

Protective Flexible Coatings on Copper by Spontaneous Polymerization

HAIPENG ZHENG, KAMAL NAINANI, JAMES P. BELL

Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269-3136

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ABSTRACT: Spontaneous polymerization (S-Poly) is a novel process for forming protective polymer coatings on metals. The S-Poly mechanism on copper is discussed for one typical monomer system. Poly(ethylene glycol) ethyl ether methacrylate (EEM), a flexible monomer, was first introduced into a styrene/*N*-phenyl maleimide system that we had used for aluminum and steel. The effects of EEM on the composition, apparent molecular weight, thermal properties, and other properties of the coatings were studied with reflectance Fourier transform infrared, gel permeation chromatography, differential scanning calorimetry, and water-uptake and adhesion experiments. *N*-(4-Fluorophenyl) maleimide (4FMI), a strongly hydrophobic monomer, was further incorporated into the EEM copolymer for improved water impermeability. The resultant coatings, which included EEM and 4FMI units, showed good bonding strength to copper and better ductility and protective properties than other coatings in both corrosion and pinhole tests. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1749–1757, 2002

Key words: spontaneous polymerization; copper; adhesion; water impermeability; corrosion resistance; copolymerization; coatings; fluoropolymers; adhesion

INTRODUCTION

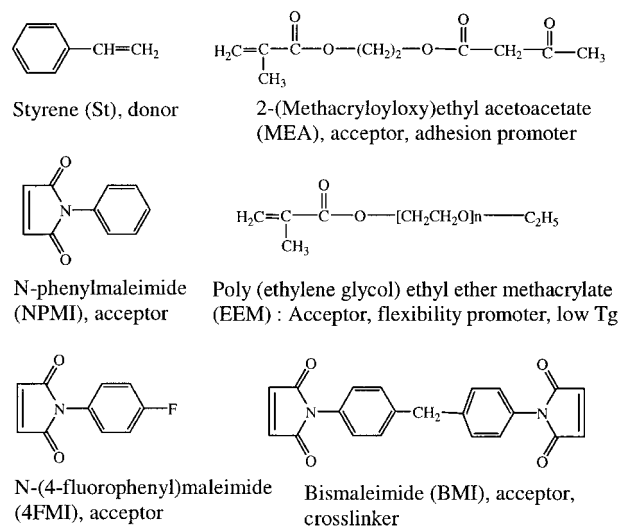
Polyimides have been extensively used in the electronics industry, especially in the manufacture of flexible printed circuit boards and semiconductor chip devices, because of their superior chemical and thermal stability.¹ Conventional methods of forming such polymer coatings are anodization coating,² conversion coating,³ dip coating,⁴ spray coating,⁵ and powder coating.⁶ Compared with these methods, the spontaneous polymerization (S-Poly) technique provides a safe and economical process that can be conducted at room temperature in an acidified, partly aqueous monomer solution.⁷ In this process, polymer coatings grow spontaneously on a metal surface with-

out any other initiators when the metal is immersed in a monomer solution. Uniform and conformal coatings 1–50 μm thick can be controlled on objects with complex topographies,⁸ but polymerization does not occur in the monomer solution.

In the S-Poly system, some feasible metals are aluminum, steel, copper, and zinc and their alloys.⁸ The syntheses and properties of highly thermally stable and rigid copolymer coatings on aluminum and steel have been reported in earlier articles.^{9–13} The S-Poly process normally involves a donor monomer such as styrene (St) and a primary acceptor monomer such as *N*-phenyl maleimide (NPMI).^{9,10} 2-(Methacryloyloxy) ethyl acetoacetate (MEA) has been incorporated into the polymer coatings as a crack-resistant reagent and adhesion promoter. A small amount of bismaleimide (BMI) has also been used as a crosslinker to prevent the sagging of thicker coatings during

Correspondence to: J. P. Bell (jbell@mail.ims.uconn.edu).

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Scheme 1 Chemical structures of the monomers.

polymerization. The S-Poly coatings have shown good thermal stability, excellent adhesion strength to aluminum, low dielectric constants, and excellent corrosion resistance.¹⁰ However, when this S-Poly technique with the same monomer composition was applied to copper pipes or panels, the coatings tended to be brittle and had low adhesion strength to copper.

In this study, new monomers were introduced to improve the ductility and adhesion of the S-Poly coatings on copper. On the basis of recent polymerization mechanism studies on aluminum^{10,14} and the redox mechanism on steel,⁸ the polymerization mechanism of the S-Poly process on copper was first investigated. Poly(ethylene glycol) ethyl ether methacrylate (EEM; Scheme 1), containing a carbonyl group and one flexible chain, was introduced into the aforementioned S-Poly system.¹⁵ The resulting copolymer coatings became more ductile with strong adhesion to copper, but at the same time they showed somewhat lower resistance in immersion and corrosion tests.

