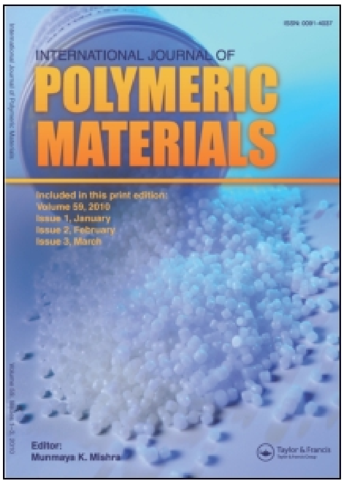

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Peroxodisuiphate/Peroxodiphosphate-Ascorbic Acid Redox Initiated Graft Copolymerization of Acrylonitrile/Methylmethacrylate onto Polyethyleneterephthalate — A Close Comparison

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Peroxodisulphate/Peroxodiphosphate-Ascorbic Acid Redox Initiated Graft Copolymerization of Acrylonitrile/Methylmethacrylate onto Polyethyleneterephthalate – A Close Comparison

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The kinetics of graft copolymerization of Poly acrylonitrile (PAN)/Poly methylmethacrylate (PMMA) onto synthetic backbones such as nylon 6/nylon 66/Poly ethylene terephthalate (PET) initiated by peroxodisulphate (PDS)/Peroxodiphosphate (PDP)-Ascorbic acid (H_2A) redox systems were studied separately. Simultaneous homopolymerizations were also followed under all conditions. A close comparison of the various rate parameters was made through analysis of results.

Keywords: Graft copolymerizations; synthetic backbones; peroxo salts-H_2A-Redox systems; kinetic parameters

INTRODUCTION

A variety of redox systems have been employed for the initiation of graft copolymerization of vinyl monomers onto synthetic or natural

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backbone [1]. Van Phung and coworkers [2] reported that acrylamide or acrylonitrile (AN) can be grafted onto nylon 6 or nylon 66 to produce N-grafted polyamides *via* redox reaction. Potassium bromate-thiourea redox system was used by Habeish and coworkers [3] for initiation of graft co-polymerization of methylmethacrylate (MMA) onto nylon 66. Lenka *et al.* [4], carried out the graft copolymerization of MMA onto nylon 6 using acetyl acetonate 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) [5, 6], Mn(IV) [7], Mn(III) [8] and azobisisobutyronitrile based redox system [9]. Peroxodiphosphate has been used as a lone initiator for the graft copolymerization of MMA onto nylon 6 [10]. Burkanudeen and coworkers [11] recently studied the polymerization of acrylamide and graft co-polymerization of acrylamide onto nylon 66 in nitrogen atmosphere using Vanadium(V)-metabisuphite as a new redox initiating system. In the grafting study, simultaneous homopolymerization was observed in all the experimental conditions. A mechanism was proposed to explain the observation of simultaneous homopolymerization during grafting.

Graft co-polymerization study of MMA onto PET fiber using hydrogen peroxide as initiator was carried out [12]. Graft copolymerization of acrylamide onto PET chips and spinning of bicomponent fibers was made [13].

Recently from our laboratory peroxomonosulphate (PMS)-Ascorbic acid (H_2A) redox initiated system was employed for grafting PAN onto nylon 6/nylon 66/PET [14, 15]. A close comparison of the various rate parameters was made during the graft co-polymerization while using the backbones nylon 6/nylon 66/PET. This work directs its attention to use different peroxosalts, Peroxodisulphate (PDS), Peroxodiphosphate (PDP) along with ascorbic acid to form redox initiating system for graft copolymerization of PAN/PMMA onto PET and to make a comparative analysis of the results.

EXPERIMENTAL PROCEDURE

A typical graft copolymerization study was carried out as given below:

PET(W_1g) and required amount of the reductant ascorbic acid (H_2A), Sulphuric acid (to adjust acidity) and sodium sulphate (to adjust ionic strength) were taken in a reaction vessel and thermostated for 30 minutes. The system was flushed with pure nitrogen gas for 30 minutes and then the required amount of monomer (acrylonitrile or methylmethacrylate) and the oxidising agent (PDS or PDP) solution were added to the reaction mixture. The time of adding the oxidising agent was taken as the starting time for the reaction (No polymerization was observed in the absence of oxidant. This was ascertained by a separate experiment). The reaction vessel was sealed with rubber gaskets to ensure inert atmosphere during reaction time. At the end of the reaction time, the reaction was arrested by immersing the reaction vessels in ice cold water (10°C) and blowing air into the tube to freeze further reaction. Constant grafting time (6 hrs) was given.

The grafted PET along with homopolymer (PAN/PMMA) was filtered from the reaction mixture using G3 sintered crucible, washed with distilled water for several times, dried (60°C for 6 hours in the case of PAN and 105°C for 5 hours for PMMA) and weighed till to get constant weight. This gives the total weight of the grafted polymer with the homopolymer (W_2g).

The mixture of grafted PET along with homopolymer PAN/PMMA was soxhlet extracted with acetone or benzene for 24 hours to separate the homopolymers. After the separation of homopolymer, the grafted sample was cooled to room temperature and weighed to constant weight (W_3g).

The difference between the weight of PET after grafting (W_3g) and the weight of original PET taken (W_1g) gives the weight of grafted PET ($W_3 - W_1$)g.

The difference ($W_2 - W_3$)g gives the weight of homopolymer PAN or PMMA formed.

Rate of PDS/PDP disappearance was determined by volumetric method [14, 15].

Rate Measurements

Graft Co-polymerization

$$\%\ \text{grafting} = \frac{\begin{array}{c}\text{(Dry weight of the grafted sample} -\\ \text{Dry weight of the backbone)}\end{array}}{\text{(Dry weight of the backbone)}} \times 100$$

$$\% \text{ efficiency} = \frac{(\text{Weight of the grafted polymer})}{(\text{Weight of the monomer used})} \times 100$$
$$= \frac{(W_3 - W_1)g}{W_4 g} \times 100$$

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

where (W_3-W_1) = Weight of the grafted polymer

V = Total volume of the reaction mixture
t = Reaction time (Sec)
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 $(W_2 - W_3)$ is the weight of homopolymer, V, t, M are as given above.

Isolation of Grafted Polymeric Chain from PET

The grafted PET was digested with phenol/trichloro phenol 10/7 volume [16] for 30 minutes. The digestion was allowed to proceed for 24 hours. The residue was washed with boiling water and dried. The separated polymer was purified.

Chain Length Measurements

Homopolymers (PAN/PMMA)

Chain length '*n*' of the separated homopolymers PAN/PMMA were determined by viscometry.
For PMMA in benzene at 25°C [17]

$$[n] = 5.20 \times 10^{-3} \times M^{-0.76}$$

For PAN in dimethylformamide at 25°C [18]

$$[n] = 2.43 \times 10^{-4} \times M^{-0.75}$$

The procedure adopted to determine chain length of homopolymer was also extended for the determination of molecular weight of PAN or PMMA isolated from the backbone.

RESULTS AND DISCUSSION

Three graft copolymerization studies were carriedout:

1. Peroxodisulphate (PDS)-Ascorbic acid (H_2A) initiated graft copolymerization of PMMA onto PET. (PDS-H_2A-MMA-PET system)
2. Peroxodiphosphate (PDP)-Ascorbic acid (H_2A) initiated graft copolymerization of PMMA onto PET. (PDP-H_2A-MMA-PET system)
3. Peroxodiphosphate (PDP)-Ascorbic acid (H_2A) initiated graft copolymerization of PAN onto PET. (PDP-H_2A-AN-PET system)

Effect of [MMA] on Graft Parameters

When PDP-H_2A and PDS-H_2A systems were used for the initiation of graft co-polymerization of PMMA onto PET, it was observed that both R_g and R_h increases with [MMA] in the range from $7.60 \times 10^{-3} \mathrm{mol\,l^{-1}}$ to $76.0 \times 10^{-3} \mathrm{mol\,l^{-1}}$. Direct plots of R_g *vs* [MMA] (Fig. 1A, C) and R_h *vs* [MMA] (Fig. 1B, D) were found to be linear for PDP-H_2A system and thereby showed first power dependences on R_g and R_h.

Kinetic chain length of the grafted polymer (n_g) and homopolymer (n_h) were determined and found that both the values decrease with [MMA]. Double logrythmic plots $\log n_g$ *vs* log [MMA] (Fig. 2A, B) and direct plots n_g *vs* [MMA] (Fig. 2C) and n_h *vs* [MMA] (Fig. 2D) gave the first order dependences of n_g and n_h.

It was observed that % grafting steadily increases with [MMA] but % efficiency show increasing trend initially and decreases there afterwards (Tab. I).

