Fenton's Reagent-Initiated Graft Copolymerization of Acrylonitrile onto Sodium Alginate

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SYNOPSIS

Graft copolymerization of acrylonitrile (AN) onto sodium alginate was studied in an aqueous medium using ferrous ammonium sulfate–hydrogen peroxide (Fenton's reagent) as the redox initiator. To optimize the reaction conditions for affording maximum percentage of grafting, the concentrations of sulfuric acid, initiator components, monomer, and also temperature and time were varied. The results are discussed and a reaction mechanism is proposed. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Grafting is a fascinating field of research with unlimited future prospects. Among chemical methods, redox-initiated grafting offers advantages since, in the presence of redox systems, grafting can be carried out under milder conditions and side reactions are at a minimum. Fenton's reagent (Fe^{+2}—H_2O_2) is a well-known redox initiator and has been successfully utilized in grafting vinyl monomers onto starch,[1] wool,[2] cellulosic,[3-5] and jute fibers.[6]

A comprehensive research program on grafting of various vinyl monomers onto chemically modified amylose,[7-10] viz., sodium salt of partially carboxymethylated amylose (Na–PCMA), as well as chemically modified starch,[11-13] viz., sodium salt of partially carboxymethylated starch (Na–PCMS) of varying degrees of substitution, has been initiated in our laboratory. This has been done to arrive at a good understanding of the kinetics and mechanisms of grafting as well as to obtain basic information needed for improvements to be made in the properties of the products.

In our previous article,[14] we reported studies on the ceric-induced grafting of acrylonitrile (AN) onto sodium alginate (SA). In the present work, grafting of AN onto SA is investigated in the presence of Fenton's reagent and the reaction conditions for graft copolymerization are optimized.

EXPERIMENTAL

Materials and Methods

Sodium alginate (SA) used in the present work was kindly supplied by Wilson and Co., Bombay. Acrylonitrile (AN), JC's chemical pure grade, was distilled at atmospheric pressure through a fractionating column and the center cut was used in the copolymerization reactions. Ferrous ammonium sulfate (FAS) was purified by recrystallization from hot water and 30% w/v hydrogen peroxide (BDH), H_2O_2, and sulfuric acid of "analar" grade was used. Nitrogen was purified by passing through a freshly prepared alkaline pyrogallol solution. Low conductivity water was used for the preparation of solutions as well as in polymerization reactions.

Graft Copolymerization

The grafting reactions were carried out under nitrogen atmosphere in a 500 mL three-necked flask equipped with a reflux condenser, a stirrer, and a gas inlet system, immersed in a constant temperature bath. In a typical reaction, SA (1.0–3.5 g) was dissolved in low conductivity water (200 mL) with constant stirring and bubbling of a slow stream of nitrogen for 30 min at the desired temperature (30–

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50°C). The freshly prepared 20 mL solution of FAS (1×10^{-3} to 7×10^{-3} M) in sulfuric acid (0.1–0.5 M) and H_2O_2 (3×10^{-3} to 10×10^{-3} M) was added and a continuous supply of nitrogen was maintained throughout the reaction period. The freshly distilled AN (4.0–16.0 mL) was added to the reaction mixture. The grafting reactions were carried out for varying time intervals (1–24 h).

After the reaction was over, the reaction mixture was filtered and the residue was extracted with dimethylformamide (DMF) for 48 h. After complete removal of polyacrylonitrile (PAN), the grafted SA was dried to a constant weight. The percentage of grafting and percentage efficiency were calculated from the increase in weight of SA after grafting, in the following manner:

$$\% \text{ Grafting} = \frac{\text{Wt of polymer grafted}}{\text{Initial wt of backbone}} \times 100$$

$$\% \text{ Total conversion} = \frac{\text{Wt of polymer grafted} + \text{Wt of homopolymer}}{\text{Wt of monomer charged}} \times 100$$

$$\% \text{ Grafting efficiency} = \frac{\text{Wt of polymer grafted}}{\text{Wt of polymer grafted} + \text{Wt of homopolymer}} \times 100$$

IR Spectra

The infrared (IR) spectra of SA, PAN, and SA-*g*-PAN samples were taken in KBr pellets using a Perkin-Elmer Model 983 spectrophotometer.