Recently, we reported that fluorinated S-Poly coatings on aluminum exhibited excellent resistance in most corrosion tests.¹⁶ The advantages of such coatings include their strong hydrophobicity, low dielectric constants, water impermeability, and low coefficient of friction.^{17–19} Here we introduced a fluorinated monomer, *N*-(4-fluorophenyl) maleimide (4FMI), into this S-Poly system on copper. The structures and compositions of the fluorinated coatings were confirmed with attenuated total reflectance Fourier transform infrared

(ATR-FTIR) spectra and X-ray photoelectron spectroscopy (XPS) data. The protective properties of the coatings were evaluated with adhesion and water-immersion measurements and corrosion and pinhole tests.

EXPERIMENTAL

Materials

St, MEA, maleic anhydride, 4-fluoroaniline, and EEM were purchased from Aldrich Chemical Co., and NPMI and BMI were acquired from Mitsui Toatsuo Chemical Co. The inhibitors in the monomers were not removed because no adverse effect of the initiators on the polymerization process was found. The monomers were used as received and stored in refrigerators. For some experiments, BMI was purified by recrystallization from tetrahydrofuran (THF). The chemical structures of the monomers are shown in Scheme 1. *N*-Methyl pyrrolidinone (NMP) was obtained from Fisher Scientific Co.

4FMI was synthesized according to the method of Rao.²⁰ Maleic anhydride (9.8 g, 0.1 mol) was dissolved in 100 mL of dry dimethylformamide, and then 9.5 mL (0.1 mol) of 4-fluoroaniline was added to the stirring solution drop by drop. The reaction solution was stirred and maintained at room temperature for 3 h. Next, 50 mL of acetic anhydride and 4 g of sodium acetate were added to this reaction solution, and the mixture was maintained at 50°C, with stirring, for another 3 h. Then, the mixture was cooled to room temperature and poured into a large amount of distilled water. When the precipitate appeared, it was filtered to obtain a brown product. The crude product was purified by recrystallization from ethanol to form yellow, needle crystals of 4FMI (15 g, 78%).

mp: 156°C. ¹H-NMR (CDCl₃, δ): 7.34–7.36 (m, 2H, *φ*-H), 7.16–7.19 (s, 2H, *φ*-H), 6.87 (s, 2H, CH=). ¹³C-NMR (CDCl₃, δ): 170.3 (C=O), 135.2 (C=C), 163.7, 128.8, 126.8, 117.1 (Ar).

Copper alloy 110 contains essentially pure copper with traces of silver. Copper pipes, supplied by United Technologies Research Center (East Hartford, CT), were made of copper 120 alloy, which had traces of silver and was 0.004–0.012 wt % phosphorus. The copper samples were degreased with Blue Gold, an industrial cleaner, and rinsed with distilled water. They were then etched in a 20 mol % nitric acid aqueous solution

for 20 s. The substrates were finally rinsed with distilled water and dried with compressed air. After this pretreatment, coatings grew immediately on the copper samples.

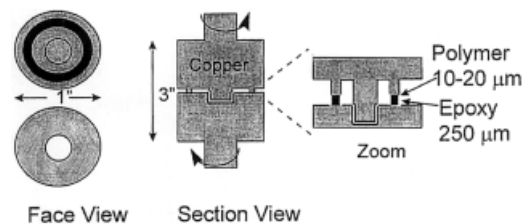
Polymerization Procedures

A monomer solution was prepared by the dissolution of monomers St, NPMI, EEM, and BMI in NMP, by their mixture with an approximate amount of H_2SO_4 -acidified distilled water, and by the addition of MEA to the mixed solution. The whole process was carried out in one ice-water bath to remove heat from the exothermic mixture. The monomer solutions were always prepared to pH 2.7–3.4. Other monomer solutions were prepared in the same way. After N_2 was purged into the monomer solutions for 20 min to reduce the dissolved oxygen to less than approximately 3 ppm, the cleaned copper panels were immersed in the monomer bath. White and swollen polymer coatings gradually formed on the surfaces. The thicknesses of the coatings were controlled by the immersion time or monomer concentration.¹⁰ The wet coatings were rinsed in a mildly stirred, 15% aqueous NMP solution for 30 min. The coatings were then dried in an air oven at 110°C for 1 h and 200°C (or 165°C) for 2 h, with a slow air purge. The samples were cooled slowly in the oven with the heat turned off.

For an evaluation of the time-dependent weight gain or coating growth rate of polymer coatings on copper, numbered copper substrates were first weighed after pretreatment of the copper but before polymerization. After polymerizations for different times, the samples were rinsed, dried, and cooled as described previously. The coating substrates were then weighed again. The weight difference divided by the coating surface area (two sides) was taken as the weight gain (mg/cm^2) of each coating sample. The samples for gel permeation chromatography (GPC) measurements were prepared by the wet polymer coatings being scraped from the substrates immediately after polymerization and by the removed material being rinsed in a large amount of methanol. The filtered material was next washed with methanol three times and dried *in vacuo* to a constant weight.