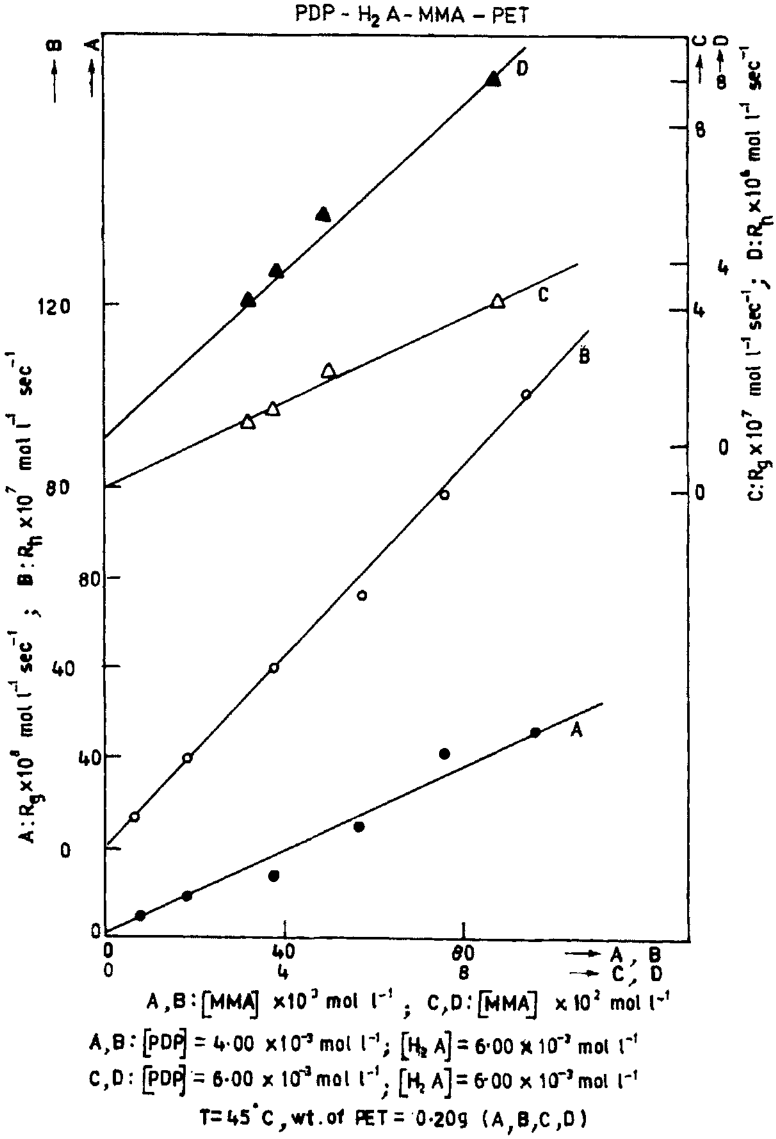


FIGURE 1 Effect of [MMA] on R_g and R_h.

R_g, R_h, n_g and n_h values obtained in the PDS-H$_2$A system also gave a similar trend towards change of [MMA] as that of PDP-H$_2$A system. (Fig. 3A–D and Fig. 4A–D).

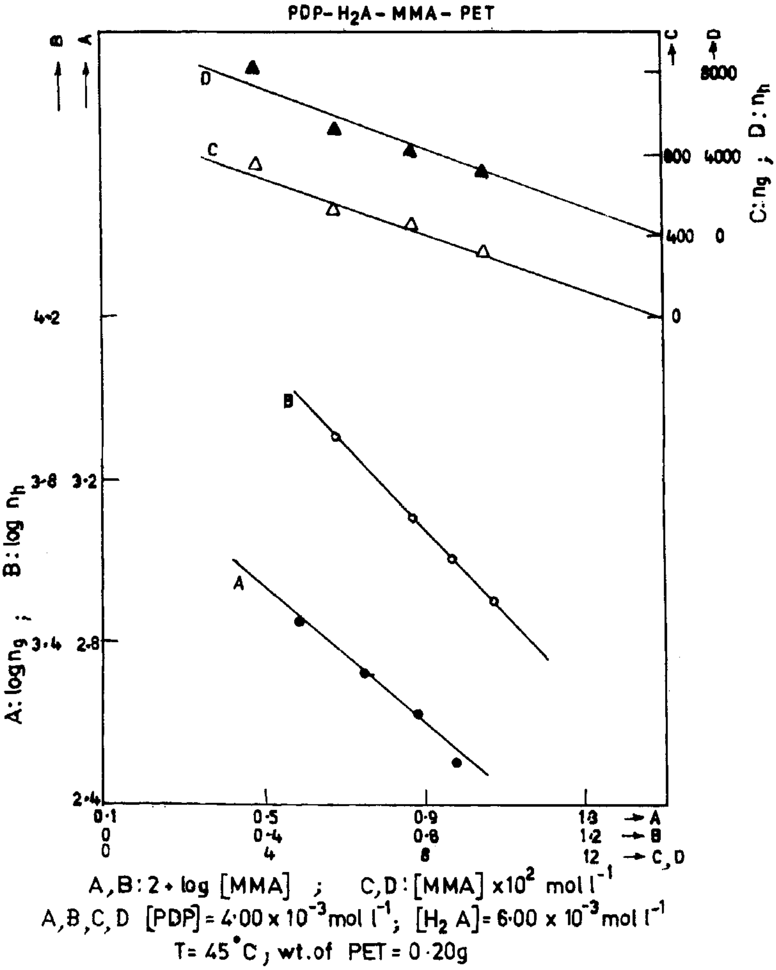


FIGURE 2 Effect of [MMA] on n_g and n_h.

Effect of [AN] on Graft Parameters

Graft copolymerization of PAN onto PET with PDP-H_2A system gave a different trend with respect to monomer variation towards R_h.

The fact that the plots of R_g *vs* [AN] (Fig. 5A, C) and R_h *vs* $[AN]^{1.5}$ (Fig. 5B, D) were linear and indicated first order and three halfth order dependences for R_g and R_h respectively. R_h, here, showed three halfth

TABLE I PDS/PDP-H_2A-MMA-PET. Effect of (MMA) on % grafting and % efficiency. (H_2A) = 6.00×10^{-3} mol l^{-1}; $T = 45$°C; Weight of PET = 0.20 g

$[MMA]^a \times 10^2$ % $mol\,l^{-1}$	% *grafting* (*a*)	% *efficiency* (*a*)	$(MMA)^b \times 10^2$ $mol\,l^{-1}$	% *grafting* (*b*)	% *efficiency* (*b*)
1.90	4.00	8.43	3.04	4.75	6.30
3.80	8.00	8.44	3.80	8.45	8.90
4.94	12.20	9.86	4.94	13.00	10.50
8.74	16.60	7.60	8.74	21.50	9.87

a = (PDS) = 6.00×10^{-3} mol l^{-1}.
b = (PDP) = 6.00×10^{-3} mol l^{-1}.

order dependence in comparison with first order in PDP-H_2A-MMA system.

n_g and n_h values were determined separately and found to increase with [AN]. Double logrythmic plots $\log n_g$ *vs* log [AN] (Fig. 16A) and $\log n_h$ *vs* log [AN] (Fig. 16B), direct plots n_g *vs* [AN] (Fig. 16C) and n_h *vs* $[AN]^{0.5}$ (Fig. 16D) were now found to be linear and indicated the first and half order dependences on n_g and n_h respectively. A different observation than in PDP-H_2A-MMA-PET system was therefore noted here in the case of homopoloymer formation.

Under identical conditions, the system with PDP as oxidant was found to have higher % grafting while grafting PAN onto PET than with PDS. The change in % grafting and % efficiency are presented (Tab. II).

Effect of [PDS]/[PDP] on Graft Parameters

In all the three systems, R_g and R_h values were determined for the variation of [PDS] or [PDS] and found that both values increases with [PDS] or [PDP].

TABLE II PDP-H_2A-AN-PET. Effect of [AN] on % grafting and % efficiency. [PDP] = 6.00×10^{-3} mol l^{-1}; $T = 45$°C. [H_2A] = 4.00×10^{-3} mol l^{-1}; Weight of PET = 0.20 g

$[AN] \times 10\,mol\,l^{-1}$	% *grafting*	% *efficiency*
1.431	3.85	2.04
2.862	8.10	2.06
4.293	12.00	2.12
5.724	15.50	2.04
7.155	17.90	1.90

