

Graft Copolymerization of Polyacrylonitrile (PAN) onto Nylon 6/Nylon 66 and Simultaneous Homopolymerization: A Comparative Study. II

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SYNOPSIS

The kinetics of graft copolymerization of polyacrylonitrile (PAN) onto nylon 6/nylon 66 and the simultaneous homopolymerization initiated by potassium peroxomonosulfate (PMS)–ascorbic acid (H₂A) redox systems were studied separately. Various kinetics parameters were evaluated and analyzed to have a comparison among the systems. The occurrence of simultaneous homopolymerization was evident through rate parameters. When the backbone was changed, the following order was observed for grafting efficiency: polyester (PET) > nylon 6 \approx nylon 66. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Graft copolymerization onto nylon appears to be a very fascinating field for research with unlimited future possibilities for improving its properties. For example, nylon grafted with styrene is insoluble in formic acid, phenol, and *m*-cresol and showed a good water repellency when more than 10% is grafted on.¹ On the other hand, it has been reported that when nylon is grafted with acrylic, methacrylic, and maleic acids, the water absorbency, heat resistance, and antistatic properties are improved.^{2–4} Considerable enhancement of the wet crease recovery is noticed when nylon is grafted with acrylamide, divinylsulfones, and *N*-vinylpyrrolidone. The dyeability of nylon is improved when grafting is carried out with the last named monomer.^{5,6}

Graft copolymerization of vinyl polymers onto substrate polymers is generally considered to involve the generation of reactive sites on the polymer in a conventional manner. This can be achieved by several means such as high-energy ra-

diation,⁷ low-energy radiation in the presence or absence of stabilizers,⁸ and chemical methods.^{9–11} Among chemical methods, redox-initiated grafting is advantageous because grafting can be carried out under milder conditions with minimum side-chain reactions.¹²

A variety of redox systems have been employed for the initiation of graft copolymerization of vinyl monomers onto synthetic or natural polymer backbones. Van Phung and co-workers¹³ reported that acrylamide or acrylonitrile can be grafted on nylon 6 or nylon 66 to produce *N*-grafted polyamides via a redox reaction. The potassium bromate–thiourea redox system was used by Hebeish and co-workers¹⁴ for the initiation of graft copolymerization of methyl methacrylate (MMA) onto nylon 66. Lenka and co-workers¹⁵ carried out graft copolymerization of MMA onto nylon 6 using the acetylacetonate complex of Mn(III), Ce(III), and Fe(III).

Recently, much attention has been focused on the graft copolymerization of vinyl monomers onto nylon 6 through chemical initiation using Ce(IV),^{16,17} Mn(IV),¹⁸ Mn(III),¹⁹ and azobisisobutyronitrile redox systems.²⁰ Peroxodiphosphate has been used as a lone initiator for the graft copolymerization of MMA onto nylon 6.²¹

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The present study deals with the kinetics of graft copolymerization of AN onto nylon 6/nylon 66 using the PMS-H₂A redox system and its simultaneous homopolymerization to obtain a comparative understanding about the mechanism.

EXPERIMENTAL

Acrylonitrile (AN) (Robert Johnson) was used after purification as described earlier.²² Potassium peroxomonosulfate (PMS) (Aldrich, USA, under the name "OXONE") was a gift sample. The ascorbic acid (H₂A) (BDH AR) sample was used as such.

Nylon 6, in the form of fiber, was a gift sample from J. K. Synthetic, Kota, Rajasthan. It was swollen in 2% phenol solution for 48 h, then washed with water and dried before use. This was done to remove any adhering impurity and to expose the reactive sites for grafting. Nylon 66, in the form of fiber, was a gift sample from M/s Garware Nylon Limited, Bombay. This was also purified as in the case of nylon 6 before use.

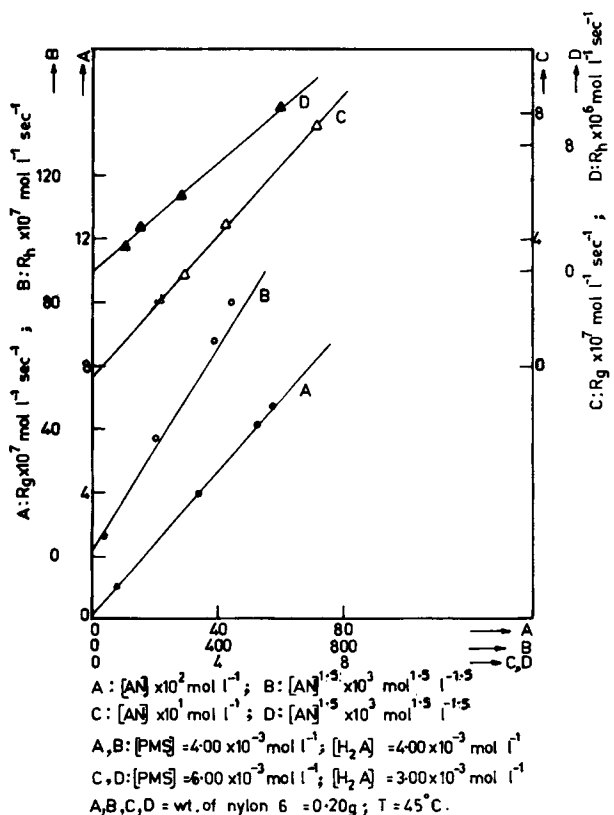


Figure 1 PMS-H₂A-AN-nylon 6: Effect of [AN] on R_g and R_h .

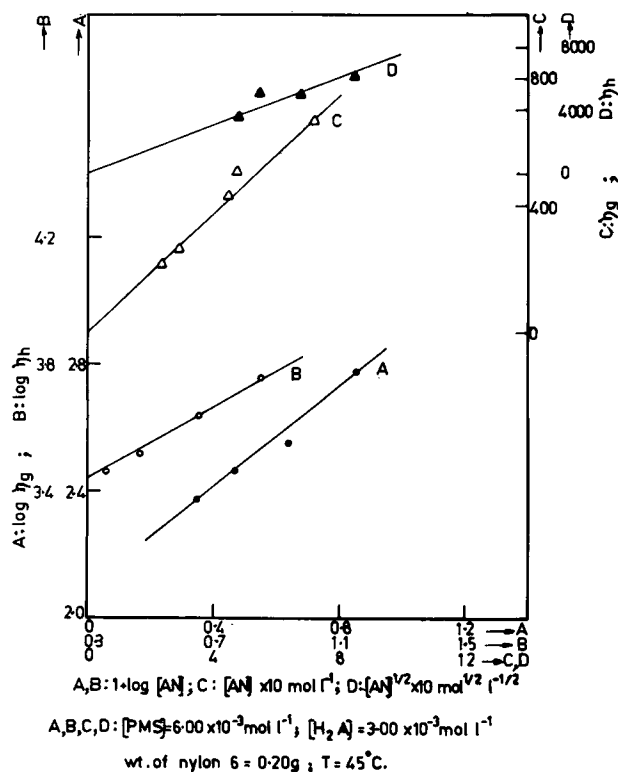


Figure 2 PMS-H₂A-AN-nylon 6: Effect of [AN] on n_g and n_h .

RESULTS

Graft Copolymerization of AN onto Nylon 6

Effect of [AN] on Graft and Homopolymerization Parameters

Graft Parameters. R_g increases steadily with [AN]. The R_g vs. [AN] [Fig. 1(A) and (C)] plot was a straight line with a slope of unity, pointing out the first-order dependence of R_g on [AN].

The kinetic chain length n_g was determined for the above conditions. n_g increases with [AN]. The plot of $\log n_g$ vs. $\log [AN]$ [Fig. 2(A)] was linear in nature with a slope of unity. n_g vs. [AN] [Fig. 2(C)] was a straight line with a slope of unity indicating first-order dependence of n_g on [AN].

