

Coating Formation by Spontaneous Polymerization on Aluminum: Various Monomers

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ABSTRACT: Spontaneous polymerization to give conformal, uniform coatings on metals has been expanded to a series of different monomers. The monomer 4-fluoro maleimide, when copolymerized with styrene, a coupling agent, and a bis-maleimide crosslinker, imparts very low dielectric constant (2.4) to the coating while retaining high temperature resistance. Diethyl fumarate, with the same comonomers, enhances ductility and provides an adjustable glass transition temperature. Addition of glycidyl acrylate to the monomer system provides reactivity of the coating to epoxy resins. Kinetic studies using these monomers were consistent with the free radical polymerization mechanism. The rate of reaction seemed limited by the diffusion of species to the reaction site. Extent of incorporation of the new monomers into the chain backbone was verified, and adhesion and corrosion resistance properties examined. The data illustrate the versatility of the conformal, chrome free spontaneous polymerization process. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 875–885, 2000

Key words: coating formation; spontaneous polymerization; aluminum; monomers; corrosion

INTRODUCTION

Spontaneous polymerization is a new process by which polymer coatings can be synthesized directly on metal surfaces. Formation of protective coatings on aluminum and steel has been discussed in earlier papers.^{1–4} The process is conducted at room temperature in a single tank of monomers, acidified water, and solvent if needed; no initiator or external driving force is required. The key difference of this process from other conventional coating processes such as dip coating, spray painting, or electrophoretic deposition is that here the polymer chains “grow” at the metal surface instead of being deposited. Significant advantages of the process are that the coatings

formed are conformal and pinhole free. As a result, uniform coatings can be formed on objects with complex topographies. The process also results in very good adhesion of the polymer coating to the metal substrate, because wetting of the metal surface is easier by monomers as compared with wetting by polymers.

The spontaneous polymerization process on aluminum involves the use of donor and acceptor monomers, such that the electron densities around the double bond, between the two monomers, are very different. Under suitable conditions such monomer pairs can polymerize rapidly at room temperature and result in an alternating copolymer. Many different initiation and polymerization mechanisms for such donor–acceptor systems have been proposed and reviewed.^{5–7} The novel aspect of the present process is that the donor (styrene) and acceptor (*N*-phenyl maleimide) monomers spontaneously copolymerize on

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aluminum surface in the absence of any externally added initiator. By controlling the solvent quality of the monomer solution the polymerization occurs only at the aluminum–solution interface.

The first coatings obtained on aluminum using spontaneous polymerization are described in a previous paper.¹ Coatings were made using styrene (St) and *N*-phenyl maleimide (NPMI), and other comonomers added were 2(methacryloyloxy)ethyl acetoacetate (MEA), and bis-maleimide (BMI). Addition of these monomers improved the uniformity and adhesion of these coatings to aluminum. Spontaneous polymerization has also been observed on steel by Zhang and Bell, where protective coatings were successfully synthesized.²

Other acceptor monomers such as 4-fluoro maleimide (4FMI), diethyl fumarate (DEF), and glycidyl acrylate (GA) were also used to synthesize coatings having different properties. In all cases, the donor monomer used was styrene, and the crosslinker used was BMI. Polymer coatings were made using 4FMI/St/MEA/BMI, NPMI/St/DEF/BMI, and NPMI/St/GA/BMI systems. In most cases, the ratio of the two acceptor monomers was varied, keeping the styrene and BMI concentrations constant.

Kinetic studies were performed in which the resultant coating thickness was measured as a function of polymerization time, temperature, and monomers ratio in feed, for the 4FMI/St/MEA/BMI system. Evidence of incorporation of DEF and GA into the NPMI/St/BMI system was obtained using infrared spectroscopy. The effect of varying monomer ratios in feed on the T_g of the resultant polymer was also measured.

Adhesion of the coatings to aluminum was measured using a torsional testing method, where the shear strengths of the joints were measured. The protective properties of the coatings were analyzed using accelerated salt fog corrosion testing and electrochemical impedance spectroscopy (EIS). Dielectric constants and electrical breakdown potentials were also measured to test for suitability of these coatings for electronic applications.

EXPERIMENTAL

Materials

Monomers

Styrene from Aldrich Chemical Co. was vacuum distilled at 40°C to remove inhibitor. NPMI and

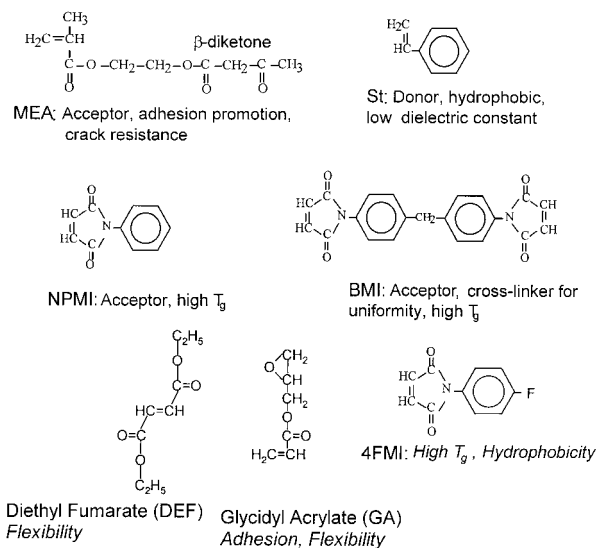


Figure 1 Monomers used for spontaneous polymerization and their roles.