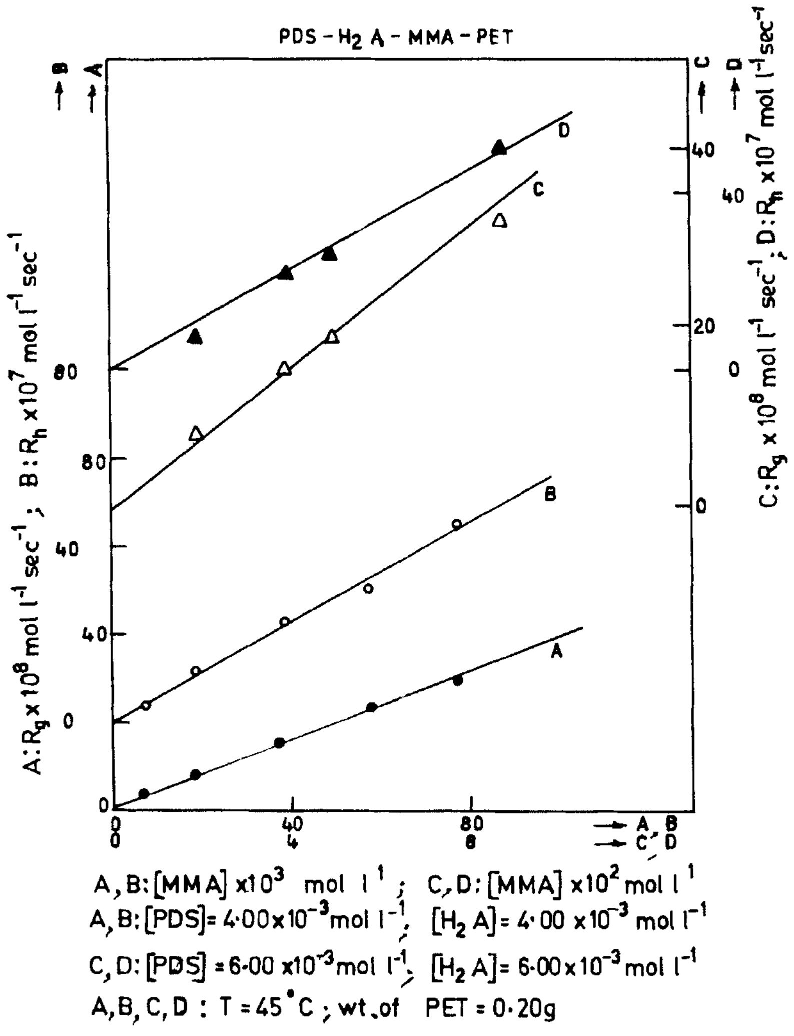


FIGURE 3 Effect of [MMA] on R_g and R_h.

The oxidants were found to have half order dependence in all the three systems. The linear nature of the plots R_g *vs* $[PDS]^{0.5}$ (Fig. 7A, C) and R_h *vs* $[PDP]^{0.5}$ (Fig. 7B, D) in the system PDS-H_2A-MMA-PET, R_g *vs* $[PDP]^{0.5}$ (Fig. 8A, C) and R_h *vs* $[PDP]^{0.5}$ (Fig. 8B, D) in the system PDP-H_2A-MMA-PET, R_g *vs* $[PDP]^{0.5}$ (Fig. 9A, C) and R_h *vs*

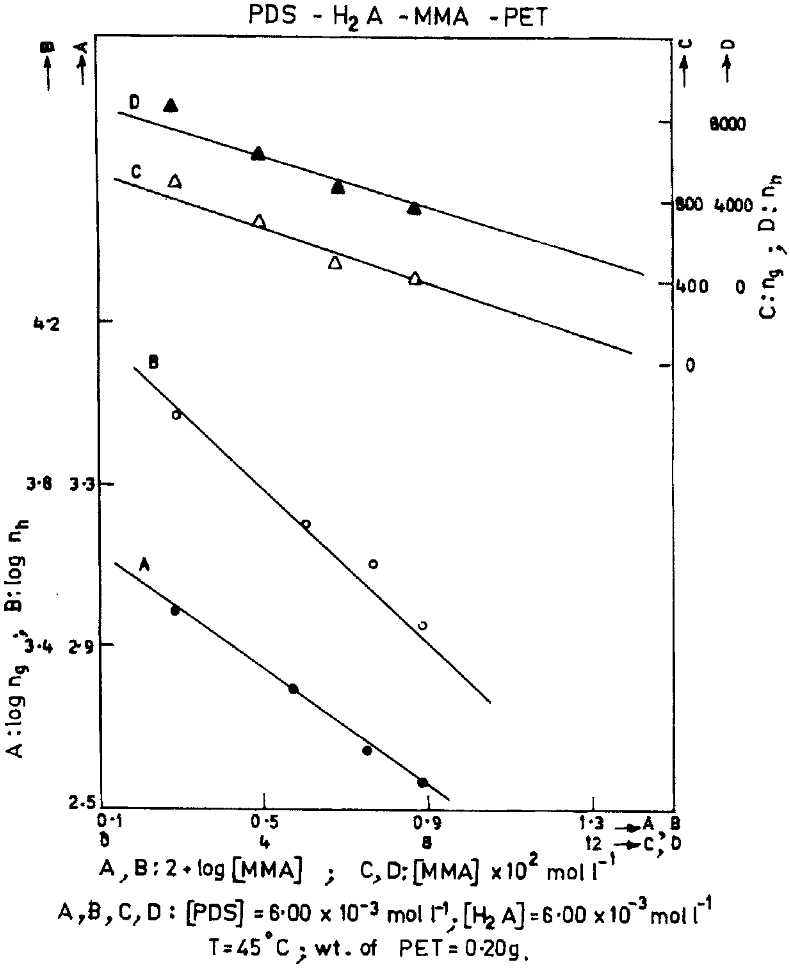
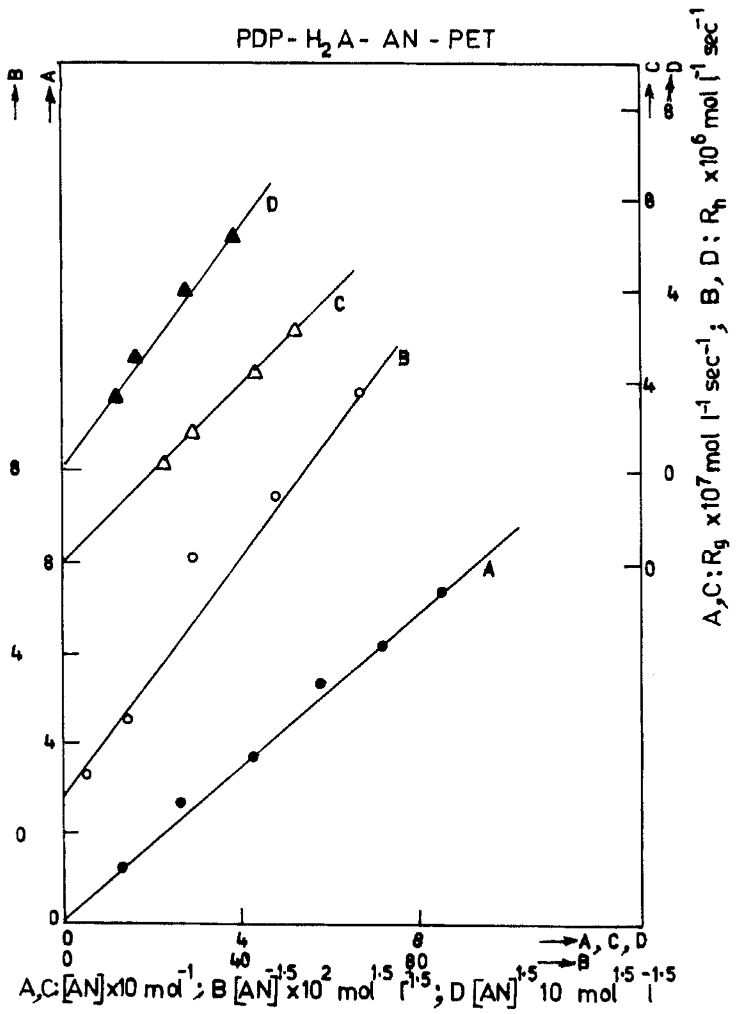


FIGURE 4 Effect of [MMA] on n_g and n_h.

$[PDP]^{0.5}$ (Fig. 9B, D) in the system PDP-H_2A-AN-PET confirmed the order dependences.

Other graft parameter like % grafting and % efficiency showed gradual increase with [PDS] or [PDP] under the conditions mentioned in Table III.

n_g and n_h values were determined independantly and found to decrease with [PDS] or [PDP]. Double logrythmic plots (Fig. 10A, B),



A,B: [PDP] = 6·00 × 10^{-3} mol l^{-1} ; [H_2A] = 4·00 × 10^{-3} mol l^{-1}
C,D: [PDP] = 5·00 × 10^{-3} mol l^{-1} ; [H_2A] = 6·00 × 10^{-3} mol l^{-1}
A,B,C,D : T = 45°C ; wt. of PET = 0·20g.