RESULTS AND DISCUSSION

Evidence of Grafting

(i) The simplest method to prove the formation of the graft copolymer is based on the difference in solubility of the graft copolymer and the nongrafted homopolymer. SA is soluble in water and homopolymer (PAN) is soluble in DMF. When a reaction product was Soxhlet-extracted with DMF and water alternately for 48 h, an insoluble solid still remained. A physical mixture of SA and PAN was treated in the same way and was found to dissolve completely. Therefore, it is apparent that the graft copolymer obtained was not a simple physical mixture, but some chemical bonds must exist between SA and PAN macromolecules.

(ii) Infrared spectral analysis has been utilized to prove grafting. For this purpose, the IR spectra of SA, PAN, and SA-*g*-PAN were taken in the range 1000–4000 cm^{-1}. The graft copolymer showed absorption bands of SA and an additional band at 2250 cm^{-1}, which has been attributed to the C≡N stretching mode, characteristic of the spectra of PAN. Thus, the presence of an additional 2250 cm^{-1} band in the graft copolymer indicates that grafting has taken place.

Determination of Optimum Reaction Conditions

To optimize the conditions for grafting, the concentrations of sulfuric acid, initiator components, monomer, and also temperature and time were varied.

Effect of Sulfuric Acid Concentration

The concentration of sulfuric acid was varied in the range 0.1–0.5 M, keeping the concentrations of all other reagents fixed. The effect of acid concentration on percent grafting is shown in Figure 1. It is seen that the percent grafting increases with increase of acid concentration up to 0.4 M, beyond which it decreases.

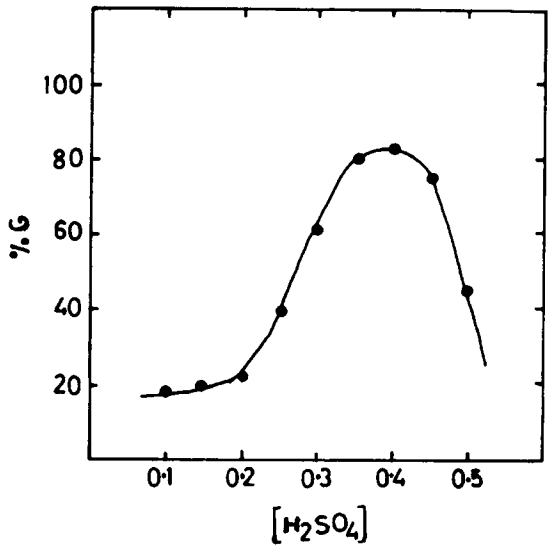

Figure 1 Effect of sulfuric acid on percent grafting (% G). SA = 2.0 g; H_2O = 200 mL; [FAS] = 6×10^{-3} M; [H_2O_2] = 6×10^{-3} M; [AN] = 0.679 mol L^{-1}; temp. = 35°C; time = 4 h.

Effect of Ferrous Ammonium Sulfate (FAS) Concentration

The influence of FAS concentration on percent grafting is shown in Figure 2. The percentage of grafting increases with the increase of [FAS] from 1×10^{-3} to 4×10^{-3} M and thereafter it decreases. The increasing trend of percentage grafting with increase of [FAS] could be ascribed to the formation of more initiating radicals, thereby facilitating the grafting reactions. When the [FAS] increases beyond 4×10^{-3} M, more and more Fe^{+3} ions might be generated that affect grafting adversely by termination of growing grafted chains.[4]

Effect of Hydrogen Peroxide (H_2O_2) Concentration

The effect of variation in H_2O_2 concentration on percent grafting is shown in Figure 3. With increase of [H_2O_2] from 3×10^{-3} to 9×10^{-3} M, the percent graft yield increases steadily. The increasing trend in percent grafting with increasing [H_2O_2] up to 9×10^{-3} M might be due to the formation of a greater number of grafting sites with increasing oxidant concentration. However, the increase of [H_2O_2] beyond 9×10^{-3} M results in a decrease of graft yield. Therefore, the optimum concentration of H_2O_2 for AN grafting onto SA was found to be 9×10^{-3} M.

