

Grafting of Acrylonitrile onto Styrene–Maleic Acid Copolymer by Tetravalent Cerium Ion

R. A. VORA,¹ H. C. TRIVEDI,² C. P. PATEL,² and M. C. TRIVEDI^{3,*}

¹The Department of Applied Chemistry, Maharaja Sayajirao University, Baroda-390 002, India; ²The Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar-388 120, India; ³Research Centre, Gujarat State Fertilizers Company Ltd., Fertilizernagar, Vadodara-391 750, India

SYNOPSIS

The graft copolymerization of acrylonitrile (AN) onto a styrene–maleic acid copolymer (SY–MAc) with ceric ammonium nitrate (CAN) as a redox initiator in an aqueous medium has been studied. The effects of various reaction parameters, including reaction time and temperature, concentrations of initiator, nitric acid, and monomer, on the grafting yields and the rates of polymerization (R_p), graft copolymerization (R_g), and homopolymerization (R_h) were studied systematically. The results are discussed. The kinetic scheme of free-radical graft copolymerization has been proposed and the equations relating the values of R_p , R_g , and R_h are also suggested. The experimental results are found to be in good agreement with the proposed kinetic scheme. The activation energies of graft copolymerization and total polymerization are calculated. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Graft copolymerization provides a general route for the modification of both the physical and the chemical properties of natural and synthetic polymers. In our previous articles, we determined the optimized reaction conditions for Fenton's reagent-initiated graft copolymerization of acrylonitrile onto sodium alginate¹ and reported the kinetics and reaction mechanism for the same.² Considerable effort has been spent on developing methods for grafting maleic anhydride (MA) or MA copolymers to the backbone of a variety of saturated and unsaturated polymeric materials.³ This communication presents the results of studies of grafting acrylonitrile onto a styrene–maleic acid copolymer (SY–MAc) using tetravalent ceric ions.

EXPERIMENTAL

A styrene–maleic anhydride (50 : 50) copolymer (SY–MA) was prepared using 2,2'-azobisisobuty-

ronitrile as an initiator.⁴ The copolymer was extracted in a Soxhlet extractor with benzene to remove free polystyrene and was further purified by the reprecipitation method. It was finally dried under vacuum at 50°C. The sample of SY–MA was hydrolyzed by mixing the copolymer with enough water to make a 1% solution and then agitated slowly on a shaker bath (Tempo, Bombay, India) at 60°C until the completion of hydrolysis of the copolymer. The completion of hydrolysis was ensured by achieving constancy in the pH of the solution. The solution of styrene–maleic acid (SY–MAc) thus obtained was filtered through a G-3 sintered glass funnel. The concentration of the stock solution of SY–MAc was determined from the dry weight of SY–MAc by evaporating a known volume of SY–MAc solution. The concentration of the stock solution of SY–MAc thus was found to be 0.43%.

Acrylonitrile (AN), JC's chemical pure grade, was distilled at an atmospheric pressure through a fractionating column and the center cut was used in the copolymerization reactions. Ceric ammonium nitrate (CAN) of reagent grade (Chiti Chem, Baroda) was used as received. Dimethylformamide (DMF) and acetone were purified by the usual procedure. Analar-grade nitric acid was used. Nitrogen was purified by passing through a freshly prepared alkaline

* To whom correspondence should be addressed.

pyrogallol solution. The low conductivity water was used for the preparation of solutions as well as in the polymerization reactions.

Graft Copolymerization

The grafting reactions were carried out under a nitrogen atmosphere in a 250 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, 50 mL (0.43%) of SY-MAC solution was taken in the flask and a slow stream of nitrogen was bubbled for 30 min, with constant stirring at the desired temperature (20–45°C). A freshly prepared 5 mL solution of CAN (0.05–0.35M) in nitric acid (0.1–0.6N) was added and stirred for 20 min. Nitrogen gas was continuously passed through the reaction mass and freshly distilled AN monomer (1.0–5.0 mL) was added. The grafting reactions were carried out for varying time intervals (0.5–15 h). After completion of the reaction, the mixture was immediately filtered and the crude copolymer product was repeatedly washed with conductivity water and finally with acetone. The crude graft copolymer sample, viz., SY-MAC-*g*-PAN, was dried at 40°C under vacuum until constant weight was obtained.

