

The *In-Situ* Synthesis of Protective Coatings on Steel Through a Surface Spontaneous Polymerization Process

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ABSTRACT: This article reports a new method of forming protective coatings on metal surfaces. The process is very simple and environmentally friendly. Polymerization occurs spontaneously on the metal surface after the immersion of a cleaned metal substrate into a dominantly aqueous monomer solution. A layer of coating with uniform thickness is formed *in situ*. The coating thickness can be controlled from 1 to 50 μm . This article will describe the spontaneous polymerization process as it occurs specifically on steel and for a 4-carboxyphenyl maleimide–styrene monomer system. The polymerization propagation mechanism is free radical, and alternating copolymers are always obtained in this system, even with significant changes in the monomer feed composition. This could be attributed to the formation of a charge transfer complex between the monomer pair. The incorporation of the rigid imide ring into the copolymer backbone significantly improves the coating's thermal properties, and styrene enhances the electrical properties. These properties are relatively insensitive to the monomer feed composition, supporting the formation of alternating copolymer. The effects of several process variables have been evaluated, including solution pH, monomer concentration, solution temperature, and monomer feed composition. The proposed initiation mechanism involves the direct electrochemical reduction of the monomer by the steel surface to generate the initiating free radicals. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1667–1680, 1997

Key words: coating; spontaneous polymerization; steel; conformed; corrosion protection; substituted maleimides

INTRODUCTION

Coatings are widely used on metal surfaces for decorative and/or protective purposes. Coating techniques that can provide high-quality coatings inexpensively and without using environmentally hazardous materials are very desirable in industrial applications. We have developed a new method of forming protective coatings on metal surfaces.^{1,2} The process is very simple and environmentally friendly. Polymerization occurs spontaneously on

the substrate surface upon immersion of a cleaned metal object into a dominantly aqueous monomer solution. A uniform layer of coating is formed *in situ*. The coating thickness is controllable in the range of 1–50 microns. A variety of monomers can be chosen to yield the desired properties, and the process is applicable to a variety of metals.

This process is superior to conventional methods in several ways. Because the coating is synthesized *in situ* on the substrate surface, uniform and pinhole free coatings can be obtained, even on objects with complex geometry. The starting monomer solution is of low viscosity, resulting in improved adhesion because the monomer solution wets the surface very well. Room temperature and atmosphere are

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used, and process control is relatively simple. Finally, dominantly aqueous systems can be used, which have the advantages of less pollution, lower cost, and easier process control.

The phenomena of spontaneous polymerization of two monomers in solution has been observed by several researchers and has been reviewed extensively.³⁻⁷ For example, maleic anhydride and phenyl vinyl sulfide spontaneously polymerize to produce alternating copolymer without the aid of an initiator.⁸ Several theories have been devised to explain this phenomenon. The most common theories involve the formation of a donor acceptor complex between the monomers.⁶ Weak electron transfer occurs from the donor monomer to the acceptor monomer, and the complex formed usually has a bright color. Such complexes have been found experimentally in many systems, such as maleic anhydride-styrene.⁹ Iwatsuki and Yamashita rationalized the polymerization behavior of charge transfer complexes according to their strength.⁷ They established a correlation using the equilibrium constant of the charge transfer complex, K , which is defined as the following:



where D is the donor monomer, A is the acceptor monomer, and DA is the charge transfer complex.

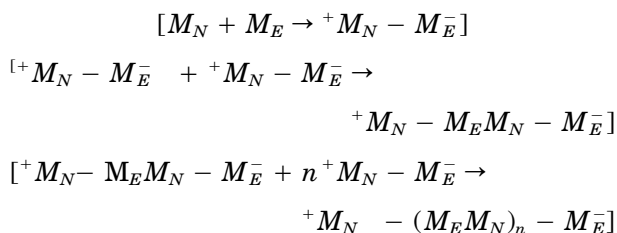
K (L/mol)	Polymerization Mechanism	Reaction Product
0-0.01	free radical with added initiator	random copolymer
0.01-0.1	free radical with added initiator	alternating copolymer
0.1-1.0	spontaneous free radical	alternating copolymer
1.0-5.0	spontaneous ionic	homopolymer
> 5.0	complete electron transfer to form stable complexes	

Iwatsuki and Yamashita believed that spontaneous polymerization can occur by either free radical or ionic mechanism when the complex is sufficiently strong, i.e., when $0.1 < K < 5$. For weak systems, initiators must be added.

The presence of a Lewis acid can enhance the electron-accepting ability of the acceptor monomer. This effect was first discovered by Hirooka

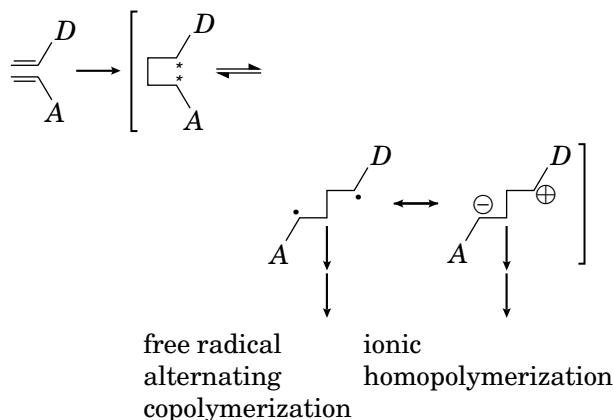
and colleagues, who used ethylaluminum dichloride to synthesize alternating copolymer of acrylonitrile and propylene.¹⁰ The generally accepted explanation¹¹⁻¹⁵ is that the Lewis acid increases the electrophilicity of the acceptor monomer by complexing with its lone pair electrons, such as those of oxygen in the carbonyl group or nitrogen in the nitrile group. Many acceptor monomers have these strong electron-withdrawing groups. Such complexation increases the polarity difference between the donor monomer and the acceptor monomer, resulting in the formation of a stronger complex.

Saegusa and coworkers have extensively explored another mechanism, over a decade of time.¹⁶⁻²¹ They proposed that the monomers form a zwitterionic intermediate, which is responsible for both initiation and propagation.¹⁶ The general scheme involves one electrophilic monomer (M_E) and one nucleophilic monomer (M_N) and is shown below.



Scheme 1

Hall has proposed a bond formation mechanism to explain the spontaneous polymerization phenomena.²² This is based on the assumption that a bond is formed between the donor monomer and the acceptor monomer to generate a tetramethylene intermediate, which is the true initiation species.



Scheme 2

Both diradical and zwitterionic tetramethylene may be formed. The actual species is a resonance hybrids of these two extreme cases and may appear in either character, depending on the monomer system used. Hall's mechanism satisfactorily explained the formation of cyclic byproducts along with polymers by spontaneous polymerization in many systems.²²⁻²⁷

While our polymerization process also occurs spontaneously, it is unique in that the metal surface is essential to the initiation process. Without the substrate, no polymerization was observed, and the monomer solution remained clear for weeks. Apparently, the initiation mechanism involves the interaction between the metal surface and the monomer. In this article, we report our studies of the spontaneous polymerization process as it occurs specifically on steel and propose a mechanism around such interaction to explain this phenomena. The monomer system described here is a 4-carboxyphenyl maleimide (4CPMI)–styrene system. The same process can also be applied to other metals, such as aluminum,² copper, zinc, tin, silver, etc.

