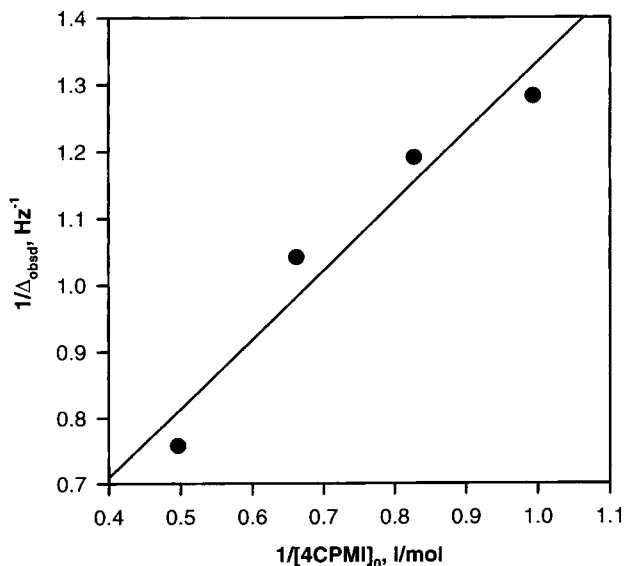
$$\frac{1}{\Delta_{obsd}^{St}} = \frac{1}{K\Delta_0^{St}} \frac{1}{[4CPMI]} + \frac{1}{\Delta_0^{St}} \quad (3)$$

where $\Delta_{obsd}^{St} = \delta_{obsd}^{St} - \delta_{free}^{St}$, and $\Delta_0^{St} = \delta_C^{St} - \delta_{free}^{St}$. The K value can be determined by linear regression from the data in Figure 2. A value of 0.28 L/mol was obtained for the 4CPMI/styrene system in d_6-DMSO. Thus, it seems that a weak charge transfer complex does exist between these two monomers, and the K value falls close to that of similar systems.[22]
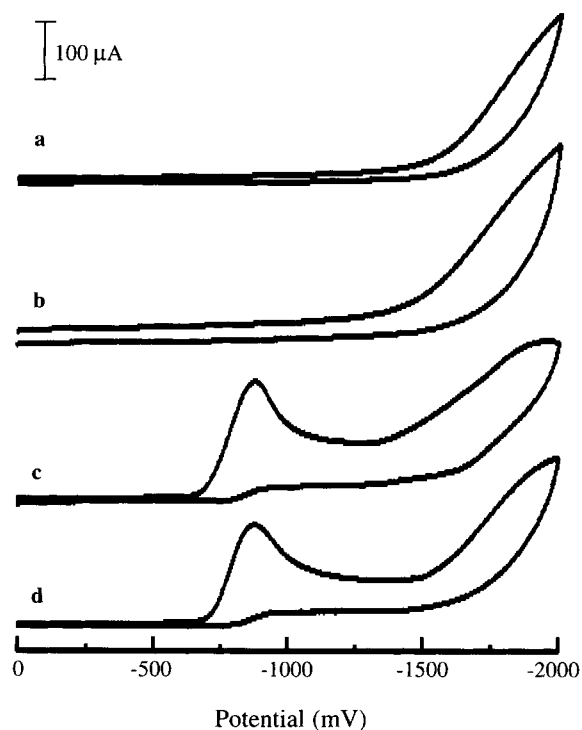
The cyclic voltammogram (CV) of $0.1M$ NaNO$_3$ blank solution is shown in Figure 3(a). The solvent used is a 50/50 mixture of NMP and water. The solution is stable up to -1.5 V vs. SCE. After that, the current increases rather rapidly due to the decomposition of water.

$$H_2O + e \rightarrow OH^- + H_2 \uparrow \quad (4)$$

The CV of styrene dissolved in the above mentioned blank solution is shown in Figure 3(b). There

Figure 3 Cyclovoltammogram of (a) blank solution, (b) $0.002M$ styrene, (c) $0.002M$ 4CPMI, and (d) $0.002M$ styrene and $0.002M$ 4CPMI. Glassy carbon working electrode. Scan rate = 200 mV/sec. Blank solution contains $0.1M$ NaNO$_3$ dissolved in a 50/50 NMP/H$_2$O mixture.