BMI were purchased from Mitsui Toatsuo Chemical Co. NPMI was purified by dissolving it in boiling cyclohexane and subsequent crystallization on cooling. Bright yellow needle-like crystals were obtained after drying at 60°C in vacuum. BMI was used as obtained. 4FMI was synthesized from 4-fluoro aniline and maleic anhydride by adapting the method of Rao.⁸ MEA from Aldrich Chemical Co. and GA from Lancaster Chemicals were purified by passing through a DHR-4 inhibitor removal column from Scientific Polymer Products. The monomers were refrigerated after purification. DEF was used as received. The structures of these monomers are shown in Figure 1. *N*-methyl pyrrolidinone (NMP) was purchased from Fisher Scientific Co. and used as received.

Aluminum Alloys and Pretreatment

The aluminum used was 2024, 6061, or 7075 alloy. Al 2024 (4.5% Cu, 1.5% Mg, 0.6% Mn) has a high shear strength and is used as a structural aircraft alloy, but is highly prone to corrosion. Al 6061 (1.0% Mg, 0.6% Si, 0.2% Cr, 0.27% Cu) is used in heavy duty structures where corrosion resistance is needed.⁹

The aluminum samples were given one of the following two pretreatments: (1) Samples were degreased with 5% aqueous Micro (a laboratory general purpose alkaline soap) solution, rinsed with distilled water, and treated with 5% hydrofluoric acid for 30 s, followed by a distilled

water rinse. (2) Samples were grit blasted using 170 mesh alumina and rinsed with distilled water. The aluminum samples were coated immediately after the cleaning process.

Monomer Feed Solution Preparation

The monomers to be used were dissolved in NMP. Dilute aqueous sulfuric acid (0.025*M*) was then added slowly to the solution while stirring. The NMP/water ratio was such that the monomers were close to their solubility limit. This ratio depends on the monomer feed composition and concentration. A higher NMP ratio improves the solvent quality, but if too high the formed polymer will dissolve. A 63/37 volume ratio of NMP/water was used for making monomer solutions containing NPMI, St, BMI, GA, and DEF. For solutions containing 4FMI, an NMP/water ratio of 70/30 was used. A clear solution was obtained by this method. Solutions containing NPMI were yellow and those with 4FMI were light brown but clear.

Polymerization Procedure

Polymerization Cell

Polymerization was conducted in Pyrex beakers of various sizes, depending on the sample size, or in custom-designed 1 × 8 × 8 cm polypropylene tank compartments. The polypropylene tanks allowed polymerization of large surface areas with small solution volumes. Typically, 3" × 3" aluminum coupons could be polymerized using 50 mL solution. The post polymerization rinsing bath was a 12 cm diameter bath, gently stirred.

Process

The monomer solution was first purged with nitrogen to reduce the dissolved oxygen concentration to less than 2 ppm, since oxygen quenches free radicals. When the cleaned aluminum was immersed in the monomer bath, a white, swollen polymer coating began to form. Polymerization time for samples in the bath was varied from 3 to 120 min.

Following the polymerization, the coated sample was immersed in a gently stirred 10–15% aqueous NMP solution for about 15 min to remove excess NMP and trapped residual monomers. The coated coupons were then oven dried at 150°C for 1 h to remove most of the water and NMP, and then at 225–250°C for 4–6 h to remove the last traces of NMP. Cooling was done slowly over 3–4 h.

Characterization

Sample Preparation

The polymers to be characterized were all spontaneously polymerized on aluminum unless stated otherwise. The swollen polymer was scraped from the coated aluminum prior to the drying step. This polymer mass was then washed with ethanol in order to remove NMP, water, and any residual monomers. The polymer precipitated to the bottom and the clear solution was decanted. This washing with ethanol was repeated 3–4 times. The polymer precipitate was then dried in vacuum at 100°C for 24 h, yielding a white powder.

Fourier Transform Infrared Spectroscopy

Fourier transform infrared (FTIR) spectra for the polymer coatings were taken using a Nicolet 60 SX FTIR spectrometer with a deuterated triglycine sulfate detector and a germanium/KBr beam splitter. Samples were prepared by pressing KBr pellets from mixtures of about 1–2 mg polymer and 150 mg KBr powder. FTIR was used to detect the incorporation of the acrylic monomers into the St–NPMI copolymer.

Thermal Analysis

A Perkin Elmer DSC-7 instrument was used to estimate the glass transition temperature (T_g) of the polymer coatings made from varying monomer feed compositions. The instrument was calibrated using indium and tin standards. A 10–12 mg sample was placed in aluminum pans and scanned over 50–300°C at a heating rate of 20°C/min. A mid point method was employed to estimate the T_g .

Adhesion Measurements

Adhesion of the polymer coatings to the aluminum substrate was measured using the torsional testing method of Bell and Lin.¹⁰ The joint assembly is shown in Figure 2. Using this test, the polymer–metal joints can be broken in a pure shear mode and the joint shear strength can be measured accurately. For water immersion tests, the joints were soaked in 60°C water for 3 days and broken. Adhesion of polymer coatings formed from various monomer feeds was measured using this method under both dry and wet conditions.

Electrical Properties

Dielectric constant measurements of the polymer coatings were performed on a Time Domain Di-

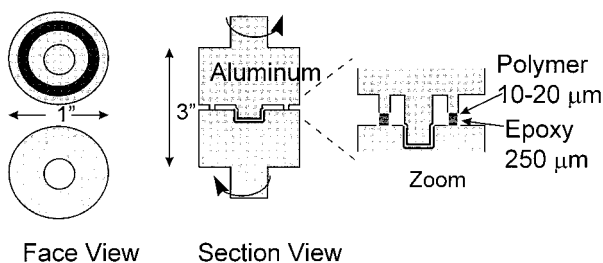


Figure 2 Schematic of the torsional testing joints.¹⁰ Dark ring is the contact face.

electric Spectrometer at room temperature. Various polymer compositions were tested in order to examine the effect of different monomers on the electrical properties. Frequencies applied ranged from 0.001 to 1000 Hz. Coatings of thickness 25–35 μm were used.