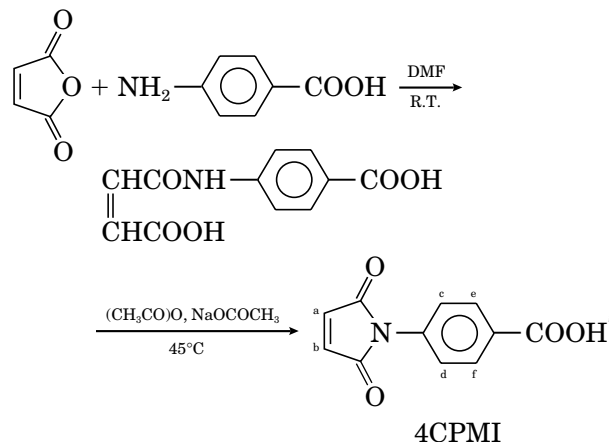
EXPERIMENTAL

Materials

SAE 1010 carbon steel coupons from Q-Panel Company were used as the substrate for this study. Styrene (Fisher Scientific Company) was distilled at 50°C under reduced pressure to remove the inhibitor. The middle fraction was collected and refrigerated until use. All other chemicals, except 4-carboxyphenyl maleimide (4CPMI), were obtained from Fisher Scientific Company and used as received.

4CPMI was prepared in this laboratory from maleic anhydride (MAn) and 4-amino-benzoic acid (ABA) according to the method of Rao²⁸ (see Scheme 3). MAn (45.2 g) and ABA (63.2 g) were dissolved in 250 mL *N,N*-dimethyl formamide (DMF). The mixture was first stirred at room temperature for 1 h. 3.6 g of anhydrous sodium acetate and 72 mL of acetic anhydride were then added, and the temperature was raised to 45°C. The mixture was stirred for another 3 h. The crude 4CPMI was obtained by pouring the reaction mixture into a large amount of water. It was subsequently filtered, washed with water three times, and dried. Recrystallization was conducted in ethanol. Monomer pu-

rity was confirmed by nuclear magnetic resonance (NMR) and differential scanning calorimetry (DSC). The thermogram showed only one sharp melting peak at 241°C.



Scheme 3

The IR spectrum (KBr disk) was as follows: 2971, 1774, 1714, 1604, 1398, 1299, 1214, 1143, 827, and 704 cm^{-1} .

¹H-NMR (*d*₆-DMSO) δ [see the hydrogen position in scheme (3)], measurements were as follows: 13.0 (broad s, 1 H, g); 8.03 (*d*, 2 H, e and f); 7.49 (*d*, 2 H, c and d); and 7.22 (s, 2 H, a and b).

Polymerization

The substrate surface was cleaned using an ammonium-based laboratory detergent, rinsed with an ample amount of distilled water, and dried in a 90°C oven for immediate use. A monomer solution was prepared by first dissolving styrene and 4CPMI in *N*-methyl-2-pyrrolidinone (NMP), then mixing with an appropriate amount of distilled water. The volume ratio of NMP and water used was 56 : 44. The pH of the solution was adjusted to be between 2.6 and 3.6 using a small amount of sulfuric acid.

The simplicity of the process allows the polymerization cell to be easily fabricated. Different sizes and geometry can be used according to the specific need. A beaker, which was the reaction vessel used in this study, suffices in many cases. The prepared monomer solution was poured into the cell, and spontaneous polymerization began on the steel coupon surface immediately after immersion into the solution. Polymerization of the monomer and deposition of the formed polymer

occurred simultaneously on the surface. A layer of white coating was usually visible on the surface within several minutes. The coating at this stage is very swollen and has a large amount of solvent and water trapped within.

After the reaction, the coupon was withdrawn from the cell and immersed in a rinsing bath for one hour. The bath contained a 10 : 90 NMP to water mixture and had mild agitation. This step was to extract the trapped monomers and most of the solvent. Experiments have shown that a small amount of solvent in the rinsing bath is necessary to obtain a clear and smooth coating in the drying process. Otherwise, a white and powdery coating is obtained. The amount of residual solvent after rinsing process can be controlled by a combination of NMP content in the rinsing bath and the rinsing time. Drying was conducted in two stages in an oven with slow air convection: 150°C for 1 hour, and 250°C for 5 hours. The dried sample was cooled down to room temperature slowly to avoid thermal shock. Drying conditions have not been fully studied as yet.

The polymer samples used for characterization were scraped off the substrate immediately after polymerization and precipitated in a large amount of methanol. The filtrate was washed with methanol three times and dried at 60°C under vacuum to constant weight. The amount of polymer formed on the surface was determined gravimetrically.

Characterization

A 500 MHz Bruker NMR spectrometer model DMX-500 was used for the analysis of the monomers and the polymer. A Nicolet 60SX Fourier transform infrared spectrometer (FTIR) was used to characterize the composition of the obtained polymer with a resolution of 4 cm^{-1} . A DSC calorimeter model 2920 and a 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 dielectric constant measurements on the coatings were conducted using a time domain dielectric spectrometer (TDDS) from IMASS, Inc.

RESULTS AND DISCUSSION

Figure 1 shows the ^1H -NMR spectrum of the polymer obtained in d_6 -DMSO. The aromatic protons from both styrene and 4CPMI form two broad

absorptions at 7.98 and 7.13 ppm. The strong absorption at 3.33 ppm is due to the moisture absorbed in the hygroscopic solvent. It also overshadowed the signal from the imide protons appearing in the vicinity. Peaks at 2.17 and 1.91 ppm are assigned to the absorption of the methylene group of styrene, while the $-\text{CH}-$ group absorbs at 2.69 ppm. Absorption of both monomers are absent in the spectrum. This confirmed that the polymerization reaction happened via the opening of the double bond of both monomers.

The IR spectrum of the polymer is shown in Figure 2. The symmetric and asymmetric stretching peaks of the carbonyl groups in the imide ring appear at 1776 and 1714 cm^{-1} , respectively. The peak at 1512 cm^{-1} is attributed to the parasubstituted phenyl ring of 4CPMI. The aromatic carbon—carbon stretching at 1608 cm^{-1} has contributions from both 4CPMI and styrene. The strong absorption at 1383 cm^{-1} is due to the symmetric C—N—C stretching of the imide ring. 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.²⁹ The C—H bending of the vinyl group at 991 and 908 cm^{-1} of styrene and the C=C stretching of imide ring at 949 cm^{-1} of 4CPMI are absent in the spectrum.