is no characteristic reduction appearing in the potential range scanned; the species is inert. A characteristic peak is present at -0.78 V in the voltammogram, as shown in Figure 3(c), for 4CPMI dissolved in blank solution. This is associated with the reduction of 4CPMI.

$$4CPMI + e^- + H^+ \rightarrow 4CPMI^\bullet \quad (5)$$
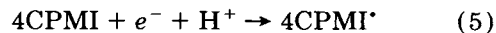
When a solution of equal concentration of 4CPMI and styrene was scanned, a reduction peak appeared at about the same potential. No shift in peak position or appearance of a secondary peak due to the complex was found. Nevertheless, this does not rule out the possibility of complex formation in the solution for the following two reasons: (1) the complex formed is a rather weak one, and its reduction potential may not be very different from that of 4CPMI. (2) Low concentration solutions ($0.002M$) are used in CV studies. Under such conditions, less than 0.1% of 4CPMI molecules would be converted to complex, and the complex signal could be overshadowed by that of free 4CPMI.
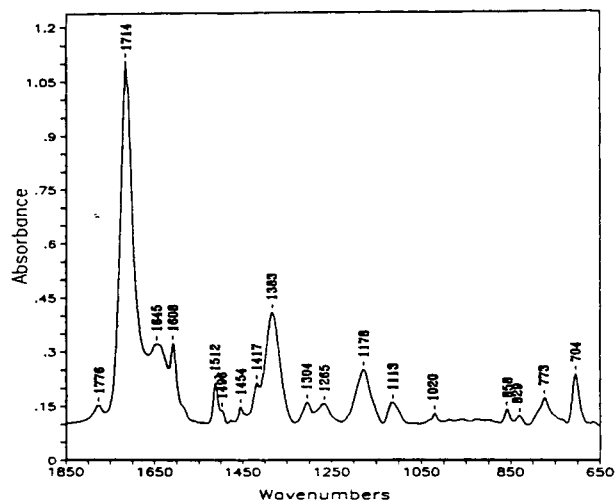

Figure 2 $1/\Delta_{obsd}$ vs. $1/[4CPMI]_0$ for styrene-4CPMI complex in d_6-DMSO [styrene] = $0.05M$, [4CPMI] = 1.0–$2.0M$.

Figure 4 Transmission IR spectrum of poly(4-CPMI/St) coating obtained by electropolymerization. Resolution 4 cm^{-1}.

Due to the electrochemical activity of the monomer system, electropolymerization studies were carried out at a constant potential of -1.5 V on cleaned steel coupons, without the addition of additional electrochemical initiator. The IR spectrum of the polymeric coating obtained is shown in Figure 4. The symmetric and asymmetric $C = O$ stretching of the carbonyl groups in the imide ring absorb at 1776 cm^{-1} and 1714 cm^{-1}, respectively. The strong absorption at 1383 cm^{-1} is due to symmetric $C - N - C$ stretching of the imide ring. The peak at 1512 cm^{-1} is attributed to the *para*-substituted phenyl ring in 4CPMI, while the aromatic $C - C$ stretching at 1608 cm^{-1} has contributions from both 4CPMI and styrene. The characteristic absorption of polystyrene at 1493 and 1452 cm^{-1} is assigned as the semicircle stretching and mixed $C - H$ bending of a monosubstituted phenyl ring.[23] The $C - H$ bending of the vinyl group at 991 cm^{-1} and 908 cm^{-1} of styrene, $C - C$ stretching of imide ring at 949 cm^{-1} of 4CPMI, are absent in the spectrum, confirming that the polymerization reaction happened via the opening of the double bond. The reaction mechanism can be taken as free radical as water is a very active chain-transfer agent for ionic polymerization. Also, ionic polymerization would yield homopolymer instead of copolymer. From the IR and DSC data, as discussed later, it is clear that the polymer obtained is not a homopolymer.