FIGURE 5 Effect of [AN] on R_g and R_h.

direct plots n_g *vs* $[\mathrm{PDS}]^{-0.5}$ (Fig. 10C), n_h *vs* $[\mathrm{PDS}]^{-0.5}$ (Fig. 10D) for PDS-H_2 A-MMA-PET system, double logrythmic plots (Fig. 11A, B), direct plots n_g $[\mathrm{PDP}]^{-0.5}$ (Fig. 11C), n_h *vs* $[\mathrm{PDP}]^{-0.5}$ (Fig. 11D) for the

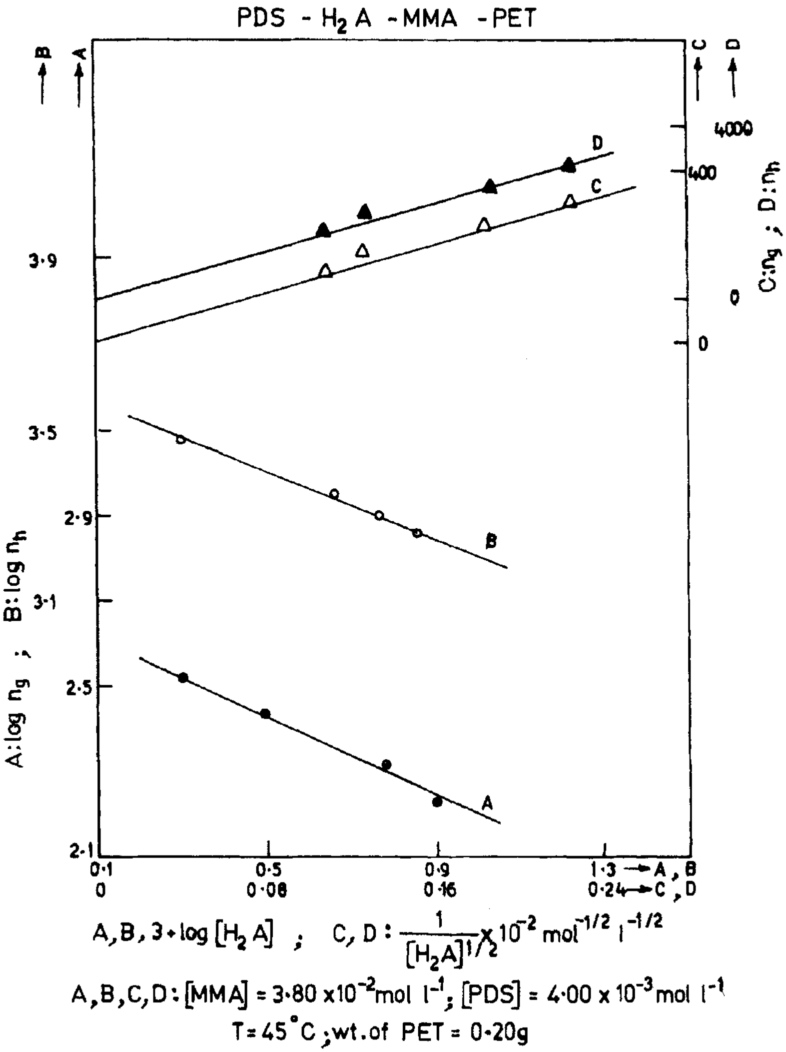
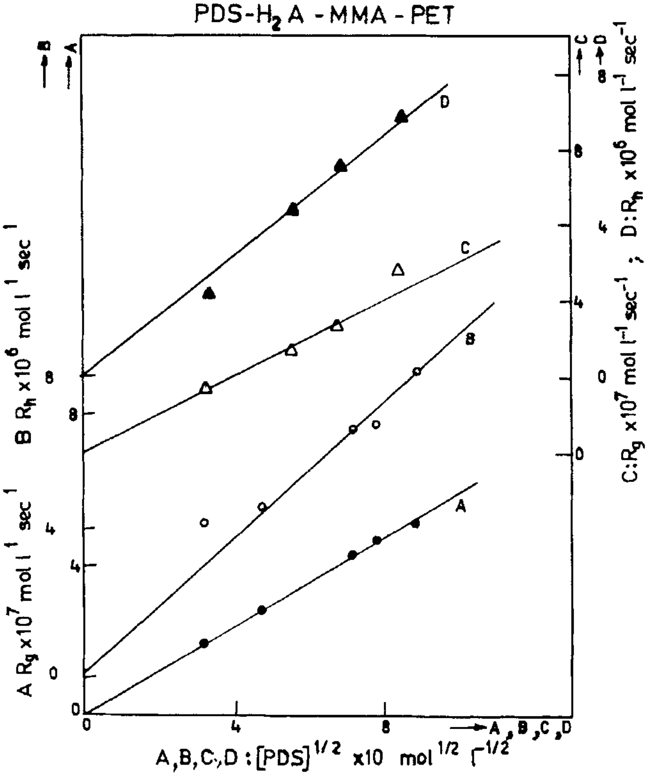


FIGURE 6 Effect of $[H_2A]$ on n_g and n_h.

system PDP-H_2A-MMA-PET and double logrythmic plots (Fig. 12A, B), direct plots n_g *vs* $[PDP]^{-0.5}$ (Fig. 12C), n_h *vs* $[PDP]^{-0.5}$ (Fig. 12D) for the system PDP-H_2A-AN-PET system were drawn to find the order dependences.



A,B : [MMA] = $3{\cdot}80 \times 10^{-2}$ mol l^{-1}; $[H_2A] = 4{\cdot}00 \times 10^{-3}$ mol l^{-1}

C, D : [MMA] = $3{\cdot}08 \times 10^{-2}$ mol l^{-1}; $[H_2A] = 6{\cdot}00 \times 10^{-3}$ mol l^{-1}

T = 45°C ; wt of PET = 0·20g

FIGURE 7 Effect of [PDS] on R_g and R_h.

Effect of [PDS] on $-R_{PDS}$′ [PDP] on $-R_{PDP}$

$-R_{PDS}/-R_{PDP}$ values were also determined and found to increase with [PDS] or [PDP] (Tab. III).

Effect of [H_2A] on Graft Parameters

In all the three systems, R_g and R_h values increase with [H_2A]. The half order dependences of H_2A were noticed through the linearity of the

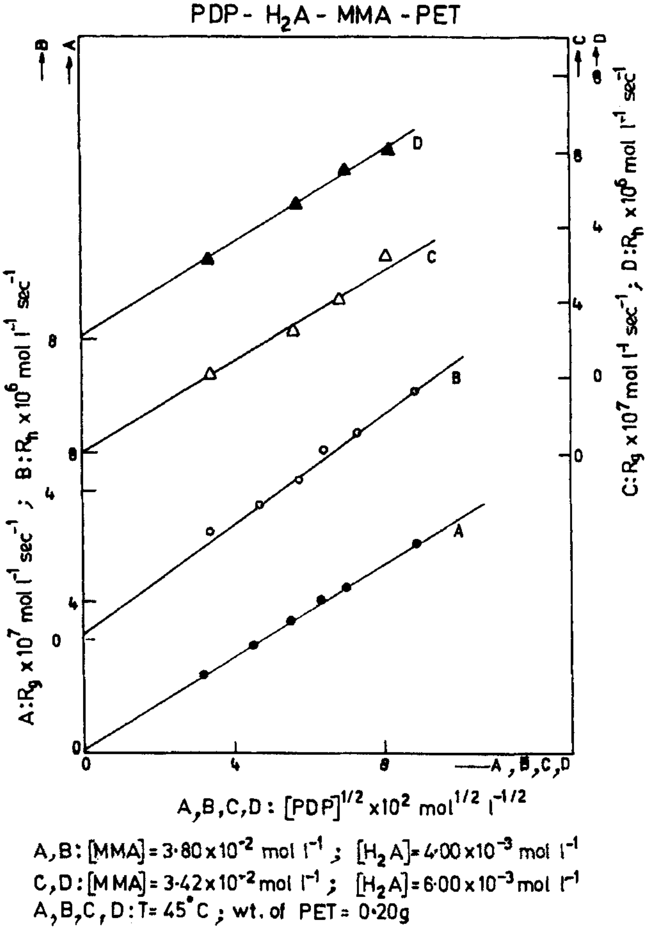


FIGURE 8 Effect of [PDP] on R_g and R_h.

direct plots R_g *vs* $[H_2A]^{0.5}$ (Fig. 13A, C), R_h *vs* $[H_2A]^{0.5}$ (Fig. 13B, D), for the system PDP-H_2A-MMA-PET, R_g *vs* $[H_2A]^{0.5}$ (Fig. 14A, C), R_h *vs* $[H_2A]^{0.5}$ (Fig. 14B, D) for the system PDS-H_2A-PET and R_g *vs* $[H_2A]^{0.5}$ (Fig. 15A, C) and R_h *vs* $[H_2A]^{0.5}$ (Fig. 15B, D) for the system PDP-H_2A-AN-PET.

n_g and n_h values were determined separately and found to decrease with increase in $[H_2A]$ in all the three systems. Double logrythmic plots