The grafting yields and the rates of polymerization (R_p), graft copolymerization (R_g), and homopolymerization (R_h) were calculated in the following manner:

Percentage grafting (% G)

$$= \frac{\text{wt of polymer grafted}}{\text{initial wt of backbone}} \times 100$$

Percentage of total conversion (% C_t)

$$= \frac{\text{wt of polymer grafted} + \text{wt of homopolymer}}{\text{wt of monomer charged}} \times 100$$

Percentage grafting efficiency (% GE)

$$= \frac{\text{wt of polymer grafted}}{\text{wt of polymer grafted} + \text{wt of homopolymer}} \times 100$$

Rate of polymerization (R_p)(mol L⁻¹ s⁻¹)

$$= \frac{\text{wt of polymer grafted} + \text{wt of homopolymer}}{\text{Mol wt of monomer}} \times 1000 \\ \times \text{reaction time in seconds} \\ \times \text{volume of the mixture (mL)}$$

Rate of graft copolymerization (R_g)(mol L⁻¹ s⁻¹)

$$= \frac{\text{wt of polymer grafted}}{\text{Mol wt of monomer}} \times 1000 \\ \times \text{reaction time in seconds} \\ \times \text{volume of the mixture (mL)}$$

Rate of homopolymerization (R_h)(mol L⁻¹ s⁻¹)

$$= \frac{\text{wt of homopolymer}}{\text{Mol wt of monomer}} \times 1000 \\ \times \text{reaction time in seconds} \\ \times \text{volume of the mixture (mL)}$$

IR Spectra

The infrared (IR) spectra of SY-MAC, polyacrylonitrile (PAN), and SY-MAC-*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 graft copolymer is based on the difference in solubility of the graft copolymer and the nongrafted homopolymer. SY-MAC is soluble in water and homopolymer (PAN) is soluble in DMF. When a reaction product was Soxhlet-extracted with DMF and water alternatively for 48 h, an insoluble solid still remained. A physical mixture of SY-MAC 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 SY-MAC and PAN macromolecules.
- (ii) Infrared spectral analysis was utilized to prove grafting. For this purpose, the IR spectra of SY-MAC, PAN, and SY-MAC-*g*-PAN were taken and it was observed that the graft copolymer showed absorption bands of SY-MAC and an additional band at around 2250 cm⁻¹, which was 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 the grafting has taken place.

Determination of Optimum Reaction Conditions

In the study of ceric ion-induced grafting of AN onto SY-Mac, various conditions were used to discover those optimum for grafting.

Effect of Initiator Concentration

Figure 1 shows the dependence of the grafting yields on initiator concentration. The percent grafting increases with increase in the initiator concentration but reaches a maximum value of 269.76% at 0.25 mol/L of CAN. A further increase in CAN concentration is accompanied by a decrease in the grafting yields. The observed increase in % *G* within the CAN concentration range of 0.05–0.25 mol/L may be because, in this concentration range, the activation along the backbone takes place immediately, followed by graft copolymerization of the monomer onto backbone. A relatively high concentration of the initiator may cause a reduction of grafting due to an increase in the number of backbone radicals terminated prior to AN addition. Furthermore, homopolymer formation at higher initiator concentration which competes with the grafting reaction for the available monomer could lead to a decrease in graft yield. Similar observations have been reported in the literature.⁵⁻⁹

In the initial stage (Fig. 1), higher *GE* has been found, which may be due to the fast dissociation of CAN, since less Ce(IV) would be available for initiation.¹⁰ Beyond the optimum concentration of CAN, a decrease in *GE* was observed which may be due to the termination of growing grafted chains.¹¹

Effect of Acid Concentration

The effect of acid concentration on the grafting yields is shown in Figure 2. It is seen that there

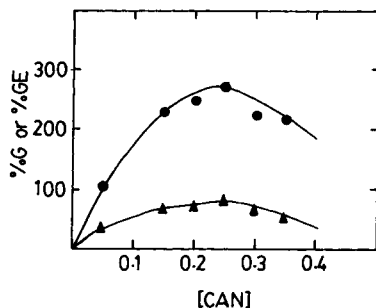


Figure 1 Effect of ceric ammonium nitrate (CAN) on (●) percent grafting, % *G*, or (▲) percent grafting efficiency, % *GE*.