Characterization

ATR-FTIR or FTIR spectra were obtained with a Nicolet 60SX-FTIR spectrometer with an IR mi-



Scheme 2 Torsion joints used for measuring the shear strengths of coatings on copper.²¹

croscope, an ATR lens, and a touching sensor. A Waters 550C-150 gel permeation chromatograph with a Waters 410 differential refractometer and Ultrastyrigel columns was used to measure the molecular weights of coatings. A PerkinElmer DSC-7 thermal analysis instrument was used at a heating rate of 10°C/min. A torsional testing method, developed by Bell and Lin,²¹ was used to determine the adhesive bonding strengths of the coatings to the copper surfaces. The joint setup is shown in Scheme 2. The adhesive between the two coated copper surfaces was prepared from a stoichiometric mixture of Shell Epon Resin 828 and methylene dianiline at 100°C. Shell Epon Resin 828 was purchased from Miller-Stephenson Chemical Co., Inc. Water-uptake experiments were done by weight gain in water at room temperature. The XPS data were obtained with a Kratos HX instrument with an $\text{Mg K}\alpha_{1,2}$ anode. The X-ray gun was operated at 15 kV and 300 W, and the pressure in the sample chamber was between 5×10^{-6} and 1×10^{-5} Pa. An acidic or basic solution of a 25% NMP and 75% (1% Na_2SO_4) aqueous salt solution (v/v), acidified to pH 4 by the addition of H_2SO_4 or made basic to pH 9 by the addition NaOH, was used in corrosion tests. The pinhole tests were carried out in a 0.35% NaCl solution with 0.2% phenolphthalein (easily showing purple bubbles at surface defects), with one 2 cm \times 5 cm Pd net as a positive electrode and with each copper sample as a negative electrode.

RESULTS AND DISCUSSION

Mechanism Studies of Polymerization

Polymerization reactions of St and maleimide derivatives have been studied for many years in the presence of initiators.^{22,23} The S-Poly process only occurs through the interaction between a monomer solution and a metal surface, without addi-

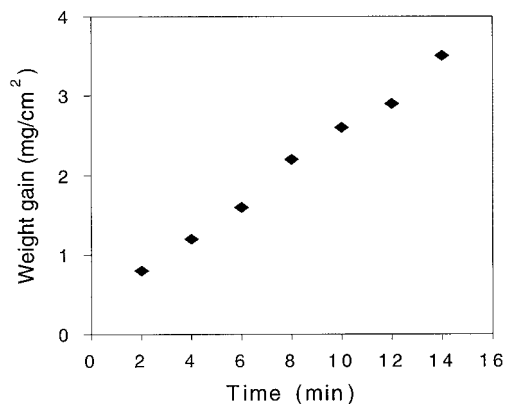
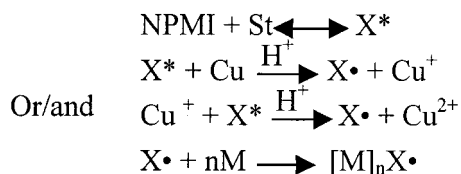


Figure 1 Coating growth on copper 110 as a function of time. The monomer solution NPMI/St/MEA/BMI (0.1/0.2/0.1/0.005M) was used.

tional initiators.^{8,10} A Lewis acid–base theory has been used to explain the initiation step in the NPMI/St/MEA/BMI system for aluminum.¹⁰ A redox mechanism has been described in the chain initiation step for steel substrates.⁸ In these S-Poly systems, St is a strong electron donor, NPMI is a strong electron acceptor, and MEA is a weak electron acceptor. NPMI and St easily form a donor–acceptor or charge-transfer (CT) complex, which is consistent with many previous studies.^{24,25} In this system, copper also requires the participation of a monomer complex in the initiation step. With respect to the actual initiation process for this S-Poly system, experimental results show that copper behaves like steel. In Figure 1, there is a linear dependence of the coating growth rate on time, which is similar to the kinetic behavior of the S-Poly system for steel.⁸ Furthermore, copper has the same order of magnitude of redox potential as steel (iron) in contrast to aluminum.²⁶ We previously discovered that polymerization occurs when a copper or Cu(I) salt appears in a monomer solution.⁸ Therefore, a possible mechanism is shown as follows:¹⁵



where X* is the CT complex, X· is the CT complex with one free radical, and M is a monomer. In the S-Poly process, when copper is immersed in the monomer solution, the copper surface is first oxi-

dized to release electrons and form Cu(I) or Cu(II) in the presence of an acid. An electron is released in each oxidation process. At the same time, the CT complex accepts electrons and reduces into a free radical or diradical, which initiates the polymerization.