Corrosion Testing

Salt Fog Testing. Corrosion protection properties of the polymer coatings were studied by exposing samples to a 5% NaCl salt fog, following the American Society for Testing and Materials (ASTM B-117) test method. Samples tested were grit blasted Al 6061 and 2024 alloy coupons and had a 25 μm thick polymer coating.

Electrochemical Impedance Spectroscopy. Electrochemical impedance studies were performed on coated samples exposed to 0.5M NaCl solution. The impedance cell was a 2" diameter, 4" high Pyrex cylinder sealed to a 3" \times 3" specimen via a Viton O-Ring, which provided an exposed specimen area of 18.3 cm^2 . The cells were open to atmosphere, permitting natural aeration. The aluminum specimen was the working electrode; the counter electrode was graphite and a saturated calomel electrode was used as a reference electrode. Impedance spectra were obtained with a Solatron Model 1250 Frequency Response Analyzer, coupled with a Solatron Model 1286 Potentiostat and an online computer. Z-plot software was used to control the experiments, and equivalent circuit modeling was performed with Boukamp's EQUICRT software.¹¹ Measurements were performed using an EG&G Princeton Applied Research model 263 potentiostat/galvanostat driven by an IBM compatible PC. Impedance spectra were recorded for various immersion times.

RESULTS AND DISCUSSION

The mechanism of spontaneous polymerization on aluminum has been discussed in detail in earlier

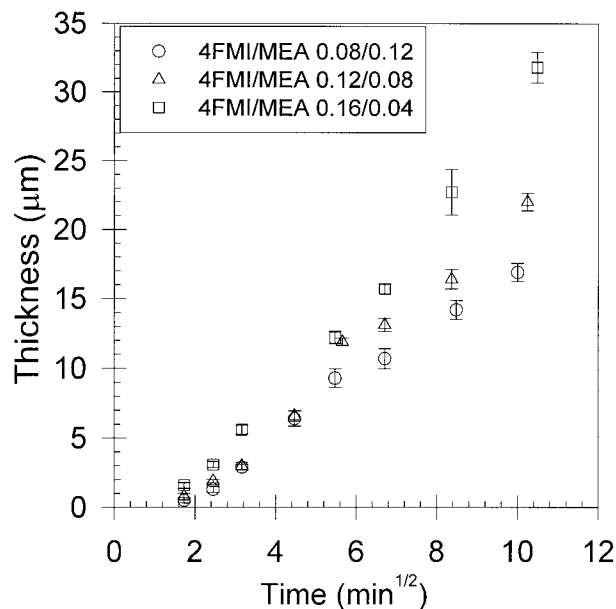


Figure 3 Dependence of polymerization kinetics on 4FMI/MEA ratio in feed 4FMI/MEA/St/BMI = $x/x/0.2/0.005M$. (Error bars indicate standard deviation.)

works.^{1,3} Various coatings made from using the new monomers mentioned above were evaluated for their kinetics and properties.

Kinetic Studies of the 4FMI/MEA/St/BMI System

In this series of experiments, the 4FMI/MEA/St/BMI system was used in an effort to make coat-

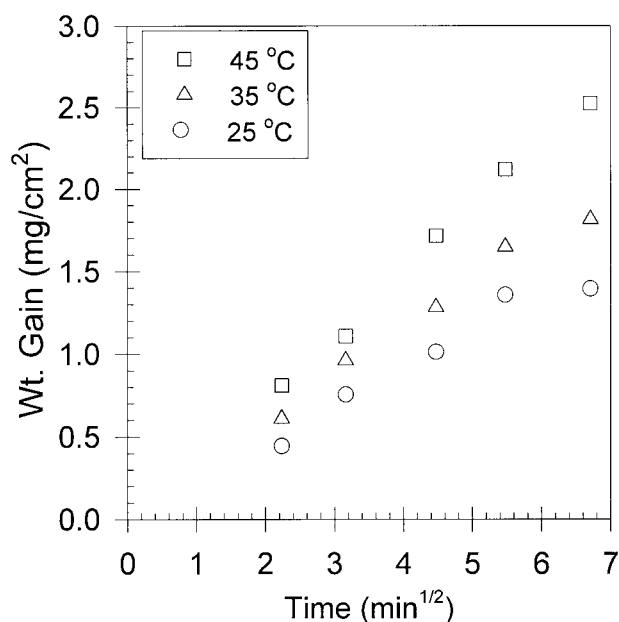


Figure 4 Dependence of polymerization kinetics of 4FMI/MEA/St/BMI system on polymerization temperature. 4FMI/MEA/St/BMI 0.1/0.1/0.2/0.005M.