Effect of Amount of Sodium Alginate (SA)

Figure 4 shows the effect of the backbone concentration on percentage grafting. It is seen that percentage grafting increases with increase in amount of SA up to 3 g and finally decreases with further increase in amount of SA. The initial increase may be due to the fact that the reactive sites increase with increase in amount of SA. The decrease is due to the destruction of radical activity on the backbone soon after it is formed due to termination between backbone–backbone and backbone–primary radicals. This is in agreement with the results obtained in the grafting of AN onto starch[15] and onto sodium salt of carboxymethylated amylose.[16]

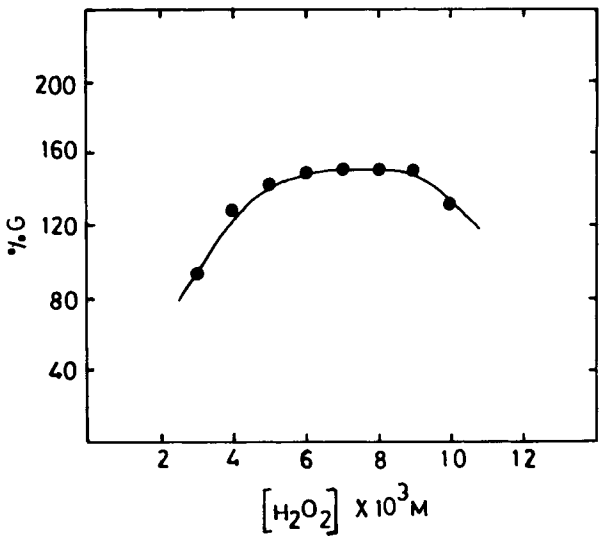

Figure 3 Effect of hydrogen peroxide [H_2O_2] on percent grafting (% G). SA = 2.0 g; H_2O = 200 mL; [H_2SO_4] = 0.4M; [FAS] = 4×10^{-3} M; [AN] = 0.679 mol L^{-1}; temp. = 35°C; time = 4 h.

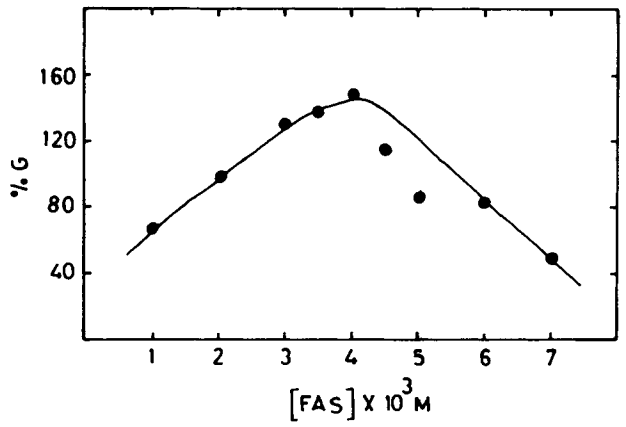

Figure 2 Effect of FAS on percent grafting (% G). SA = 2.0 g; H_2O = 200 mL; [H_2SO_4] = 0.4M; [H_2O_2] = 6×10^{-3} M; [AN] = 0.679 mol L^{-1}; temp. = 35°C; time = 4 h.

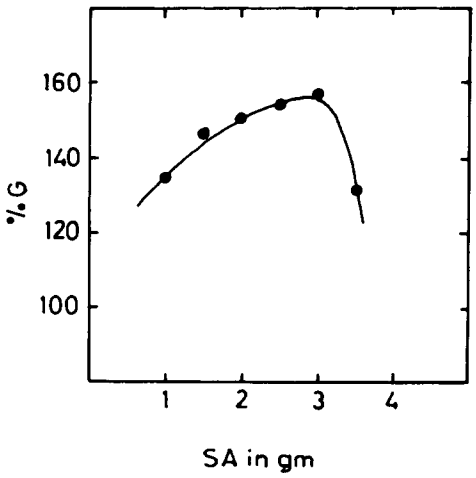

Figure 4 Effect of amount of SA on percent grafting (% G). H_2O = 200 mL; [H_2SO_4] = 0.4M; [FAS] = 4×10^{-3} M; [H_2O_2] = 9×10^{-3} M; [AN] = 0.679 mol L^{-1}; temp. = 35°C; time = 4 h.