To determine the composition of the coating, a calibration was obtained using homopolymers of 4CPMI and styrene. Figure 5(a) and (b) are transmission IR spectra of polystyrene and

poly(4CPMI), respectively, obtained by solution polymerization in THF. The spectrum of the blend of the homopolymers agrees with that of the copolymer with no additional peaks appearing, as shown in Figure 5(c). A calibration plot was then constructed using blends of these two homopolymers at various ratios. The absorption peaks at 1510 cm^{-1} for styrene and that at 1493 cm^{-1} for 4CPMI were chosen as the characteristic peaks for 4CPMI and styrene, respectively. When the absorbance ratio of these two peaks is plotted vs. the molar ratio of poly(4CPMI) to polystyrene present in the blend, as shown in Figure 6, very good linearity is obtained.

The polymerization was controlled to be at low monomer conversion levels, in which case the monomer concentrations can be assumed to be constant during the reaction course. The compositions of the copolymers obtained at various monomer feed ratios were then determined using the above calibration method. Despite the 4CPMI content in the feed changing from 20 to 60 mol %, the ratio of 4CPMI and styrene incorporated into the polymer is always close to 1, as shown in Figure 7.
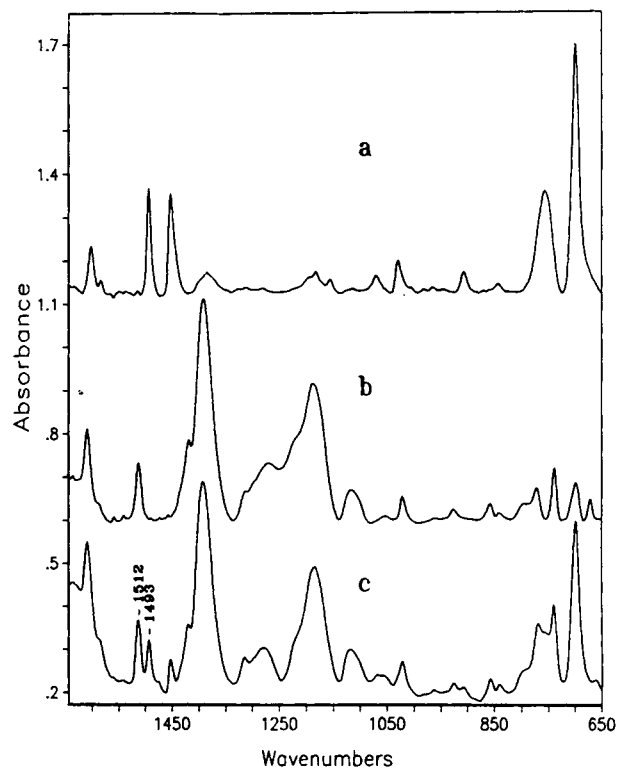
Figure 5 Transmission IR spectra of (a) poly(4-CPMI), (b) polystyrene, and (c) blend of the two homopolymers obtained by solution polymerization. Resolution 4 cm^{-1}.
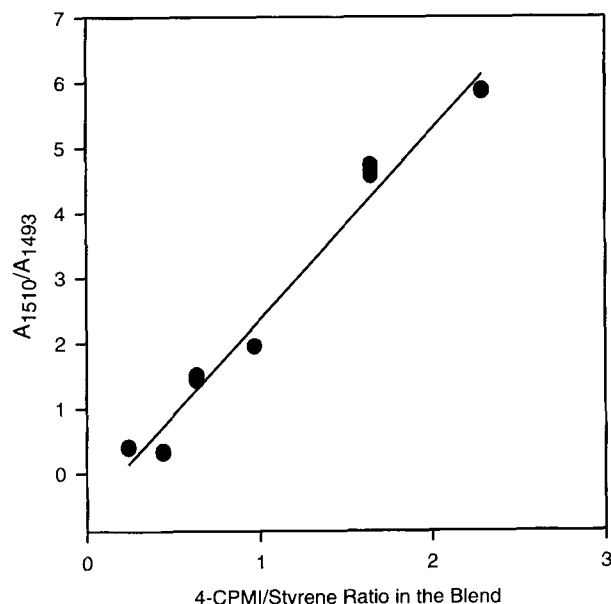
Figure 6 Absorbance ratio of 1510 cm^{-1} to 1493 cm^{-1} vs 4-CPMI/styrene ratio in the blend.