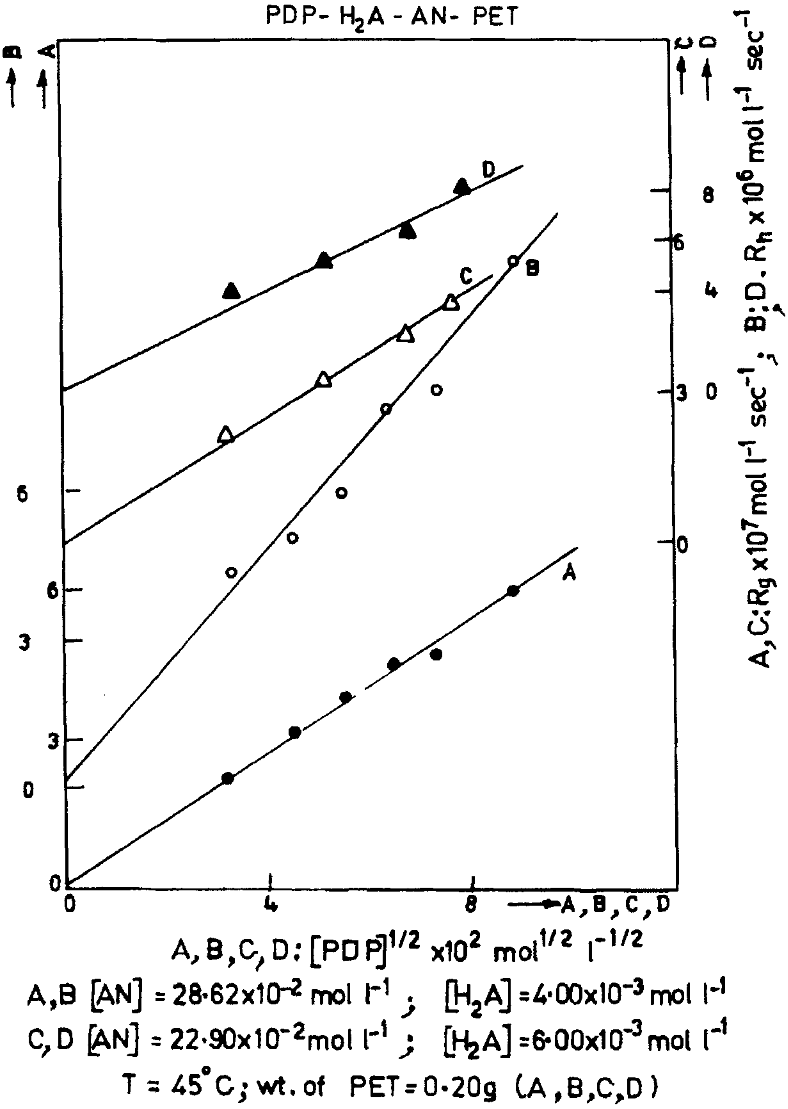


FIGURE 9 Effect of [PDP] on R_g and R_h.

(Figs. 6A, B, 17A, B, 18A and B) and direct plots n_g *vs* $[H_2A]^{0.5}$ (Figs. 6C, 17C and 18C) n_h *vs* $[H_2A]^{-0.5}$ (Figs. 6D, 17D and 18D) were used to identify the order dependences of PDS/PDP on n_g and n_h.

TABLE III PDS/PDP-H_2A-MMA-PET. Effect of [PDS]/[PDP] on % grafting, % efficiency and $-R_{PDS}/R_{PDP}$. $T = 45°C$; Weight of PET = 0.20 g

$(PDS)^a \times 10^4 / (PDP)^{b,c}$ $mol\,l^{-1}$	% grafting			% efficiency			$-R_{PDS} \times 10^7$ $mol\,l^{-1}\,sec^{-1}$	$-R_{PDP'} \times 10^7$ $mol\,l^{-1}\,sec^{-1}$	$-R_{PDP} \times 10^7$ $mol\,l^{-1}\,sec^{-1}$
	a	*b*	*c*	*a*	*b*	*c*	*a*	*b*	*c*
10.00	10.4	10.8	6.42	10.8	11.4	1.68	2.96	3.16	2.61
20.00	15.9	15.2	9.05	16.8	16.1	2.38	7.31	7.63	7.75
50.00	26.2	23.6	13.6	24.9	24.8	3.58	21.1	21.2	15.0
80.00	28.7	30.4	17.8	30.2	32.1	4.56	34.5	34.8	25.2

a,b: $[MMA] = 3.80 \times 10^{-2}\,mol\,l^{-1}$; $[H_2A] = 4.00 \times 10^{-3}\,mol\,l^{-1}$.
c: $[AN] = 28.62 \times 10^{-2}\,mol\,l^{-1}$; $[H_2A] = 4.00 \times 10^{-3}\,mol\,l^{-1}$.

TABLE IV PDS/PDP-H_2A MMA PET. Effect of H_2A on % grafting and % efficiency. $T = 45°C$; Weight of PET = 0.20 g

$(H_2A)^{a,b,c} \times 10^4$ $mol\,l^{-1}$	% Grafting			% Efficiency		
	a	*b*	*c*	*a*	*b*	*c*
10.00	10.3	17.5	3.10	10.9	18.4	0.79
20.00	14.5	19.6	4.50	15.3	20.7	1.18
30.00	18.3	24.2	5.70	19.3	25.5	1.50
60.00	26.5	33.3	8.10	27.9	35.1	2.13
80.00	31.5	35.3	9.06	33.3	37.2	2.58

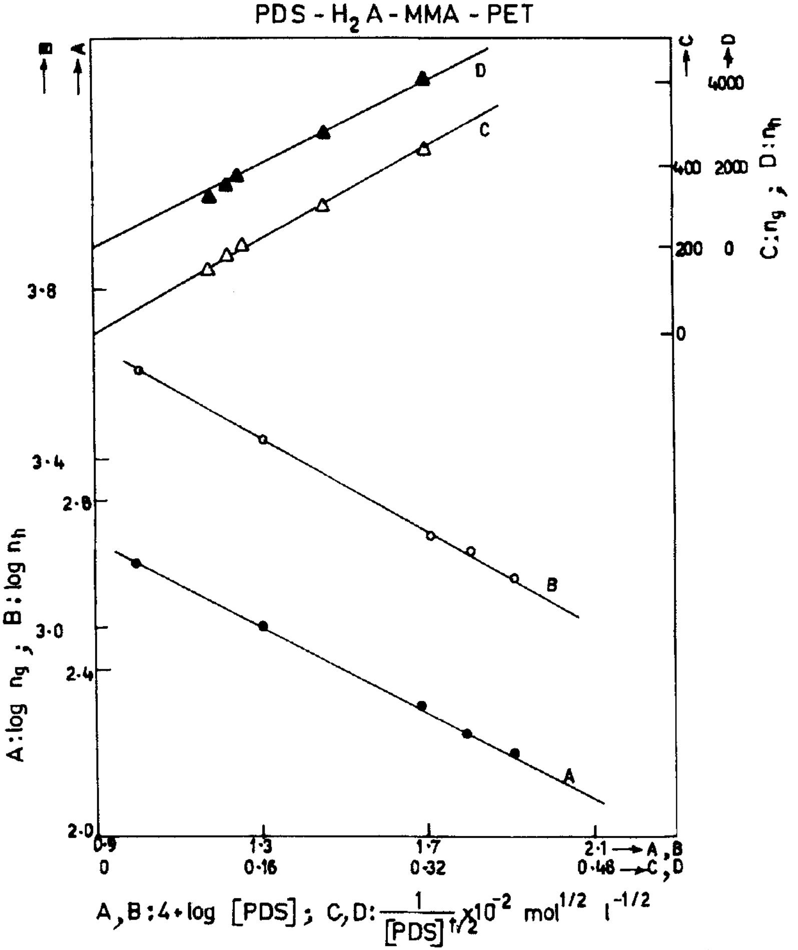
a,b: $[MMA] = 3.80 \times 10^{-2}\,mol\,l^{-1}$; b,c: $[PDP] = 6.00 \times 10^{-3}\,mol\,l^{-1}$;
a: $[PDS] = 4.00 \times 10^{-3}\,mol\,l^{-1}$; c: $[AN] = 28.62 \times 10^{-2}\,mol\,l^{-1}$.

The % grafting and % efficiency increase with [H_2A] under the conditions mentioned in Table IV for the three systems.

Effect of PET on Graft Parameters

In all the three systems, for the variation of backbone material, PET fibre, R_g and R_h values increase steadily with backbone amount. Direct plots R_g *vs* (Weight of PET)$^{0.5}$ (Fig. 19A, C), R_h *vs* (Weight of PET)$^{0.5}$ (Fig. 19B, D) for the system PDS-H_2A-MMA-PET, R_g *vs* (Weight of PET)$^{0.5}$ (Fig. 20A, C), R_h *vs* (weight of PET)$^{0.5}$ (Fig. 20B, D) for the system PDP-H_2A-MMA-PET and R_g *vs* (Weight of PET)$^{0.5}$ (Fig. 21A, C), R_h *vs* (Weight of PET)$^{0.5}$ (Fig. 21B, D) for the system PDP-H_2A-AN-PET were used to infer the half order dependences.

n_g and n_h measurements were carried out under the grafting conditions mentioned. It was observed that both values decrease with backbone amount. The slopes of the double logrythmic plots Figures



A, B, C, D: $[MMA] = 3{\cdot}80 \times 10^{-2}$ mol l^{-1} ; $[H_2A] = 4{\cdot}00 \times 10^{-3}$ mol l^{-1}
T = 45°C ; wt of PET = 0·20g

FIGURE 10 Effect of [PDS] on n_g and n_h.

22A and B, 23A and B, 24A and B are found to be – 0.5 indicating the inverse half ordere dependences of n_g and n_h towards backbone amount.