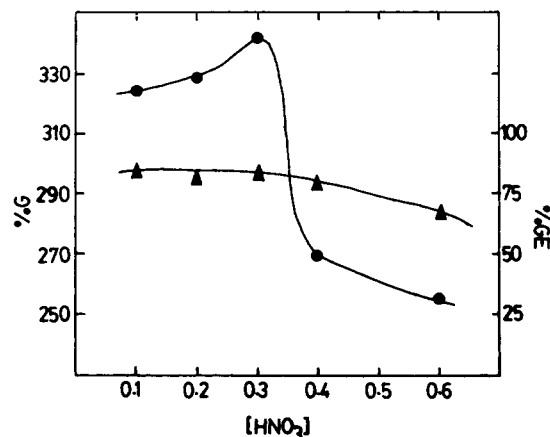


Figure 2 Effect of nitric acid on (●) percent grafting, % *G*, or (▲) percent grafting efficiency, % *GE*.

exists an optimum concentration of nitric acid (0.30 mol/L) which affords maximum percent grafting. Beyond this concentration of nitric acid, the percentage grafting decreases. In the beginning, the percentage of grafting increases with increase in $[H^+]$. This is attributed to the increases in the concentrations of $[Ce(OH)_3]^{3+}$ and Ce^{4+} at the expense of $(Ce-O-Ce)^{6+}$. Ceric (Ce^{4+}) and $[Ce(OH)_3]^{3+}$, being smaller in size, are more effective in their ability to form complexes with SY-MAc than is $(Ce-O-Ce)^{6+}$. With a further increase in nitric acid concentration beyond 0.30 mol/L, it is observed that % *G* as well as % *GE* (Fig. 2) decreases. This is not only due to the recombination and disproportionation of the graft macroradicals but also might be due to the decrease in complexation efficiency of SY-MAc at high acid concentrations. The results obtained in the present case are similar to the grafting of acrylamide onto starch,⁷ methylmethacrylate (MMA) onto starch,¹² and AN onto carboxymethyl amylose,¹³ sodium alginate,⁹ and carboxymethylated starch.¹⁴

Effect of Temperature

The effect of temperature on percentage of grafting as well as grafting efficiency is depicted in Figure 3. It is apparent from this figure that with an increase in temperature from 20 to 45°C, % *G* as well as % *GE* increases significantly. These findings can be explained by the fact that the solubility of SY-MAc, the solubility of the monomer, and its diffusion rates are enhanced by increasing the temperature, and as a result, graft yields are found to be increased. Similar types of results are also reported in the literature.^{12,15,16}

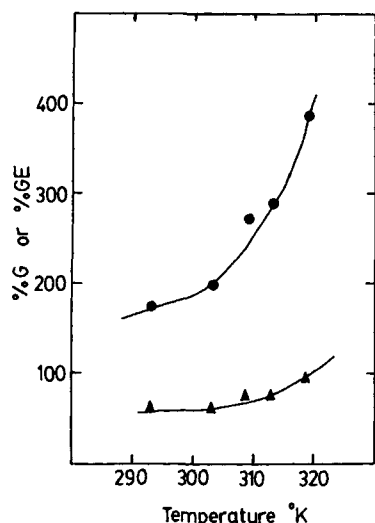


Figure 3 Effect of temperature on (●) percent grafting, % *G*, or (▲) percent grafting efficiency, % *GE*.

Effect of Monomer Concentration

The effect of monomer (AN) concentration on the percentage of grafting (% *G*) as well as percent grafting efficiency (% *GE*) is shown in Figure 4, from which it is clear that the percent grafting increases rapidly with increase in monomer concentration but beyond AN = 0.786 mol/L, the percent grafting increases gradually. This can be explained by the fact that (i) at the higher monomer concentration a larger

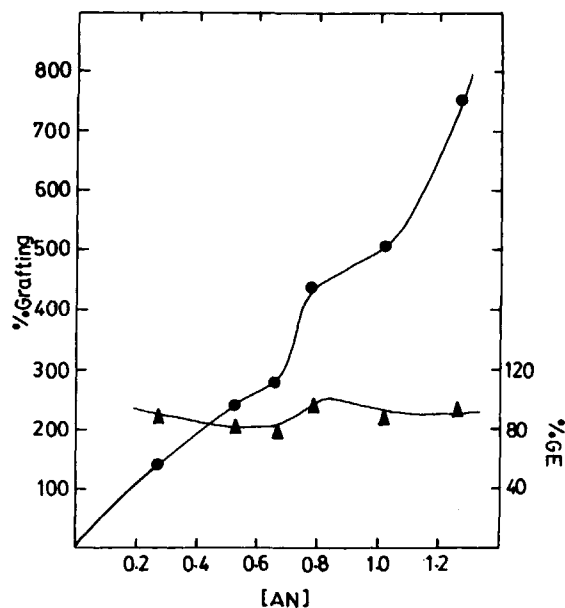


Figure 4 Effect of monomer concentration on (●) percent grafting % *G*, or (▲) percent grafting efficiency, % *GE*.

