

Graft Copolymerization of Polyacrylonitrile (PAN) onto Polyester (PET) and Simultaneous Homopolymerization: A Kinetic Study. I

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SYNOPSIS

The kinetics of graft copolymerization of polyacrylonitrile (PAN) onto polyester (PET) and the simultaneous homopolymerization initiated by the potassium peroxomonosulfate (PMS)–ascorbic acid (H₂A) redox system were studied separately. Results on the graft copolymerization was adequately explained by a mechanism which also accounts for the reason for simultaneous homopolymerization. The observed homopolymerization results agreed with the proposal. Kinetic chain-length measurements on the graft copolymer and homopolymerization were used to evaluate the kinetic parameters. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Graft copolymerization of vinyl monomers onto substrate polymers is generally considered to involve the generation of reactive sites on the polymer. This can be achieved by several means, such as high-energy radiation,¹ low-energy radiation in the presence or absence of stabilizers,² and chemical methods.^{3–5} Among chemical methods, redox-initiated grafting is advantageous because grafting can be carried out under milder conditions.⁶

A variety of redox systems have been employed for the initiation of graft copolymerization of vinyl monomers onto a synthetic or natural polymer backbone.⁷ The oxidation of ascorbic acid (H₂A) has been studied extensively using a variety of reagents and conditions^{8–12} and the oxidation was proved to proceed via radical mechanism in these studies. Although the peroxosalts have been exhaustively studied, the use of peroxomonosulfate (PMS), one component of the redox pair in the graft copolymerization, is of comparatively recent origin.¹³

While using redox pairs for grafting-initiation purposes, it is quite reasonable to expect simulta-

neous homopolymerization also to occur. Under these circumstances, a systematic kinetic study of the graft copolymerization and the simultaneous homopolymerization separately would reveal the mechanism of such independent reactions. Such knowledge about these mechanisms would be useful in the control of homopolymerization over grafting by the proper choice of conditions, if needed. This study directs its attention to elucidate the mechanism of graft copolymerization of acrylonitrile (AN) on polyester poly(ethylene terephthalate) (PET), using the PMS–H₂A system and its simultaneous homopolymerization by a systematic kinetic study.

EXPERIMENTAL

Materials and Methods

Acrylonitrile (Robert Johnson) was used after purification as described earlier.¹⁴ Potassium peroxomonosulfate (Aldrich, USA, under the name "OXONE") was a gift sample. A stock solution of oxone (0.1M) was prepared by dissolving 6.147 g of the sample in water in a 100 mL standard measuring flask. The acidity of the solution was determined by titrating against standard alkali using a methyl orange indicator. The % of active oxygen in the freshly

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prepared stock solution was estimated by iodimetry and found to be 4.86 as against the theoretical value of 5.20.

The ascorbic acid (H₂A) (BDH AR) sample was used as such, and the solution of H₂A was prepared freshly for each experiment. PET in the form of fiber, a gift sample from Madura Coats, India, was purified by rinsing with hot water and cold water and dried at room temperature. This was finally extracted with methyl alcohol for 24 h to remove any adhering material.¹⁵

Procedure

A typical graft copolymerization study was carried out as given below: PET (W_1g) and the required amount of the reductant (H₂A), sulfuric acid (to adjust acidity), and sodium sulfate (to adjust ionic strength) were taken in a reaction vessel and thermostated for 30 min and the required amount of the monomer (AN) and the oxidizing agent (PMS) solution were added to the reaction mixture. The time of adding the oxidizing agent was taken as the starting time for the reaction (polymerization conditions were selected in such a way that no polymerization occurred in the absence of added oxidant. This was ascertained by a separate experiment). The reaction vessel was sealed with rubber gaskets to ensure an inert atmosphere during reaction time intervals.

At the end of the reaction time, the reaction was arrested by immersing the reaction vessel in cold water ($\sim 10^\circ\text{C}$) and blowing air into the tube to freeze further reactions. The grafted PET along with the homopolymer (polyAN) was filtered from the reaction mixture using a C-3 sintered crucible, washed with distilled water several times, dried (60°C for 6 h), and weighed to constant weight. This gives the total weight of the grafted polymer with the homopolymer (W_2g).

The mixture of grafted PET along with the homopolymer PAN was Soxhlet-extracted with acetone for 24 h to separate the homopolymer. After the separation of the homopolymer, the grafted sample was cooled to room temperature and weighed to constant weight (W_3g). The difference ($W_3 - W_1$)g gives the weight of the grafted polymer. The difference ($W_2 - W_3$)g gives the weight of the homopolymer (PAN).

The rate of PMS disappearance ($-R_{\text{PMS}}$) was determined by following the unreacted [PMS] by iodimetric titration.¹⁶ The rate of disappearance of PM: $-R_{\text{PMS}}$ was calculated as follows:

$$-R_{\text{PMS}} = \frac{[\text{PMS}]_{\text{initial}} - [\text{PMS}]_{\text{at reaction time}}}{\text{reaction time}}$$

By blank titration, it was ascertained that the presence of H₂A did not interfere with the above titration procedure.

Rate Measurements

Graft Copolymerization

The rate of grafting (R_g), rate of homopolymerization (R_h), % grafting, and % efficiency were calculated as follows:

$$\% \text{ Grafting} = \frac{\text{(dry weight of the grafted sample)} - \text{(dry weight of the backbone)}}{\text{dry weight of the backbone}}$$

% Grafting efficiency

$$\begin{aligned} &= \frac{\text{weight of the grafted polymer}}{\text{weight of monomer used } (W_4g)} \times 100 \\ &= \frac{(W_3 - W_1)}{W_4} \times 100 \end{aligned}$$

$$\text{Rate of grafting } (R_g) = \frac{1000(W_3 - W_1)}{V.t.M.}$$

where ($W_3 - W_1$) = weight of the grafted polymer, V = total volume of the reaction mixture, t = reaction time (s), and M = molecular weight of the monomer used.

Simultaneous Homopolymerization

R_h was calculated as follows:

$$R_h = \frac{1000(W_2 - W_3)}{V.t.M.}$$

where ($W_2 - W_3$) = weight of the homopolymer and V , t , and M are as given above.

Isolation of Grafted Polymeric Chain from Polyester (PET)

The grafted PET was digested with phenol/trichlorophenol 10/7 volume for 30 min. The digestion was allowed to proceed for 24 h.¹⁷ The residue was washed with boiling water and dried.