Effect of Reaction Time

The effect of variation of polymerization time on percent grafting (% G) and percent grafting efficiency (% GE) is shown in Figure 5. It can be seen from this figure that the percentage grafting increases rapidly with time up to 3 h, after which it levels off but the percent grafting efficiency remains almost unchanged. The increase in percent grafting is accounted for by the increase in number of grafting sites in the initial stages of the reaction.[17] The leveling of grafting with time could be attributed to a decrease in concentration for both initiator and monomer as well as to a reduction in the number of sites on the SA backbone accessible for grafting as the reaction proceeds. It has been observed that grafting efficiency does not change appreciably during the course of the reaction. This result is similar to the grafting of vinyl monomers onto cellulose[18] and grafting of butylacrylate onto gelatin[19] with ceric ion as an initiator.

The percent total conversion (Fig. 6) increases linearly for the first 3 h. After this time, it reaches a constant value of about 97% C_t. Thus, it can be observed that 3 h is the optimum time duration for the grafting reaction.

Effect of Temperature

The graft copolymerization of AN onto SA has been studied at four different temperatures, i.e., 35, 40, 45, and 50°C. The effect of temperature on percent grafting is shown in Figure 7. It is observed that the percentage of grafting increases with increase of temperature from 35 to 45°C and decreases with further increase of temperature to 50°C. The dependence of percentage of grafting on temperature can be ascribed to the solubility of SA and enhancement of the rate of diffusion of the monomer. With further increase of temperature, the graft copolymerization occurs with poor selectivity and various hydrogen abstraction and chain-transfer reactions might be accelerated, leading to the decrease of percentage of grafting.

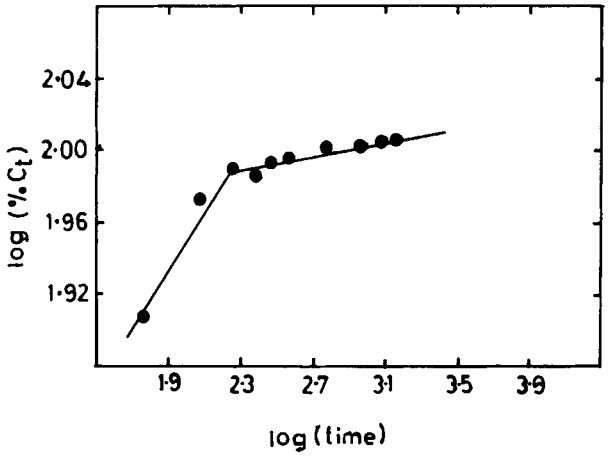

Figure 6 Plot of log (% C_t) vs. reaction time.

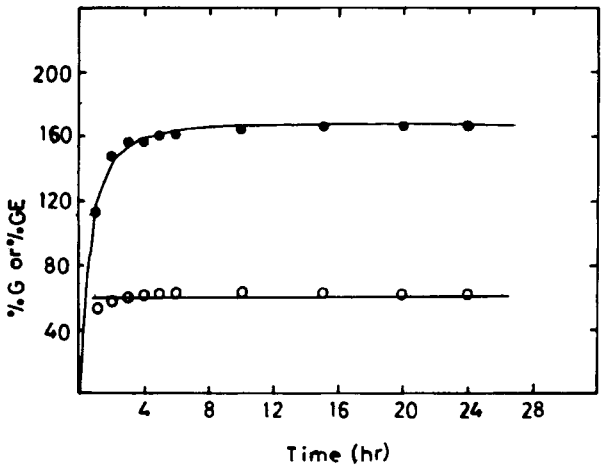

Figure 5 Effect of reaction time on percent grafting, % G (●), or percent grafting efficiency, % GE (○). SA = 3.0 g; H_2O = 200 mL; [H_2SO_4] = 0.4M; [FAS] = 4 × 10^{-3} M; [H_2O_2] = 9 × 10^{-3} M; [AN] = 0.679 mol L^{-1}; temp. = 35°C.

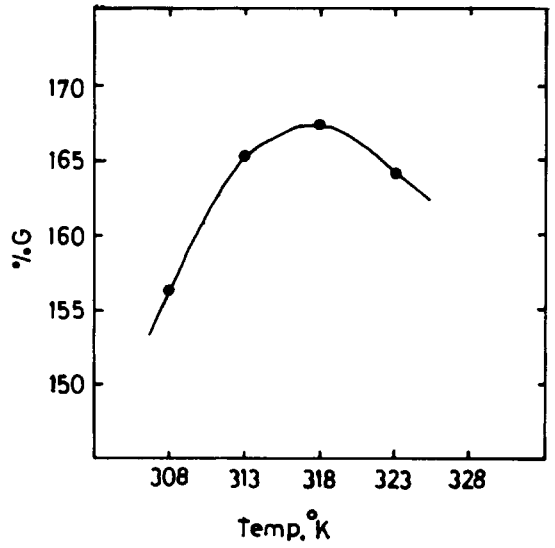

Figure 7 Effect of temperature on percent grafting (% G). SA = 3.0 g; H_2O = 200 mL; [H_2SO_4] = 0.4M; [FAS] = 4 × 10^{-3} M; [H_2O_2] = 9 × 10^{-3} M; [AN] = 0.679 mol L^{-1}; time = 3 h.