amount of the growing polymeric chains that are formed are involved in generating additional active sites onto SY-MAc by the chain-transfer reaction and (ii) with the increase of monomer concentration the viscosity of the medium would be increased owing to the solubility of PAN in its own monomer, which will hinder termination, particularly by the coupling of growing polymer chains.

Figure 5 shows that an increase in AN concentration increases the rate of polymerization (R_p). The rate of graft copolymerization (R_g) also increases rapidly up to AN = 0.786 mol/L and beyond which it increases slowly. But grafting efficiency (Fig. 4) was found to level off after a certain monomer concentration, showing that even when the percent grafting (Fig. 4) and R_g (Fig. 5) are increased, they have not contributed to a progressive increase in grafting efficiency. Egboh and Jinadu¹² and Lenka et al.¹⁵ also made similar observations in the case of grafting of MMA onto starch and cellulose, respectively. The increase in R_h beyond the optimum monomer concentration may be explained by the fact that an increase in the monomer concentration favors homopolymerization.

Effect of Reaction Time

The effect of reaction time on the percentage grafting of AN onto SY-MAc is shown in Figure 6. With an increase in grafting reaction time, the percentage of grafting is found to be increased. After 3 h, the percentage of grafting reaches a plateau level due to

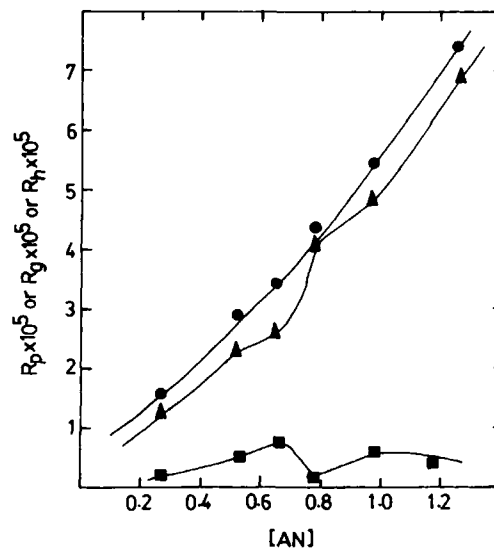


Figure 5 Plot of (●) $R_p \times 10^5$, (▲) $R_g \times 10^5$, or (■) $R_h \times 10^5$ vs. monomer concentration.

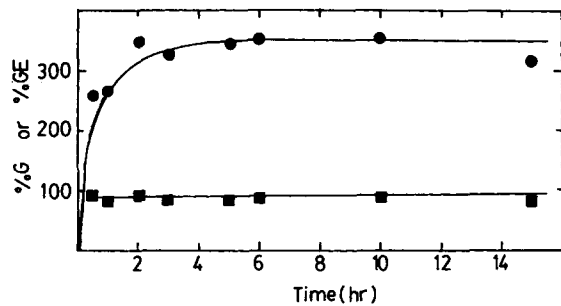


Figure 6 Effect of reaction time on (●) % G or (■) % GE.

the depletion of the monomer and initiator concentration as well as a shortage of the available grafting sites as the reaction proceeds. It can be observed from this figure that grafting efficiency does not change appreciably during the course of the reaction. Similar results were also reported earlier.^{13,17,18}

From Figure 7, it can be seen that % C_t increases up to 3 h and then attains a constant value of about 87%. We thus observe that 3 h is the best duration for this grafting reaction, because the amount of copolymer produced is maximum and the amount of homopolymer is small, and after that time, the other grafting parameters increase slowly until 15 h is reached.