Chain-length Measurements

Homopolymer (PAN). The chain length " n " of the separated homopolymer PAN was determined by viscometry in dimethylformamide at 25°C ¹⁸ using

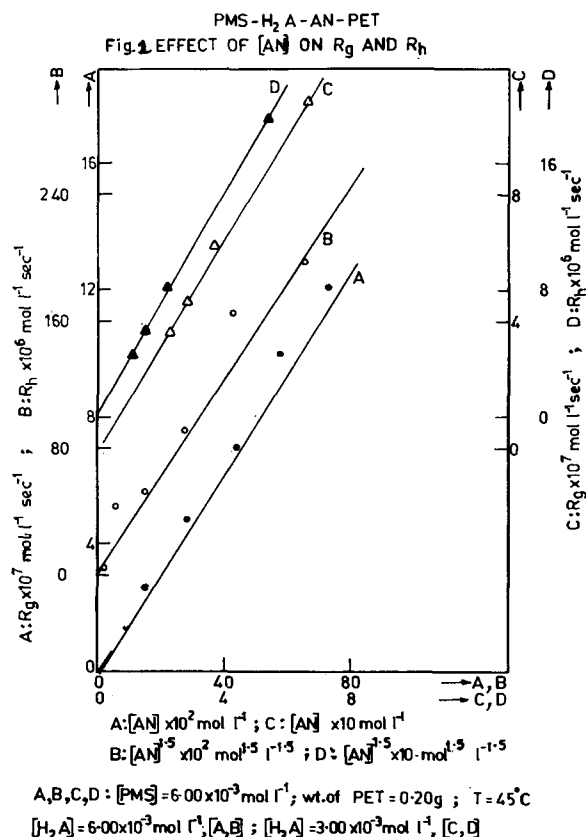


Figure 1 PMS-H₂A-AN-PET: Effect of [AN] on R_g and R_h .

$$[\eta] = 2.43 \times 10^{-4} \times M_v^{-0.75}$$

Grafted Polymer. The determination of the molecular weight of grafted chains of PAN onto PET was carried out viscometrically as above.¹⁸

RESULTS AND DISCUSSION

The kinetic results on the graft copolymerization was found to be smooth (though the medium was heterogeneous) during graft copolymerization. This was evident from the following kinetic observations:

Effect of [AN] on Graft Parameters

The rate of grafting (R_g), kinetic chain length of grafted chains of PAN (n_g), % grafting, and % efficiency were followed for different [AN] by keeping other experimental conditions constant.

R_g increases steadily with [AN]. The direct plot R_g vs. (AN) [Fig. 1(A) and (C)] were drawn and found to be a straight line passing through the origin

and, thus, confirming the order of R_g with respect to AN as unity. The clear first-order dependence of R_g on [AN] at different experimental conditions is an indication of the smoothness of the kinetic results.

The kinetic chain length of the grafted backbone (n_g) was determined for the above conditions. n_g increases with [AN]. The plot $\log n_g$ vs. $\log[AN]$ [Fig. 2(A)] was found to be a straight line with a slope of unity, thus confirming the first-order dependence of n_g on [AN]. A direct plot n_g vs. [AN] [Fig. 2(C)] was also a straight line and found to pass through the origin.

The effect of change in [AN] on % grafting and % efficiency are given in Table I. It was observed that % grafting increases steadily with increase in [AN] but that % efficiency shows an increasing trend initially and then decreases.

Effect of [AN] on Homopolymerization Parameters

The rate of homopolymerization (R_h) was also found under the identical conditions at which the grafting

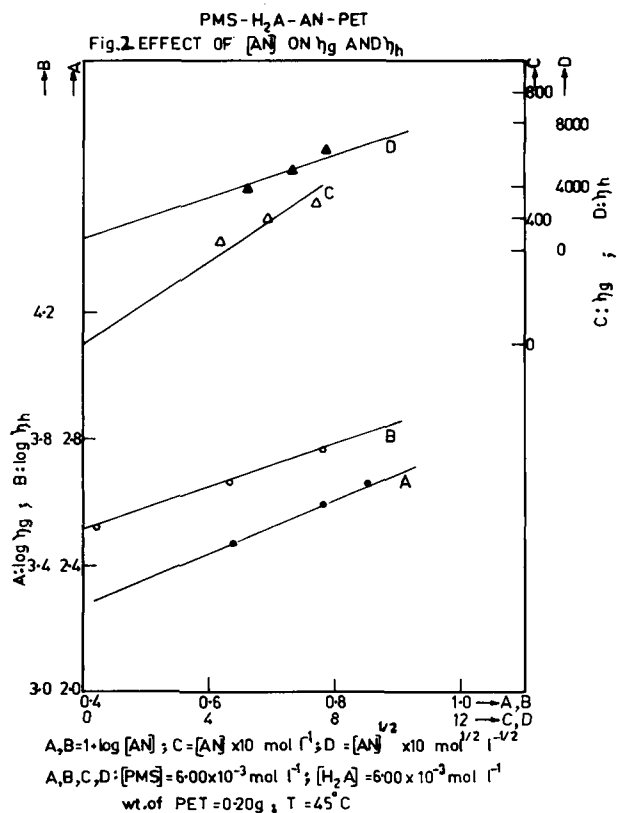


Figure 2 PMS-H₂A-AN-PET: Effect of [AN] on n_g and n_h .

Table I Effect of [AN] and [PMS] on % Grafting and % Efficiency ($[H_2A] = 3.00 \times 10^{-3}$ mol L $^{-1}$; $T = 45^\circ C$; Weight of PET = 0.20 g)

	% Grafting	% Efficiency
[AN] ^a × 10 ¹ mol L ⁻¹		
2.290	10.2	3.36
2.862	12.5	3.68
3.721	18.1	3.67
6.583	31.3	3.58
[PMS] ^b × 10 ⁴ mol L ⁻¹		
10.0	3.38	0.901
26.0	5.40	1.420
46.0	7.00	1.84
66.0	8.80	2.32

^a [PMS] = 6.00×10^{-3} mol L⁻¹.

^b [AN] = 22.9×10^{-2} mol L⁻¹.

reactions were carried out. However, in the absence of PET, homopolymerization was found to occur with a very low rate of homopolymerization (R_h) under the same conditions of grafting. The direct plot R_h vs. $(AN)^{1.5}$ [Fig. 1(B) and (D)] were found to pass through the origin and pointed out the three-half-order dependence of R_h on [AN].

The kinetic chain length of the homopolymer (n_h) was determined separately by a viscometric method. The plot $\log n_h$ vs. $\log[AN]$ [Fig. 2(B)] was a straight line with a slope value of 0.5. The direct plot n_h vs. $(AN)^{0.5}$ [Fig. 2(D)] was also a straight line and found to pass through the origin.

Rate of Disappearance of PMS ($-R_{PMS}$)

$-R_{PMS}$ was followed volumetrically under all the conditions at which graft copolymerization was carried out. It was found that $-R_{PMS}$ values remain invariant for the conditions mentioned in Table I.

Effect of (PMS) on Graft Parameters

The values of R_g obtained by changing [PMS] showed an increasing trend. The direct plot R_g vs. $[PMS]^{0.5}$ [Fig. 3(A) and (C)] were found to be straight lines with a slope of 0.5. This indicates a square-root-order dependence of [PMS] on R_g .

