

Polymerization of Acrylamide Compounds onto Fe Plates: An Alternative Route for Applying Polymer Coatings

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Synopsis

Acrylamide and some of its derivatives were polymerized onto the surface of Fe plates by causing a slight corrosion of Fe to Fe^{2+} in the presence of perdioxy compounds. In water within a suitable pH range, the acrylamide monomers are likely to store at the metal-solution interface and to adsorb on the iron surface. Thus, the polymerization takes place in situ, leading to the formation of uniform film coatings; the presence in the solution of a radical inhibitor imparts considerable stability to the bulk of the system. The dependence of the polymerization kinetics on several variables such as pH, monomer concentration, and peroxide concentration has been determined, and some characteristics of the resulting coatings were investigated.

INTRODUCTION

In water medium most of the organic compounds, because of their low surface tension, store at the interfaces: acrylamide and its derivatives are furthermore likely (within some pH range) to adsorb strongly onto metal surfaces owing to the interaction of π bonds and $-\text{NH}_2$ groups with the metal lattice.

Under suitable conditions acrylamide and its derivatives may consequently polymerize onto the surface of metal articles with the formation of coherent coatings, as was obtained by electrolysis by polarizing cathodically the metal article into an acid solution containing the monomer and some compound that formed free radicals by reduction.¹⁻⁷

It seems likely that the polymerization of the same acrylamide monomers onto Fe articles may be performed by a more straightforward route, that is, the production of free radicals at the metal surface through a slight corrosion of Fe to Fe^{2+} in the presence of a perdioxy compound.⁸⁻¹⁰ The present work discloses the feasibility of this polymerization in situ as an alternative route for applying protective coatings and investigates its peculiarities.

EXPERIMENTAL

The polymerizations were performed in a glass cell (Fig. 1) which at any run was filled with a 150 ml standard volume of water solution comprising monomer, corrosion agent of Fe, and peroxide. The cover of the cell (a) had a slit with the border in relief (b), which was used to immerse the iron plate (c) into the solution and to withdraw the same once coated. The cell cover was further equipped with

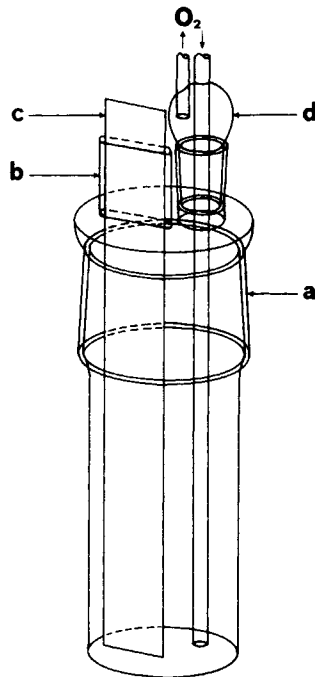


Fig. 1. Cell used for the *in situ* polymerization.

an inlet-outlet glass tube (d) for bubbling a continuous slight current of oxygen or air inside the cell.

In this very simple system, conditions favoring polymerization *in situ* are likely to occur for the following reasons:

1. Within a suitable range of pH the spontaneous corrosion of the Fe sheet provides not only the formation of the active partner (Fe^{2+}) of the redox catalyst, but also the accumulation of the monomer onto the metal surface. The Fe sheet acquires, in fact, a static potential ($-0, 2-0, 3$ V versus NHE) very near to Fe zero charge potential ($-0, 4$ V versus NHE), which favors maximum absorption of the monomer.¹¹

2. Oxygen, the concentration of which attains a steady value in the solution, is a powerful inhibitor for the polymerization in the bulk of acrylamide monomers, whereas it proves ineffective in the interfacial region. Thus, stability of monomer solutions during repeated coating operations is attained.

The formation of polymer film coatings, which clearly depends on the nature of the monomer-polymer system, too, has been obtained from diacetone acrylamide (DAA), diacetone acrylamide/*N,N*-methylenebisacrylamide (NNMBA), and acrylamide/*N,N*-methylenebisacrylamide.

Most of the work has been focused on the polymerization kinetics of these systems, which were investigated as follows: On immersing successively several Fe sheets in the same solution, the amount of polymer coating formed onto their surface after different reaction times was determined by weighing. Thus, the kinetic curves could be plotted by points, allowing assessment of the peculiarities of the coating process and its validity range at variance with peroxide concentration, pH, and monomer concentration.