The influence of reaction time on rates of polymerization (R_p), graft copolymerization (R_g), and homopolymerization (R_h) is shown in Figures 8, 9, and 10, respectively. The rate of polymerization, R_p (Fig. 8), decreased with increasing time for the grafting reaction. This effect can be attributed to the fact that the relative increment in the total yield is very much less when compared to that of time, and in the expression for R_p , the numerator becomes

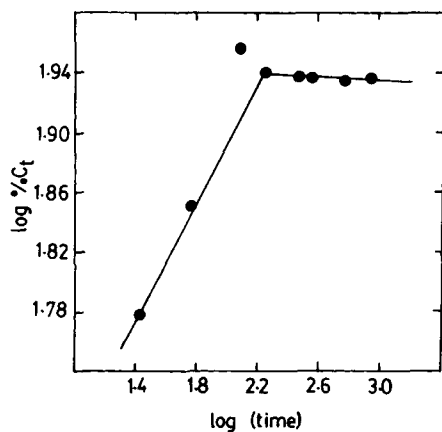


Figure 7 Plot of $\log(\% C_t)$ vs. reaction time.

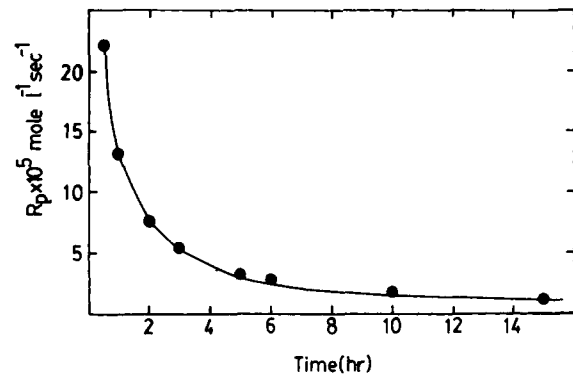


Figure 8 Influence of reaction time on rate of polymerization (R_p).

almost constant, and when the time for the reaction is raised, the denominator becomes larger and the R_p will reduce accordingly. Since R_g and R_h are related to R_p , the relative decrease of R_g (Fig. 9) and R_h (Fig. 10) with time can be understood. Their decrease may also be due to the depletion of the initiator and monomer with time.

The results obtained for the influence of reaction time on the grafting yields and the rates of various reactions are similar to the grafting of MMA onto amylose,¹⁹ AN onto carboxymethyl amylose,¹³ and MMA onto cellulose and oxycellulose.²⁰

Thus, from the above discussion, the optimized reaction conditions obtained in the graft copolymerization of AN onto SY-MAc are CAN = 0.25 mol/L, HNO_3 = 0.3 mol/L, temperature = 45°C, AN = 0.786 mol/L, and time = 3 h.

Kinetics and Mechanism

In the case of SY-MAc, the reactive groups are carboxyl. These groups are known to form a complex

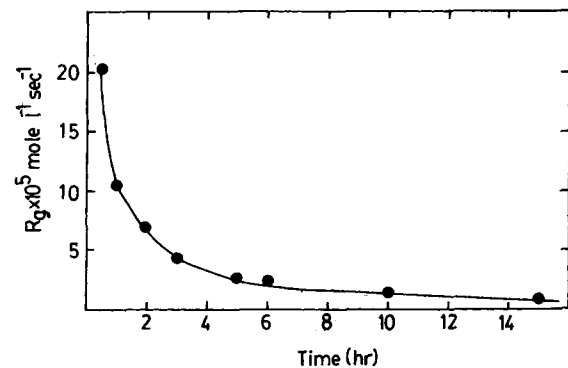


Figure 9 Influence of reaction time on rate of grafting (R_g).

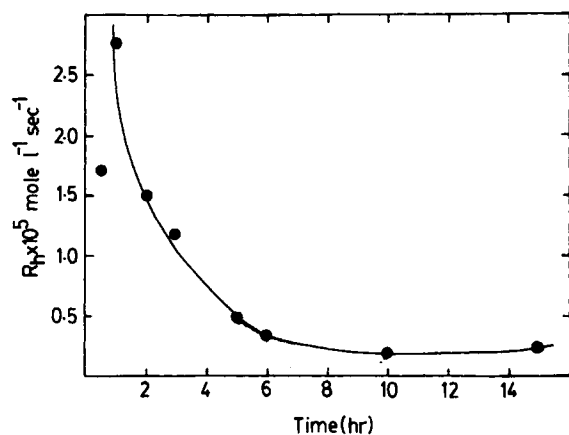
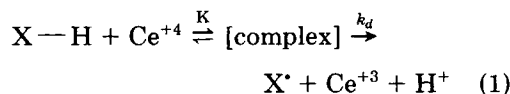