The kinetic chain length of the grafted backbone (n_g) was determined by a viscometric method for the above conditions: n_g decreases with [PMS]. The plot $\log n_g$ vs. $\log[PMS]$ [Fig. 4(A)] was a straight line with a slope of -0.5 . A direct plot of n_g vs. $(PMS)^{-1/2}$ [Fig. 4(C)] was also drawn in order to confirm the inverse square root order with respect to n_g on [PMS].

Table I gives the % grafting and % efficiency obtained during grafting on the change in (PMS). It was observed that with % grafting and % efficiency steadily increase with increase in [PMS].

Effect of [PMS] on Homopolymerization Parameters

R_h was found to increase with (PMS). A direct plot of R_h vs. $(PMS)^{1/2}$ [Fig. 3(B) and (D)] were found to be straight lines with a slope of 0.5, suggesting a square-root-order dependence of R_h on [PMS].

n_h was found to decrease with [PMS]. The $\log n_h$ vs. $\log[PMS]$ [Fig. 4(B)] plot was a straight line with a slope of the value of negative 0.5. The linearity in the plot n_h vs. $(PMS)^{-1/2}$ [Fig. 4(D)] confirms the above observation.

$-R_{PMS}$ was found to increase steadily with (PMS). $\log(-R_{PMS})$ vs. $\log(PMS)$ [Fig. 5(A) and (B)] were straight lines with the slope of unity. The unit-order dependence of $-R_{PMS}$ on [PMS] was further evident from the linear nature of $-R_{PMS}$ vs. [PMS] [Fig. 5(C) and (D)].

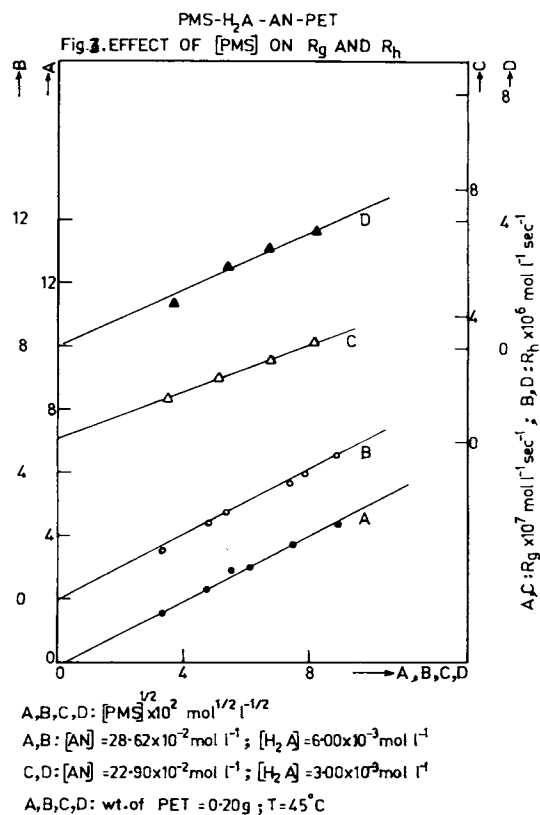


Figure 3 PMS-H₂A-AN-PET: Effect of [PMS] on R_g and R_h .

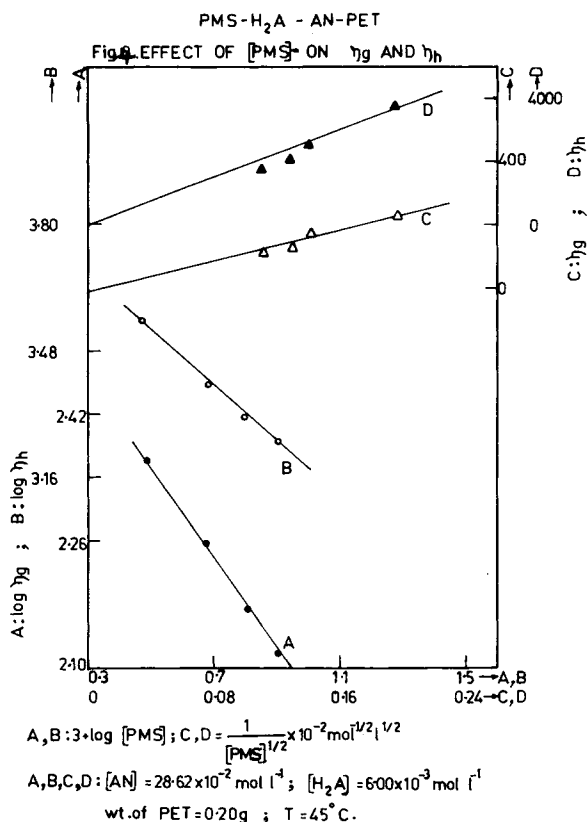


Figure 4 PMS-H₂A-AN-PET: Effect of [PMS] on n_g and n_h .

Effect of [H₂A] on Graft Parameters

The R_g values obtained by varying [H₂A] showed an increasing trend with H₂A. R_g vs. $[H_2A]^{1/2}$ [Fig. 6(A) and (C)] were straight lines passing through the origin, suggesting half-order dependence of R_g on [H₂A].

n_g decreases with increase in [H₂A]. Log n_g vs. log[H₂A] [Fig. 7(A)] was a straight line with a slope of -0.5. The inverse square-root-order dependence of n_g on [H₂A] was also ascertained from the fact that the plot n_g vs. $(H_2A)^{-1/2}$ [Fig. 7(C)] was a straight line passing through the origin. The % grafting and % efficiency values while changing [H₂A] were found to increase with [H₂A] (Table II).

Effect of [H₂A] on Homopolymerization Parameters

R increases with [H₂A]. A direct plot of R_h vs. $[H_2A]^{1/2}$ [Fig. 6(B) and (D)] were found to be straight lines, indicating the half-order dependence of R_h on [H₂A]. n_h decreases with increase in [H₂A]. The log n_h vs. log(H₂A) [Fig. 7(B)] plot was a straight line and gives a slope of negative 0.5. The plot n_h vs.

$(H_2A)^{-1/2}$ [Fig. 7(D)] gives support to the negative half-order dependence. $-R_{PMS}$ values remain almost constant for the conditions mentioned in Table II.

Effect of [PET] Amount on Graft Parameters

R_g showed an increasing trend while increasing the PET amount. A direct plot R_g vs. (weight of PET)^{0.5} [Fig. 8(A) and (C)] were straight lines with a slope of 0.5 and suggesting half-order dependence of R_g on PET.

n_g was found to decrease with the PET amount. The log n_g vs. log(weight of PET) [Fig. 9(A)] plot was a straight line with a slope of negative 0.5. n_g vs. (weight of PET)^{-0.5} [Fig. 9(C)] was drawn to confirm the inverse square-root-order dependence of n_g on the backbone amount.