Homopolymerization Parameters. R_h was found to increase with [AN] under identical conditions. The direct plot of R_h vs. $[AN]^{1.5}$ [Fig. 1(B) and (D)] was found to pass through the origin, indicating a three-half-order dependence of R_h on AN.

n_h shows an increasing trend with [AN]. $\log n_h$ vs. $\log [AN]$ [Fig. 2(B)] was a straight line with a slope of 0.5. The n_h vs. $[AN]^{1/2}$ [Fig. 2(D)] plot was drawn. The linearity in the plot supports the above observation. The rate of disappearance of PMS

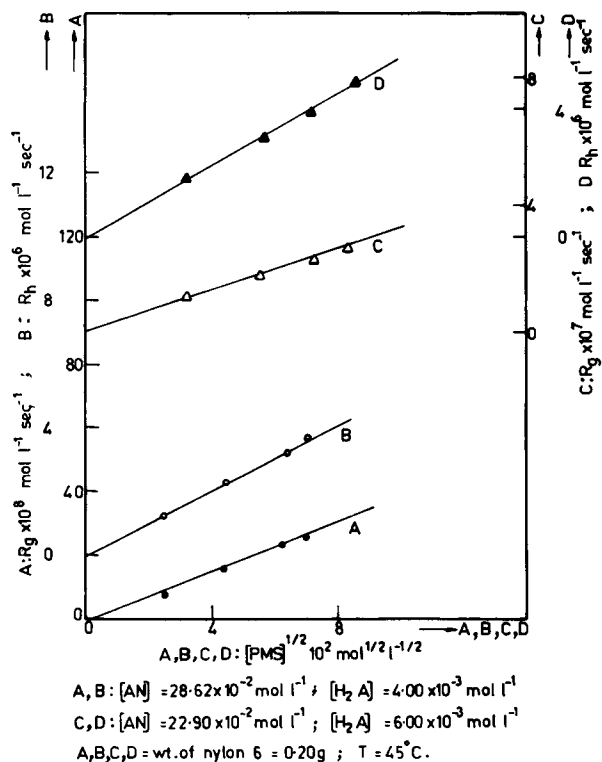


Figure 3 PMS-H₂A-AN-Nylon 6: Effect of [PMS] on R_g and R_h .

($-R_{PMS}$) values remains almost constant for the above conditions.

Effect of [PMS] on Grafted Homopolymerization Parameters

R_g increases with increase in [PMS]. The direct plot R_g vs. $[PMS]^{1/2}$ [Fig. 3(A) and (C)] was a straight line with a slope of 0.5, suggesting half-order dependence of PMS on R_g .

n_g decreases with PMS. The $\log n_g$ vs. $\log[PMS]$ [Fig. 4(A)] plot was a straight line with a slope of negative 0.5. The n_g vs. $[PMS]^{-1/2}$ [Fig. 4(C)] plot was linear in nature, thus supporting negative 0.5-order dependence of n_g on PMS.

R_h values increase with PMS. The R_h vs. $[PMS]^{1/2}$ [Fig. 3(B) and (D)] plot was linear in nature with a slope of 0.5.

n_h values decrease with increase in [PMS]. The plot of $\log n_h$ vs. $\log[PMS]$ [Fig. 4(B)] was a straight line with a slope of -0.5 . n_h vs. $[PMS]^{-1/2}$ [Fig. 4(D)] was linear in nature, thus confirming -0.5 -order dependence of n_h on PMS.

$-R_{PMS}$ values increase with PMS. $\log -R_{PMS}$ vs. $\log[PMS]$ [Fig. 5(A) and (B)] was linear with a slope of unity. The $-R_{PMS}$ vs. $[PMS]$ [Fig. 5(C) and (D)] plot was a straight line passing through the origin, confirming unity-order dependence of $-R_{PMS}$ on PMS.

Effect of [H₂A] on Graft and Homopolymerization Parameters

Graft Parameters. R_g increases steadily with $[H_2A]$. The R_g vs. $[H_2A]^{1/2}$ [Fig. 6(A) and (C)] plot was a straight line with a slope of 0.5, indicating half-order dependence of R_g on $[H_2A]$.

n_g decreases with $[H_2A]$. The plot of $\log n_g$ vs. $\log[H_2A]$ [Fig. 7(A)] was linear with a slope of negative 0.5. The n_g vs. $[H_2A]^{-1/2}$ [Fig. 7(C)] plot was a straight line passing through the origin, thus confirming negative 0.5-order dependence of n_g on $[H_2A]$.

Homopolymerization Parameters. R_h values were found to increase with $[H_2A]$. The plot of R_h vs. $[H_2A]^{1/2}$ [Fig. 6(B) and (D)] was linear in nature with a slope of 0.5, pointing out half-order dependence of R_h on H_2A . n_h values decrease with $[H_2A]$. The $\log n_h$ vs. $\log[H_2A]$ [Fig. 7(B)] plot was a straight line with a slope of inverse square-root order, indicating -0.5 -order dependence of n_h on $[H_2A]$. The direct plot n_h vs. $[H_2A]^{-1/2}$ [Fig. 7(D)] was linear, confirming -0.5 -order dependence of n_h on H_2A . $-R_{PMS}$ values remain almost constant for the above conditions.

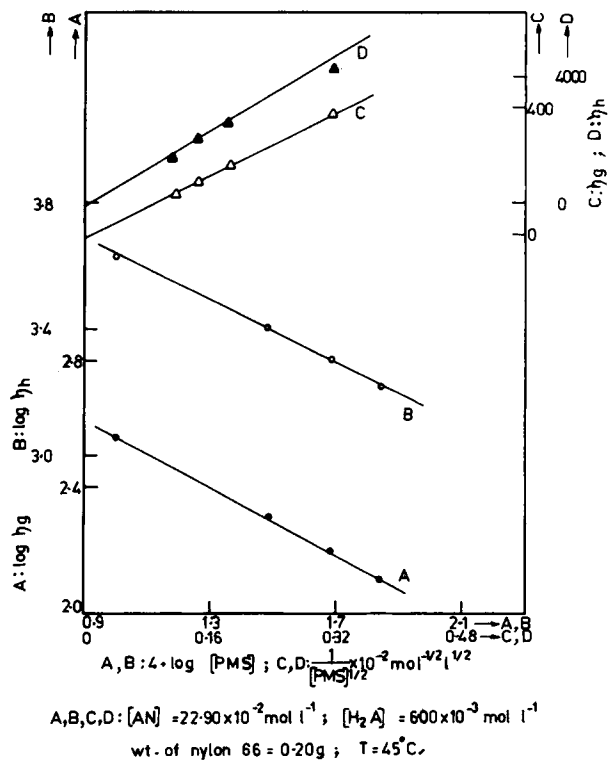


Figure 4 PMS-H₂A-AN-nylon 6: Effect of [PMS] on n_g and n_h .

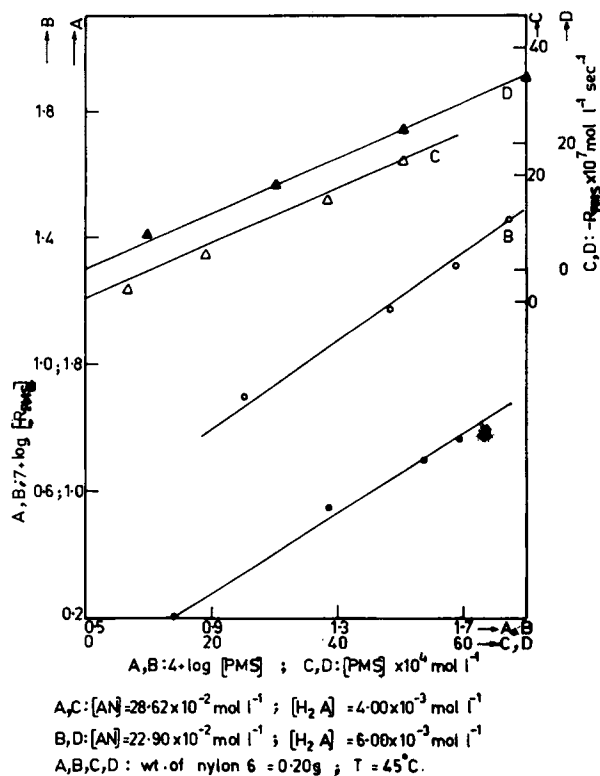


Figure 5 PMS-H₂A-AN-nylon 6: Effect of [PMS] on $-R_{PMS}$.