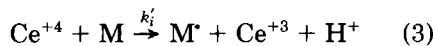
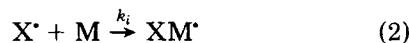
Figure 10 Influence of reaction time on rate of homopolymerization (R_p).

with ceric ion. The complex may dissociate, giving rise to free-radical sites onto SY-MAc. The mechanism of free-radical graft copolymerization of AN onto SY-MAc is expected to proceed according to the following proposed scheme¹³:

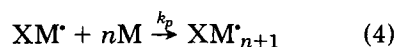
(i) Radical generation:



(ii) Initiation:

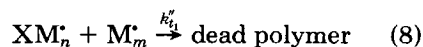
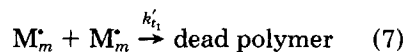
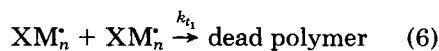


(iii) Propagation:



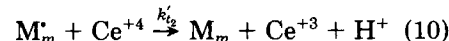
(iv) Termination: Two types of termination may take place—

(a) At lower Ce^{+4} concentrations, the growing chain is terminated by the recombination of double radicals:

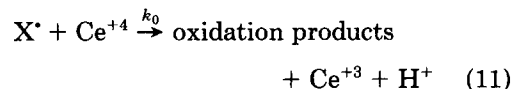


(b) At higher Ce^{+4} concentrations, the

growing chain is terminated by a single radical:



(v) Oxidation:



where X—H denotes the reactive group of SY-MAC, M is the monomer, K is the equilibrium constant, and K_d , k_i , k'_i , k_p , k'_p , k_{t1} , k'_{t1} , k''_{t1} , k_{t2} , k'_{t2} , and k_0 are the rate constants of the respective reactions. It is assumed that $k_p = k'_p$, $k'_{t1} = k''_{t1}$ and $k_{t2} = k'_{t2}$.

For the case of double-radical termination, assuming a steady state, the rate of graft copolymerization, R_g , is given by¹³

$$R_g = \frac{k_p k_d^{0.5} K [\text{X—H}][\text{M}][\text{Ce(IV)}]^{0.5}}{k_{t1}^{0.5} (k_d K [\text{X—H}] + k_i [\text{M}])^{0.5}} \quad (12)$$

the rate of homopolymerization R_h is

$$R_h = \frac{k_p k'_i}{k_{t1}^{0.5}} \frac{[\text{M}]^2 [\text{Ce(IV)}]^{0.5}}{(k_d K [\text{X—H}] + k_i [\text{M}])^{0.5}} \quad (13)$$

and the total rate of polymerization, R_p , would be

$$R_p = R_g + R_h \quad (14)$$

Similarly, for the case of single-radical termination,

$$R_g = \frac{k_p k_d K}{k_{t2}} \frac{[\text{M}]^2 [\text{X—H}]}{[\text{M}] + (k_0/k_i)[\text{Ce(IV)}]} \quad (15)$$

Table I Rates of Graft Copolymerization (R_g) and Polymerization (R_p) for Grafting of AN onto SY-MAc at Various Initiator Concentrations^a

[CAN] (mol L ⁻¹)	$R_g \cdot 10^5$ (mol L ⁻¹ s ⁻¹)	$R_p \cdot 10^5$ (mol L ⁻¹ s ⁻¹)
0.05	0.98	2.67
0.15	2.21	3.54
0.20	2.39	3.67
0.25	2.62	3.36
0.30	2.14	3.39
0.35	2.09	3.92

^a SY-MAc = 50 mL (0.43%), HNO_3 = 0.3M, temperature = 45°C, AN = 0.786M, time = 3 h.

Table II Rates of Polymerization (R_p) and Graft Copolymerization (R_g) for Grafting of AN onto SY-MAc at Different Temperatures^a

Temperature (K)	$R_p \cdot 10^5$ (mol L ⁻¹ s ⁻¹)	$R_g \cdot 10^5$ (mol L ⁻¹ s ⁻¹)
293.15	2.62	1.68
303.15	3.05	1.87
308.15	3.36	2.62
313.15	3.64	2.78
318.15	3.95	3.74

^a SY-MAc = 50 mL (0.43%), CAN = 0.25M, HNO₃ = 0.3M, AN = 0.786M, time = 3 h.