This is certainly consistent with the complex formation shown by the NMR results. It is also in agreement with literature reports on similar monomer systems,[16-19] which suggest that despite the low concentration of the complex present in the system, its reactivity is presumably significantly higher than that of either one of two monomers, resulting in alternating copolymer formation under all monomer feed ratios. There have been reports in the literature concerning the dependence of complexation on various factors, such as solvent character and temperature.[27-30] Generally, the concentration of complex is expected to be reduced in a polar environment. This is because most polar solvents, such as DMSO and NMP used in this research, are Lewis bases and compete with donor monomer to complex with the acceptor monomer. Water, despite its high dielectric constant, is not a strong Lewis base. This is shown in its donor number of 18, compared with 29.8 of DMSO. This, coupled with the relatively large equilibrium constant and high monomer concentrations used, leads us to believe that the charge transfer complex observed in the NMR experiment will also exist with an appreciable concentration in the NMP/water solution despite the aqueous environment of the experiment. Also, water is a nonsolvent for both 4CPMI and styrene. This further hinders its ability to interact with 4CPMI and styrene and influence complex formation. Complexation is a slightly exothermic reaction. The complex concen-

tration will be decreased at high temperatures. Our experiments were conducted at room temperature, practically eliminating the temperature factor.

Similar experimental results have also been explained in terms of crosspropagation theories in the literature. Such theories[16,35] attribute the alternating structure formation to the much greater tendency of a donor radical to react with an acceptor monomer and an acceptor radical with a donor monomer. Such a tendency is manifested in the reactivity ratio data. For example, values of $r_1 = 0.005$ and $r_2 = 0.050$ are reported for the maleic anhydride/styrene system. The classical copolymerization theory predicts alternating copolymer formation for such reactivity ratios. Different theories have offered different explanations for this strong cross propagation tendency. Price[16] believes that the transition state is stabilized by partial electron transfer between the electron-donor radical and electron-acceptor monomer, or electron-acceptor radical and electron-donor monomer decreasing the activation energy for crosspropagation.
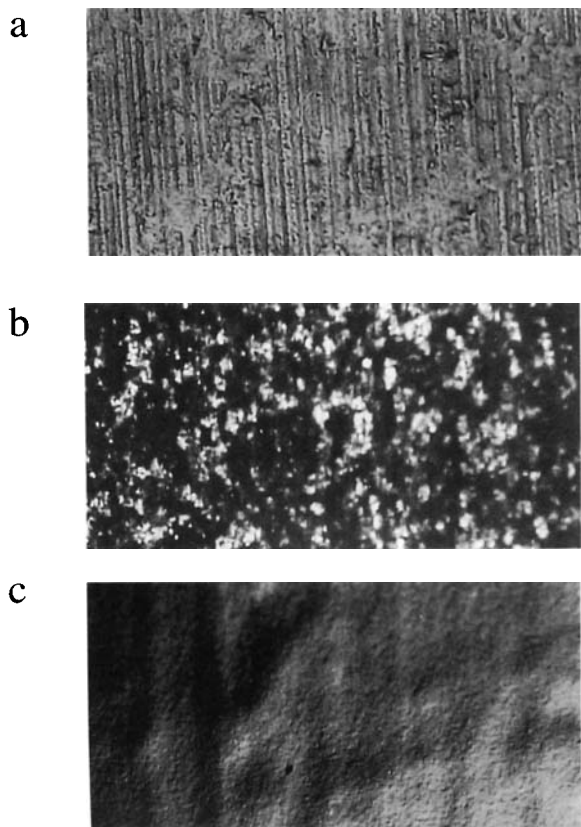
Our experimental findings thus far are consistent with the complex mechanism. However, as discussed above, there is not enough experimental evidence to exclude the cross-propagation mechanism as a cause for alternating structure at the same point. Unequivocal proof of complex participation will have to be obtained from further kinetic and stereochemistry studies.
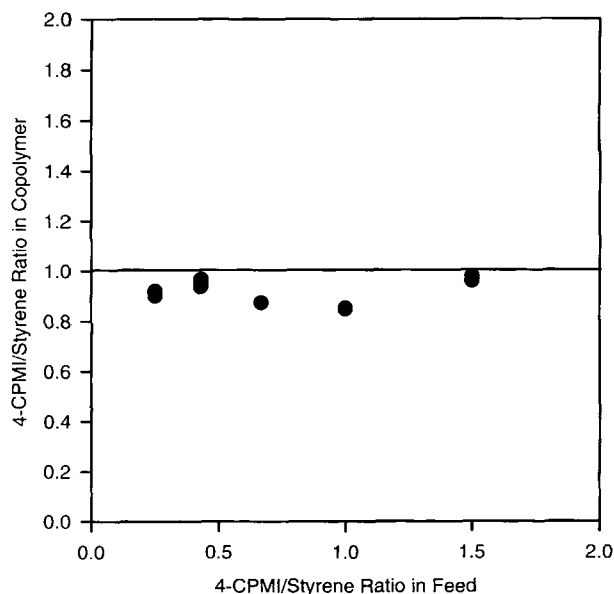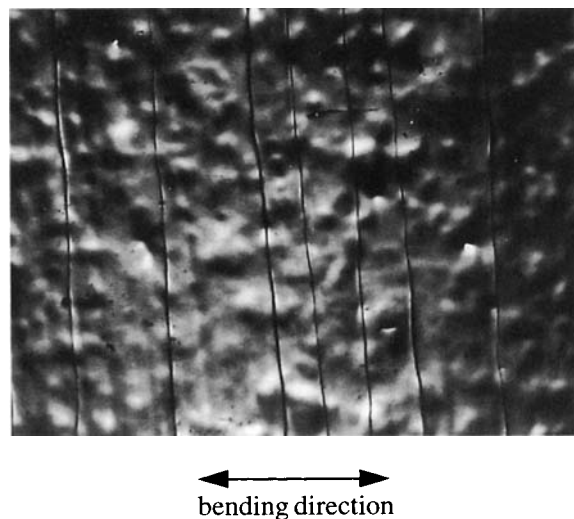