Effect of Nylon 6 on Graft and Homopolymerization Parameters

R_g increases steadily with increase in the backbone material. R_g vs. [weight of nylon 6]^{1/2} [Fig. 8(A) and (C)] plot was linear in nature, suggesting half-order dependence of R_g on the weight of nylon 6. n_g decreases with the backbone amount. The log n_g vs. log[weight of nylon 6] [Fig. 9(A)] plot was linear, pointing out inverse square-root-order dependence of n_g on the backbone amount. The direct plot n_g vs. [weight of nylon 6]^{-1/2} [Fig. 9(C)] was also a straight line, thus confirming the above order -0.5 .

R_h values increase with the amount of nylon 6. The R_h vs. [weight of nylon 6]^{1/2} [Figs. 8(B) and (D)] plot was a straight line passing through the origin, indicating half-order dependence of R_h on nylon 6.

n_h values show a decreasing trend with respect to the amount of nylon 6. Log n_h vs. [weight of nylon 6] [Fig. 9(B)] was a straight line with a slope of -0.5 . The direct plot n_h vs. [weight of nylon 6]^{-1/2} [Fig. 9(D)] was a straight line with a slope of $-1/2$, indicating $-1/2$ -order dependence of n_h on the weight of nylon 6.

Graft Copolymerization of AN onto Nylon 66

Similar observations such as first-power dependence on [AN] [Fig. 10(A) and (C)] and square-root-order dependencies on [PMS] [Fig. 12(A) and (C)], [H₂A] [Fig. 14(A) and (C)], and [wt of nylon 66] [Fig. 16(A) and (C)] with respect to R_g were observed when nylon 66 was used as a backbone material; first-power dependence on [AN] [Fig. 11(C)] and inverse square-root-order dependencies on [PMS] [Fig. 13(C)], [H₂A] [Fig. 15(C)], and [wt of nylon 66] [Fig. 17(C)] with regard to n_g ; three-half-order dependence on [AN] [Fig. 10(B) and (D)] and square-root-order dependencies on [PMS] [Fig. 12(B) and (D)], [H₂A] [Fig. 14(B) and (D)], and [wt of nylon 66] [Fig. 16(B) and (D)] with respect to R_h ; and half-order dependence on [AN] [Fig. 11(D)] and negative 0.5-order dependencies on [PMS] [Fig. 13(D)], [H₂A] [Fig. 15(D)], and [wt of nylon 66] [Fig. 17(D)], with respect to n_h were made.

DISCUSSION

The observation made with the systems using nylon 6 and nylon 66 as backbone materials is almost similar to the one as seen in graft copolymerization

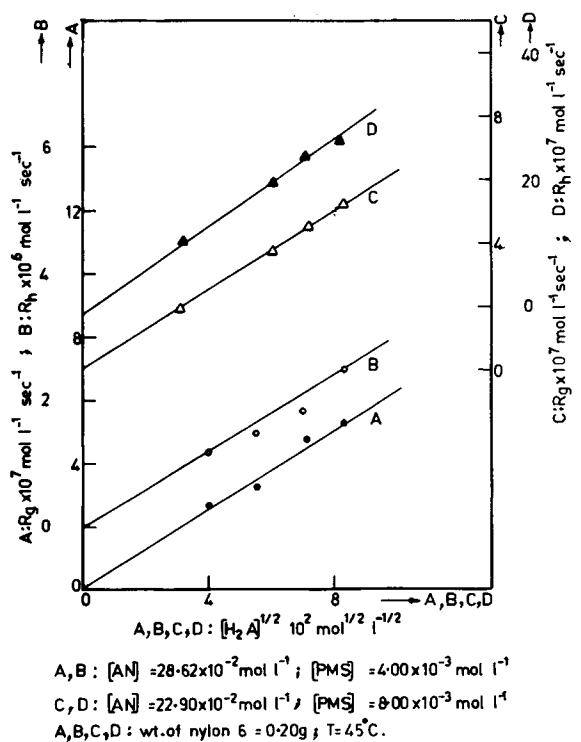


Figure 6 PMS-H₂A-AN-nylon 6: Effect of [H₂A] on R_g and R_h .

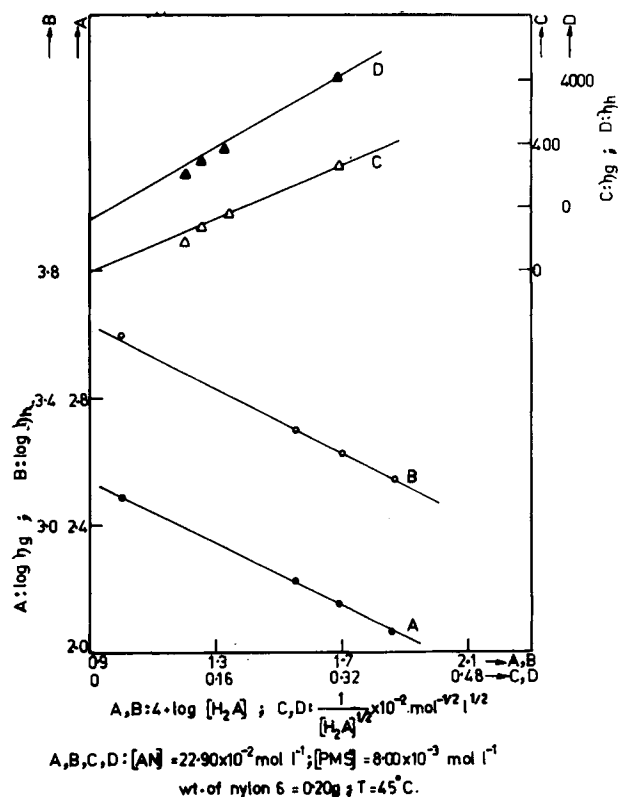
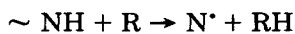


Figure 7 PMS-H₂A-AN-nylon 6: Effect of [H₂A] on *n_g* and *n_h*.

of AN onto poly(ethylene terephthalate) (PET) through initiation by the PMS-H₂A redox pair (Part I). This points out that the probable reaction schemes would be the same as in the previous case discussed in Part I.

Hence, a similar sequence of reactions as represented for the graft copolymerization of AN initiated by the PMS-H₂A redox pair onto PET with a change in the backbone as nylon 6 would be selected as the most probable one.

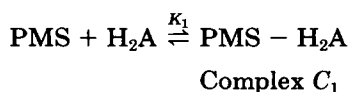
The grafting of nylon 6 was reported to be initiated by the production of the nylon radical by the abstraction of a proton from the NH grouping in the backbone polymer¹⁶:



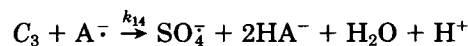
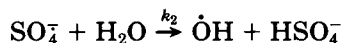
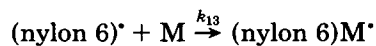
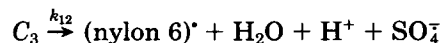
where "R" can be a radical or a metal ion.

Selected Most Probable Scheme

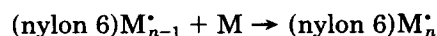
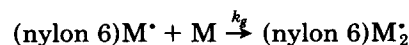
Initiation:



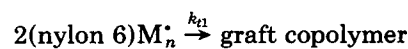
Complex C₃



Propagation:



Termination:



For the simultaneous homopolymerization, a similar mechanism would be as follows:

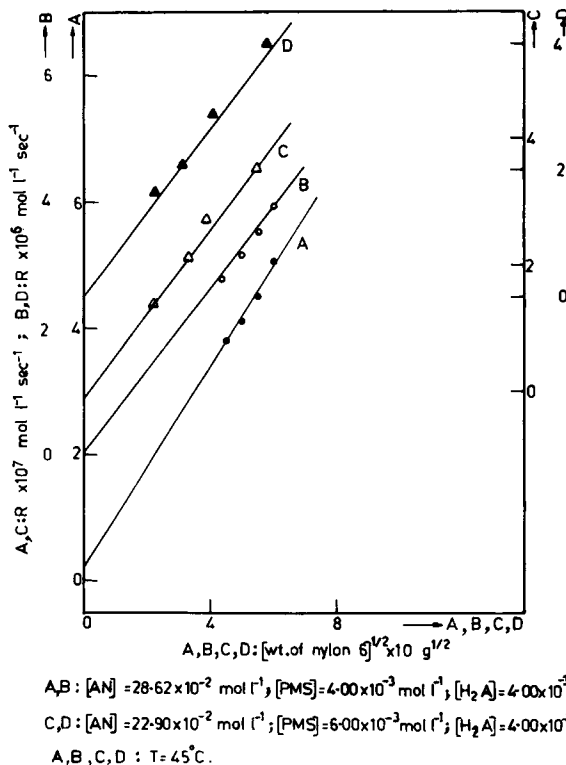


Figure 8 PMS-H₂A-AN-nylon 6: Effect of weight of nylon 6 on *R_g* and *R_h*.