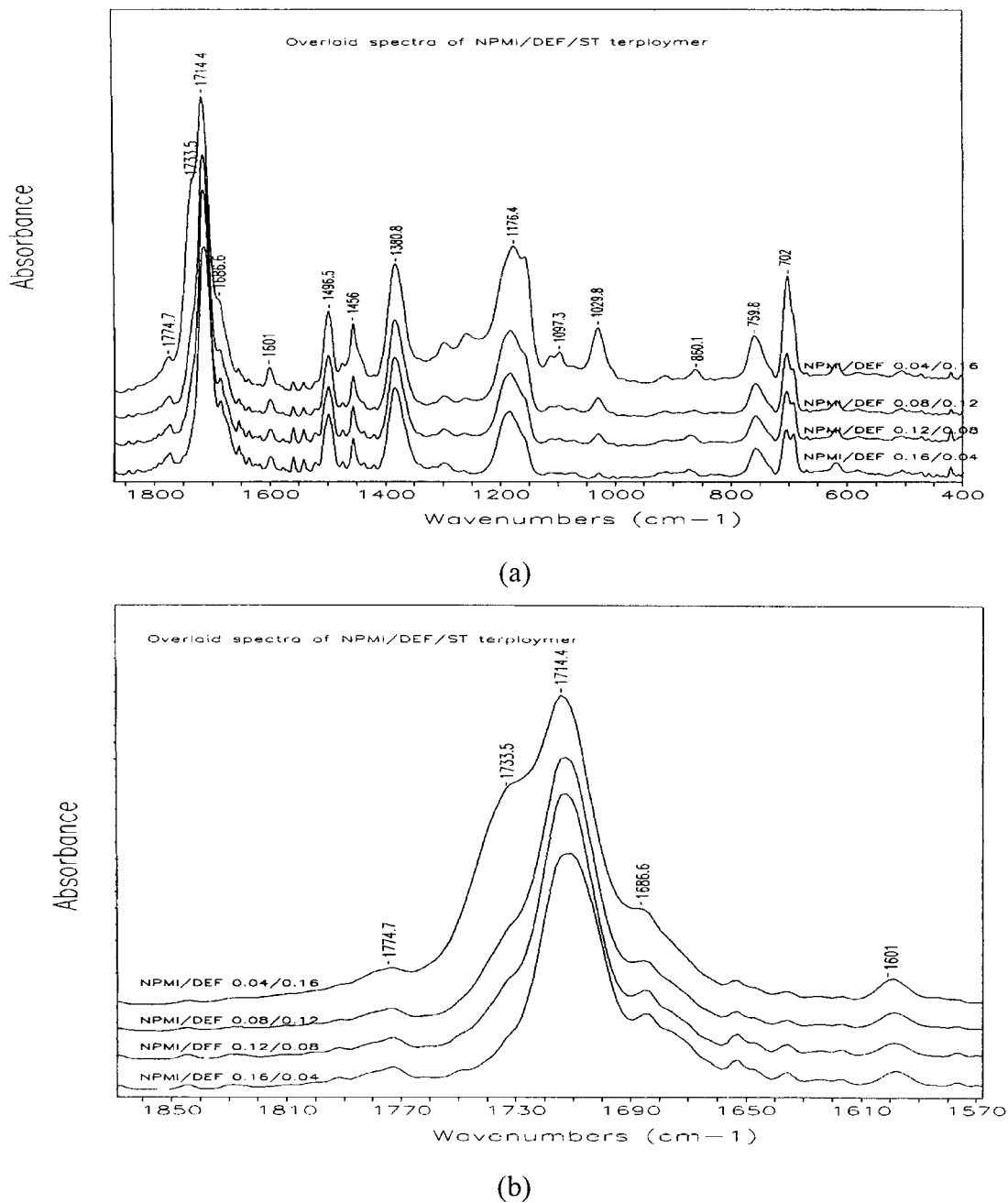


Figure 5 FTIR showing incorporation of DEF in increasing amounts in the coating, as the DEF/NPMI ratio is increased, by the appearance of the 1733 cm⁻¹ peak.

ings with high corrosion resistance associated with its hydrophobic properties and low surface energy. For the 4FMI–St copolymers, molecular weight was in the range of 70,000 g/mol, based on gel permeation chromatography, using polystyrene standards. The kinetics of this system are shown in Figure 3. The coating thickness increased linearly as a function of the square root of

time, which indicates the rate of polymerization was diffusion controlled. The rates for the three compositions showed dependence on the maleimide–MEA ratio, and decreased with decreasing 4FMI in the system; a similar effect was reported for the *N*-phenyl maleimide/MEA/styrene/BMI system.³ Kinetic studies were also performed as a function of temperature and are shown in Figure

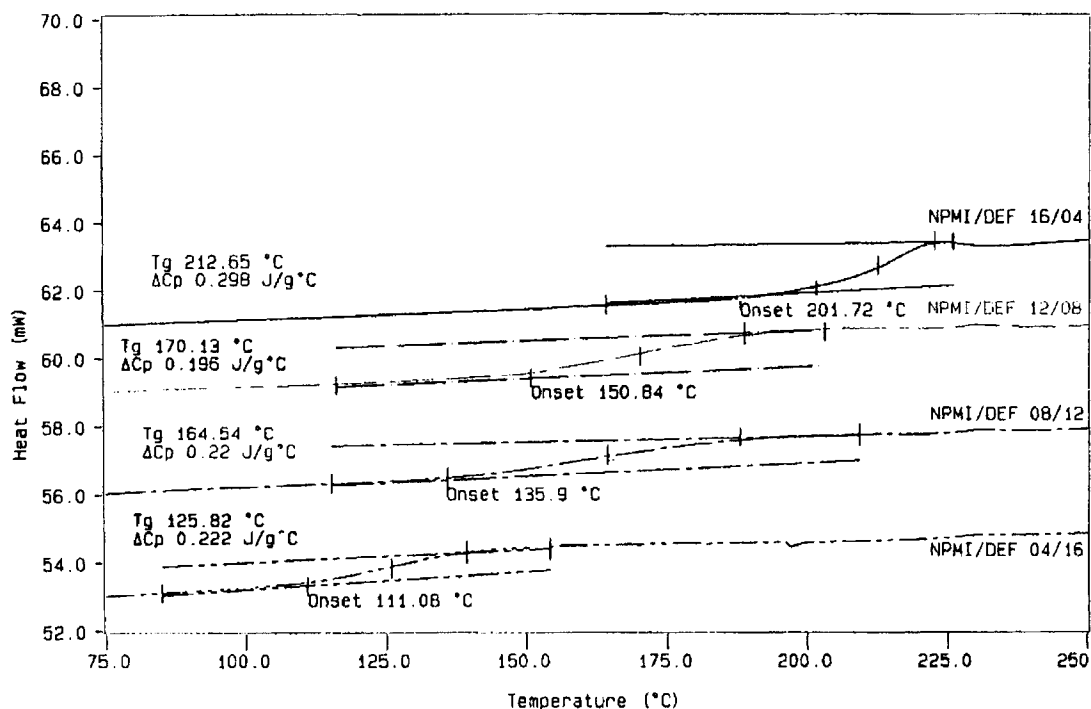


Figure 6 Differential scanning calorimeter thermograms for NPMI/DEF/St polymers from various NPMI/DEF feed ratios.