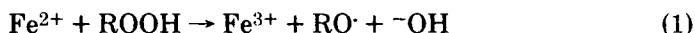
RESULTS AND DISCUSSION

Kinetics of Diacetone Acrylamide Polymerization

When a Fe sheet is immersed into an aqueous solution saturated with oxygen or air containing 0.59 mol/l diacetone acrylamide, 0.88×10^{-3} mole/l *tert*-butylhydroperoxide, and 10^{-1} mole/l HCl, a continuous polymer film is formed on the surface of the plate in a few seconds. On coating this way several sheets, one obtains, by the procedure described above, curve a shown in Fig. 2, which shows that the coating weight (mg/cm^2) grows steadily with the reaction time although at a decreasing rate. On increasing the peroxide concentration (curves d, e, and c), the coating yield increases but tends to a limiting value. The highest peroxide concentration (curve c) seems, moreover, to cause an efficiency decrease for the process, especially for the longest reaction times.

When a small amount of CuCl_2 (8.8×10^{-3} mole/l) is added to the solution for the same conditions of curve d, a light copper layer is at first deposited on the plate, and the polymer coating builds up thereon in this case, too (curve b).

These results are explained as follows: Fe corrosion is caused by HCl leading to production of Fe^{2+} (anodic reaction) and H_2 development (cathodic reaction). The Fe^{2+} ions then react with the peroxide according to the well-known process¹⁰



This is the main initiation route. One must also consider the direct interaction of the peroxide with the Fe sheet as a possible source of free radicals. When CuCl_2 is added to the monomer-peroxide solution, the corrosion of Fe involves the plating of Cu onto the sheet, and Cu^+ (formed from Cu^{2+} and Cu) are possibly involved in the free-radical production.¹⁰

It is however clear that, whatever the route followed by radical formation,

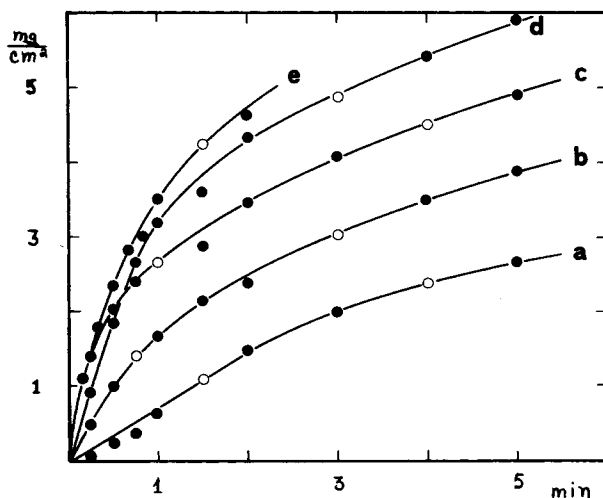


Fig. 2. Kinetics of diacetone acrylamide polymerization at 25°C onto Fe sheets for different *tert*-butyl hydroperoxide (TBIP) concentrations. Full points refer to hardened steel sheets, empty points to soft steel. TBIP (moles/l): (a) 0.88×10^{-3} ; (b) 2.20×10^{-3} in the presence of 8.80×10^{-3} mole/l CuCl_2 ; (c) 13.60×10^{-3} ; (d) 2.20×10^{-3} ; (e) 6.60×10^{-3} .

maximum radical concentration is attained at the surface of the Fe sheet and the polymerization takes place there at the highest rate.

But the heterogeneous polymerization rate depends on the initiation stage as long as other variables do not control the process. Production of initiator which exceeds the monomer concentration may conversely cause oligomerization, thus degrading the coating process. The kinetic influence of pH differs only quantitatively from that for the peroxide concentration. An acidity minimum (pH 2.5) is necessary to start the polymerization in situ, but a low kinetic dependence on pH is soon reached. For pH 0.5, the coatings become very poor, and eventually no polymer may be formed.

The effects of peroxide and pH offer some ideas of the growing mechanism of the polymer. The polymerization takes place heterogeneously mainly, as a continuous film is formed on the sheet surface from the very start of the reaction. Further increase in thickness either involves chain transfer reactions between solid phase and monomer or some permeability of the film to the partners of the redox catalyst. Clearly at this stage, pH and peroxide cannot fully control the kinetics of film growing which will mainly depend on coating morphology and monomer supply. As a matter of fact, runs performed for different monomer concentrations have outlined the linear dependence of the kinetics on this last variable at any time of the process.