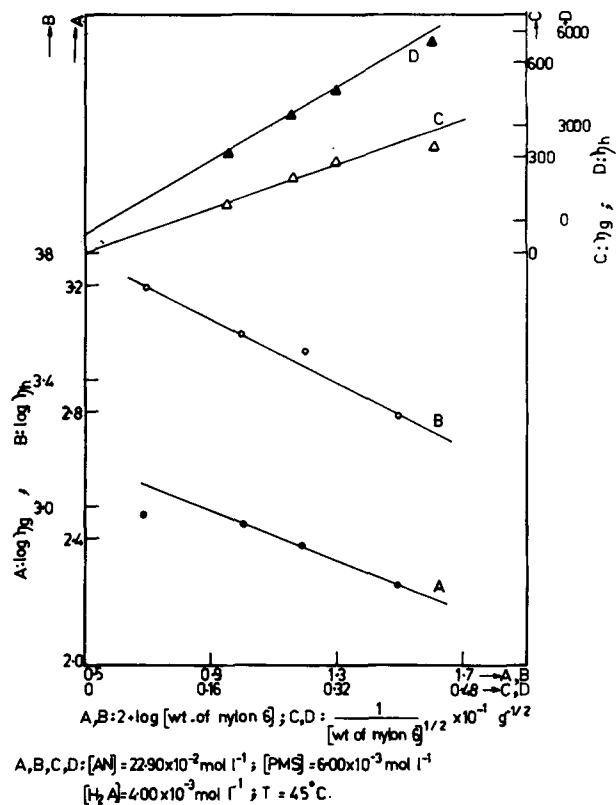
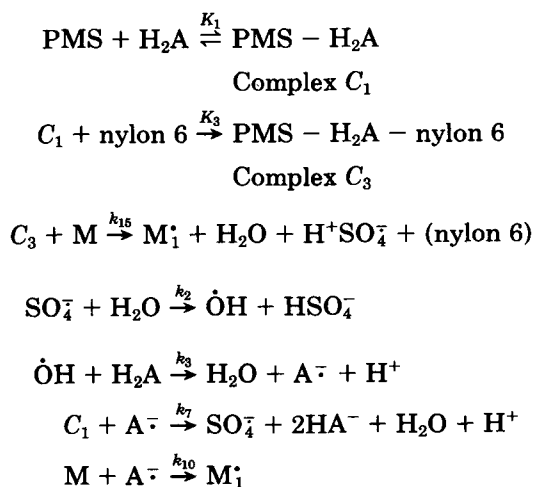
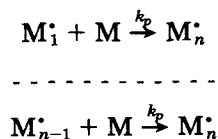


Figure 9 PMS-H₂A-AN-nylon 6: Effect of weight of nylon 6 on n_g and n_h .

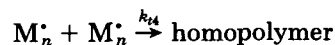
Initiation:



Propagation:



Termination:



For this scheme, the expressions for R_g , n_g , R_h , and n_h can be written based on the discussion in Part I as

$$R_g = k_g \left(\frac{2k_{12}K_1K_3}{k_{t1}} \right)^{1/2} \times [M][\text{nylon 6}]^{1/2}[\text{PMS}]^{1/2}[\text{H}_2\text{A}]^{1/2} \quad (\text{E}_1)$$

$$n_g = \frac{k_g[M]}{(k_{t1})^{1/2}(2k_{12}K_1K_3)^{1/2}(\text{nylon 6})^{1/2} \times (\text{PMS})^{1/2}(\text{H}_2\text{A})^{1/2}} \quad (\text{E}_2)$$

$$R_h = R_p \left(\frac{2k_{15}K_1K_3}{k_{t4}} \right)^{1/2} [M]^{3/2}(\text{nylon 6})^{1/2} \times (\text{PMS})^{1/2}(\text{H}_2\text{A})^{1/2} \quad (\text{E}_3)$$

$$n_h = \frac{k_p[M]^{1/2}}{(k_{t4})^{1/2}(2k_{15}K_1K_3)^{1/2}(\text{nylon 6})^{1/2} \times (\text{PMS})^{1/2}(\text{H}_2\text{A})^{1/2}} \quad (\text{E}_4)$$

Nylon 66

When nylon 66 was used as the backbone, the following changes are required in the mechanism:

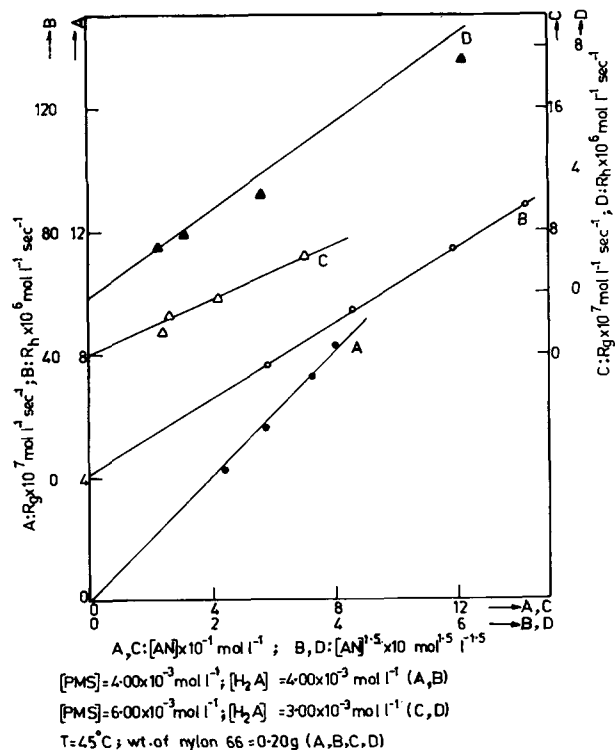


Figure 10 PMS-H₂A-AN-nylon 66: Effect of $[AN]$ on R_g and R_h .

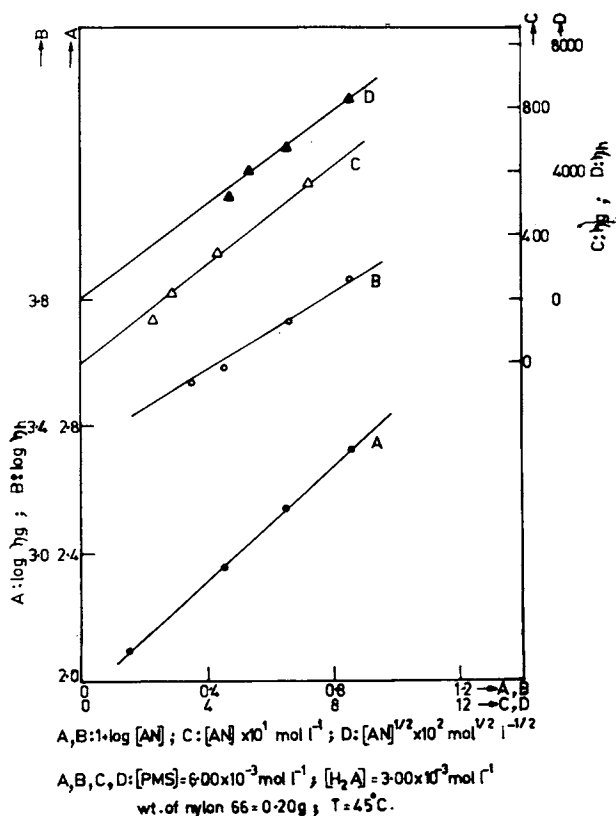
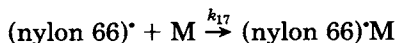
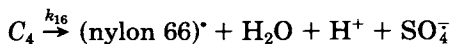
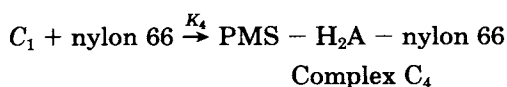


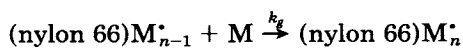
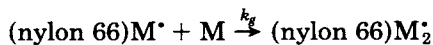
Figure 11 PMS-H₂A-AN-nylon 66: Effect of [AN] on n_g and n_h .