Figure 7 4-CPMI/styrene ratio in the copolymer vs. that in the feed. Total monomer concentration 0.4 M.

When the polymerization proceeded to high conversion, in the case of styrene and 2,4,6-tribromophenyl maleimide (TBPMI),[25] a mixture of alternating copolymer and pure polystyrene was formed by a batch emulsion polymerization process with excess styrene in the feed. The reason is probably that TBPMI is almost exhausted at a high conversion and then the homopolymerization of styrene takes place.

Smooth and uniform coatings were obtained on the steel surface by electropolymerization. Figure 8(a) shows the original metal surface as received. The surface is rough, and there is apparent mill scale on it. The layer of porous oxide on the surface is mechanically weak, preventing strong adhesion of the coating to the substrate. The citric acid etching process removed this layer and, as shown in Figure 8(b), roughened the surface, introducing many anchor sites for polymer chains to interlock to the substrate. This would be expected to significantly improve the adhesion of the coating. The coated substrate surface, shown in Figure 8(c), is uniform and much smoother than the original surface. Figure 9

bending direction

Figure 9   Micrograph of a coated steel coupon subject to a 90° bend. Magnification = 45×.

Figure 8   Micrograph of (a) original, (b) citric acid etch, and (c) coated steel surface. Magnification = 175×.

shows the tip portion of a sample that has been bent 90°. The coating fractured perpendicular to the bending direction, due to its glassy nature at room temperature. However, there was no delamination from the substrate, indicating good adhesion of the coating.

The molecular weight of the polymer formed was fairly high, with the weight average molecular weight, $\bar{M}_w$, of 146,000 by GPC, and a polydispersity index, $\bar{M}_w/\bar{M}_n$, of 2.4. This is typical for free radical polymerization in that high molecular weight polymer can usually be obtained relatively easily. What needs to be kept in mind is that the molecular weight obtained is based on a calibration of polystyrene, and the actual molecular weight could be somewhat lower, considering the copolymer will have a stiffer backbone than polystyrene and, therefore, larger hydrodynamic volume for the same molecular weight.