4. The polymerization rate increased significantly with increasing temperature.

The kinetic data show that polymerization rates are dependent upon monomer concentrations and temperature. Alternatively, the desired coating thickness can easily be controlled by varying polymerization time, as illustrated on Figure 4. In absence of MEA, the 4FMI/St/BMI coatings alone are brittle, as one might expect from the high glass transition temperature. Adhesion measurements and protective properties of these coatings are discussed in a later section.

Incorporation of Other Monomers into the NPMI/St/BMI System

In order to modify the properties of the polymer coatings, other acceptor monomers were introduced into the feed. Incorporation of such other types of monomers allows coating properties to be tailored to meet specific applications.

Incorporation of Diethyl Fumarate

DEF is a good acceptor monomer due to the presence of C=O groups on each of the carbons (Fig. 1); it does not homopolymerize under normal con-

ditions. Copolymerization of various substituted fumarates with donor monomers such as styrene and N-vinyl carbazole has been reported.¹²⁻¹⁴ DEF has a high reactivity toward styrene and alternating copolymers have been reported.¹³

Polymer coatings were formed by varying the NPMI/DEF ratio while keeping the styrene concentration constant. The incorporation of DEF was visible clearly through FTIR, as shown in Figure 5. As the amount of DEF in polymer increased, a shoulder at 1733 cm⁻¹ from the carbonyl ester appeared, and also a distinctive band at 1029 cm⁻¹ from the {—C—O—(C=O)—} group in DEF increased in intensity. The T_g of the polymer also decreased to as low as 125°C. The DSC results are shown in Figure 6. The molecular weight of the NPMI/DEF/St polymer showed a slight decrease with increasing amount of DEF. Incorporation of DEF offers the possibility of synthesizing flexible coatings with good adhesion.

Incorporation of GA

GA is a weak acceptor monomer and was used for two reasons: (1) adding epoxide groups to the polymer, and (2) reducing the T_g of the resultant coatings. The presence of the epoxide groups can

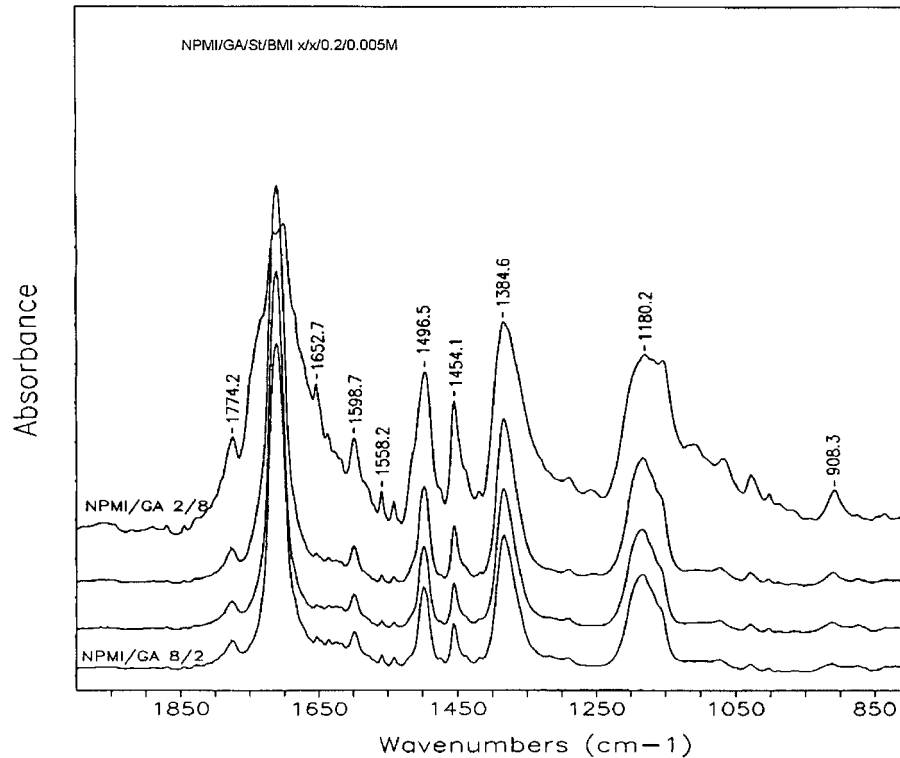


Figure 7 FTIR spectra showing incorporation of GA in increasing amounts into coating, as the GA/NPMI ratio in feed was increased, from the increasing intensity of the 908 cm^{-1} peak from the oxirane group.

make the coatings top coatable by providing good intercoat adhesion with epoxy based powder coat systems, where the spontaneously formed coating serves the function of a primer. The homopolymer of GA, poly(glycidyl acrylate), has a low T_g of about 10°C . Thus its incorporation should make the coatings more flexible and crack resistant. Coatings were made using varying NPMI/GA ratios and keeping the St and BMI amounts constant. The incorporation of GA into the polymer coating was again confirmed using FTIR; the spectra are shown in Figure 7. As the concentra-