Effect of Monomer Concentration

Figure 8 shows the effect of monomer (AN) concentration on percent grafting as well as percentage grafting efficiency. The percent grafting increases as the monomer concentration increases from 0.272 to 0.679 mol/L, and, thereafter, it decreases with further increase of monomer concentration. The rapid increase of grafting by increasing monomer concentration up to 0.679 mol/L could be ascribed to the greater availability of grafting sites to monomer. However, the decreasing trend of percent grafting beyond optimum monomer concentration is probably due to the competition between homopolymerization and graft copolymerization, where the former prevails over the latter at higher AN concentration. Similar observations have also been reported.[20]

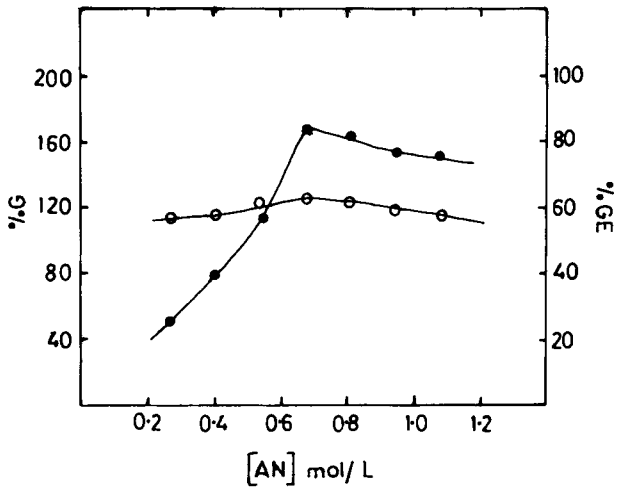

Figure 8 Effect of [AN] on percent grafting, % G (●), or percent grafting efficiency, % GE (○). SA = 3.0 g; H_2O = 200 mL; $[H_2SO_4] = 0.4M$; $[FAS] = 4 \times 10^{-3} M$; $[H_2O_2] = 9 \times 10^{-3} M$; temp. = 45°C; time = 3 h.

Reaction Mechanism

Fenton's reagent is well known for its ability to effect vinyl polymerization. The mechanism by which Fenton's reagent participates in the chain reaction was elucidated by Haber and Weiss,[21,22] who postulated that $^{\bullet}OH$ formed by interaction of hydrogen peroxide and FAS is responsible for initiating vinyl polymerization. In the grafting reaction initiated by Fenton's reagent, a similar mechanism involving generation of free-radical sites on polymeric backbone SA by $^{\bullet}OH$ may also hold. In a system containing H_2O_2, FAS, and SA, H_2O_2 may interact with FAS (Fe^{+2}) to form $^{\bullet}OH(R^{\bullet})$. The hydroxy radical ($R^{\bullet}$) thus formed abstracts hydrogen from the SA backbone to produce SA macroradicals ($SA^{\bullet}$) that interact with a suitable monomer (M) to initiate grafting. The following reaction mechanism has been suggested:

$$Fe^{+2} + H-O-O-H \rightarrow {}^{\bullet}OH(R^{\bullet}) + Fe^{+3} + OH^{-} \quad (1)$$

$$R^{\bullet} + M \rightarrow R-M^{\bullet} \xrightarrow{nM} R-(M)^{\bullet}_{n+1} \quad (2)$$

$$R^{\bullet} + SA \rightarrow SA^{\bullet} + H_2O \quad (3)$$

$$R-(M)^{\bullet}_{n+1} + SA \rightarrow SA^{\bullet} + R-(M)_{n+1}-H \quad (4)$$

$$SA^{\bullet} + M \rightarrow SAM^{\bullet} \xrightarrow{nM} SA(M)^{\bullet}_{n+1} \quad (5)$$

$$SA-(M)^{\bullet}_{n+1} + R^{\bullet} \rightarrow SA-(M)_{n+1}-OH \quad (6)$$

$$SA-(M)^{\bullet}_{n+1} + Fe^{+3} \rightarrow SA-(M)_{n+1} + Fe^{+2} \quad (7)$$

$$M^{\bullet}_{n+1} + Fe^{+3} \rightarrow M_{n+1} + Fe^{+2} + H^{+} \quad (8)$$

$$SA-(M)^{\bullet}_{n+1} + M^{\bullet}_{m} \rightarrow SA-(M)_{n+m+1} \quad (9)$$