The first trace of the DSC thermogram has a large broad peak due to evaporation of residual NMP solvent. A second run shows only one glass transition at 231°C, shown in Figure 10. This high T_g compared to polystyrene is due to the incorporation of the rigid five-member ring of 4CPMI into the backbone, significantly hindering segmental rotation, thus stiffening the chain. The incorporation of 4CPMI into polymer backbone also results in improved thermal stability as compared with polystyrene. The TGA samples were further dried for 30 min at 250°C in the TGA chamber to remove the residual solvent observed in the DSC experiments. Under nitrogen atmosphere, the TGA thermogram in Figure 11(a)
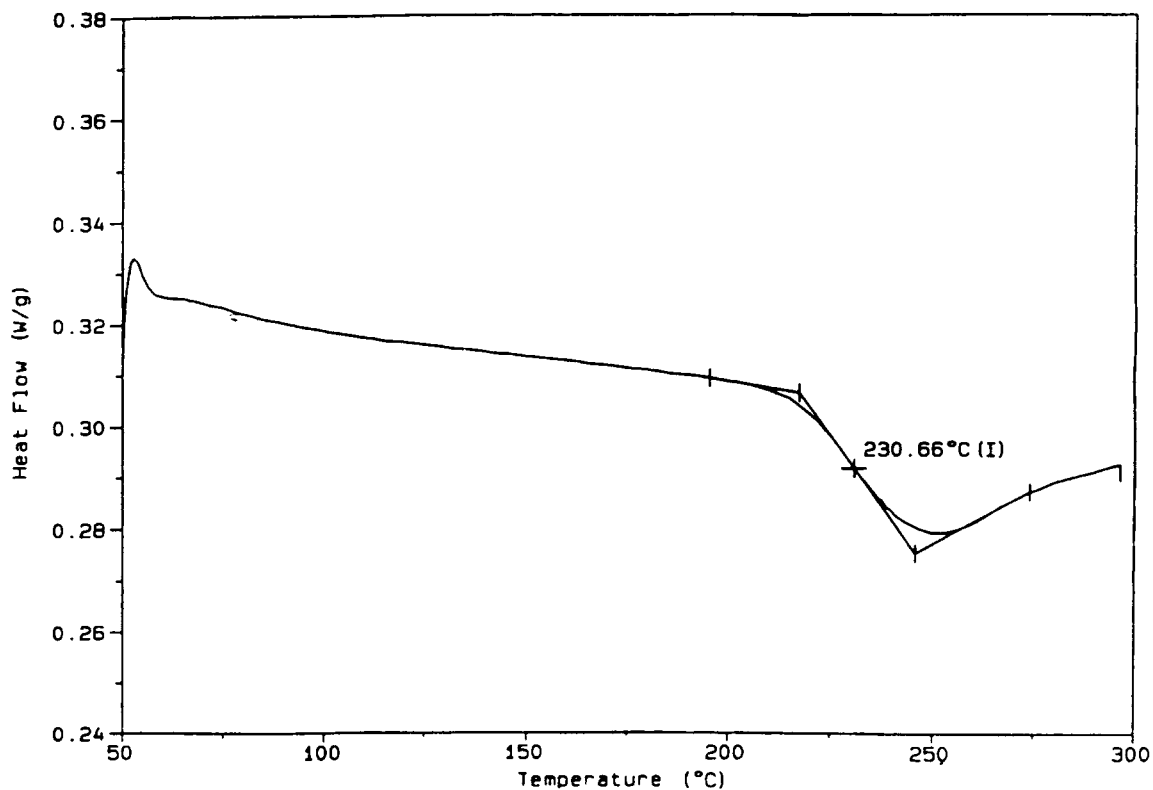
Figure 10 DSC thermogram of Poly(4-CPMI/St) coating obtained by electropolymerization. Heating rate = 10°C min.
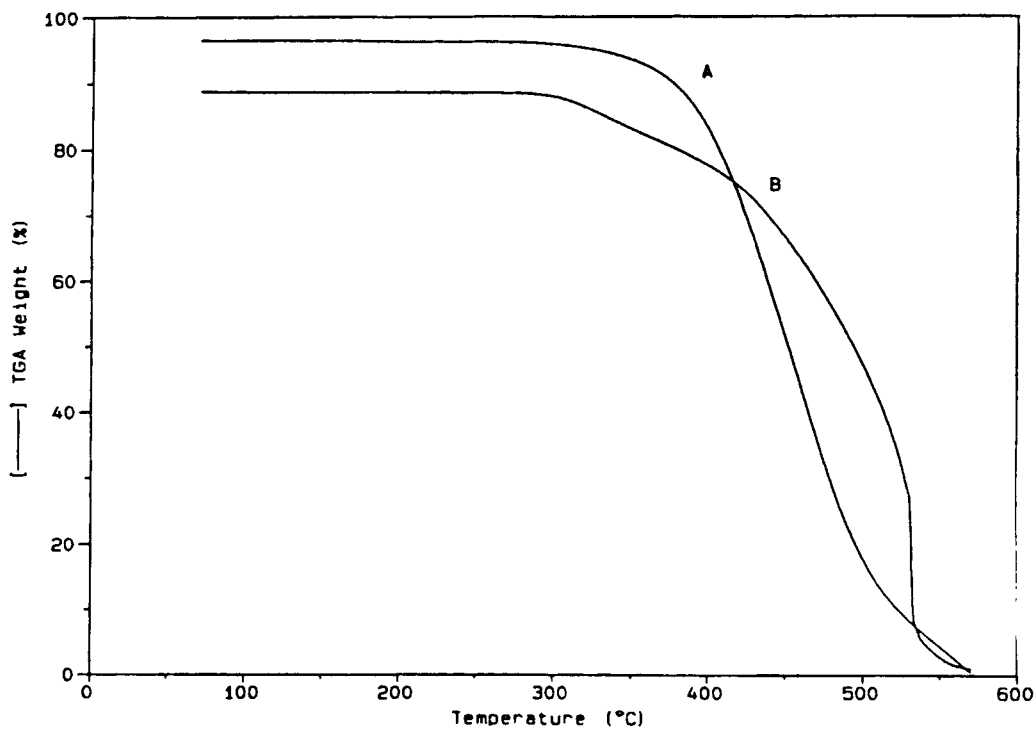