The % grafting and % efficiency values obtained for the conditions mentioned (Table II) showed that % grafting initially increases and thereafter decreases. On the other hand, % efficiency increases with the backbone material.

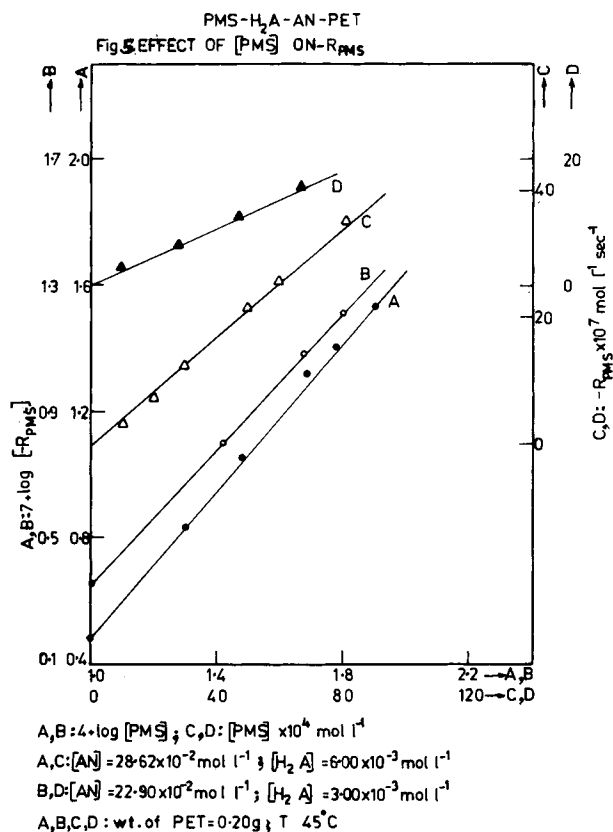


Figure 5 PMS-H₂A-AN-PET: Effect of [PMS] on $-R_{PMS}$.

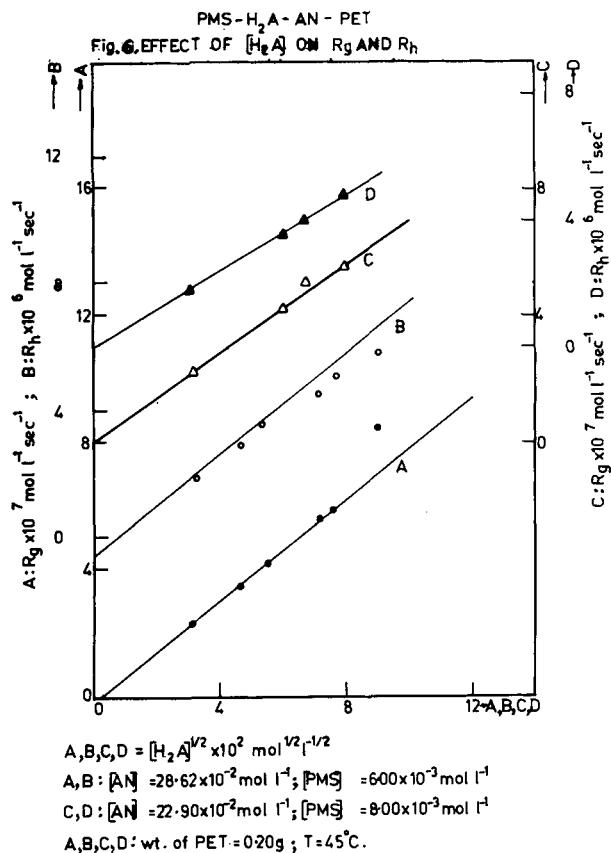


Figure 6 PMS-H₂A-AN-PET: Effect of [H₂A] on R_g and R_h.

Effect of [PET] Amount on Homopolymerization Parameters

R_h values steadily increase with the PET amount. The clear straight line nature of R_h vs. (wt of PET)^{0.5} [Fig. 8(B) and (D)] points out the half-order dependence of R_h on PET.

n_h decreases with the PET amount. The log n_h vs. log(weight of PET) [Fig. 9(B)] plot was found to be straight line with a slope of minus 0.5, indicating the inverse square-root-order dependence of the n_h on PET.

A direct plot n_h vs. (wt of PET)^{0.5} [Fig. 9(D)] was also drawn to confirm the above order dependence. -R_{PMS} was found to be unaffected by the change in PET amount (Table II).

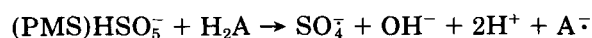
RESULTS

The observed smooth kinetic results clearly point out that reactions of trapped radicals during precipitation in the medium and the consequent autocatalytic effect were not present at these experimental

conditions. Hence, for the proposal of mechanisms, reactions are considered based on the polymerization conditions without an autocatalytic effect during polymerization.

Polymerization of AN by the potassium peroxydiphosphate (PDP)-H₂A system and polymerization of acrylamide, methacrylamide, and methyl methacrylate (MMA) by the potassium peroxydisulfate (PDS)-H₂A system were reported to be initiated by the ascorbate anion radical [A⁻] produced during the interaction between the oxidant and reductant.^{19,20}

A similar type of initiation can therefore be thought of for the present graft copolymerization using the PMS-H₂A system:



A likely additional possibility is the fast step²¹:



The $\dot{O}H$ can now interact with H₂A to generate A⁻ as²²

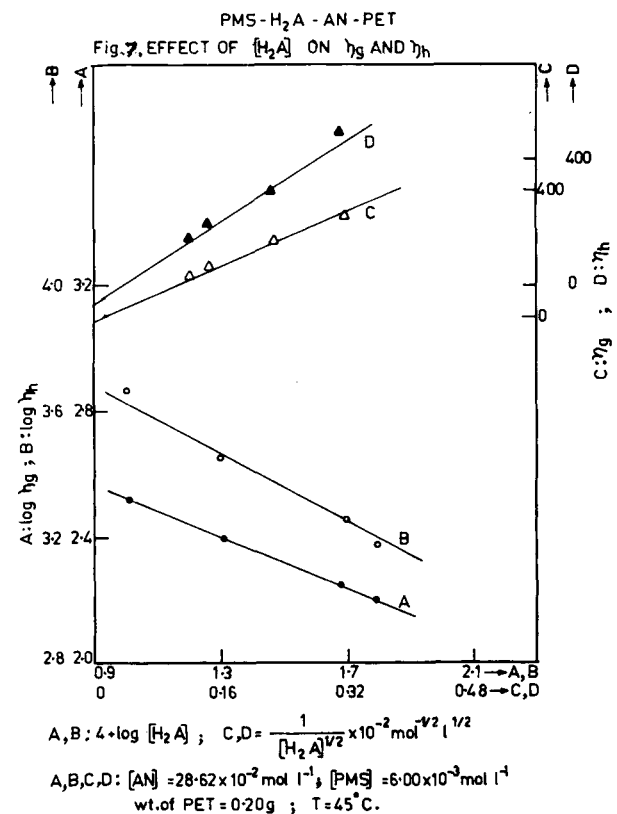


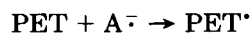
Figure 7 PMS-H₂A-AN-PET: Effect of [H₂A] on η_g and η_h.