It is apparent from the above mechanism that initiation of grafting can occur by processes (3) and (4). Since the concentration of Fenton's reagent is very small, generation of active sites by process (3) involving abstraction of the hydrogen atom from SA is unlikely. $^{\bullet}OH$ will, instead, preferentially interact with AN to give the growing polymeric chains, which then are expected to create active centers on SA by a hydrogen abstraction process (4). If the growing polymeric chain is responsible for initiation of grafting, the percentage of grafting would be expected to increase with increase in monomer concentration, as evidenced in Figure 8. As seen in Figure 7, the percentage of grafting increases with increase in temperature, which also supports the assumption that initiation of grafting primarily occurs by a hydrogen abstraction process that has higher activation energy.

REFERENCES

1. R. C. Burr, G. F. Fanta, C. R. Russell, and C. E. Rist, *J. Macromol. Sci.-Chem.*, **2**, 93 (1968).
2. M. Lipson, *Nature*, **64**, 576 (1949).
3. B. N. Misra, R. Dogra, I. K. Mehta, and J. K. Jassal, *J. Polym. Sci. Polym. Chem. Ed.*, **17**, 1861 (1979).
4. B. N. Misra, R. Dogra, and I. K. Mehta, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 749 (1980).
5. B. N. Misra, I. K. Mehta, and R. C. Khetarpal, *J. Polym. Sci. Polym. Chem. Ed.*, **22**, 2767 (1984).
6. J. Das, A. K. Mohanty, and B. C. Singh, *J. Polym. Mater.*, **6**, 91 (1989).

7. B. K. Patel, V. K. Sinha, and H. C. Trivedi, *J. Polym. Mater.*, **8,** 321 (1991).
8. S. B. Shah, B. K. Patel, C. P. Patel, and H. C. Trivedi, *Starch/Stärke,* **44,** 108 (1992).
9. B. K. Patel, C. P. Patel, and H. C. Trivedi, *J. Polym. Mater.*, **9,** 171 (1992).
10. B. K. Patel, C. P. Patel, and H. C. Trivedi, *Starch/Stärke,* **45,** 70 (1993).
11. V. K. Sinha, C. P. Patel, and H. C. Trivedi, *Prajna Jr. Sardar Patel Univ. India,* **2,** 25 (1992).
12. B. K. Patel, V. K. Sinha, C. P. Patel, and H. C. Trivedi, *Starch/Stärke,* **45,** 178 (1993).
13. V. K. Sinha, C. P. Patel, and H. C. Trivedi, *J. Polym. Mater.*, **10,** 209 (1993).
14. S. B. Shah, C. P. Patel, and H. C. Trivedi, *High Performance Polym.*, **4,** 151 (1992).
15. R. Mehrotra and B. Ranby, *J. Appl. Polym. Sci.*, **21,** 3407 (1977).
16. B. K. Patel, PhD Thesis, Sardar Patel University, India, 1990.
17. T. Nagabhushanam, K. T. Joseph, and M. Santappa, *J. Polym. Sci. Polym. Chem. Ed.*, **16,** 3287 (1978).
18. D. J. McDowall, B. S. Gupta, and V. T. Stannett, *Prog. Polym. Sci.*, **10,** 1 (1984).
19. Z.-C. Li, Z.-F. Fu, M.-Z. Huang, and N. Lian, *J. Macromol. Sci.-Chem.*, **A25**(12), 1487 (1988).
20. V. K. Sinha, PhD Thesis, Sardar Patel University, India, 1990.
21. F. Haber and J. Weiss, *Naturwiss,* **29,** 948 (1932).
22. F. Haber and J. Weiss, *Proc. R. Soc. Lond. Ser. A,* **147,** 332 (1934).

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