Figure 11 TGA thermogram of Poly(4-CPMI/St) coating obtained by electropolymerization under (a) nitrogen and (b) oxygen. Heating rate = 20°C/min.

shows that the copolymer is stable up to 400°C, after which it undergoes a one-stage decomposition. The thermal stability is still excellent under oxygen atmosphere, where the onset temperature for degradation is only lowered by about 50°C, to 350°C, as shown in Figure 11(b). The great improvement in thermal properties compared to polystyrene is due to the large proportion of 4CPMI incorporated into the polymer chain, namely, an almost alternating structure, in agreement with the IR result. Of interest is that when the first heat of the DSC was scanned up to 350°C, instead of the 300°C used in the previous experiments, a higher T_g of 275°C was obtained in the second trace. Probably a crosslinking reaction and removal of trace amounts of solvent occurred in the high temperature range leading to the T_g enhancement observed in the second heating run. Of both factors, crosslinking is the dominating one, as the previously soluble polymer became insoluble in NMP after the DSC run.

Dielectric properties are very critical for insulation applications. A low dielectric constant is always desirable. Dielectric constant measurements on this system at selected frequencies are listed in Table I. The coating has a dielectric constant of about 2.6 in the frequency range investigated, comparable to or slightly lower than that of commercial polyimides, which are widely used for insulation in the electronic and electrical industries. Thus, it seems that the coating developed will be an attractive candidate for such applications.

CONCLUSION

The electrocopolymerization of 4-carboxyphenyl maleimide with styrene was studied on a steel substrate. A charge transfer complex, although not observed directly in the polymerization solvent system, was shown to be formed between the two monomers in DMSO, with an equilibrium constant of 0.28. The reduction potential was estimated to be −0.78 V. Copolymers were obtained when electropolymerization was conducted under constant potential of −1.5 V. The composition of the formed polymer at low conversion is always 1 : 1 in 4CPMI and styrene, despite large changes in monomer feed ratio. The coating obtained has a T_g of 231°C and a dielectric constant of about 2.6. It is stable up to 400°C under nitrogen, and 350°C under oxygen. There is also indication of good adhesion between the substrate and the coating. The high temperature stability and good dielectric properties make the coating a potential

Table I Dielectric Constant of 4CPMI/Styrene Copolymers

Frequency (Hz)	Dielectric Constant
1	2.68
10	2.65
60	2.64
100	2.64
600	2.63
1000	2.63
6000	2.60
10000	2.55

candidate for high temperature, and especially insulation, applications.

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