Table I Dependence of T_g on the NPMI/GA Feed Ratio

Monomer Feed NPMI/GA/St/BMI (M)	Glass Transition Temp T_g ($^\circ\text{C}$)
0.16/0.04/0.20/0.0025	218
0.12/0.08/0.20/0.0025	208
0.08/0.12/0.20/0.0025	191
0.04/0.16/0.20/0.0025	176

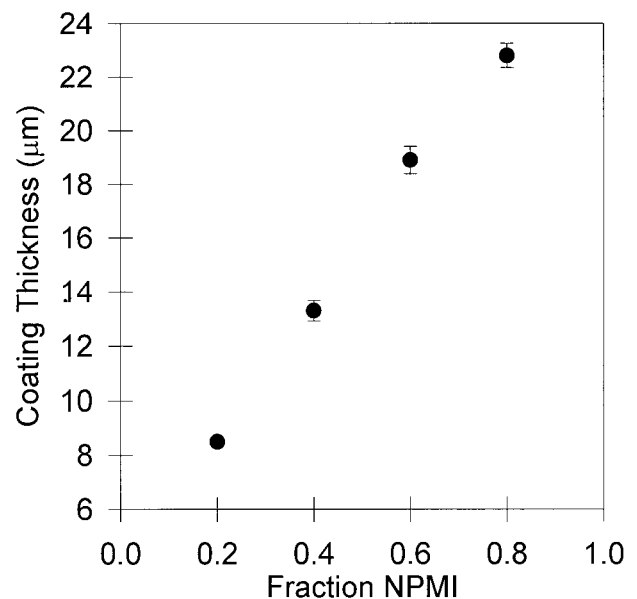


Figure 8 Coating thickness obtained for different NPMI/GA ratios in feed. NPMI/St/GA/BMI = $x/0.1M/(1-x)/0.0025M$. Ninety minute polymerization.

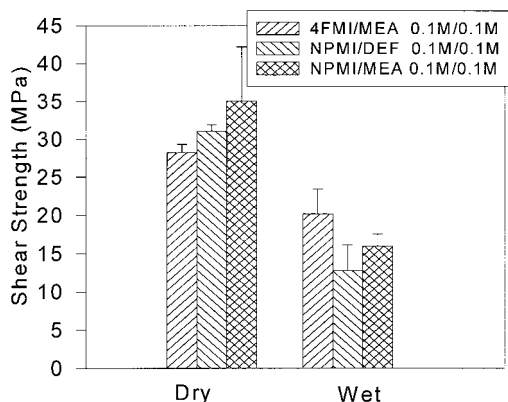


Figure 9 Adhesion measurements of coating compositions under dry conditions and after 3 days immersion in 60°C water (error bars indicate 95% confidence interval). Styrene and BMI were also present in same amounts of 0.2 and 0.005M, respectively, in all three systems.

tion of GA in feed increased, the peak at 910 cm^{-1} due to the epoxide groups increased in intensity along with the increase in the weak 1030 cm^{-1} band $\{-\text{C}-\text{O}-(\text{C}=\text{O})-\}$. The glass transition temperatures of the polymers formed also decreased with increasing concentration of GA in polymer as shown in Table I, from 212 to 125°C. This decrease in T_g indicated that more flexible coatings can be made by incorporating low T_g monomers in larger amounts into the coating. Again, the rate of coating formation decreased with decreasing NPMI concentration in feed. The coating thickness obtained for various NPMI/GA feed ratios, shown in Figure 8, decreases linearly with decreasing NPMI concentration in feed for a given polymerization time. This again is an indication that only the NPM–St diradical is the initiating intermediate in this monomer system.

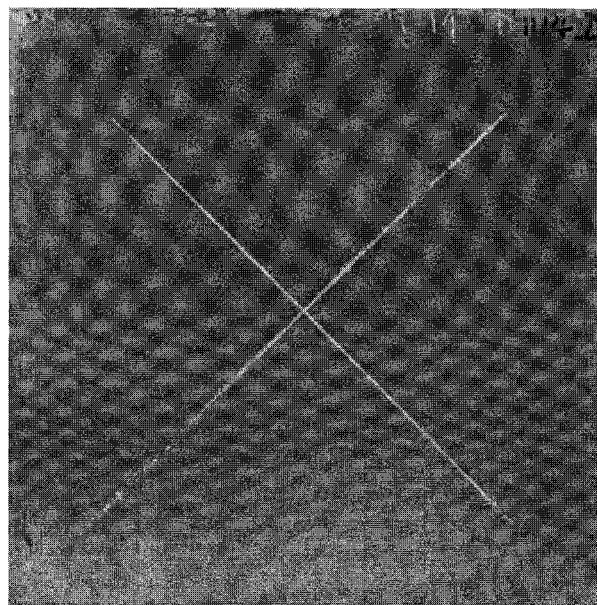


Figure 10 Al 2024 sample coated from 4FMI/MEA/St/BMI 0.1/0.1/0.2/0.005M coating bath after 2000 h exposure to salt fog at 35°C (ASTM B-117 method).

Adhesion Studies

The shear strengths of systems containing NPMI/MEA, NPMI/DEF, and 4FMI/MEA, along with styrene and BMI, are shown in Figure 9. The dry strength was highest for the system containing NPMI/MEA, at 35 MPa, and lowest for the system containing 4FMI/MEA, at 28 MPa. The wet strength for the 4FMI/MEA system was measured at 21 MPa, however, which was considerably higher than wet results for the other two systems. This points to the more hydrophobic nature of coatings containing 4FMI.