Direct plots n_g *vs* (weight of PET)$^{-0.5}$ (Fig. 22C), n_h *vs* (weight of PET)$^{-0.5}$ (Fig. 22D), n_g *vs* (Weight of PET)$^{-0.5}$ (Fig. 23C), n_h *vs* (weight of PET)$^{-0.5}$ (Fig. 23D), n_g *vs* (weight of PET)$^{-0.5}$ (Fig. 24C) and n_h *vs* (weight of PET)$^{-0.5}$ (Fig. 24D) were drawn and found to be

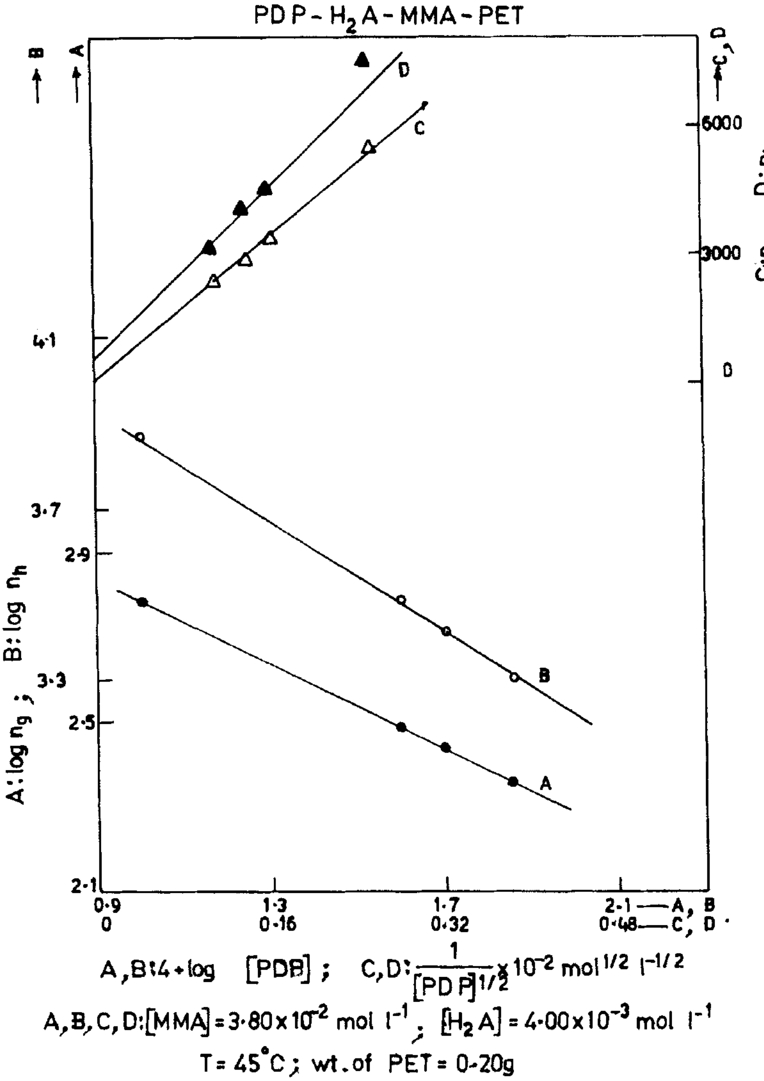


FIGURE 11 Effect of [PDP] on n_g and n_h.

linear in all cases suggesting an inverse half order dependences of n_g and n_h on PET.

The increase in % grafting was sharp in all the systems. The % efficiency increases steadily under the conditions mentioned in Table V.

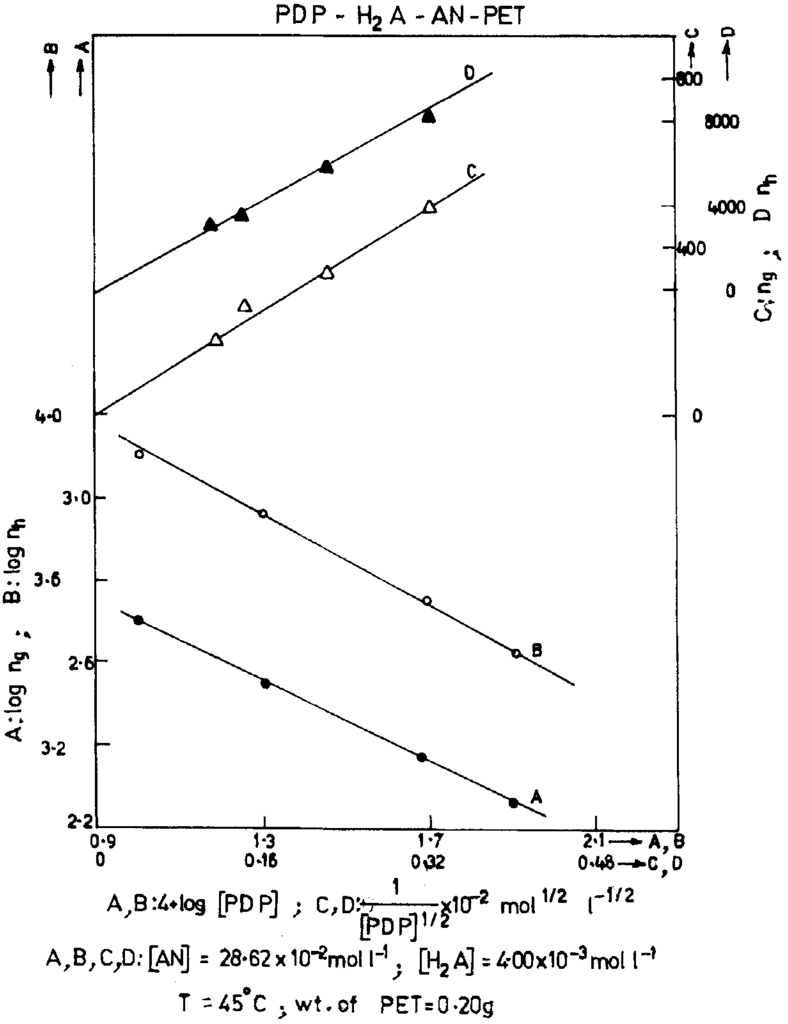


FIGURE 12 Effect of [PDP] on n_g and n_h.

DISCUSSION

The results obtained with PDP-H_2A redox initiated graft co-polymerization of PAN onto PET was similar to the one obtained for the graft co-polymerization of PAN onto PET using PMS-H_2A system [14,15]. Hence the mechanism for the graft co-polymerization

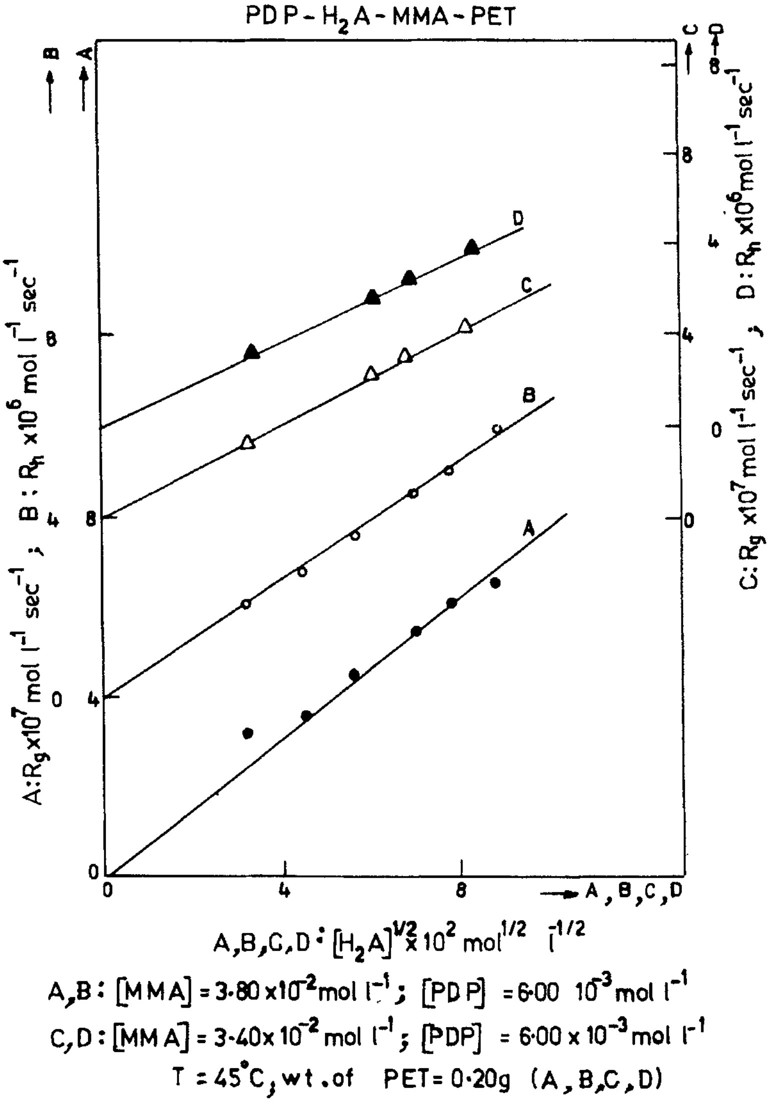


FIGURE 13 Effect of $[H_2A]$ on R_g and R_h.

of PAN onto PET and its simultaneous homopolymerization would be similar to the PMS-H_2A system with suitable replacement of oxidant as PDP.