The termination reaction may involve combination, chain transfer to a monomer and/or solvent, or disproportionation between two growing chains.²⁷ If the termination occurs exclusively by disproportionation, the expected polydispersity index (PDI) is around 1.5. If the combination reaction totally dominates, the PDI should be approximately 2.0.^{28,29} However, the PDI has been found to vary between 2 and 6 in our S-Poly systems, which may suggest that neither disproportionation nor combination reactions are the sole cause of terminating polymer chains. Further studies of the reaction kinetics are required to determine if a chain-transfer reaction dominates termination of the polymer chains.

Incorporation of EEM into the Copolymer

Previous work¹⁰ has shown that copolymer coatings obtained from the NPMI/St/MEA/BMI system include a close to 1/1 ratio of NPMI and St units and random MEA units. Here two experiments were performed to determine how the three monomers (NPMI, St, and EEM) were incorporated into the polymer chains. First, concen-

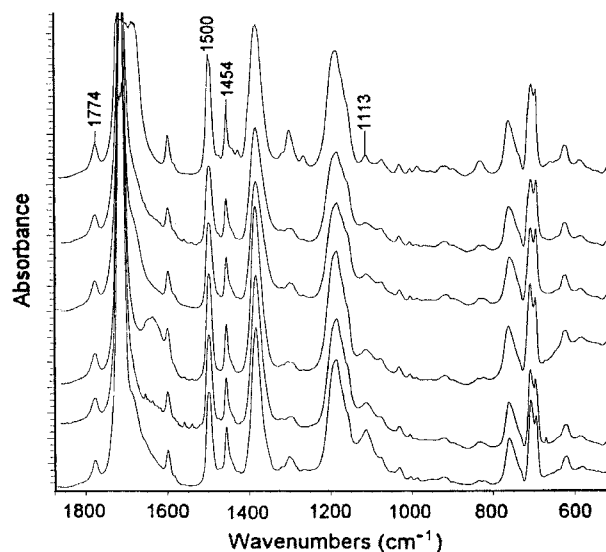


Figure 2 FTIR spectra of the NPMI/St/EEM copolymers for which the NPMI/EEM concentration ratios were 0.18/0.02, 0.15/0.05, 0.12/0.08, 0.1/0.1, 0.05/0.15, and 0.02/0.18M from top to bottom ([St] = 0.2M).

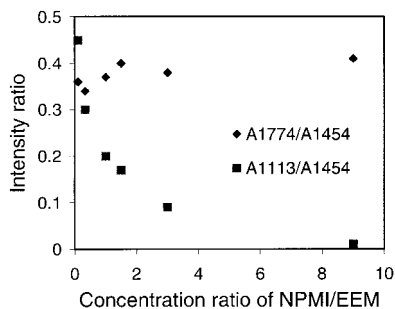


Figure 3 FTIR intensity ratios of NPMI and EEM peaks to St as functions of the NPMI/EEM concentration ratio in monomer solutions ($[St] = 0.2M$).

tration ratios of NPMI to EEM were varied, with concentrations of both St and the total acceptors being kept at $0.2M$. Wet polymer coatings were scraped from the copper surface, washed with ethanol, and dried. The relative quantities of NPMI, St, and EEM in the copolymer coatings were confirmed by a comparison of the peak intensities in FTIR spectra (Fig. 2). The spectra for each composition were normalized with the intensity of the peak at 1454 cm^{-1} , which is a characteristic absorption peak of the St unit. Two other peaks at 1113 and 1774 cm^{-1} were assigned to the $-\text{C}-\text{O}-\text{C}(=\text{O})-$ group of EEM and $-\text{C}=\text{O}$ group of NPMI, respectively. The A1774/A1454 and A1113/A1454 intensity ratios are plotted in Figure 3. The A1774/A1454 ratio is independent of the monomer concentrations (ca. 0.4), showing an approximate 1/1 ratio of NPMI and St units in the copolymers.¹⁰ However, the ratio of EEM units to St units decreased significantly as the relative amount of NPMI increased and the concentration of EEM decreased. This indicates the random incorporation of EEM units into the St/NPMI copolymer. This result is further confirmed in Figure 4. The peak intensity ratio was obtained with the same calculation method. When the concentration of NPMI and St was kept at 0.1 and $0.2M$, respectively, and the concentration of EEM was varied from 0.025 to $0.2M$ in the monomer solution, the ratio of NPMI units and St units still remained about 1/1 in the polymer. However, the relative amount of EEM increased gradually as the concentration of EEM in the feed increased.