Table II Effect of (H₂A) and (Weight of PET) on % Grafting and % Efficiency ([AN] = 28.62 × 10⁻² mol L⁻¹; [PMS] = 6.00 × 10⁻³ mol L⁻¹; T = 45°C)

	% Grafting	% Efficiency
[H ₂ A] ^a × 10 ⁴ mol L ⁻¹		
10.0	6.0	1.58
20.0	9.2	2.42
40.0	12.6	3.12
50.0	16.1	4.23
60.0	17.5	4.61
80.0	24.3	6.43
(Wt of PET) ^b g		
0.05	3.69	2.42
0.10	28.60	3.77
0.15	20.30	4.02
0.25	13.9	4.57
0.30	13.5	5.35
0.35	13.2	6.56

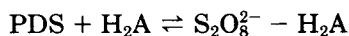
^a Wt of PET = 0.20 g.

^b (H₂A) = 6.00 × 10⁻³ mol L⁻¹.



Based on the above consideration, in the present system, initiation through A[·] may be taken as predominant, although OH[·] and SO₄^{·-} are produced during the interaction between PMS and H₂A.

In the polymerization of AN by PDS-H₂A, Ariff and co-workers²³ proposed a complex formation between PDS and H₂A:



A transfer of A[·] to the monomer during interaction between the PDS-H₂A complex and the monomer was reported to be the initiation step in such a study.²³ A similar complexation may be considered for the present case with PMS as the oxidant:

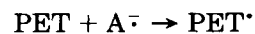


The present work relates to the graft copolymerization of AN onto PET. Hence, the role of the backbone PET must also be taken into consideration in the initiation step. The fact that the observed R_g showed a square-root-order dependence on the backbone [Fig. 8(A) and (B)] and the dependence of the PET amount on n_g [Fig. 9(A) and (C)] gives

an indication of such a probable involvement. Therefore, three probable grafting initiation routes can be taken for consideration to select the most probable one.

In the first route of the grafting initiation, the A[·] radical produced by the decomposition of H₂A-PMS complex can interact with the backbone and generate a radical site in the backbone.

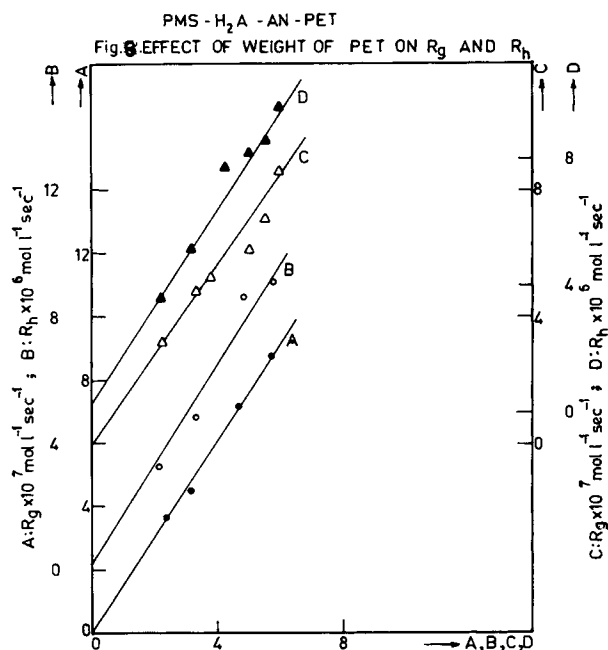
Initiation I:



where PET[·] is produced by the abstraction of a proton from the —CH₂ group in the main chain of the backbone by the A[·] radical.

A similar proton abstraction reaction was reported to cause initiation of graft copolymerization onto nylon 6/nylon 66 from the group —NH—²⁴ in the graft copolymerization of MMA onto nylon 6 with the tetravalent cerium–thiourea complex.

The second possible initiation path may be of the following type:



A, B, C, D: [wt of PET]^{1/2} × 10 g^{1/2}
 A, B: [AN] = 22.90 × 10⁻² mol l⁻¹; [PMS] = 6.00 × 10⁻³ mol l⁻¹
 [H₂A] = 4.00 × 10⁻³ mol l⁻¹
 C, D: [AN] = 28.62 × 10⁻² mol l⁻¹; [PMS] = 6.00 × 10⁻³ mol l⁻¹
 [H₂A] = 6.00 × 10⁻³ mol l⁻¹
 A, B, C, D: T = 45°C.

Figure 8 PMS-H₂A-AN-PET: Effect of weight of PET on R_g and R_h .

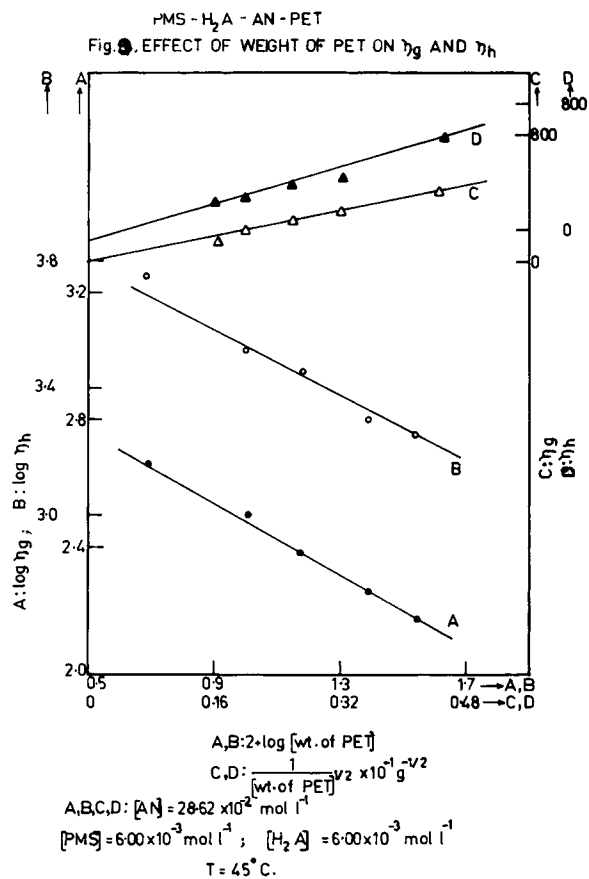
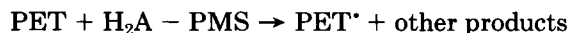


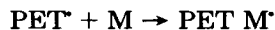
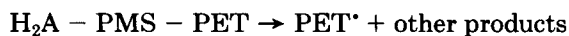
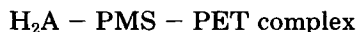
Figure 9 PMS-H₂A-AN-PET: Effect of weight of PET on η_g and η_h .