To determine the composition of the coating, a calibration was constructed using blends of homopoly (4CPMI) and polystyrene, obtained by solution polymerization. The absorption peak at 1510 cm^{-1} for 4CPMI and that at 1493 cm^{-1} for styrene were chosen as the characteristic peaks. Very good linear correlation was obtained between the absorbance ratio of the two peaks, $A_{1510} : A_{1493}$, and the molar content of poly(4CPMI) in the blend, as shown in Figure 3. All polymerization experiments were stopped at low monomer conversion, and the monomer concentration was assumed to be constant in the analysis. The composition of the copolymers obtained at a wide range of monomer feed ratios was determined using the above calibration, as shown in Figure 4. The molar ratio of 4CPMI and styrene incorporated was found to be always close to 1, despite 4CPMI feed content varying from 20 to 70 mol %. This is in agreement with literature reports on similar monomer systems.^{30–32} Several theories exist to explain such phenomena. One theory accepted by many researchers is the donor—acceptor—complex theory. Presumably, the complex has a significantly higher reactivity than that of either donor

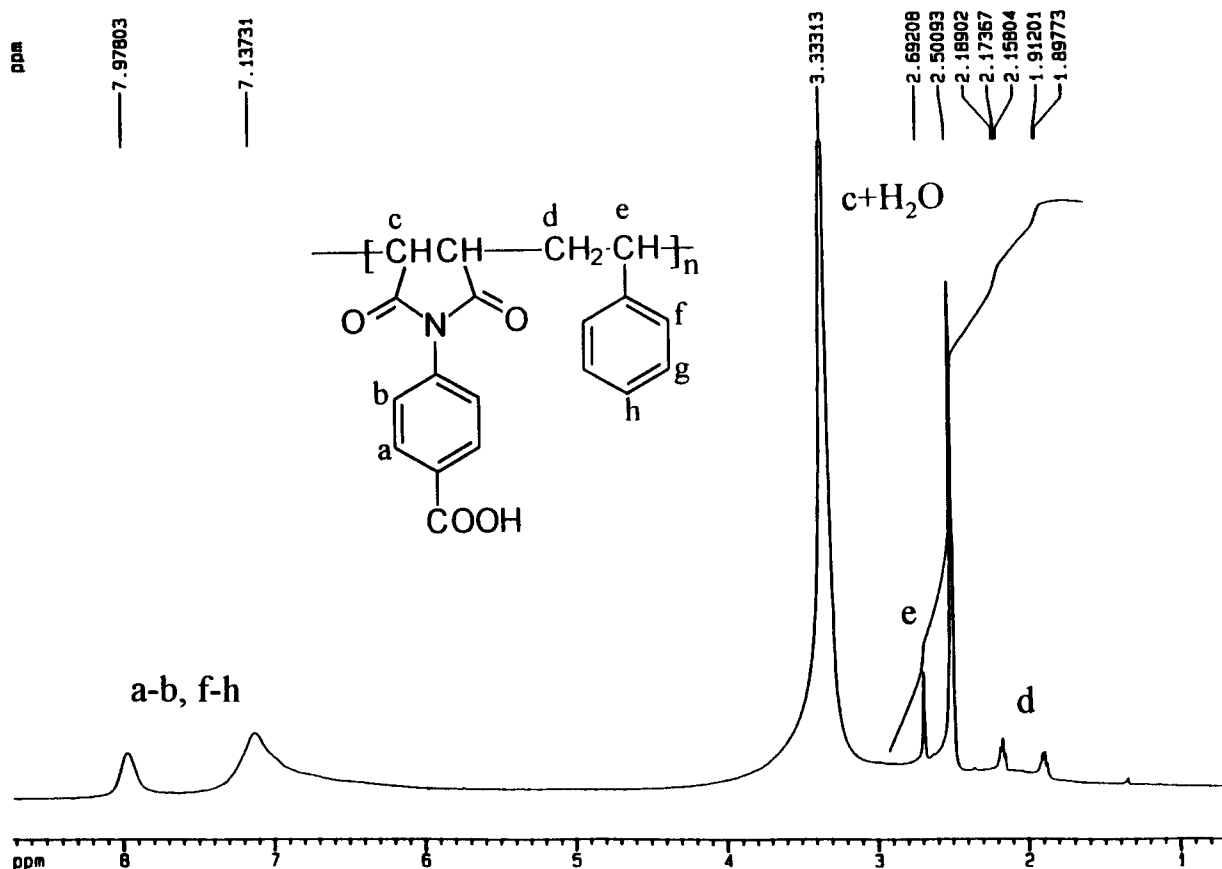


Figure 1 $^1\text{H-NMR}$ spectrum of poly(4CPMI-styrene) in d_6 -DMSO.

or acceptor monomer, resulting in formation of alternating copolymer under all monomer feed compositions. Our previous study on this system has shown that 4CPMI and styrene does form a charge transfer complex.³³ The IR result is therefore consistent with the previous results.

The first trace of the DSC thermogram on the polymer has a broad hump in the low temperature range due to residual methanol. A glass transition temperature of 275°C was observed, as shown in Figure 5. This transition is very reproducible. Thermograms of three subsequent reheats are also included in Figure 5. The transition showed no sign of shifting and is the only transition observed in all four heats. The high T_g is due to the incorporation of 4CPMI into the polymer backbone. The rigid imide ring significantly hinders segmental rotation and thus stiffens the chain. The incorporation of 4CPMI also significantly improved the thermal stability of the copolymer. Under nitrogen atmosphere, the copolymer is stable up to 400°C, as illustrated in the TGA thermogram of Figure 6.

After that, a one-stage decomposition is observed. The improvement in thermal properties as compared to polystyrene suggests that a large proportion of 4CPMI is incorporated into the copolymer. Figure 7 shows the variation of the glass transition temperature as well as the thermal decomposition temperature with the molar content of 4CPMI in the monomer solution. Both properties remained relatively unchanged for polymers obtained from different feed percentages of 4CPMI. This behavior also supports a 1 : 1 copolymerization of 4CPMI and styrene into the polymer chain, in agreement with the FTIR data.

The dielectric constant of the 4CMI-styrene was measured at selected frequencies, shown in Table I. The constant is about 2.6 in the frequency range investigated. This is lower than that of commercial polyimides, which are widely used for insulation in the electronic and electrical industries. On the other hand, it is very close to that of polystyrene. This low value may be due to having a structure similar to polystyrene. In a separate di-