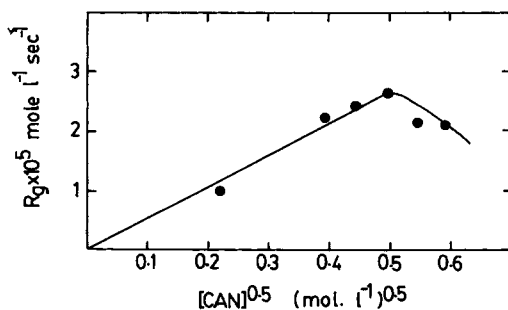
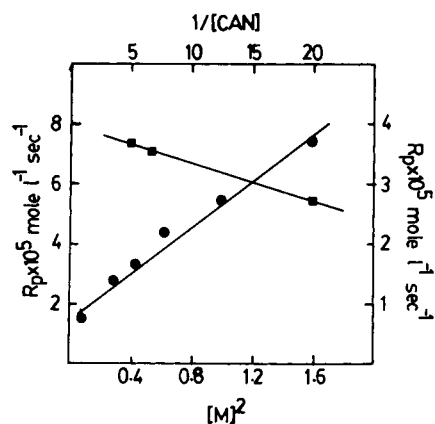
$$R_h = \frac{k_p k'_i}{k_{t_2}} [M]^2 \quad (16)$$

$$R_p = R_g + R_h = \frac{k_p}{k_{t_2}} [M]^2 \left\{ \frac{k_d K [X-H]}{[M] + (k_0/k_i)[Ce(IV)]} + k'_i \right\} \quad (17)$$

The above discussion can more or less be illustrated by the data in Tables I and II and Figure 5. The plot of R_g vs. $[CAN]^{0.5}$ should be linear at lower $[CAN]$, according to eq. (12) (Fig. 11). From this figure, it is seen that the plot is linear at lower $[CAN]$, which agrees with termination by recombination of double radicals [eq. (12)]. But, at higher $[CAN]$, the plot deviates from linearity. This may be due to single-radical termination [eq. (15)], which decreases the rate of graft copolymerization.

Katai et al.²¹ reported that $k_0/k_i = 50$ for the study of the ethylene glycol acrylonitrile system and further stated that k_0 is, in general, considerably larger than is k_i . Accordingly, one can write

$$(k_0/k_i)[Ce^{+4}] \gg [M] \quad (18)$$

**Figure 11** Plot of $R_g \times 10^5$ vs. $[CAN]^{0.5}$.**Figure 12** Plots of (●) $R_p \times 10^5$ vs. $[M]^2$ and (■) $R_p \times 10^5$ vs. $1/[Ce^{+4}]$.

and, hence, eq. (15) as well as eq. (17) reduces to

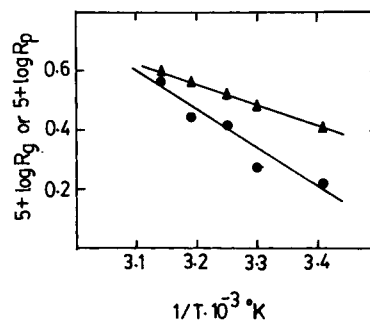
$$R_g = \frac{k_p k_d K}{k_{t_2}} \frac{[M]^2 [X-H]}{(k_0/k_i)[Ce(IV)]} \quad (19)$$

and

$$R_p = \frac{k_p}{k_{t_2}} [M]^2 \left\{ \frac{k_d K [X-H]}{(k_0/k_i)[Ce(IV)]} + k'_i \right\} \quad (20)$$

respectively.

The effect of the concentration of the initiator as well as that of the monomer on the overall rate of polymerization (R_p) (Table I and Fig. 5) as expected from the above relation is exemplified in Figure 12. The plots of R_p vs. $[M]^2$ and R_p vs. $1/[Ce^{+4}]$ are found to be linear, which supports the above scheme. From the Arrhenius plot of $\log R_p$ vs. $1/T$ as well as $\log R_g$ vs. $1/T$ (Fig. 13), the overall activation energy for polymerization (R_p) and the activation energy

**Figure 13** Plot of (▲) $5 + \log R_p$ and (●) $5 + \log R_g$ in mol L⁻¹ s⁻¹ vs. $1/T$.

for graft copolymerization (R_g) were found to be 5.56 and 10.70 kJ/mol, respectively.

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