Initiation II:



The third initiation possibility may involve the following sequence:

Initiation III:



A complexation involving the backbone prior to initiation was considered by Nayak and co-workers²⁵ in the graft copolymerization of MMA onto nylon by the hexavalent chromium ion, by Gupta and Gupta²⁶ in the grafting of *N,N'*-methylenebisacrylamide onto silk using the vanadyl acetate complex, by Pradhan and co-workers²⁷ in the graft copoly-

merization of MMA onto nylon 6 using the Fe²⁺-thiourea redox system, and by Sahoo and co-workers²⁸ in the grafting of acrylamide onto cotton using the PMS-Co(II) redox system.

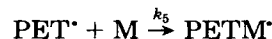
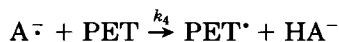
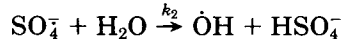
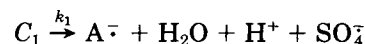
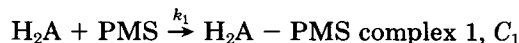
With mutual termination and conventional propagation for graft copolymerization, the following reaction possibilities can be explored:

VARIOUS POSSIBLE REACTION SCHEMES

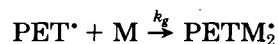
Schemes I-III consider initiation by the first route with production of A⁻ and its consequent initiation steps and with three different termination possibilities.

Scheme I

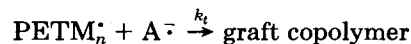
Initiation:



Propagation:



Termination:

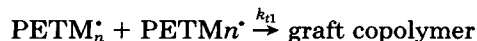


Scheme II

Initiation: As in Scheme I.

Propagation: As in Scheme I.

Termination:

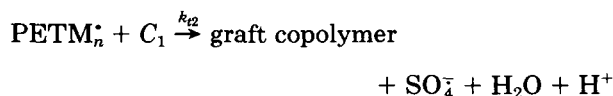


Scheme III

Initiation: As in Scheme I.

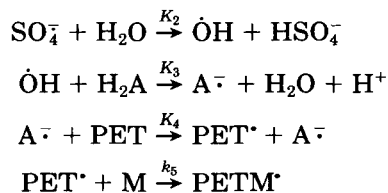
Propagation: As in Scheme I.

Termination:



The formed SO_4^- during termination by transfer can reinitiate the grafting reaction.

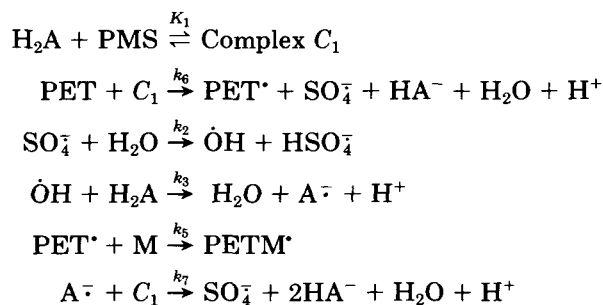
Reinitiation:



If direct interaction between the H_2A -PMS complex and the backbone is assumed, then with the relevant termination reaction, Schemes IV-VI can be constituted.

Scheme IV

Initiation:



Propagation: As in Scheme I.

Termination: As in Scheme I.

Scheme V

Initiation: As in Scheme IV.

Propagation: As in Scheme I.

Termination: As in Scheme II.

Scheme VI

Initiation: As in Scheme IV.

Propagation: As in Scheme I.

Termination: As in Scheme III.

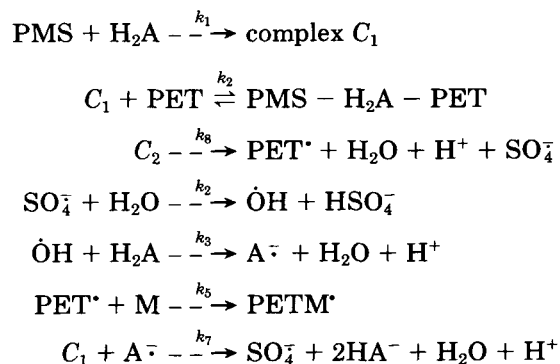
Reinitiation: As in Scheme III.

If the two complexes, one between H_2A and PMS and another between H_2A -PMS and backbone PET, are considered to be involved in the initiation,

Scheme VII or VIII, or IX or X, would be the reaction mechanism.

Scheme VII

Initiation:

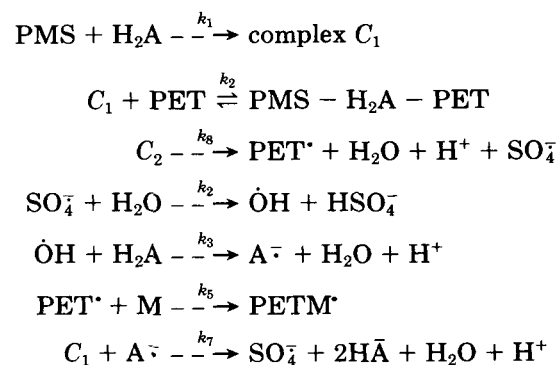


Propagation: As in Scheme I.

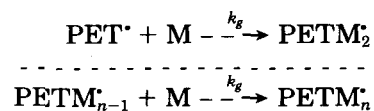
Termination: As in Scheme I.

Scheme VIII

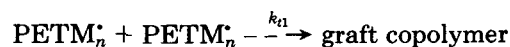
Initiation:



Propagation:



Termination:



Scheme IX

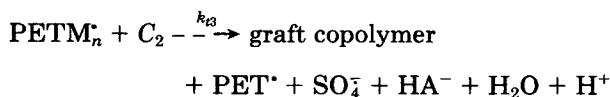
Initiation: As in Scheme VII.

Propagation: As in Scheme I.

Termination: As in Scheme III.
Reinitiation: As in Scheme III.

Scheme X

Reinitiation: As in Scheme VII.
Propagation: As in Scheme I.
Termination:



Reinitiation: As in Scheme III.

SELECTION OF MOST PROBABLE SCHEME

For the 10 above-proposed schemes, one can derive an expression for the rate of graft copolymerization under stationary-state conditions and compare it with the experimental results obtained. The reaction mechanism which can explain suitably all the experimental observations relating to grafting and homopolymerization in a concurrent manner would then be selected as the most probable one.