Dielectric Constant

The dielectric constant value was lower than 3.0 for coatings made from the three different mono-

Table II Dielectric Constants Measured for Various Polymers

Frequency (Hz)	Dielectric Constant		
	NPMI/MEA/St/BMI 0.05/0.05/0.10/0.0025	NPMI/DEF/St/BMI 0.05/0.05/0.10/0.0025	4FMI/MEA/St/BMI 0.05/0.05/0.10/0.0025
0.001	2.80	2.73	2.49
0.01	2.73	2.69	2.42
0.1	2.68	2.66	2.39
60	2.63	2.62	2.34
1000	2.62	2.60	2.33
10000	2.62	2.60	2.32

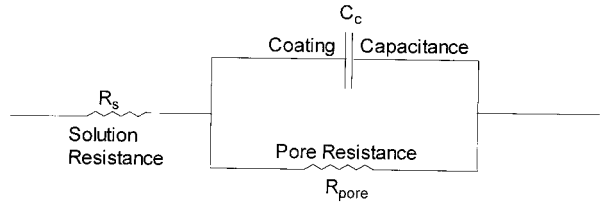


Figure 11 Equivalent circuit diagram used to fit the electrochemical impedance spectra.

mer systems, in the frequency range from 10^{-3} to 10^4 Hz (Table II). Values for commercial polyimides such as Pyralin are higher at about 2.8.¹⁵ The low dielectric constant for these polymers is probably due to the presence of relatively nonpolar styrene units in an alternating sequence along the main chain, and the high T_g of the polymer. The dielectric constant was highest for the NPMI/MEA/St/BMI system, which has a relatively higher concentration of polar groups. For the NPMI/DEF/St/BMI system the dielectric constant was lower, and fluorinated maleimide further lowered the dielectric constant to the range of 2.4. The low dielectric constants of these coatings, especially at low frequencies, make them suitable for use as dielectrics in electronic applications such as circuit boards, where high resistance to heat and potential are required.

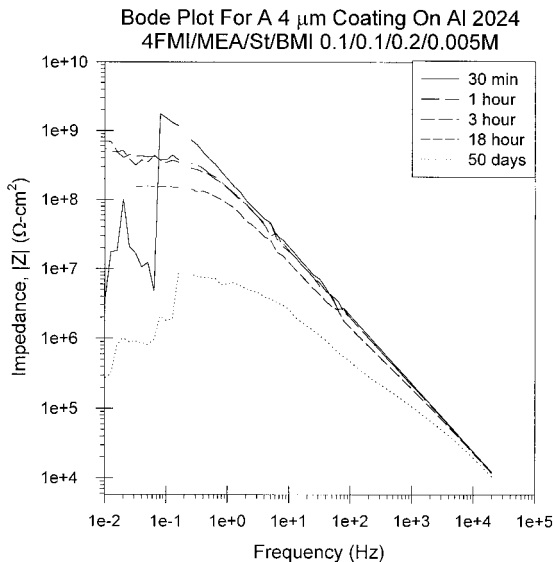


Figure 12 Bode plots at various immersion times of a $4\ \mu\text{m}$ thick coating on Al 2024 made from 4FMI/MEA/St/BMI 0.1/0.1/0.2/0.005M coating bath.

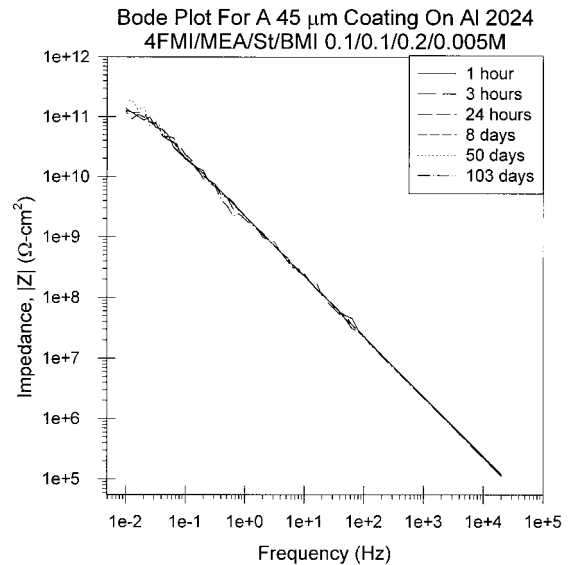


Figure 13 Bode plots at various immersion times of a $45\ \mu\text{m}$ thick coating on Al 2024 made from 4FMI/MEA/St/BMI 0.1/0.1/0.2/0.005M coating bath.

Corrosion Studies

Salt Fog Corrosion Testing

The protective qualities of the polymer coatings were evaluated using the ASTM B-117 salt fog accelerated corrosion test.¹⁶ Both 6061 and 2024 alloys were tested. The 2024 alloy is highly prone to corrosion due to presence of 4–5% copper. Figure 10 shows results from an Al 2024 sample coated from a 4FMI/MEA/St/BMI 0.1/0.1/0.2/0.005M solution exposed for 2000 h. A 0–1 mm creep was seen around the scribed “X,” and no field blisters were seen. Samples with the 4FMI coating thickness of $10\ \mu\text{m}$ also did not show any visible corrosion after 3000 h exposure. These results are consistent with those previously reported for the NPMI/St/MEA/BMI system.¹

Electrochemical Impedance Spectroscopy

EIS is a very widely used technique to study corrosion behavior of systems such as polymer coated metals.^{17,18} By applying the AC signal over a wide range of frequencies and recording the current, the resistive and capacitive components of system can be calculated using a simple equivalent circuit such as one shown in Figure 11.