Also the copolymerization of diacetone acrylamide with lower amounts of N,N-methylenebisacrylamide (10/1 ratio by weight) has been investigated. This reaction showed the same kinetic dependence on pH and peroxide as seen for diacetone acrylamide alone. It was kinetically remarkable that small amounts of N,N-methylenebisacrylamide gave a substantial increase in the overall rate of the polymerization in situ.

Kinetics of Acrylamide/N,N-Methylenebisacrylamide

Neither acrylamide nor N,N-methylenebisacrylamide when used separately may be polymerized with the formation of polymer film coatings by the procedure described above. However, coherent films were obtained by copolymerizing acrylamide with minor amounts of N,N-methylenebisacrylamide (ratios of acrylamide/NNMBA ranging from 5 to 30 by weight were utilized). Moreover, it was found that a satisfactory adhesion of the films to the metal substrate may be obtained only when either Cu^{2+} is used as the corrosion agent of Fe or some polyalcohol (glycerol, for instance) is added to the monomer solution.

With respect to peroxide and pH influence on the coating kinetics, a strict similarity exists with what was seen above for the polymerization of diacetone acrylamide. As shown in Figure 3, the polymerization rate reaches its maximum in the pH range of 1.2–2.8. For pH 4, the coating morphology is degraded; whereas for pH 0.5, there is a drop in the propagation rate of the process. When either the overall concentration of the monomers or their ratios were varied, an approximate linear dependence of the rates on the concentration of each monomer could be determined within the examined range of concentrations (acrylamide was varied from 0.7 to 2.0 moles/l; NNMBA from 3.2×10^{-2} to 1.3×10^{-1} mole/l).

In view of a possible practical utilization of this system for large-scale coating operations, a great number of sheets (several tens) were immersed one after the

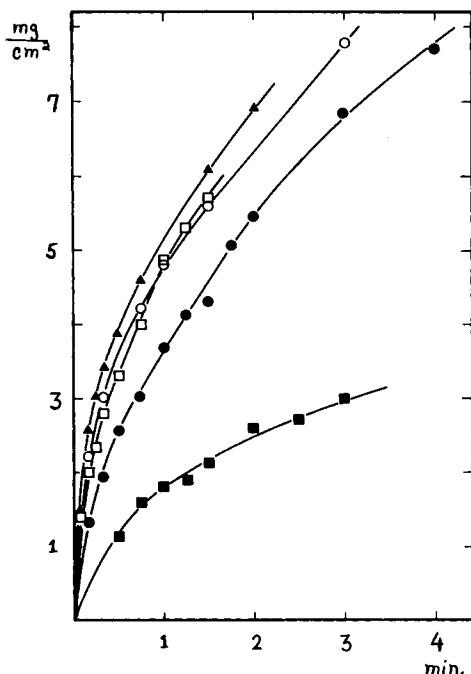


Fig. 3. Kinetics of acrylamide/N,N-methylenebisacrylamide copolymerization at 25°C onto Fe sheets for different pH values. pH: (■) 0.5; (●) 0.82; (□) 2.8; (○) 1.2; (▲) 2.2. Other conditions: acrylamide = 1.4 mole/l; NNMBA = 6.5×10^{-2} mole/l; $K_2S_2O_8$ = 1.66×10^{-2} mole/l; $CuCl_2$ = 8.8×10^{-3} mole/l.

other in the same solution, leaving each to interact with the monomer peroxide system for a standard time. Good film coatings were obtained in every case. However, when the polymer coated on each sheet was plotted as a function of the progressive number of the sheet, a slow efficiency decrease was noted for the coating process as it went on. This fact can mainly be explained by the progressive monomer depletion taking place in the equipment shown in Figure 1 for repeated coating operations. As an example, when the solution had lost about 30% of its initial volume, 60% of the monomer had been consumed. This seems interesting in that it supports the view of either monomer storing up at the metal-solution interface or a polymer growing mechanism which involves the diffusion of monomer from the bulk to the active centers of the metal and the ejection of solvent from the film.

A serious handicap for large-scale coating operations might be constituted by the accumulation of Fe^{3+} ions which, over some concentrations (5×10^{-2} mole/l), were found to inhibit the polymerization in situ. Anyway, an alkalization of the solution allows the separation of Fe^{3+} as hydroxide from the system, which may be restored again to the initial performances.