The observed result in the graft copolymerization studies clearly indicates that R_g showed square-root-order dependence on $[\text{PMS}]$ [Fig. 3(A) and (C)], (H_2A) [Fig. 6(A) and (C)], and PET [Fig. 8(A) and (C)]. This obviously suggested a mutual-type termination operating in the graft copolymerization.^{26,29,30} Hence, only Schemes II, V, and VIII are taken for consideration with mutual termination.

For Scheme II, applying a steady-state approximation for all radicals, the following expressions can be obtained:

$$R_g = k_g \left(\frac{2k_1, K_1}{k_{t1}} \right)^{0.5} [\text{M}][\text{PMS}]^{0.5} [\text{H}_2\text{A}]^{0.5} \quad (\text{E}_1)$$

$$n_g = \frac{k_g[\text{M}]}{k_t^{1/2}(2K_1k_1)^{0.5}[\text{PMS}]^{0.5}[\text{H}_2\text{A}]^{0.5}} \quad (\text{E}_2)$$

E_1 and E_2 did not contain any terms related to PET and, hence, Scheme II may not be suitable to explain the observation.

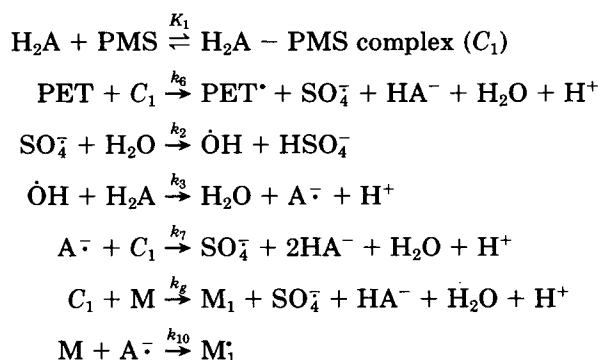
Considering initiation through the second possibility and taking into account only termination by the mutual type,³⁰ for Scheme V, R_g and n_g expressions can be derived as

$$R_g = k_g \left(\frac{2k_6, k_1}{k_{t1}} \right)^{0.5} (\text{M})(\text{PMS})^{0.5} \\ \times [\text{H}_2\text{A}]^{0.5} (\text{PET})^{0.5} \quad (\text{E}_3)$$

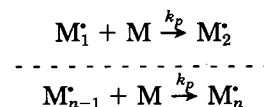
$$n_g = \frac{k_g(\text{M})}{k_t^{0.5}(k_6K_1)^{0.5}(\text{PMS})^{0.5}(\text{H}_2\text{A})^{0.5}(\text{PET})^{0.5}} \quad (\text{E}_4)$$

(E_3) and (E_4) could explain all the results related to R_g and n_g in the kinetics of graft copolymerization. Hence, the primary reaction in Scheme V may be taken to consider the possible simultaneous homopolymerization.

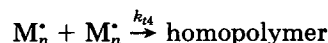
Simultaneous homopolymerization:



Propagation:



Termination:



For the above mechanism, the derived expression for R_h would be

$$R_h = \frac{k_p[(k_1(\text{H}_2\text{A})(\text{PMS})^{0.5}(2(k_g[\text{M}] + k_6[\text{PET}]^{0.5}(\text{M})))]}{k_{t4}^{0.5}} \quad (\text{E}_5)$$

When $k_g \gg k_6 [\text{PET}]$,

$$R_h = \frac{k_p[2K_1k_g(\text{H}_2\text{A})[\text{PMS}]^{1/2}[\text{M}]^{3/2}]}{k_{t4}^{1/2}} \quad (\text{E}_6)$$

When $k_g[M] \ll k_6[\text{PET}]$,

$$R_h = \frac{k_p[K_1k_6(\text{H}_2\text{A})[\text{PMS}][\text{PET}]^{1/2}[\text{M}]}{k_{t4}^{1/2}} \quad (\text{E}_7)$$

(E₆) fails to explain the square-root-order dependence on (PET) [Fig. 8(C) and (D)] and (E₇) fails to account for the three half-order dependence on (M) [Fig. 1(C) and (D)]. Hence, Scheme V may not be suitable to explain the simultaneous homopolymerization.

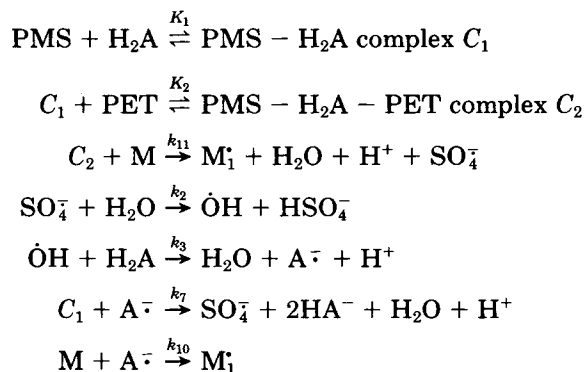
For Scheme VIII, R_g and n_g expressions were derived under steady-state conditions as

$$R_g = k_g \left(\frac{2k_8K_1K_2}{k_{t1}} \right)^{0.5} [\text{M}][\text{PET}]^{0.5} \times [\text{PMS}]^{0.5}[\text{H}_2\text{A}]^{0.5} \quad (\text{E}_8)$$

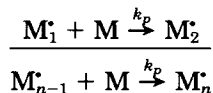
$$n_g = \frac{k_g(\text{M})}{(k_{t1})^{0.5}(2k_8K_1K_2)^{0.5}[\text{PET}]^{0.5}[\text{H}_2\text{A}]^{0.5}[\text{PMS}]^{0.5}} \quad (\text{E}_9)$$

In (E₈) and (E₉), all the experimental observations toward R_g and n_g such as first-power dependence of R_g on [AN] [Fig. 1(A) and (C)], square-root-order dependencies on [PMS] [Fig. 3(A) and (C)], [H₂A] [Fig. 6(A) and (C)] and [PET] [Fig. 8(A) and (C)] and first-order dependence of n_g on (AN) [Fig. 2(C)], and inverse square-root-order dependencies on [PMS] [Fig. 4(C)], H₂A [Fig. 7(C)], and (PET) [Fig. 9(C)] could be clearly seen.

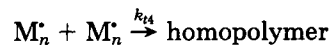
Through primary reactions in initiation III, the possible simultaneous homopolymerization can take place by



Normal propagation:



Mutual termination:



For the above mechanism, the expressions for R_h and n_h would be

$$R_h = k_p \left(\frac{2k_{11}K_1K_2}{k_{t4}} \right)^{1/2} (\text{PET})^{1/2}(\text{H}_2\text{A})^{1/2} \times (\text{PMS})^{1/2}(\text{M})^{3/2} \quad (\text{E}_{10})$$

$$n_h = \frac{K_p}{(k_{t4}^{1/2})(2k_{11}K_1K_2)^{1/2}(\text{PET})^{1/2}(\text{H}_2\text{A})^{1/2}(\text{PMS})^{1/2}} \quad (\text{E}_{11})$$

(E₁₀) and (E₁₁) explain all the experimental results toward R_h and n_h , respectively, such as 1.5-order dependence of R_h on [AN] [Fig. 1(B) and (D)], square-root-order-dependence on [PMS] [Fig. 3(B) and (D)], (H₂A) [Fig. 6(B) and (D)], and (PET) [Fig. 8(B) and (D)], half-order dependencies of n_h on (AN) [Fig. 2(D)], and inverse square-root-order dependencies on (PMS) [Fig. 4(D)], (H₂A) [Fig. 7(D)], and (PET) [Fig. 9(D)].