For Graft Copolymerization

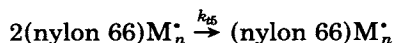
Initiation:



Propagation:

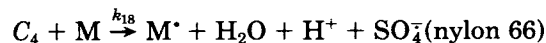
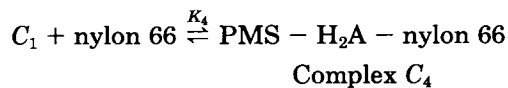


Termination:



For the Simultaneous Homopolymerization

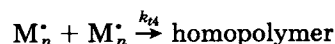
Initiation:



Propagation:



Termination:



The corresponding expressions R_g , n_g , R_h , and n_h for the nylon 66 system would be

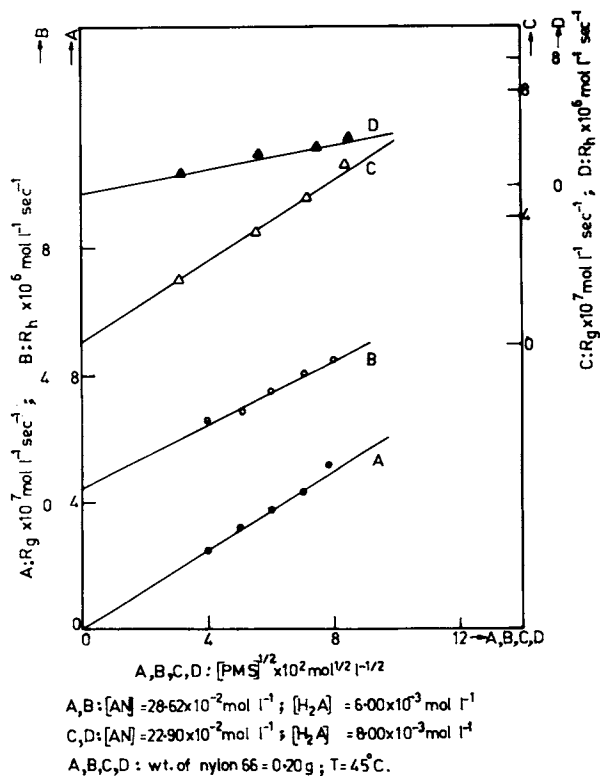


Figure 12 PMS-H₂A-AN-nylon 66: Effect of [PMS] on R_g and R_h .

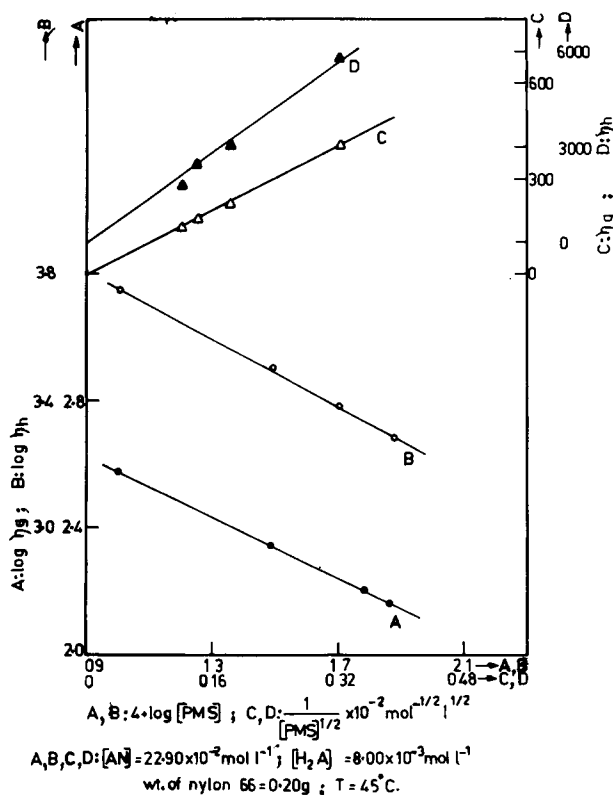


Figure 13 PMS-H₂A-AN-nylon 66: Effect of [PMS] on n_g and n_h .

$$R_g = k_g \left(\frac{2k_{16}K_1K_4}{k_{t5}} \right)^{1/2} \times [M](\text{nylon 66})^{1/2}(\text{PMS})^{1/2}(\text{H}_2\text{A})^{1/2} \quad (\text{E}_5)$$

$$n_g = \frac{k_g[M]}{(k_{t5})^{1/2}(2k_{16}K_1K_4)^{1/2}(\text{nylon 66})^{1/2} \times (\text{PMS})^{1/2}(\text{H}_2\text{A})^{1/2}} \quad (\text{E}_6)$$

$$R_h = k_p \left(\frac{2k_{18}K_1K_4}{k_{t4}} \right)^{1/2} (\text{nylon 66})^{1/2}(\text{H}_2\text{A})^{1/2} \times (\text{PMS})^{1/2}(\text{M})^{3/2} \quad (\text{E}_7)$$

$$n_h = \frac{k_p[M]^{1/2}}{(k_{t4})^{1/2}(2k_{18}K_1K_4)^{1/2}(\text{nylon 66})^{1/2} \times (\text{PMS})^{1/2}(\text{H}_2\text{A})^{1/2}} \quad (\text{E}_8)$$

That the rate expressions for R_g given by (E₁) and (E₅) are the suitable choice for nylon 6 and nylon 66 as backbones was confirmed by the fact that the composite rate constants remain invariant for all the variations of [AN], [PMS], [H₂A], and nylon 6/nylon 66. The values so obtained through different routes can be seen in Tables III and IV. The average value of the composite rate constants from R_g measurements with nylon 6 and nylon 66 as backbones,

respectively, are $4.47 \times 10^{-4} \text{ mol}^{-1} \text{ L g}^{-1/2} \text{ s}^{-1}$ and $3.98 \times 10^{-4} \text{ mol}^{-1} \text{ L g}^{-1/2} \text{ s}^{-1}$.

From the rate expression given by (E₂) and (E₆) for n_g , the average values of the composite rate constants from n_g measurements for nylon 6 and nylon 66 systems are $25.3 \text{ mol}^{-1} \text{ L s}^{-1}$ and $23.0 \text{ mol}^{-1} \text{ L s}^{-1}$, respectively. The way of obtaining them is described in Tables I and II.

By multiplying the composite rate constants from R_g and n_g measurements, $k_g/k_t^{1/2}$ values were obtained as $0.106 \text{ mol}^{-1/2} \text{ L}^{1/2} \text{ g}^{-1/2} \text{ s}^{-1/2}$ and $0.096 \text{ mol}^{-1/2} \text{ L}^{1/2} \text{ g}^{-1/2} \text{ s}^{-1/2}$ for nylon 6 and nylon 66 systems, respectively. The closeness of the two values support the proposed mechanism, since the propagation rate constant must be independent of the chain length.

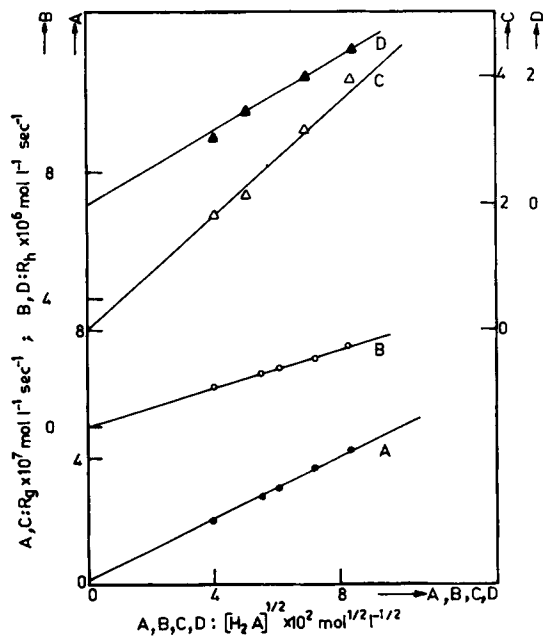
Taking the ratio of the values of the composite rate constants from R_g and n_g measurements, the values $k_{12}K_1K_3$ and $k_{16}K_1K_4$ for the nylon 6/nylon 66 systems are calculated as $1.77 \times 10^{-5} \text{ mol}^{-1} \text{ L s}^{-1}$ and $1.74 \times 10^{-5} \text{ mol}^{-1} \text{ L s}^{-1}$, respectively. In comparison with the value obtained for PET (Part I), $2.43 \times 10^{-5} \text{ mol}^{-1} \text{ L s}^{-1}$, it is inferred that nylon 6 and nylon 66 are less effective for grafting than is PET and the grafting efficiency would follow the order PET > nylon 6 \approx nylon 66.