Effect of EEM on the Molecular Weight

In the NPMI/St S-Poly system, the molecular weight of the NPMI/St copolymer changed considerably when the monomer concentration and so-

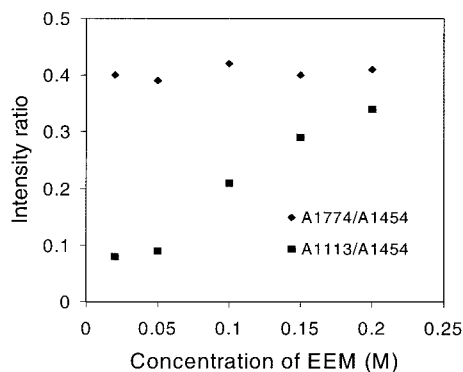


Figure 4 FTIR intensity ratios of NPMI and EEM peaks to St as functions of the EEM concentration in monomer solutions ($[St]/[NPMI] = 0.2/0.1M$).

lution pH were varied.¹⁰ In these experiments, the coating time was fixed at 5 min and the solution pH was held at 3.0. If the concentrations of St and NPMI were maintained at 0.2 and $0.1M$, respectively, the resulting NPMI/St copolymer had a number-average molecular weight (\overline{M}_n) of about 33,000 and a weight-average molecular weight (\overline{M}_w) of 122,000. Figure 5 shows that the apparent \overline{M}_n value of the copolymer coating increased gradually with increasing EEM concentration in the monomer solution, which means that the random introduction of EEM units into the copolymer slightly affects the polymerization kinetics. However, \overline{M}_w doubled when the concentration of EEM was increased to $0.15M$, perhaps resulting from the variance in the molecular weight of EEM.¹⁵ Because EEM is a mixture of monomers, the average number of units (n) in its chemical structure is 3 (from the manufacturer; see Scheme 1).

Effect of EEM on the Thermal Properties

The coatings were prepared from NPMI/St/MEA/BMI ($0.1/0.2/0.1/0.005M$) solutions with different

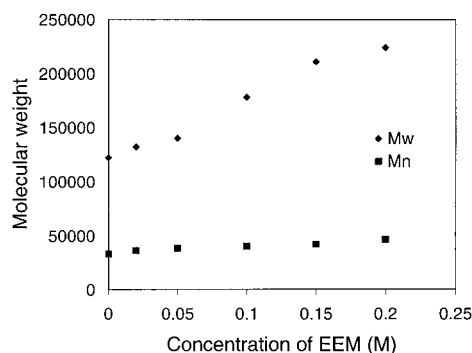


Figure 5 Effects of EEM concentrations in monomer solutions on the apparent molecular weights of the NPMI/St/EEM copolymers ($[St]/[NPMI] = 0.2/0.1M$).

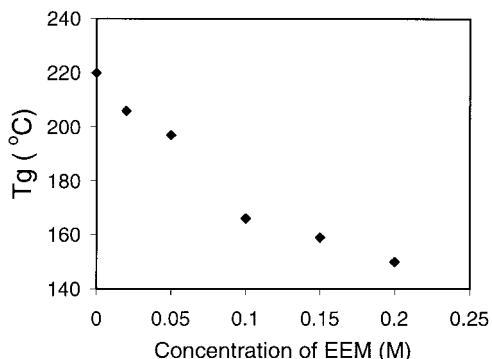


Figure 6 Effects of EEM concentrations in monomer solutions on T_g values of the NPMI/St/EEM copolymers ($[\text{St}]/[\text{NPMI}] = 0.2/0.1M$).

added concentrations of EEM. Thermogravimetric analysis results showed that the decomposition temperatures of these coatings were 385–405°C. Figure 6 shows the effect of EEM on the glass-transition temperature (T_g). T_g values of the coatings decreased significantly when the concentration of EEM in the feed was increased. It was only 148°C when the EEM concentration in the monomer solution was 0.2M. At the same time, the wet coating adhesion seemed to decrease.

Effect of EEM on Other Properties

To produce low- T_g and stable S-Poly coatings, we selected the monomer solution NPMI/St/EEM/MEA/BMI (0.1/0.2/0.1/0.1/0.005M), and the following coating properties were measured. Figure 7 shows that the coatings without EEM had lower adhesive bond shear strength (27 MPa) to copper than to aluminum (35 MPa), perhaps resulting from the different roughnesses of metal surfaces or slightly different copolymer compositions. When EEM was introduced into the copolymer, the adhesive bonding strength of the coatings increased to 32 MPa. The carbonyl group in the EEM structure may be helpful for adhesion to the copper substrate.

Measurements of water uptake show that water absorption was only 1.58 wt % for coatings without EEM after 3 days but 3.02 wt % when EEM was introduced (0.1M). This is probably related to the oxygen groups present in EEM, which easily form hydrogen bonds with water. This is very similar to the effect of increased MEA concentration in the monomer solution;¹⁰ a higher MEA content in the polymer also increased water absorption.

Formation of Fluorinated Coatings

S-Poly coatings including EEM obtained from an NPMI/St/EEM/MEA/BMI monomer solution (0.1/0.2/0.1/0.1/0.005M) had lower T_g 's and good adhesion to copper but greater water absorption. To further reduce water absorption and improve other properties, we prepared fluorinated coatings (E/F) with a 4FMI/St/EEM/MEA/BMI solution (0.1/0.2/0.1/0.1/0.005M). Two kinds of coatings, labeled E and F, were compared from an NPMI/St/EEM/MEA/BMI solution (0.1/0.2/0.1/0.1/0.005M) and a 4FMI/St/MEA/BMI solution (0.1/0.2/0.1/0.005M), respectively.