In expressions (E₈), (E₉), (E₁₀), and (E₁₁) derived for R_g , n_g , R_h , and n_h using Scheme VIII, all the experimental observations are therefore found. Hence, Scheme VIII may be a suitable choice to explain the graft copolymerization and its simultaneous homopolymerization.

EVALUATION OF COMPOSITE RATE CONSTANTS FOR THE SYSTEM

The composite rate constant

$$k_g \left(\frac{2k_8K_1K_2}{k_{t1}} \right)^{1/2}$$

in (E₈), was evaluated from the slope of the plots R_g vs. (AN) [Fig. 4(A) and (C)], R_g vs. (PMS)^{1/2} [Figs. 3(A) and (C)], R_g vs. (H₂A)^{1/2} [Figs. 6(A) and (C)], and R_g vs. (wt of PET)^{1/2} [Figs. 8(A) and (C)] to be $5.77 \times 10^{-4} \text{ mol}^{-1} \text{ L}^1 \text{ g}^{-1/2} \text{ s}^{-1}$ at 45°C. The closeness of the two values through different plots support the above-proposed scheme for the grafting reaction.

From the slope of the plots n_g vs. (AN) [Fig. 2(C)], n_g vs. (PMS)^{-1/2} [Fig. 4(C)], n_g vs. (H₂A)^{-1/2} [Fig. 7(C)], and n_g vs. (wt of PET)^{1/2} [Fig. 9(C)], the average value

$$\frac{k_g}{k_{t1}^{1/2}(k_8K_1K_2)^{1/2}}$$

in (E₉) was calculated to be 23.8 mol⁻¹ L s⁻¹ at 45°C. The closeness of the two values here again support the above-proposed scheme for the grafting reaction.

Multiplying these two composite rate constants obtained from R_g and n_g measurements, the $(k_g/k_{t1}^{1/2})$ value was obtained as 0.117 mol^{-1/2} L^{1/2} g^{-1/2} s^{-1/2} at 45°C. Taking the ratio of the two rate constants, the value of $k_8K_1K_2$ was calculated to be 2.43 × 10⁻⁵ mol⁻¹ L s⁻¹ at 45°C.

The composite rate constant in (E₁₀),

$$k_p \left(\frac{2k_{11}K_1K_2}{k_{t4}} \right)^{1/2}$$

in the homopolymerization expression was evaluated from the slope of the plots. The average value was calculated to be 1.13 × 10⁻² mol^{-1/2} L^{3/2} g^{-1/2} s⁻¹ at 45°C.

The composite rate constant in (E₁₁),

$$\frac{k_p}{(k_{t4})^{1/2}(2k_{11}K_1K_2)^{1/2}}$$

was evaluated from the slope of the plots n_h vs. (AN)^{1/2} [Fig. 2(D)], n_h vs. (PMS)^{-1/2} [Fig. 4(D)], n_h vs. (H₂A)^{-1/2} [Fig. 7(D)], and n_h vs. (wt of PET)^{-1/2} [Fig. 9(D)]. The average value was calculated to be 211 mol⁻¹ L^{1/2} g^{-1/2} at 45°C.

Multiplying the composite rate constants obtained from the R_h and n_h measurements, the $K_p/k_{t1}^{1/2}$ value was obtained as 1.53 mol^{-5/4} L^{5/4} g^{-1/2} s^{-1/2}. Taking the ratio of the composite rate constants from R_h and n_h , the value $k_{11}K_1K_2$ was calculated to be 5.36 × 10⁻⁵ mol⁻¹ L s⁻¹ at 45°C.

Knowing the $k_8K_1K_2$ value from R_g and n_g as 2.43 × 10⁻⁵ mol⁻¹ L s⁻¹ and the $k_{11}K_1K_2$ value from R_h and n_h measurements as 5.36 × 10⁻⁵ mol⁻¹ L s⁻¹, the ratio k_8/k_{11} was obtained as 0.453. The ratio indicates that $k_8 < k_{11}$, suggesting that during graft copolymerization studies with AN onto PET using the PMS-H₂A redox pair graft copolymerization should be accompanied by homopolymerization and the R_g value must be lower than R_h . This fact is actually reflected in the present study.

For this mechanism, an expression for $-R_{PMS}$ can be written as

$$-R_{PMS} = \frac{(k_{11}K_1K_2)(M)(PMS)_T[H_2A][PET] + k_8K_1K_2(PMS)(H_2A)(PET)}{1 + K_1(H_2A) + K_1K_2(H_2A)(PET)}$$

where $[PMS]_T$ = initial (PMS) taken when $K_1K_2[H_2A][PET] \gg 1 + K_1[H_2A]$, the expression becomes $-R_{PMS} = k_{11}[M] + k_8[PMS]$.

The values obtained from the slopes of the plots $-R_{PMS}$ vs. (PMS) [Figs. 5(C) and (D)] are 8.77 × 10⁻⁴ s⁻¹ and 2.50 × 10⁻⁴ s⁻¹, respectively, for two different (M). Using the slopes and knowing that $-R_{PMS}$ is independent of the change in [H₂A] and PET, the two equations $k_{11}[M] + k_t$ with two different [M] values are solved to obtain the ratio k_8/k_{11} . This was calculated to be 0.286. This again supports that $k_8 < k_{11}$, as was inferred through the grafting measurements.

The increase in % grafting (Table I) with increase in the monomer can be explained by the same reasoning as reported earlier.^{31,32} A similar effect on % grafting with (M) was found by Shukla and Sharma³³ and Verma and Ray.³⁴ Verma and Ravisankar³⁵ reported that the grafting efficiency was good only at a low concentration of the monomer by another system.

The increase in % grafting and % efficiency by the parameters such as (PMS) (Table I), (H₂A) (Table II), and (PET) (Table II) could be due to the involvement of all these components in the grafting-initiation step. The decrease in % grafting at a higher backbone amount may be due to the increase in diffusibility of the monomer toward the active site generated with a larger backbone matrix. The low % efficiencies in all these cases may be due to the occurrence of the simultaneous homopolymerization, originating from the PMS-H₂A-PET complex.

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Received February 2, 1994

Accepted November 21, 1994