Physical Properties of the Coatings

The physical properties shown by poly(diacetone acrylamide) coatings prepared by the described procedure are very similar to those reported for the coatings prepared by electrolysis.¹⁻⁵ The molecular weights \bar{M}_n (by osmometry)

TABLE I
Physical and Mechanical Properties of Coatings

Bath composition	Thickness, μ	In situ polymerized coatings				Overpainted coatings ^a			
		Adhesion		Organic solvent resistance ^e	Film porosity, f N/m ²	Salt fog resistance ^g	Conical mandrel adhesion ^d	Salt fog resistance ^h	
		Cross cut ^c	Conical mandrel ^d					Unscratched	Scratched
Acrylamide 10%, NNMBA 1%	23	poor	very poor	good	0	very poor (film removal)	very poor	poor (blistering)	poor (film cut off)
Acrylamide 10%, NNMBA 1%, glycerol 3.3%	9	very poor	very poor	good	14.400	very poor (film removal)	very poor	poor	poor
Acrylamide 10%, NNMBA 1%, ethylene glycol 3.3%	23	good	good	good	0	(film removal)	very poor	(blistering)	(film cut off)
Acrylamide 10%, NNMBA 1%, MVK 1%	25	very poor	very poor	good	1.100	very poor	sufficient	good	poor
Acrylamide 10%, NNMBA 1%, ethylene glycol 2%	27	very poor	very poor	good	200.000	(film removal)	very poor	good	(film cut off)
Acrylamide 10%, NNMBA 1%, MVK 0.4%, CuCl ₂ 0.15%	14	good	good	good	200.000	(blistering)	good	poor	poor
Acrylamide 10%, NNMBA 1%, MVK 0.4%, CuCl ₂ 0.15%, glycerol 2%	10	good	good	good	130.000	(film removal)	good	(blistering)	(film cut off)
						(film removal)	good	(blistering)	(film cut off)

Acrylamide 5%, NNMBA 1%, diacetone acrylamide 5%	c. Acrylamide-Diacetone Acrylamide-Acrylic Acid-Based Coatings									
	23	sufficient	poor	good	0	very poor	very poor	very poor	very poor	very poor
Acrylamide 7%, DAA 3%, NNMBA 1%, acrylic acid 2.7%, glycerol 3%	38	very poor	very poor	good	1.100	very poor	very poor	very poor	very poor	very poor
						(film removal)	(film removal)	(film removal)	(film removal)	(film removal)

^a On in situ polymerized coatings, 40 μm film of Alkyd-Melamine-epoxy resin-based surfacer, cured at 150°C, was spray applied.

^b Thickness was measured by magnetic gauge supplied by Aminco.

^c Cross-cut adhesion test was performed by making a series of parallel cuts in one direction and a second series at right angle to the first, applying an adhesive tape and stripping.

^d Conical mandrel test was performed with the apparatus described in ASTM Method D 522.

^e Organic solvent resistance was tested by immersing test specimens in painting solvent mixture for 24 hr.

^f Film porosity was tentatively tested by an electrographic method which, by chemical reaction of $\text{K}_3\text{Fe}(\text{CN})_6$ with the $\text{Fe}(\text{II})$ ions electrochemically released by the metal, provides evidence of the presence of the pores and allows one to count them and determine their position.

^g Salt fog resistance of in situ polymerized coating was tested by ASTM Method B 117 for only 16 hr and without scratch.

^h Salt fog resistance of overpainted coatings was tested by ASTM Method B 117 for 96 hr with and without scratch.

range between 2500 and 5000. The lower weights were obtained from the most acid systems, thus suggesting a decrease in the propagation rate in the same direction.

The characteristics of the coatings obtained by acrylamide/*N,N*-methylenebisacrylamide copolymerization were investigated more thoroughly. Although these coatings are insoluble in every solvent owing to the crosslinked structure, their major lack is the very poor resistance to water and to protogenic solvents. The resistance to water may be, however, increased by postheating the coatings at 200°C. Good improvement may also be obtained by performing the reaction in situ in the presence of organic additives which are compatible with the polyacrylamide chains.

The data reported in Table I show the significant effects on some physical properties of the coatings determined by this route.

CONCLUSION

The polymerization in situ of suitable monomer systems undoubtedly appears to be an advantageous route for applying protective polymer coatings on Fe materials. The advantages are evident for a method which does not require any electric power supply and at the same time turns a two-stage process (the preparation of the polymer and the deposition of the same onto the metal) into a single operation. Clearly, the technological potential of the process must be assessed by the properties of the resulting coatings, and any further research should be turned into that direction.

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