Characterization of Fluorinated Coatings

ATR-FTIR spectra in Figure 8 show that the F coatings have three obvious peaks at 1508, 1230, and 832 cm^{-1} that are different from those of the E coatings and are assigned to the aromatic C—C stretch vibration, the *N*-phenyl stretch vibration, and the maleic out-of-plane C—H bend vibration, respectively. There is one characteristic peak at 1113 cm^{-1} in the spectrum of the E coatings. The E/F coatings have all absorption peaks of the F coatings, along with one broad shoulder at 1113 cm^{-1} .

XPS data were obtained to determine how much fluorine was present near the surfaces of the samples (see Table I). There was no fluorine in the E coatings, and there was 2.7% fluorine in the E/F coatings. The F coatings had about 3.5% fluorine on the surface. Furthermore, the surface compositions of these coatings could be approximately confirmed. For the F coatings, the copolymer units were 4FMI ($\text{C}_{10}\text{H}_6\text{FNO}_2$), St (C_8H_8), MEA ($\text{C}_{10}\text{H}_{12}\text{O}_5$), and BMI ($\text{C}_{21}\text{H}_{14}\text{N}_2\text{O}_4$). The BMI units were neglected because of the very

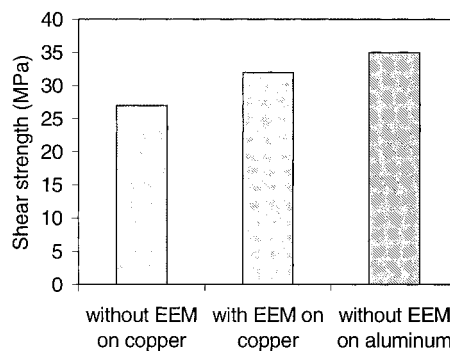


Figure 7 Joint shear strengths of coatings on aluminum and copper.

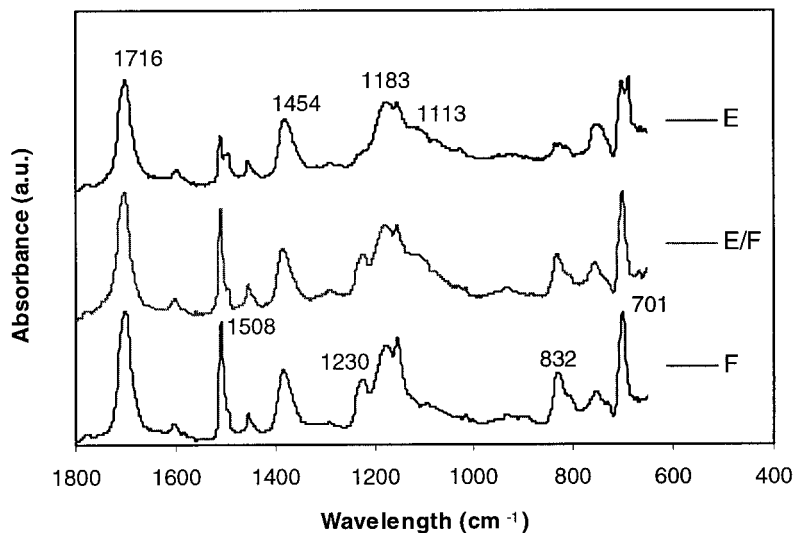


Figure 8 ATR-FTIR spectra of E, E/F, and F coatings on copper.

small amount of BMI present in the monomer solution. Based on the relationship of the atomic concentrations of C, O, and F (or N) and the atomic ratio of each unit, the ratio of 4FMI/St/MEA units in the copolymer was calculated to be 5.0/4.9/2.0 (42.0/41.2/16.8%) or 5.6/4.9/2.0 (44.8/39.2/16.0%). In both cases, the 4FMI/St ratio was somewhat higher than 1, which might have resulted from experimental error in the XPS analysis or the presence of a compositional gradient in the coatings.

For the E and E/F coatings, it was difficult to determine the ratio of each coating unit on the surface because the MEA, EEM, and St units were all composed of C and O atoms. However, we can estimate the total content of MEA and EEM units in the copolymer coatings. Suppose that maleimide derivatives and St still form a 1/1 copolymer^{10,16} even when MEA, EEM, or BMI is introduced. Therefore, the ratio of 4FMI/St/MEA/EEM units of the E/F coatings can be regarded as $a/a/b/c$. The EEM unit structure is $C_{12}H_{20}O_5$ if n is 3 on average (see Scheme 1). Therefore, two equations are obtained based on the atomic concentra-

tions of F and O for the E/F coating surface in Table I:

$$a = 2.7 \quad (1)$$

$$2a + 5b + 5c = 15.1 \quad (2)$$

There are three unknowns but two equations. However, if we want to know the total contents of MEA and EEM units in the copolymer, we can still solve these equations. $a/a/(b + c)$ is 2.7/2.7/1.94, which means 36.8/36.8/26.4% for the ratio of 4FMI/St/(MEA + EEM) units. Based on the atomic concentrations of N and O, this ratio will change to 3.2/3.2/1.74 (39.3/39.3/21.4%). With the same method, the ratio of NPMI/St/(MEA + EEM) units is 36.1/36.1/27.8% for the E coatings.