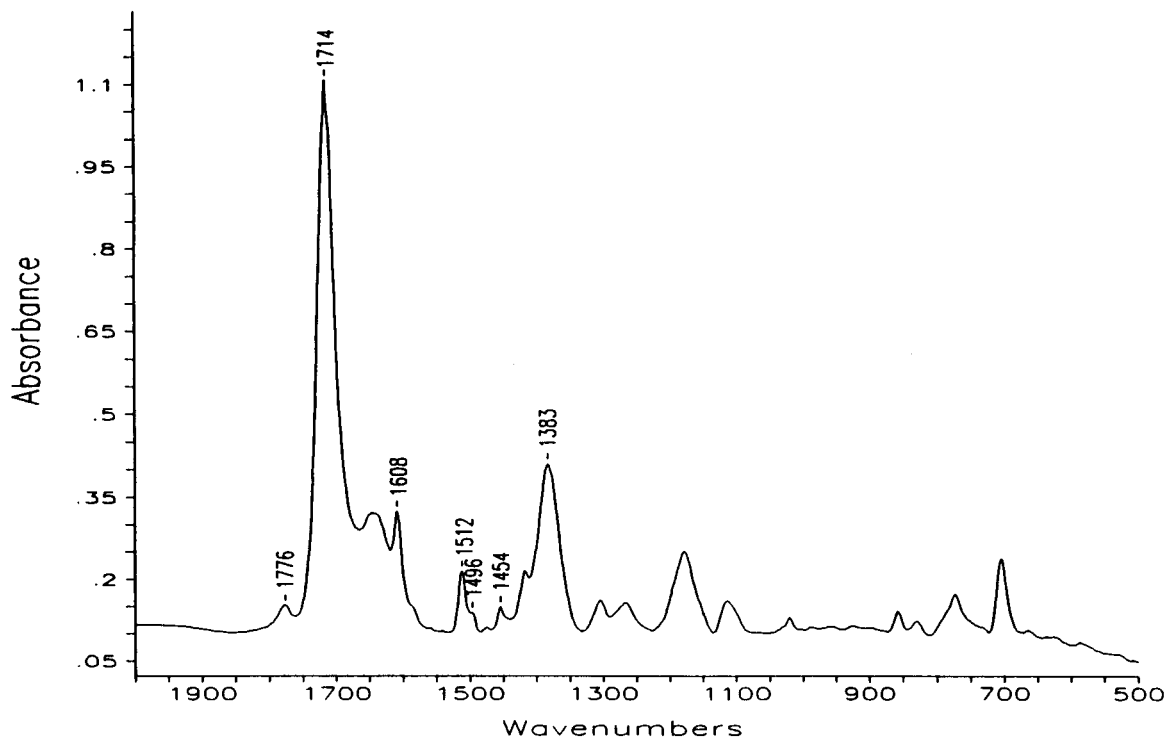


Figure 2 Transmission IR spectrum of poly(4CPMI-styrene) obtained by spontaneous polymerization (4 cm^{-1} resolution).

electric breakdown test, a coating of $15 \mu\text{m}$ thickness withstood 2500 V AC without failure. Thus, it seems that the coating system developed will be very attractive for insulation applications.

This polymerization process is different from the conventional processes in several ways. The monomer is involved in both the initiation and the propagation step. The initiation occurs through a

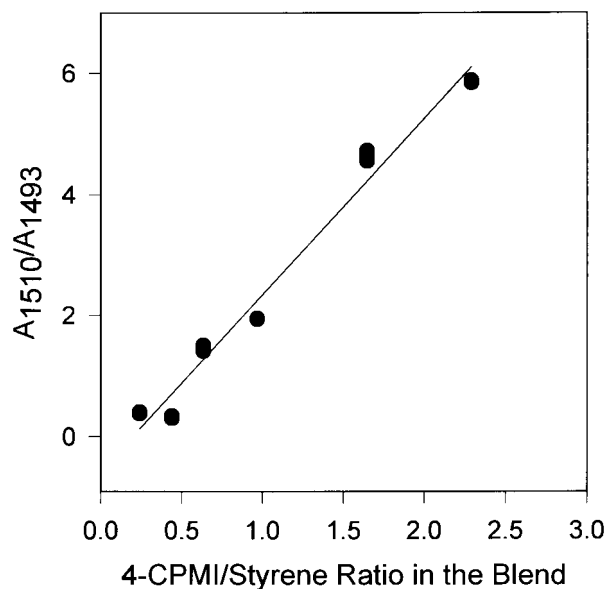


Figure 3 Absorbance ratio of 1510 to 1493 cm^{-1} versus poly(4CPMI) and polystyrene ratio in the blends.

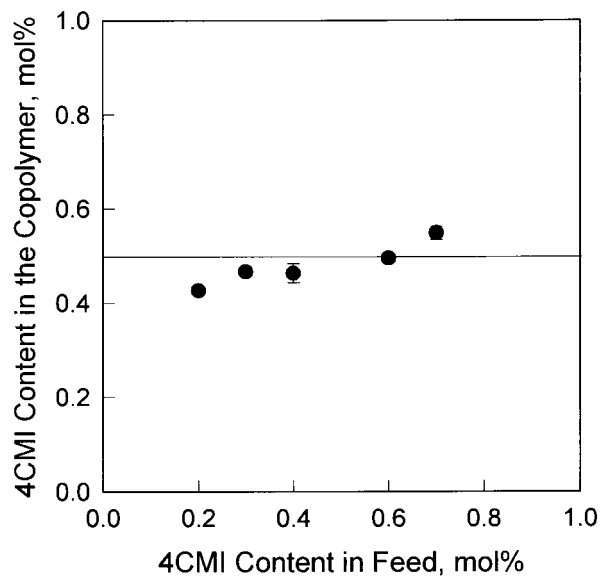


Figure 4 4CMI content in the copolymer versus that in the feed. Total monomer concentration $0.3M$.

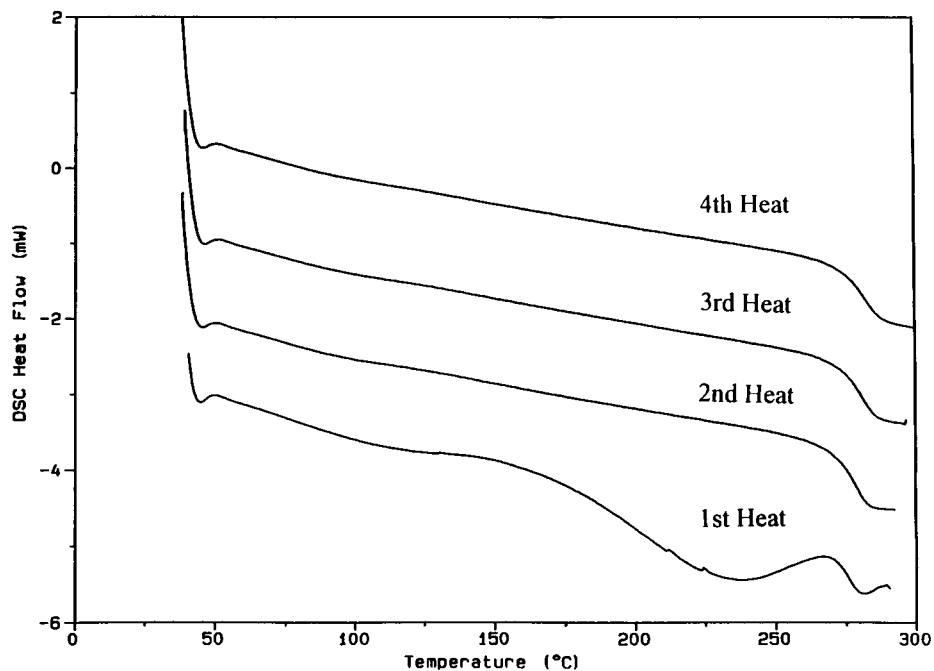


Figure 5 DSC thermograms of poly(4CPMI-styrene) obtained by spontaneous polymerization. Heating rate = 10°C min.

heterogeneous reaction between the metal surface and the monomer. Free radicals are generated, as discussed below, and react with monomers close

to the surface to form polymer. The NMP to water ratio has been adjusted so that the monomer dissolves in the mixture but the polymer formed only