This can be understood from the % efficiency values for the three backbones, PET, nylon 6, and nylon 66, under identical conditions: [PMS] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$; [H₂A] = $3.00 \times 10^{-3} \text{ mol L}^{-1}$; [AN] = $2.862 \times 10^1 \text{ mol L}^{-1}$; $T = 45^\circ \text{C}$; wt of backbone: PET/Nylon 6/Nylon 66 = 0.20 g.

Backbone	% Efficiency
PET	3.68
Nylon 6	2.18
Nylon 66	1.46

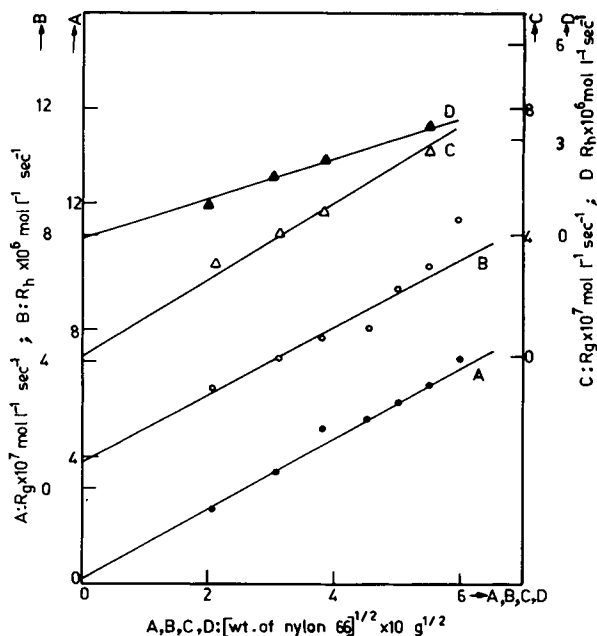
That the rate expression R_h given by (E₃) and (E₇) for nylon 6 and nylon 66 as backbone materials is the right choice was verified by evaluating the composite rate constants through different routes. It is found that the value is invariant for all the variations of [AN], [PMS], [H₂A], and nylon 6/nylon 66. The closeness of the two values support the proposed mechanism. The values so obtained are given in Tables I and II.

The average value of the composite rate constants from R_h measurements using nylon 6 and nylon 66 as backbone materials are $8.75 \times 10^{-3} \text{ mol}^{-1/2} \text{ L}^{3/2} \text{ s}^{-1}$ and $9.01 \times 10^{-3} \text{ mol}^{-1/2} \text{ L}^{3/2} \text{ g}^{-1/2} \text{ s}^{-1}$, respectively. Through rate expressions for n_h



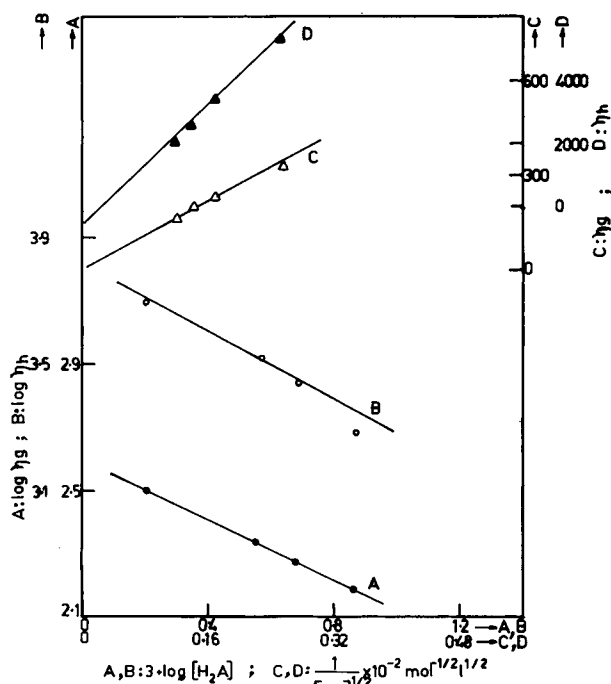
A, B: [AN] = $28.62 \times 10^{-2} \text{ mol l}^{-1}$; C, D: [AN] = $22.90 \times 10^{-2} \text{ mol l}^{-1}$
 [PMS] = $6.00 \times 10^{-3} \text{ mol l}^{-1}$ [PMS] = $6.00 \times 10^{-3} \text{ mol l}^{-1}$
 A, B, C, D: wt. of nylon 66 = 0.20 g; T = 45°C.

Figure 14 PMS-H₂A-AN-nylon 66: Effect of [H₂A] on R_g and R_h.



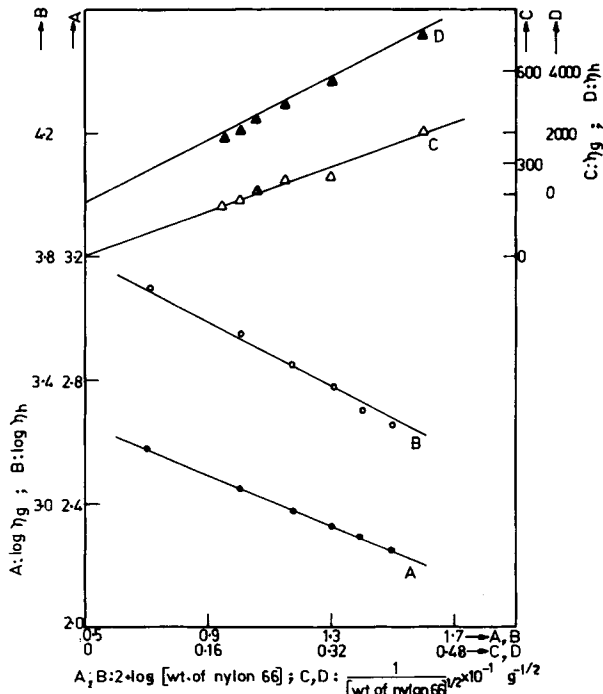
A, B: [AN] = $28.26 \times 10^{-2} \text{ mol l}^{-1}$; [PMS] = $6.00 \times 10^{-3} \text{ mol l}^{-1}$; [H₂A] = $6.00 \times 10^{-3} \text{ mol l}^{-1}$
 C, D: [AN] = $22.90 \times 10^{-2} \text{ mol l}^{-1}$; [PMS] = $6.00 \times 10^{-3} \text{ mol l}^{-1}$; [H₂A] = $6.00 \times 10^{-3} \text{ mol l}^{-1}$
 A, B, C, D: T = 45°C.

Figure 16 PMS-H₂A-AN-nylon 66: Effect of weight of nylon 66 on R_g and R_h.



A, B, C, D: [AN] = $28.62 \times 10^{-2} \text{ mol l}^{-1}$; [PMS] = $4.00 \times 10^{-3} \text{ mol l}^{-1}$
 wt. of nylon 66 = 0.20 g; T = 45°C

Figure 15 PMS-H₂A-AN-nylon 66: Effect of [H₂A] on n_g and n_h.



A, B, C, D: [AN] = $28.62 \times 10^{-2} \text{ mol l}^{-1}$; [PMS] = $6.00 \times 10^{-3} \text{ mol l}^{-1}$
 [H₂A] = $6.00 \times 10^{-3} \text{ mol l}^{-1}$; T = 45°C

Figure 17 PMS-H₂A-AN-nylon 66: Effect of weight of nylon 66 on n_g and n_h.