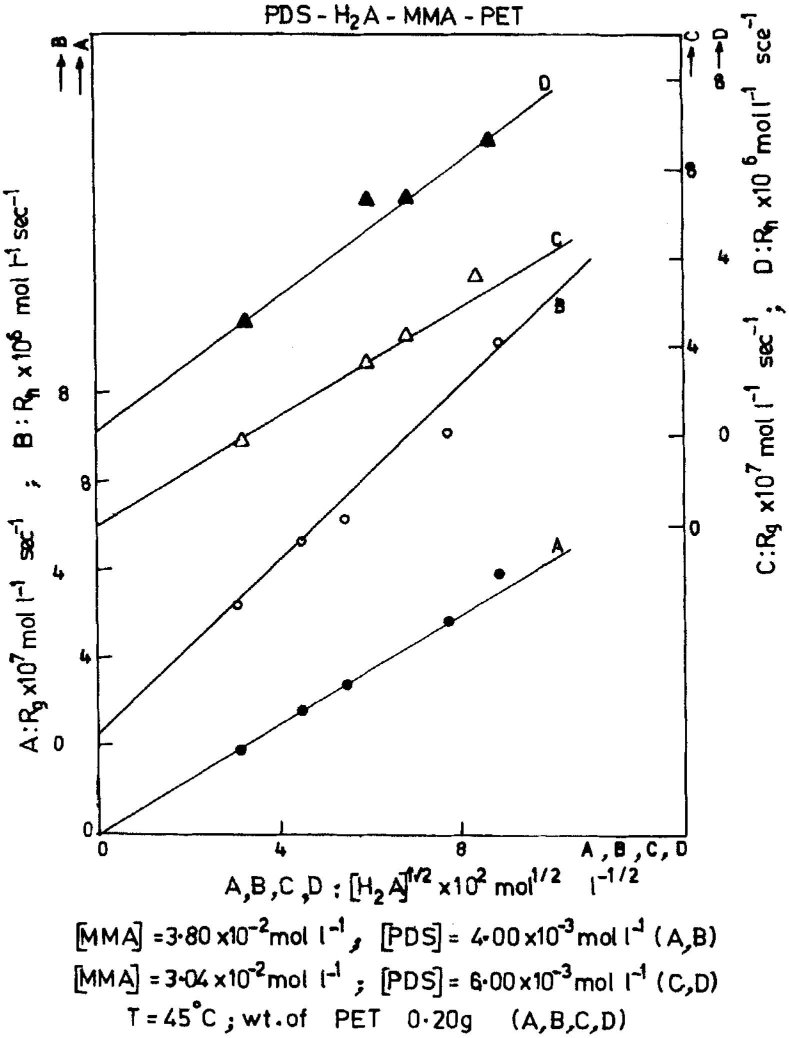
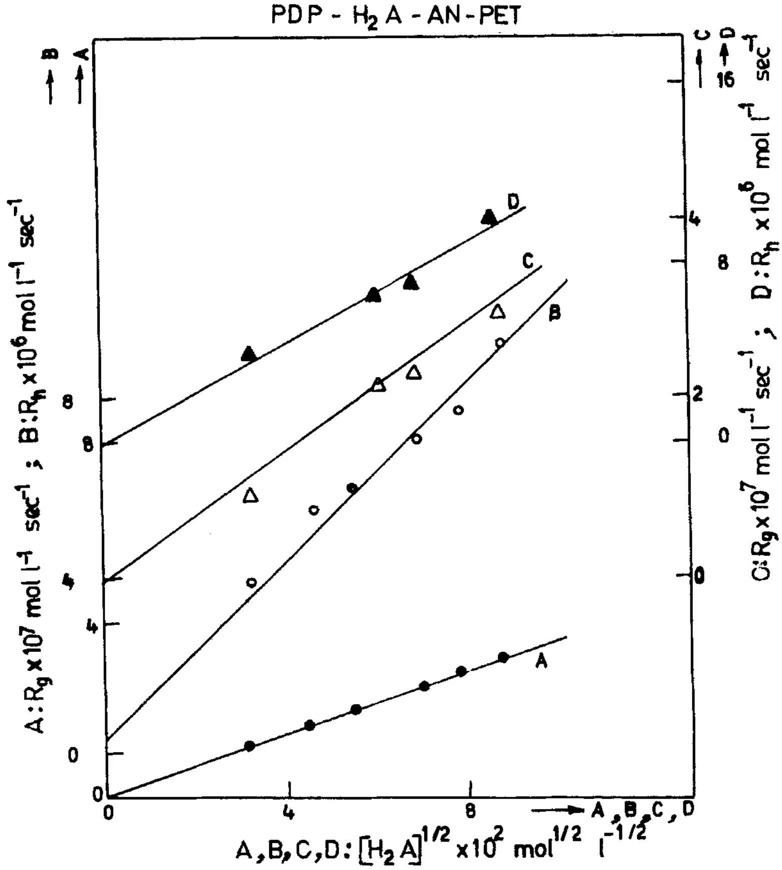


FIGURE 14 Effect of $[H_2A]$ on R_g and R_h.

Selected Reaction Scheme

Initiation

$$\text{PDP} + \text{H}_2\text{A} \overset{K_1}{\rightleftarrows} \begin{array}{c}\text{PDP-H}_2\text{A}\\ \text{Complex}_1\ \text{C}_1\end{array}$$



A, B: [AN] = 28·62 x 10^{-2} mol l^{-1}; [PDP] = 6·00 x 10^{-3} mol l^{-1}
C, D: [AN] = 22·90 x 10^{-2} mol l^{-1}; [PDP] = 5·00 x 10^{-3} mol l^{-1}
A, B, C, D: T = 45°C; wt of PET = 0·20 g.

FIGURE 15 Effect of $[H_2A]$ on R_g and R_h.

$$C_1 + \text{PET} \underset{}{\overset{K_2}{\rightleftarrows}} \underset{\text{complex}_2\ C_2}{\text{PDP-H}_2\text{A-PET}}$$

$$C_2 \xrightarrow{k_1} \text{PET} + H_2O + H^+ + HPO_4^- + PO_4^-$$

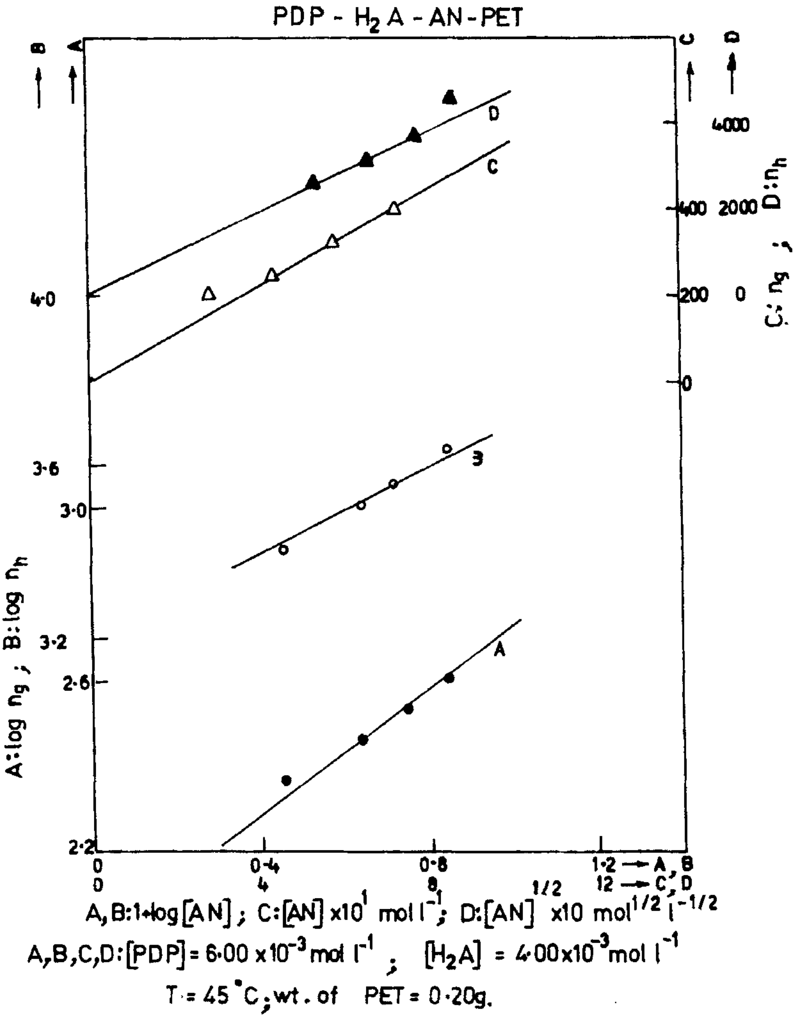


FIGURE 16 Effect of [AN] on n_g and n_h.