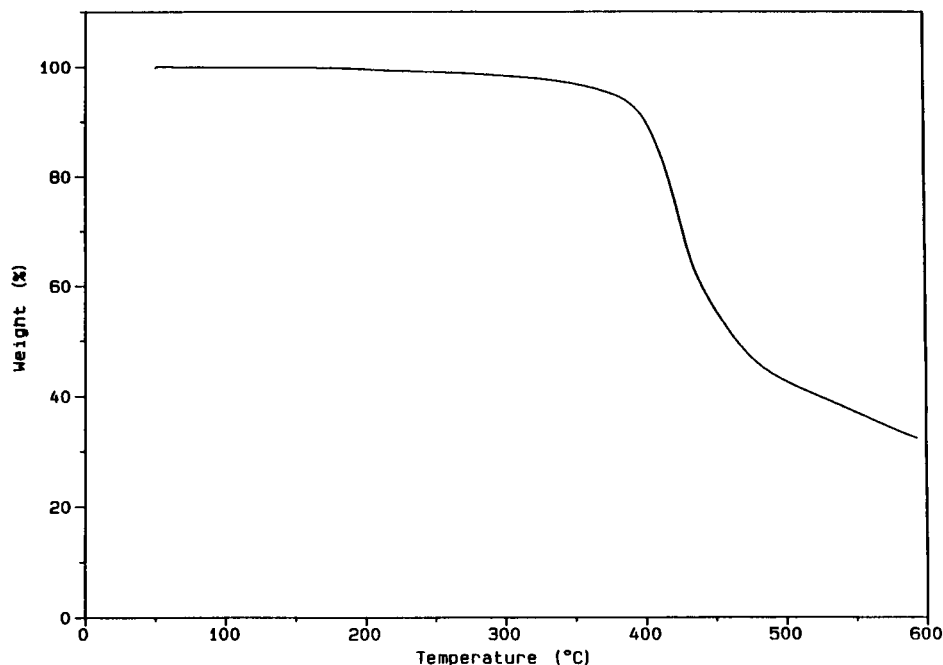


Figure 6 TGA thermogram of poly(4CPMI-styrene) obtained by spontaneous polymerization. Heating rate = 20°C min. Nitrogen atmosphere.

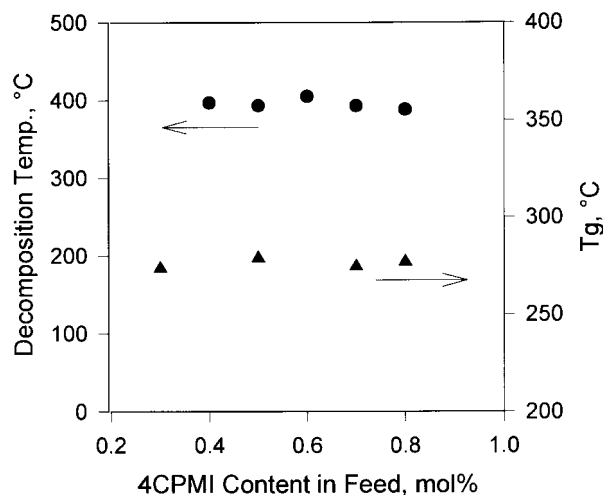


Figure 7 Variation of T_g and thermal stability of poly(4CPMI-styrene) with 4CPMI feed composition.

swells. As the polymer chain grows, its solubility in the solution decreases and it precipitates to form a layer of coating. However, the swelling of the polymer is essential to promote the diffusion of the monomers through the coating.

For the system of monomers and solvents used in this study, the polymer chains propagate by a free radical mechanism. A small amount of sulfuric acid was added to adjust the solution pH to be between 2.6 and 3.6. The carboxyl group of 4CPMI will also dissociate partially in the solution. In such an acidic reaction solution, anionic propagating species would be quenched. On the other hand, maleimide and its derivatives do not polymerize by a cationic mechanism.³⁴ The double bond of maleimides is very electrophilic because of the two strongly electron-withdrawing carbonyl groups on the imide ring. For a cationic mechanism, propagation will only occur through styrene

Table I Dielectric Constant of Poly(4CPMI-*alt*-Styrene) Copolymer

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

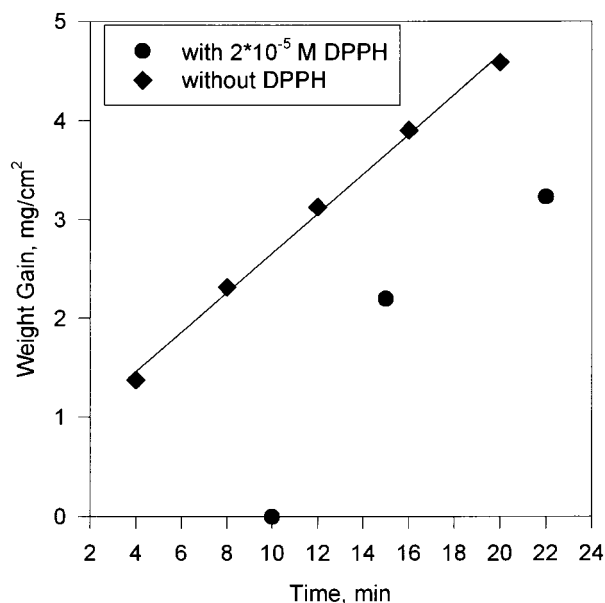


Figure 8 Effect of DPPH on the spontaneous polymerization process. DPPH = $3.0 \times 10^{-5} M$. Styrene = 4CPMI = $0.1 M$.

to form homopolystyrene. However, as we have seen from the IR and DSC data, a copolymer was indeed obtained; the monomers do not polymerize individually.

Diphenylpicryl hydrazyl hydrate (DPPH), a free radical inhibitor, has been found to quench the reaction completely. The monomer solution shows a purple color when a concentration of $3.0 \times 10^{-5} M$ of DPPH is added. After the immersion of the substrate, no coating formation could be observed initially, but the color of the solution gradually became lighter. The reaction product of DPPH with radicals is colorless. This suggests that radicals were generated on the steel substrate surface and reacted with the DPPH. After 10 minutes, polymerization began, as shown in Figure 8. The DPPH in the solution was depleted at this point. The polymerization rate was about the same as that of a control experiment in which no DPPH was added to the solution.

Process variables can influence the kinetics through both the initiation and the propagation steps. Figure 9(a) shows the effect of monomer concentration, which is involved in both initiation and propagation. Studies were conducted at five different total monomer concentrations ranging from 0.1 to 0.3 M, while the ratio of 4CPMI and styrene was maintained at 1 : 1 in all cases. A linear dependence of polymer weight gain on reac-