Table II shows that the T_g value of the fluorinated coatings is 192.4°C. However, the E/F coatings have a T_g value very close to that of the E coatings because of the replacement of rigid NPMI units with rigid 4FMI units. Sometimes, small cracks on the surfaces of the F coatings were observed under an optical microscope (50×), perhaps resulting from the low contents of MEA units in the copolymer or the higher T_g value of the F coatings. There is a large difference among their \bar{M}_n values and small changes for their \bar{M}_w values, resulting in different PDIs; the reason for the lower \bar{M}_n value for the F coatings is not clear. Actually, the incorporation of EEM into the coatings may cause a difference in the correspondence

Table I Atomic Concentrations (%) of the S-Poly Coatings

Coating	F	O	N	C
E	—	16.4	2.8	79.0
F	3.5	14.0	3.7	76.3
E/F	2.7	15.1	3.2	76.8

Table II T_g 's and Apparent Molecular Weights of the Coatings

Coating	T_g (°C)	Coatings Without MEA and BMI ^a		PDI
		\overline{M}_n	\overline{M}_w	
E	166.2	40,100	178,000	4.44
F	192.4	21,800	179,200	8.22
E/F	161.5	32,500	159,600	4.91

^a The E, F, and E/F coatings were crosslinked copolymers that could not be measured by GPC because of their low solubility. By the removal of the crosslinkers MEA and BMI from the monomer solutions, the obtained coatings were measured with THF as a solvent.

of the samples to the GPC calibration with polystyrene. All of the molecular weight measurements should be considered apparent because of this calibration.

Adhesion and Immersion Measurements

The shear strength of the E/F coatings was 31 MPa, similar to that of the E coatings. However, the F coatings showed lower bonding strength to copper (~23 MPa) because of the introduction of fluorinated groups into the copolymer coatings. Water-uptake results showed that the weight gain of the E coatings increased to almost 4.1% after a 25-day immersion in water at room temperature. If there were no cracks on the F coatings, they showed very good hydrophobicity, only 1.7% water absorption. The E/F coatings showed somewhat higher weight gain than the F coatings (2.2%).

Most fluorinated materials have very weak adhesion to substrates (or metals) because of their low surface energy.^{10,16,30,31} However, the E/F coatings retained good adhesive bonding strength and showed much better water impermeability when 4FMI replaced NPMI and EEM was introduced into the copolymer. In this system, the total ratio of EEM and MEA units was 21.4–26.4% for the coating surface, which means there were 20–30% EEM and MEA units in the bulk copolymer. Perhaps these E/F copolymers showed obvious amphiphilic properties^{32,33} because of the strong hydrophobicity of 4FMI units and the hydrophilicity of MEA and EEM units. During the drying process (a higher temperature than T_g), the E/F copolymers might have formed a partly ordered layer structure on copper, which provided more

chances for MEA and EEM units to form strong interactions with copper effectively and prevented water from moving through or penetrating the coatings easily.

Corrosion and Pinhole Tests

Sharp corners on copper test pieces tended to result in cracking and lower deposition at the edges. It was advantageous to round the sharp edges. Although most of the coating surfaces appeared defect-free, in some cases cracks were observed on the surface of the F coatings. After the samples were immersed in an acidic (pH 4; see the Characterization section for details) or basic solution (pH 9) for 10 h, there was a considerable difference, as shown in Table III. In pinhole tests, when the applied voltage was 20 V, most of the E coatings showed bubbles on the surface. For the F coatings, 3 of 10 samples were cracked (the cracks were found under an optical microscope) before immersion in the acidic solution. There were another two samples showing bubbles after immersion, resulting in 50% defect-free samples. Eighty percent of the E/F coatings retained bubble-free surfaces at 20 V for 5 min. However, most of the samples showed better resistance in the pinhole tests after immersion in the basic solution. There were no bubbles on any of the E/F coatings, on 70% of the F coatings (except for two coupons that exhibited cracks before immersion), and on 40% of the E coatings. Therefore, the E/F coatings exhibited excellent resistance in the corrosion and pinhole tests, and more coatings remained bubble-free on the surface after immersion in the basic solution than in the acidic solution.

Table III Percentage of the Samples Passing the Pinhole Tests

Sample	Pinhole Tests at 20 V for 5 min ^a	
	In an Acidic Solution (pH 4)	In a Basic Solution (pH 9)
E	None	40%
F ^b	50%	70%
E/F	80%	100%

^a There were 10 coupons of samples with 20–25- μ m-thick coatings in each test.