Table I PMS-H₂A-AN-Nylon 6

Evaluation of Rate Constants Using R_g and n_g ($T = 45^\circ\text{C}$; $u = 0.24 \text{ mol L}^{-1}$; $[\text{H}^+] = 8.00 \times 10^{-2} \text{ mol L}^{-1}$)		Composite Rate Constants from Grafting Studies			
Variation and Range	Condition	Figure (Plot)	From R_g		From n_g
			Slope	k^a ($\text{mol}^{-1} \text{ L g}^{-1/2} \text{ s}^{-1}$)	Slope
[AN] mol L ⁻¹ 8.586-57.24	[PMS] = $4.00 \times 10^{-3} \text{ mol L}^{-1}$ [H ₂ A] = $4.00 \times 10^{-3} \text{ mol L}^{-1}$ Weight of nylon 6 = 0.20 g	1(A)	$1.16 \times 10^{-6} \text{ s}^{-1}$	4.50×10^{-4}	—
2.29-7.155	[PMS] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ [H ₂ A] = $3.00 \times 10^{-3} \text{ mol L}^{-1}$ Weight of nylon 6 = 0.20 g	2(C)	—	—	1.00×10^5
[PMS] mol L ⁻¹ 6.0-50.0	[AN] = $28.62 \times 10^{-2} \text{ mol L}^{-1}$ [H ₂ A] = $4.00 \times 10^{-3} \text{ mol L}^{-1}$ Weight of nylon 6 = 0.20 g	3(A)	$4.38 \times 10^{-6} \text{ mol}^{1/2} \text{ L}^{-1/2} \text{ s}^{-1}$	3.89×10^{-4}	—
10.0-70.0	[AN] = $22.9 \times 10^{-2} \text{ mol L}^{-1}$ [H ₂ A] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ Weight of nylon 6 = 0.20 g	4(C)	—	—	$11.4 \times 10 \text{ mol}^{1/2} \text{ L}^{-1/2}$
[H ₂ A] mol L ⁻¹ 1.60-7.00	[AN] = $28.62 \times 10^{-2} \text{ mol L}^{-1}$ [PMS] = $4.00 \times 10^{-3} \text{ mol L}^{-1}$ Weight of nylon 6 = 0.20 g	6(A)	$5.88 \times 10^{-6} \text{ mol}^{1/2} \text{ L}^{-1/2} \text{ s}^{-1}$	5.14×10^{-4}	—
10.0-70.0	[AN] = $22.90 \times 10^{-2} \text{ mol L}^{-1}$ [PMS] = $8.00 \times 10^{-3} \text{ mol L}^{-1}$ [AN] = $22.9 \times 10^{-2} \text{ mol L}^{-1}$ [H ₂ A] = $4.00 \times 10^{-3} \text{ mol L}^{-1}$ [PMS] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ Same as above three lines	7(C)	—	—	$10 \times 10 \text{ mol}^{1/2} \text{ L}^{-1/2}$
[Weight of nylon 6] g 0.05-0.30	[AN] = $22.9 \times 10^{-2} \text{ mol L}^{-1}$ [H ₂ A] = $4.00 \times 10^{-3} \text{ mol L}^{-1}$ [PMS] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ Same as above three lines	8(C)	$0.689 \times 10^{-6} \text{ mol L}^{-1} \text{ g}^{-1/2} \text{ s}^{-1}$	4.34×10^{-4}	—
		9(C)	—	—	$8.5 \times 10^2 \text{ g}^{-1/2}$

Table I (Continued)

Evaluation of Rate Constants Using R_h and n_h ($T = 45^\circ\text{C}$; $u = 0.24 \text{ mol L}^{-1}$; $[\text{H}^+] = 8.00 \times 10^{-2} \text{ mol L}^{-1}$)		Composite Rate Constants from Homopolymerization Studies				
Variation and Range	Condition	Figure (Plot)	From R_h		From n_h	
			Slope	k^c ($\text{mol}^{-1/2} \text{ L}^{3/2} \text{ g}^{-1/2} \text{ s}^{-1}$)		Slope
[AN] mol L ⁻¹ 2.29-7.155	[PMS] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ [H ₂ A] = $3.00 \times 10^{-3} \text{ mol L}^{-1}$ Weight of nylon 6 = 0.20 g Same as above three lines	1(D)	1.69×10^{-5} mol ^{-1/2} L ^{1/2} s ⁻¹	6.68×10^{-3}	—	—
	2.29-7.155	2(D)	—	—	0.76×10^5 mol L ⁻¹	203
[PMS] mol L ⁻¹ 10.0-70.0	[AN] = $22.9 \times 10^{-2} \text{ mol L}^{-1}$ [H ₂ A] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ Weight of nylon 6 = 0.20 g Same as above three lines	3(D)	5.00×10^{-5} mol ^{1/2} L ^{-1/2} s ⁻¹	9.33×10^{-3}	—	—
	10.0-70.0	4(D)	—	—	20.3×10^2 mol ^{1/2} L ^{-1/2}	205
[H ₂ A] mol L ⁻¹ 10.0-70.0	[AN] = $22.9 \times 10^{-2} \text{ mol L}^{-1}$ [PMS] = $8.00 \times 10^{-3} \text{ mol L}^{-1}$ [Weight of nylon 6] = 0.20 g Same as above three lines	6(D)	4.33×10^{-5} mol ^{1/2} L ^{-1/2} s ⁻¹	7.00×10^{-3}	—	—
	10.0-70.0	7(D)	—	—	21.3×10^2 mol ^{1/2} L ^{-1/2}	240
[Weight of nylon 6] g 0.05-0.30	[AN] = $22.9 \times 10^{-2} \text{ mol L}^{-1}$ [PMS] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ [H ₂ A] = $4.00 \times 10^{-3} \text{ mol L}^{-1}$ Same as above three lines	8(D)	0.579×10^{-5} mol L ⁻¹ g ^{-1/2} s ⁻¹	7.64×10^{-3}	—	—
	0.05-0.30	9(D)	—	—	$16.1 \times 10_3$ g ^{-1/2}	233

^a $k_d(2k_{12}K_1K_3/k_{11})^{1/2}$
^b $k_{12}/(k_{11})^{1/2} (2k_{12}K_1K_3)^{1/2}$
^c $k_{12} (2k_{12}K_1K_3/k_{11})^{1/2}$
^d $k_{12}/(k_{11})^{1/2} (2k_{12}K_1K_3)^{1/2}$

Table II PMS-H₂A-AN-Nylon 66

Evaluation of Rate Constants Using R_g and n_g ($T = 45^\circ\text{C}$; $\mu = 0.24 \text{ mol L}^{-1}$; $[\text{H}^+] = 8.00 \times 10^{-2} \text{ mol L}^{-1}$)						
Composite Rate Constants from Grafting Studies						
Variation and Range	Condition	Figure (Plot)	From R_g			From n_g
			Slope	k^a ($\text{mol}^{-1} \text{ L g}^{-1/2} \text{ s}^{-1}$)	Slope	k^b ($\text{mol}^{-1} \text{ L s}^{-1}$)
[AN] mol L ⁻¹ 2.29-7.155	[PMS] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ [H ₂ A] = $3.00 \times 10^{-3} \text{ mol L}^{-1}$ [Weight of nylon 66] = 0.20 g Same as above three lines	10(C)	$1.00 \times 10^{-6} \text{ s}^{-1}$	5.27×10^{-4}	—	—
2.29-7.155		11(C)	—	—	$0.079 \times 10^5 \text{ mol}^{-1/2} \text{ L}^{1/2}$	21.2
[PMS] mol L ⁻¹ 10.0-70.0	[AN] = $22.9 \times 10^{-2} \text{ mol L}^{-1}$ [PMS] = $8.00 \times 10^{-3} \text{ mol L}^{-1}$ [Weight of nylon 66] = 0.20 g Same as above three lines	12(C)	$6.06 \times 10^{-6} \text{ mol}^{1/2} \text{ L}^{-1/2} \text{ s}^{-1}$	6.12×10^{-4}	—	—
10.0-70.0		13(C)	—	—	$11.9 \times 10 \text{ mol}^{1/2} \text{ L}^{-1/2}$	25.5
[H ₂ A] mol L ⁻¹ 1.60-7.00	[AN] = $28.62 \times 10^{-2} \text{ mol L}^{-1}$ [PMS] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ [Weight of nylon 66] = 0.20 g	14(A)	$5.26 \times 10^{-6} \text{ mol}^{1/2} \text{ L}^{-1/2} \text{ s}^{-1}$	5.31×10^{-4}	—	—
1-7.00	[AN] = $28.62 \times 10^{-2} \text{ mol L}^{-1}$ [PMS] = $4.00 \times 10^{-3} \text{ mol L}^{-1}$ [Weight of nylon 66] = 0.20 g	15(C)	—	—	$13.3 \times 10 \text{ mol}^{1/2} \text{ L}^{-1/2}$	22.8
[Weight of nylon 66] g 0.05-0.35	[AN] = $28.62 \times 10^{-2} \text{ mol L}^{-1}$ [PMS] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ [H ₂ A] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ Same as above three lines	16(A)	$1.00 \times 10^{-6} \text{ mol L}^{-1} \text{ s}^{-1} \text{ g}^{-1/2}$	5.82×10^{-4}	—	—
0.05-0.35		17(C)	—	—	$7.41 \times 10^2 \text{ g}^{1/2}$	22.6