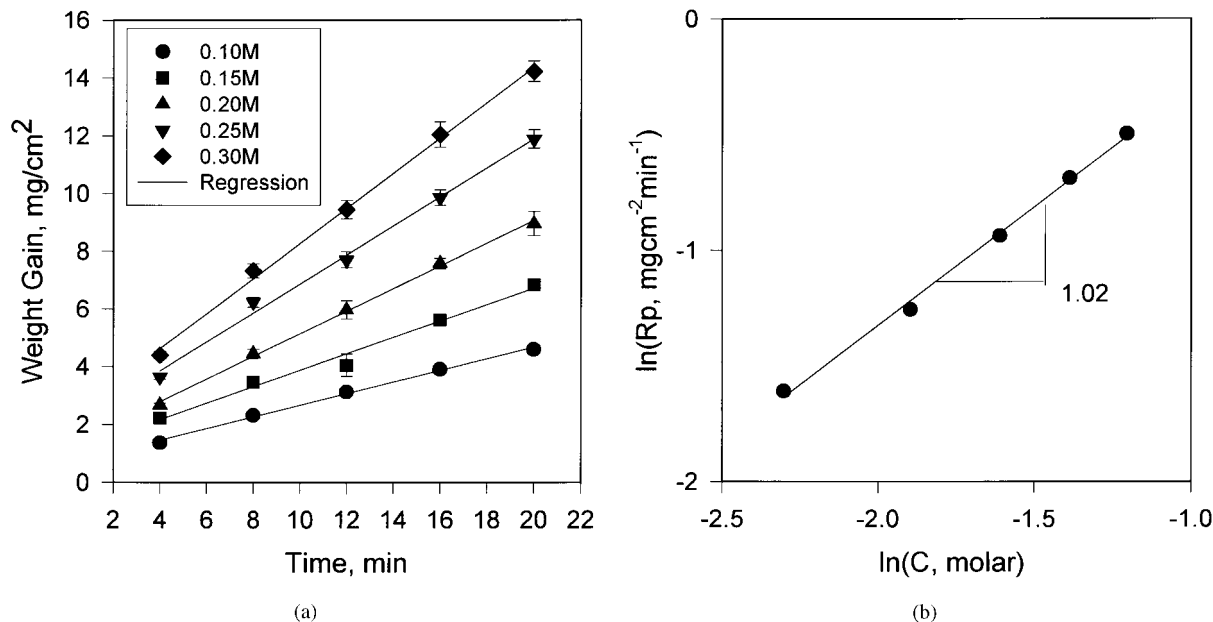


Figure 9 (a) The dependence of the weight of poly(4CPMI-styrene) coatings formed onto steel surface on the reaction time at different monomer concentrations. 4CPMI-styrene feed ratio is 1 : 1. (b) Variation of the spontaneous polymerization rate with monomer concentration.

tion time was observed in all five cases. In many heterogeneous reactions, the diffusion of reactant to the surface is slow, and the reaction rate is limited by diffusion. Our results suggest that the process is kinetically controlled in this system. If diffusion were controlling, the polymer weight gain would level off at longer reaction time and a time dependence of one-half power would provide a better fit to the experimental data. The reaction rate, which is the slope of weight gain versus time curve, also increases with increasing monomer concentration. The highest monomer concentration gives the highest reaction rate. The reaction rate was plotted versus the monomer concentration on a log-log scale to determine the exponent of monomer concentration dependence. A straight line of slope 1.02 is observed, as shown in Figure 9(b).

Such dependence can be explained qualitatively by adapting conventional chain polymerization kinetics to our system. Since the polymerization is initiated on the surface, only monomers adjacent to the surface will participate in the initiation process. The availability of monomer on the surface instead of bulk monomer concentration is more applicable in our case, while the former will be of a power of less than one of the latter. We assumed an exponent of 2/3 simply because the bulk monomer concentration is re-

lated to volume, the cube of length, and the availability of monomer on the surface to area, the square of length. Therefore, the expression of initiation rate is

$$R_i = f k_i [M]^{2/3} [\text{Metal Sites}] \quad (2)$$

where k_i is initiation rate constant; $[M]$ is the bulk monomer concentration; and f is the initiation efficiency, which is defined as the fraction of the radicals produced that initiate polymer chains. The concentration of metal sites can be considered as a constant and is lumped into k_i in subsequent derivation. Termination can occur either through bimolecular termination (coupling or disproportionation) or transfer to a chain transfer agent.

$$R_t = 2k_t [M^* d]^2 \quad (3)$$

$$R_t = k_{ts} [M^*] [SH] \quad (4)$$

where k_t and k_{ts} are the reaction rate for bimolecular and chain transfer termination, respectively, and $[SH]$ is the concentration of a chain transfer agent. The radical concentration, $[M^*]$, can be solved by invoking the steady-state assumption of radical concentration. Propagation rate can then

be obtained by substituting $[M^*]$ into the expression, as follows:

$$R_p = k_p[M][M^*] \quad (5)$$

to give

bimolecular termination

$$R_p = k_p \left[\frac{f k_i}{2k_{tc}} \right]^{1/2} [M]^{4/3} \quad (6)$$

$$\text{Chain transfer} \quad R_p = \frac{f k_i k_p [M]^{5/3}}{k_{ts} [SH]} \quad (7)$$

In the special case of chain transfer to monomer, $[M] = [SH]$,

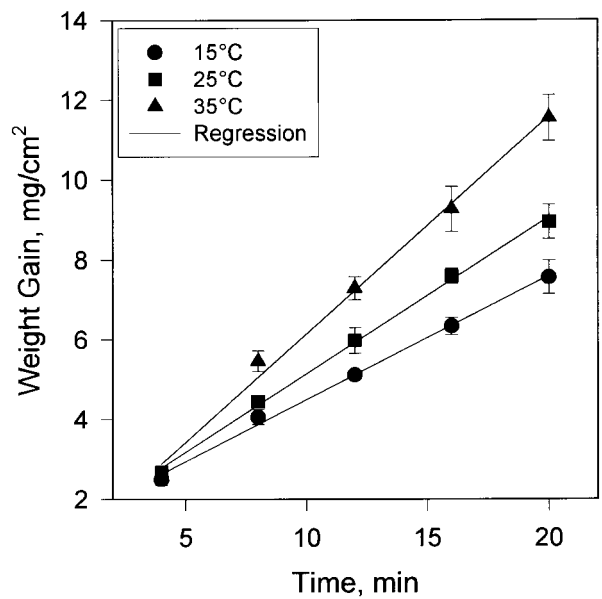
$$R_p = \frac{f k_i k_p}{k_{ts}} [M]^{2/3} \quad (8)$$

Therefore, $R_p \propto [M]^{4/3}$ in the case of bimolecular termination, and $R_p \propto [M]^{2/3}$ in the case of chain transfer to monomer. Our experimental result lies within these two limits. This suggests that both mechanisms are likely operative in our system. Chain transfer to monomer is a reasonable mechanism in our process, considering coatings up to 50 microns can be obtained, and it is difficult for a single chain to grow across the whole thickness.

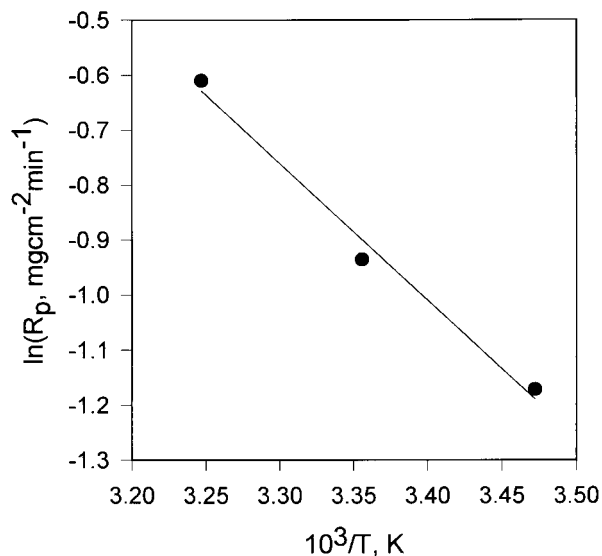
Increasing temperature will increase the kinetic energy of the molecules and enhance both the initiation and propagation reaction. This is certainly observed in the 4CPMI–styrene system, as shown in Figure 10(a). With the same reaction time, more polymer is obtained at higher temperature. The reaction rate increases in the order of 15, 25, and 35°C. A linear dependence of weight gain on time is also observed in this case. When the logarithm of the rate is plotted versus the inverse of temperature, a straight line is observed as in Figure 10(b). This suggests that an Arrhenius-type behavior fits this system.