^b Two or three coupons of the F coatings showed defects without acidic or basic corrosion due to the initial cracks on the sample surfaces.

CONCLUSIONS

A redox mechanism for the initiation polymerization of the S-Poly process on copper was first proposed in an NPMI/St/MEA/BMI system. When EEM was introduced into this system, FTIR studies indicated the random introduction of EEM units into the copolymer coatings. The copolymer had a similar apparent value of \overline{M}_n but a much higher apparent value of \overline{M}_w with an increasing concentration of EEM in the monomer solution. The T_g value of these coatings decreased to about 150°C when the concentration of EEM was increased to 0.2M. The coatings exhibited good adhesion strength to copper but lower resistance in immersion and corrosion tests. However, when 4FMI was incorporated into the aforementioned S-Poly system, fluorinated coatings including EEM units (E/F) possessed a strong bonding strength to copper and good water impermeability. They also showed better protective properties than other kinds of coatings in corrosion and pin-hole tests.

REFERENCES

- Kowalczyk, T. C.; Kosci, T. Z.; Singer, K. D.; Beuhler, A. J.; Wargowski, D. A.; Cahill, P. A.; Seager, C. H.; Meinhardt, M. B.; Ermer, S. *J Appl Phys* 1995, 78, 5876.
- Hussmann, E. K. *Proc Soc Photo-Opt Inst* 1983, 381, 152.
- McGovern, W. R.; Schmutz, P.; Buchheit, R. G.; McCreery, R. L. *J Electrochem Soc* 2000, 147, 4494.
- Kozuka, H.; Kajimura, M. *J Am Ceram Soc* 2000, 83, 106.
- Ju, D. Y.; Nishida, M.; Hanabusa, T. *J Mater Process Tech* 1999, 93, 243.
- Geier, J.; Oestman, E.; Lessmann, H.; Fuchs, T. *Contact Dermatitis* 2001, 44, 43.
- Zhang, X.; Bell, J. P. *J Appl Polym Sci* 1996, 62, 1303.
- Zhang, X.; Bell, J. P. *J Appl Polym Sci* 1997, 66, 1667.
- Agarwal, R.; Bell, J. P. *Polym Prep (Am Chem Soc Div Polym Mater Sci Eng)* 1996, 75, 341.
- Agarwal, R.; Bell, J. P. *Polym Eng Sci* 1998, 38, 299.
- Agarwal, R.; Bell, J. P. *J Appl Polym Sci* 2000, 76, 875.
- Zhang, X.; Bell, J. P. *Polym Eng Sci* 1999, 39, 119.
- Zhang, X.; Bell, J. P. *Mater Sci Eng A* 1998, 257, 273.
- Baker, N. Ph.D. Dissertation, University of Connecticut, 2001.
- Nainani, K. M.S. Dissertation, University of Connecticut, 1998.
- Zheng, H.; Davis, G.; Bell, J. P. *Polym Eng Sci* 2001, 41, 1970.
- McCulloch, I.; Yoon, H. *J Polym Sci Part A: Polym Chem* 1995, 33, 1177.
- Bongiovanni, R.; Malucelli, G.; Messori, M.; Pilati, F.; Priola, A.; Tonelli, C.; Toselli, M. *J Appl Polym Sci* 2000, 75, 651.
- Kim, J.-H.; Lee, S.-B.; Kim, S. Y. *J Appl Polym Sci* 2000, 77, 2756.
- Rao, B. S. *J Polym Sci Part C: Polym Lett* 1988, 26, 3.
- Bell, J. P.; Lin, C. J. *J Appl Polym Sci* 1972, 16, 1721.
- Horowitz, C.; Mangaraj, D.; Iorio, J. A. U.S. Pat. 4,106,955 (1978).
- Dichter, M.; Horowitz, C. U.S. Pat. 4,421,569 (1982).
- Cheng, H.; Zhao, G.; Yan, D. *J Polym Sci Part A: Polym Chem* 1992, 30, 2181.
- He, J.; Wang, J.; Si, S. *Acta Polym Syn* 2000, 5, 559.
- Fontana, M. G. *Corrosion Engineering*; New York: McGraw-Hill, 1986.
- Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Elsevier Science: Oxford, 1995.
- Baker, C. A.; Williams, R. J. P. *J Chem Soc* 1956, 2352.
- Dawkins, J. V.; Yeaden, G. *Polymer* 1979, 20, 981.
- Bay, F.; Bouchard, P. O.; Darque-Cretti, E.; Felder, E.; Scoto-Sheriff, S. *J Adhes Sci Technol* 1999, 13, 931.
- Li, X.; Aoki, A.; Miyashita, T. *Langmuir* 1996, 12, 5444.
- Sekiya, A.; Ishida, H.; Tamura, M.; Watanabe, M. *Chem Lett* 1987, 1593.
- Rodriguez-Parada, J. M.; Kaku, M.; Sogah, D. Y. *Macromolecules* 1994, 27, 1571.