Table II (Continued)

Evaluation of Rate Constants Using R_h and n_h ($T = 45^\circ\text{C}$; $\mu = 0.24 \text{ mol L}^{-1}$; $[\text{H}^+] = 8.00 \times 10^{-2} \text{ mol L}^{-1}$)		Composite Rate Constants from Homopolymerization Studies			
Variation and Range	Condition	Figure (Plot)	From R_h		From n_h
			Slope	k^c ($\text{mol}^{-1/2} \text{ L}^{3/2} \text{ g}^{-1/2} \text{ s}^{-1}$)	
[AN] mol L^{-1} 2.29-7.155	[PMS] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ [H ₂ A] = $3.00 \times 10^{-3} \text{ mol L}^{-1}$ [Weight of nylon 66] = 0.20 g Same as above three lines	10(D)	1.64×10^{-5} $\text{mol}^{1/2} \text{ L}^{-1/2} \text{ s}^{-1}$	8.63×10^{-3}	—
2.29-7.155		11(D)	—	—	154
[PMS] mol L^{-1} 10.0-70.0	[AN] = $22.9 \times 10^{-2} \text{ mol L}^{-1}$ [H ₂ A] = $8.00 \times 10^{-3} \text{ mol L}^{-1}$ [Weight of nylon 66] = 0.20 g Same as above three lines	12(D)	3.48×10^{-5} $\text{mol}^{1/2} \text{ L}^{-1/2} \text{ s}^{-1}$	7.94×10^{-3}	—
10.0-70.0		13(D)	—	—	161
[H ₂ A] mol L^{-1} 1.60-6.60	[AN] = $22.9 \times 10^{-2} \text{ mol L}^{-1}$ [PMS] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ [Weight of nylon 66] = 0.20 g Same as above three lines	14(D)	2.92×10^{-5} $\text{mol}^{1/2} \text{ L}^{-1/2} \text{ s}^{-1}$	7.69×10^{-3}	—
1.60-6.60		15(D)	—	—	167
[Weight of nylon 66] g 0.05-0.35	[AN] = $22.9 \times 10^{-2} \text{ mol L}^{-1}$ [PMS] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ [H ₂ A] = $8.00 \times 10^{-3} \text{ mol L}^{-1}$ [AN] = $28.62 \times 10^{-2} \text{ mol L}^{-1}$ [PMS] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$ [H ₂ A] = $6.00 \times 10^{-3} \text{ mol L}^{-1}$	16(D)	0.67×10^{-5} $\text{mol L}^{-1} \text{ g}^{-1/2} \text{ s}^{-1}$	8.80×10^{-3}	—
		17(D)	—	—	153

^a $k_p(2k_{1e}K_1K_4/k_{10})^{1/2}$.^b $k_p/(k_{10})^{1/2} 2(k_{1e}K_1K_4)^{1/2}$.^c $k_p(2k_{1e}K_1K_4/k_{10})^{1/2}$.^d $k_p(k_{10})^{1/2} (2k_{1e}K_1K_4)^{1/2}$.

given by (E_4) (nylon 6 as backbone) and (E_8) (nylon 66 as backbone), the average values for the individual cases are 220 and 224 mol^{-1/2} L^{1/2} s⁻¹, respectively. Multiplying the composite rate constants from R_h and n_h measurements, $k_p/k_t^{1/2}$ values were calculated to be 1.39 mol^{-3/4} L^{-3/4} g^{1/2} s⁻¹ and 1.42 mol^{-3/4} L^{3/4} g^{1/2} s⁻¹.

Taking the rate of the composite rate constants obtained from R_h and n_h measurements, $k_{15}K_1K_3$ and $k_{18}K_1K_4$ values are calculated to be 3.98×10^{-5} mol^{-3/2} L^{3/2} s⁻¹ and 4.02×10^{-5} mol^{-3/2} L^{3/2} s⁻¹ for the systems with nylon 6 and nylon 66 as backbone materials, respectively. By knowing the ($k_{12}K_1K_3$) value from the R_g and n_g measurements as 1.77×10^{-5} mol⁻¹ L s⁻¹ and $k_{15}K_1K_3$ from R_h and n_h measurements as 3.98×10^{-5} mol^{-3/2} L^{3/2} s⁻¹ for the system with nylon 6 as the backbone material, the ratio of the two values k_{12}/k_{15} was calculated to be 0.445 mol^{1/2} L^{-1/2}. By knowing the $k_{16}K_1K_4$ value from R_g and n_g as 1.74×10^{-5} mol⁻¹ L s⁻¹ and the $k_{18}K_1K_4$ value from R_g and n_g as 4.02×10^{-5} mol^{-3/2} L^{3/2} s⁻¹ for the system with nylon 66 as the backbone, the ratio of the two values k_{16}/k_{18} was calculated to be 0.433 mol^{1/2} L^{-1/2}.

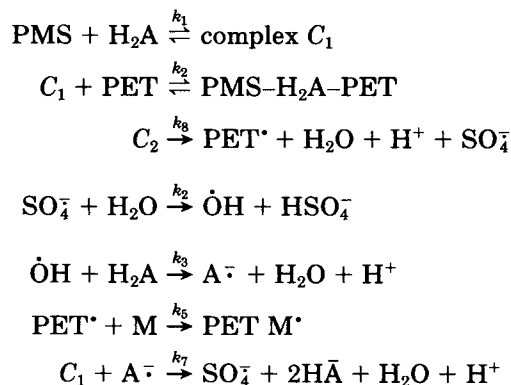
The values obtained for $k_{15}K_1K_3$ and $k_{12}K_1K_3$ from the slopes of the plots $-R_{PMS}$ vs. [PMS] [Fig. 5(C) and (D)] are 6.14×10^{-4} s⁻¹ and 2.30×10^{-4} s⁻¹, respectively, using the slopes, and knowing that $-R_{PMS}$ was invariant to the change in [H₂A] and [nylon 6], the two equations [$k_{15}[M] + k_{12}$] with two different [M] values are solved to obtain the ratio (k_{12}/k_{15}) and the calculated value was 0.374. This reveals that $k_{12} < k_{15}$ and this may be the reason for the homopolymerization to occur while grafting reactions are carried out. The analogous procedure for the nylon 66 system shows k_{16}/k_{18} as 0.581 and favors simultaneous homopolymerization.

The % grafting and % efficiency changes with the [AN], [PMS], [H₂A], and nylon 6/nylon 66 amounts were found to be similar to the one observed with the peroxomonosulfate-H₂A-initiated graft copolymerization of AN onto PET. The same reasoning is therefore reckoned with based on earlier reports.^{23,24} Shukla and co-workers²⁵ and Verma and Ray¹⁸ found a similar effect on % grafting with [M]. Verma and Ravisankar¹⁹ reported that the grafting efficiency was good only at a low concentration of the monomer by another system.

The low % efficiencies in all these cases may be due to the occurrence of simultaneous homopolymerization. This obviously suggested that most of the redox catalyst may be absorbed by the backbone (nylon 6/nylon 66) and initiates grafting and homopolymerization simultaneously.

APPENDIX: PROPOSED MECHANISM FOR THE GRAFT COPOLYMERIZATION OF MMA ONTO PET AND SIMULTANEOUS HOMOPOLYMERIZATION WHEN PMS-H₂A WAS USED AS THE REDOX INITIATOR

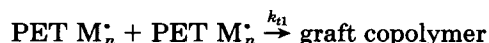
Initiation:



Propagation:



Termination:



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