The process has a complex dependence on solution pH, which affects primarily the initiation step of the process in two ways. As the radicals are generated on the substrate surface, the initiation rate depends strongly on the metal surface condition, which is a strong function of the solution pH. On the other hand, a hydrogen ion may also chemically participate in the initiation reaction. We have found that while the reaction stops com-

pletely under neutral conditions, a lower pH increases the reaction rate, as shown in Figure 11(a). This increase is largely due to the increasing initiation rate. Preliminary results showed that under constant monomer concentrations, polymers obtained at lower solution pH tend to



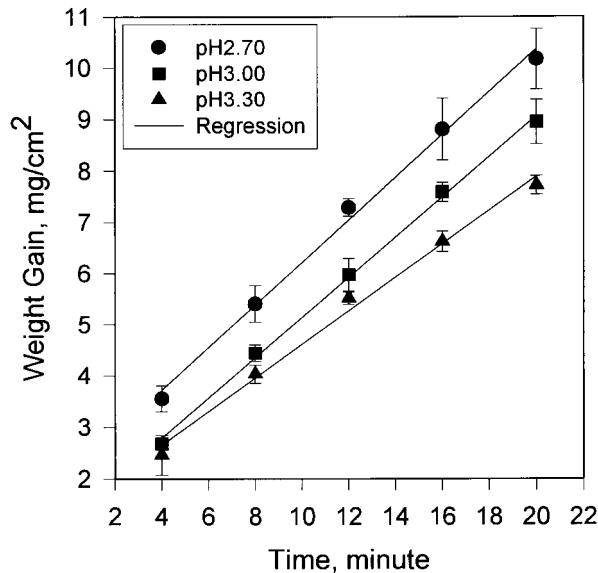
(a)



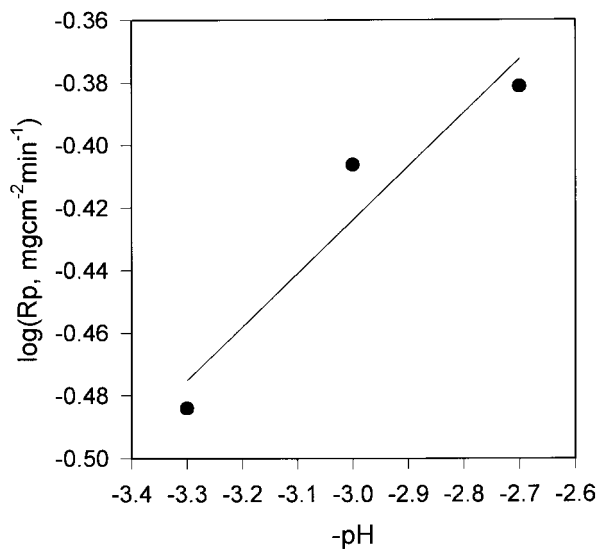
(b)

Figure 10 (a) The dependence of the weight of poly(4CPMI–styrene) coatings formed onto the steel surface on the reaction time at different solution temperatures. The 4CPMI–styrene feed ratio is 1 : 1. (b) Variation of the spontaneous polymerization rate with solution temperature.

have a lower molecular weight. This is because more chains are initiated simultaneously at lower pH. The same linear dependence of weight gain on time is also observed. A plot of the logarithm of the reaction rate versus $-\text{pH}$, i.e., $\log[\text{H}^+]$, was made to determine the rate dependence on pH. An exponent of 0.23 was obtained from Figure



(a)



(b)

Figure 11 (a) The dependence of the weight of poly(4CPMI-styrene) coatings formed onto the steel surface on the reaction time at different solution pH. The 4CPMI-styrene feed ratio is 1 : 1. (b) Variation of the spontaneous polymerization rate with solution pH.

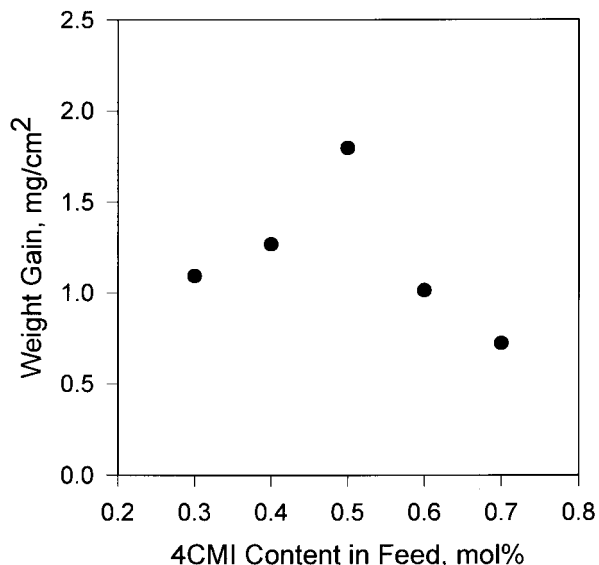
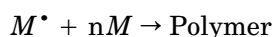
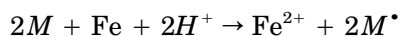


Figure 12 The dependence of the weight of poly(4CPMI-styrene) coatings formed onto the steel surface on the 4CPMI feed content. Reaction time is 5 min; total monomer concentration is 0.3M.

11(b). It is difficult to explain this exponent at present stage without a clear understanding of the interaction between H^+ and the metal surface.

The reaction rate, as shown in Figure 12, reaches a maximum at 1 : 1 monomer feed ratio under a fixed total concentration. Such dependence on the monomer feed composition could be attributed to the formation of a 1 : 1 donor acceptor complex between 4CPMI and styrene. Such a complex was previously observed in d_6 -DMSO solvent using an NMR technique.³³ A simple calculation will show that the complex concentration is at maximum at 1 : 1 feed ratio of donor and acceptor monomers. As such a complex is presumably more reactive than individual monomers, the reaction rate will also reach its maximum at this ratio. The dependence is not symmetrical with respect to the 1 : 1 line. A higher reaction rate is observed at high styrene content. This can be explained in terms of the reactivity ratio data of similar systems. The reactivity ratio for the solution copolymerization of maleic anhydride with styrene has been reported to be $r_1 = 0.005$ and $r_2 = 0.05$, respectively.³⁵ Although both monomers prefer cross propagation, the tendency for styrene to self-propagate will be much greater than that for 4CPMI. This could affect the reaction rate when the composition is away from 1 : 1 and the complex concentration is low.