Figure 12 shows a Bode plot of a $4\ \mu\text{m}$ thick coating on Al 2024 alloy. The impedance of the coating decreased with exposure time. This indicates the permeation of salt and water through

Table III Values of the Various Elements of the Equivalent Circuit Obtained by Fitting the Data for an Al 2024 with a 4 μm Coating Made from 4FMI/MEA/St/BMI 0.1/0.1/0.2/0.005M Solution

Immersion Time	R_{po} ($\Omega\text{-cm}^2$)	C_c ($\mu\text{F}/\text{cm}^2$)	R_{sol} ($\Omega\text{-cm}^2$)
1 h	2.26e7	1.87e-2	-20
3 h	1.82e7	1.84e-2	-20
18 h	8.78e6	3.3e-2	-60
50 days	5.05e5	39.7e-2	-20

some pores and possible initiation of localized corrosion. After 50 days of exposure, the impedance was still much higher than that for bare aluminum. A drop in the impedance of a coating can also occur if only a few defects are present in the coating. No corrosion was seen upon visual inspection. Thus EIS analysis reveals corrosion processes occurring at the microscopic level, which cannot be simply correlated to visual observations. Figure 13 shows the Bode plot for a 45 μm thick coating, made from 4FMI/MEA/St/BMI 0.1/0.1/0.2/0.005M solution, for exposure up to 106 days. No significant change was observed in the impedance of the coating, indicating excellent resistance to salt and water diffusion. Further, no corrosion could be detected upon visual inspection.

In order to gain some insight into the corrosion process, the impedance behavior of the 4 μm thick coating was modeled using the simple equivalent circuit described earlier. This circuit can be used to model behavior of polymer coated metal systems. The values of the pore resistance R_{po} and coating capacitance C_c after fitting the data are shown in Table III.

A decrease in the pore resistance indicates the formation of conductive paths and possible damage to the coating.¹⁸ An increase in the coating capacitance occurs due to the salt water uptake by the polymer. Since the dielectric constant of the salt solution is much greater than that of the polymer, even a small amount of water uptake is detected as an increase in the coating capacitance. A negative value of the solution resistance R_{sol} is because of a relatively large error in measuring a small resistance. An overlay of modeled data with the experimental data for 3 h immersion time is shown in Figure 14. In the Nyquist plots shown in the figures, the phase angle θ is defined as $\tan(\theta) = Z_{imag}/Z_{real}$ (Z''/Z'). The simple equivalent circuit model fits the data well in the

initial exposure times. Some deviations between the experimental data and the model were seen for 50 days of exposure time because the entire corrosion process is much more complex than the one represented by the equivalent circuit model.

CONCLUSIONS

The spontaneous polymerization process was applied successfully to form uniform conformal coatings on aluminum using three different monomer systems. Polymerization occurred only on the surface of the metal and not in the solution. In all systems discussed here, the rate of polymerization seemed to be limited by diffusion of the monomers to the reaction site, based upon the linear increase in the thickness of the coatings formed as a function of the square root of polymerization time. The rate constants for different coatings were dependent on the specific monomers; however, a coating of desired thickness could be obtained by varying either polymerization time or temperature. Varying monomer concentration in-

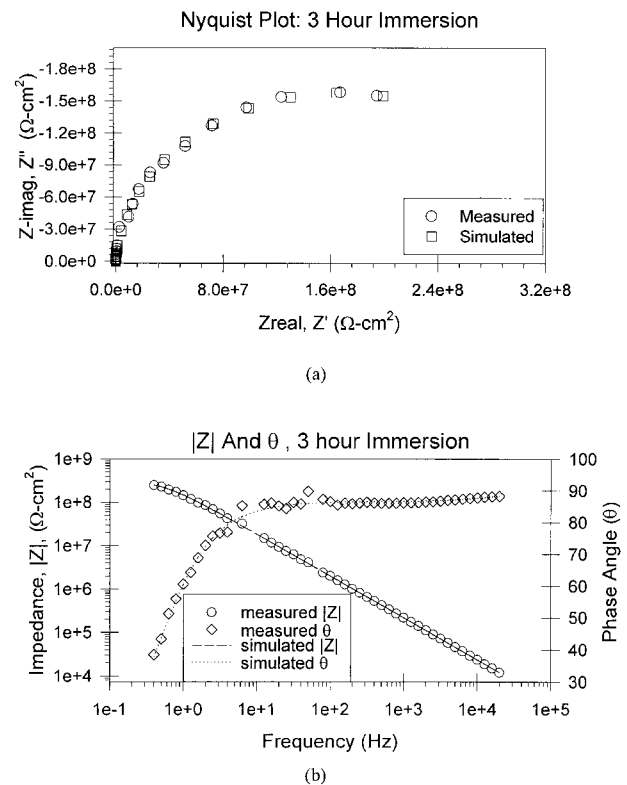


Figure 14 Nyquist and Bode plots along with equivalent circuit model fits for sample from Figure 12: 3 h immersion.

fluences both the polymerization rate and the molecular weight of the coating.^{1,2}

The coating compositions investigated had excellent adhesion to the aluminum substrate, and after soaking in 60°C water the 4FMI test joints retained to up to 70% of their dry strength value. These results correlated well with impedance values on the same coating system, where a very little drop was seen as a function of immersion time in salt water. Both these observations indicate low water uptake in the coatings. Coatings less than 10 μm thick also exhibited excellent protective behavior. Salt spray results were also excellent in light of the fact that no passivating pretreatment was provided to the aluminum.

High glass transition temperatures and low dielectric constant data for the tested coatings make them suitable for use as conformal coatings in electronic applications.

Final properties of the coatings made by spontaneous polymerization can be tailored to specific requirements by using different monomers in different ratios. Increasing amounts of GA and DEF were found in the polymer, from their infrared spectra, as their ratio relative to NPMI was increased. Increasing amounts of GA or DEF also lowered the glass transition temperatures of the coatings and made them more flexible. Other acrylate and methacrylate monomers can be incorporated and more complex polymer systems can be formed in order to obtain a wider range of physical and chemical properties. Thus the spontaneous polymerization process provides a novel method to form protective coatings using an environmentally benign, chrome free process.

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