For the initiation of the spontaneous polymerization process on iron, and perhaps also applicable to some other metals, we propose a redox mechanism. The metal surface and the monomer forms an electrochemical cell. The metal surface is oxidized and loses electrons. The monomer accepts the electrons and is reduced to a radical form in an aqueous environment, which then initiates the polymerization. The process is thermodynamically favored and occurs spontaneously. The following is a schematic of the proposed reaction mechanism:



Such a mechanism is reasonable for iron-steel and perhaps other systems. In fact, we know that ferrous compounds have been used with hydrogen peroxide as a classical redox initiation system and are widely used for emulsion polymerization initiation. 4CPMI is very electrophilic and relatively easy to reduce. It has a reduction potential of only about -0.8 V relative to a saturated calomel electrode.³³ Both Fe^0 and Fe^{2+} can be easily oxidized to a higher oxidation state and are capable of ini-

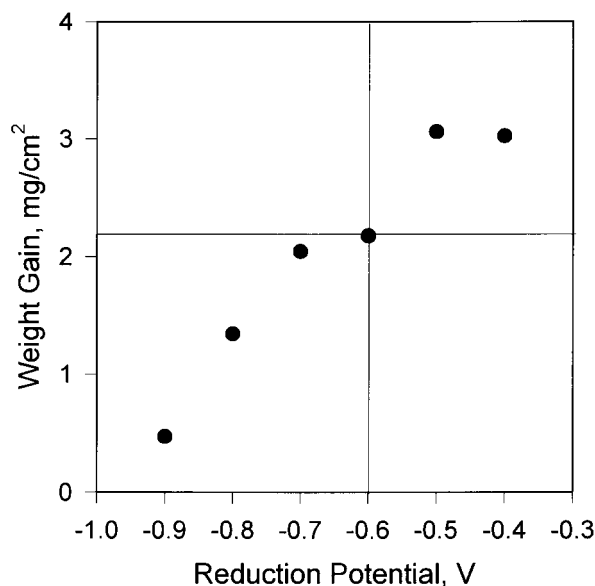


Figure 13 The dependence of the weight of poly(4CPMI-styrene) coatings formed on steel on the applied reduction potential. Reaction time is 10 min. Styrene = 4CPMI = 0.1M.

Table II Results of Spontaneous Polymerization on Different Metals

Metal	Polymerizability
Fe	+
FeSO ₄ solution	+
Fe ₂ (SO ₄) ₃ solution	-
FeO powder	+
Fe ₂ O ₃ powder	-
Cu	+
CuCl solution	+
CuSO ₄ solution	-
Al	+
Al ₂ (SO ₄) ₃ solution	-
Zn	+
ZnCl ₂ solution	-
ZnO powder	-
Pt	-
Au	-

tiating polymerization. The addition of several drops of ferrous sulfate water solution to a vial containing the 4CMI-styrene monomer solution induced nearly instantaneous polymerization within the whole vial. On the other hand, the addition of Fe^{3+} ions did not induce polymerization at all, and the solution remained clear. This is consistent with our proposed mechanism because the ferric ion is already in its highest oxidation state and cannot donate further electrons.

The redox mechanism is also supported by the strong influence of potential on the process. When the steel substrate is immersed in the monomer solution, it has a rest potential of about -0.6 V relative to a saturated calomel electrode, and polymerization occurs rapidly on the surface. If we apply a small perturbation potential around this value, drastic changes in reaction rate can be observed, as shown in Figure 13. At more negative potential, the reaction becomes much slower; while at more positive potential, the reaction rate increases. This is because the applied potential changed the oxidation rate of the metal surface and thus the polymerization initiation rate. At lower potentials, the surface is more difficult to oxidize. Meanwhile, higher potentials effectively enhance the oxidation process. The slight decrease of reaction rate at -0.4 V is due to the presence of gas bubbles on the surface, generated by the oxidation of water. This prevented a large portion of the surface area from being accessible to monomers. An appreciably higher reaction rate is otherwise expected.

We have also tested the spontaneous polymerization process on several other metals. In these experiments, we have added either pure metal, metal ion solutions, or metal oxide powders to the monomer solution. The observations are summarized in Table II. The process occurs on copper, zinc, and aluminum. This is consistent with our proposed mechanism. These three metals are very active and can be easily oxidized. Two noble metals, gold and platinum, induce no polymerization at all. This is because these two metals are inert and very difficult to oxidize. Out of the oxides/ions tested, Al^{3+} , Zn^{2+} , Cu^{2+} , and ZnO are already in the highest oxidation state and are ineffective for the process; while Cu^+ induces polymerization because it can be further oxidized to Cu^{2+} . Metal surface conditions will also influence the process. Many active metals have a layer of oxides on the surface. Such oxides become a barrier for electron transfer if they are impermeable and nonconductive. Vigorous surface treatment is necessary to remove such a layer or to replace it with a layer of porous oxides so that the oxidizable surface is accessible to the monomers. The oxide layer on iron is porous and unstable in our acidic reaction environment by nature and therefore requires minimal surface treatment for the process.

The exact identity of the chemical species involved in the initiation is still unclear at this point. Because the donor acceptor complex formed by 4CPMI and styrene is rather weak, its reduction potential will be close to that of 4CPMI alone and may also be capable of initiation. But the existence of a charge transfer complex is not a prerequisite for the polymerization process. In a separate correspondence, we will report our results on a 4CPMI–methyl methacrylate system. Both 4CPMI and methyl methacrylate are electron donors in this case and cannot form a charge transfer complex. However, we have successfully obtained random copolymers of 4CPMI and methyl methacrylate by the same spontaneous polymerization process.

This process is by no means limited to the present monomer system. If reaction indeed occurs through the proposed mechanism, monomers with a reduction potential lower than a threshold value should be able to, at least theoretically, polymerize on a specific oxidizable substrate surface. The reduction potential of a specific monomer can be conveniently determined by electrochemical techniques, such as cyclic voltammetry. We can also significantly broaden the application scope of the

spontaneous polymerization process through another route. A small amount of monomer that is capable of spontaneously polymerizing can be used as initiator to polymerize other monomers that are otherwise unpolymersizable by this process. The effectiveness of this method is determined by the reactivity ratio of the monomer system. We have successfully incorporated several monomers in the laboratory and developed three-component and even four-component monomer systems. This enables us to select and tailor monomer systems to yield coatings of different properties according to need.

CONCLUSION

The spontaneous polymerization process was studied on a steel substrate using a 4-carboxyphenyl maleimide–styrene system. The copolymer formed has a T_g of 275°C and a thermal decomposition temperature of 400°C. Its dielectric constant is about 2.6. IR analysis showed that the polymer formed is an alternating copolymer, with composition remaining constant despite large changes in monomer feed composition. Its thermal properties are therefore also insensitive to feed composition. The alternating structure can be explained by the formation of a charge transfer complex between 4CPMI and styrene, or, alternatively, by the comonomer reactivity ratios. Kinetic studies show that the reaction depends on monomer concentration, pH, temperature, and monomer feed composition. A kinetic scheme is presented to explain the first power dependence of the reaction rate on the monomer concentration. A redox mechanism is proposed for the spontaneous initiation of the process. It involves the direct electrochemical reduction of the monomer by the metal surface to generate the initiating radical.

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