$$\mathrm{PET} + \mathrm{M} \xrightarrow{k_2} \mathrm{PETM}^{\cdot}$$

$$\mathrm{PO}_4^{-} + \mathrm{H_2O} \xrightarrow{k_3} \mathrm{HPO}_4^{-} + \dot{\mathrm{O}}\mathrm{H}$$

$$\mathrm{OH} + \mathrm{H_2A} \xrightarrow{k_4} \mathrm{H_2O} + \mathrm{A}^{\bar{\cdot}} + \mathrm{H}^{+}$$

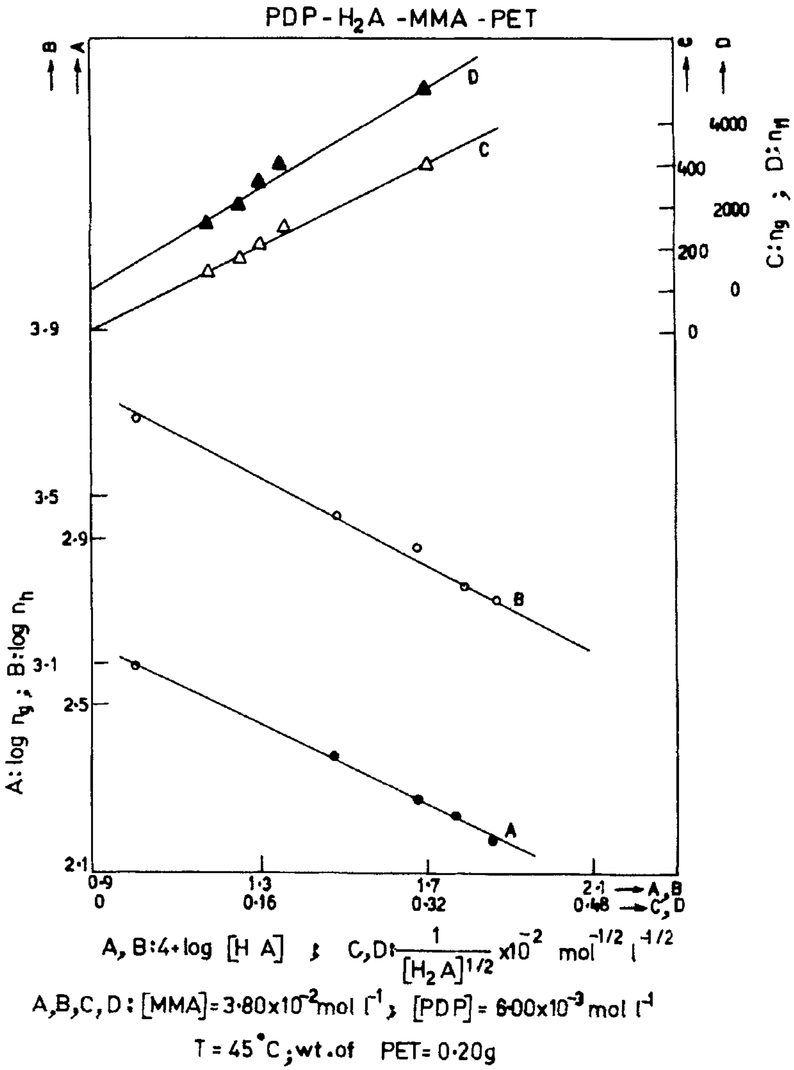


FIGURE 17 Effect of $[H_2A]$ on n_g and n_h.

$$C_2 + A^{\cdot} \xrightarrow{k_5} HPO_4^- + PO_4^- + H^+ + PET$$

$$M + A^{\cdot} \xrightarrow{k_6} M_1^{\cdot}$$

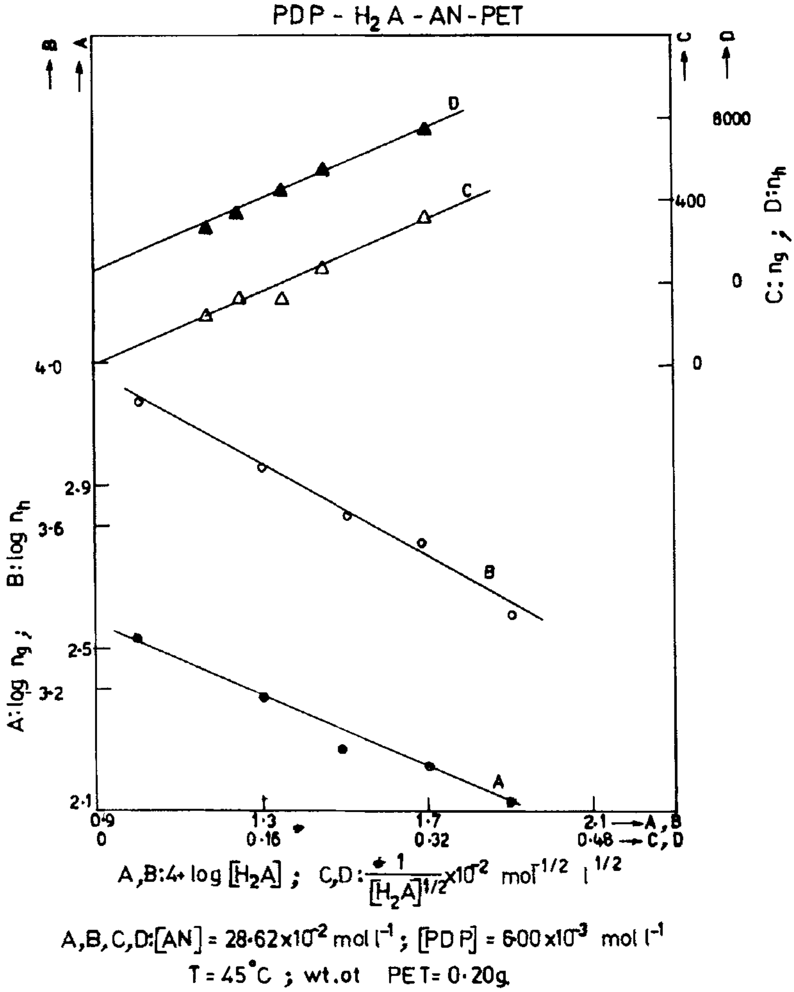


FIGURE 18 Effect of $[H_2A]$ on n_g and n_h.

Propagation

$$\begin{array}{c} M_1^{\cdot} + M \xrightarrow{\quad k_g \quad} M_2^{\cdot} \\ \hline M_{n-1}^{\cdot} + M \xrightarrow{\qquad\quad} M_n^{\cdot} \end{array}$$

TABLE V PDS/PDP-H_2A-MMA-PET. Effect of weight of PET on % grafting and % efficiency. $H_2A = 4.00 \times 10^{-3}$ mol l^{-1}; $T = 45°C$

(*Wt. of PET*)$^{a,b,c} \times 10^{-2}$	% *Grafting*			% *Efficiency*		
	a	*b*	*c*	*a*	*b*	*c*
5.00	3.03	6.29	2.94	7.99	16.6	1.94
15.00	31.5	18.0	15.5	14.9	23.8	3.06
30.00	25.0	22.2	11.5	26.4	25.1	4.54
35.00	21.5	22.4	7.30	39.7	37.7	4.78

a, b : [MMA] = 3.80×10^{-2} mol l^{-1}; b, c : [PDP] = 6.00×10^{-3} mol l^{-1};
a : [PDS] = 4.00×10^{-3} mol l^{-1}; c : [AN] = 28.62×10^{-2} mol l^{-1}.

Termination

$$M_n^{\cdot} + M_n^{\cdot} \xrightarrow{k_{t1}} \text{Graft copolymer}$$

For the above mechanism, the suitable expression for R_g and n_g would now be written based on the discussions in our earlier works [14, 15] as

$$R_g = k_g \frac{(k_1 K_1 K_2)^{1/2}}{(k_{t1})^{1/2}} [\mathrm{M}](\mathrm{PET})^{0.5}[\mathrm{PDP}]^{0.5}\,[\mathrm{H_2A}]^{0.5} \qquad \mathrm{E_1}$$

$$n_g = \frac{k_g[\mathrm{M}]}{(k_{t1})^{1/2}(2k_1 K_1 K_2)^{0.5}[\mathrm{PET}]^{0.5}[\mathrm{PDP}]^{0.5}\,[\mathrm{H_2A}]^{0.5}} \qquad \mathrm{E_2}$$

All the experimental results towards R_g and n_g such as first order dependence on [M], half order dependences on (PET), [H_2A] for R_g and first order dependence on [M], inverse half order dependences on (PET), [PDP] and [H_2A] for n_g could be seen in Eqs. (1) and (2) respectively.

For Simultaneous Homopolymerization

Initiation

$$\mathrm{PDP + H_2A} \underset{}{\overset{K_1}{\rightleftarrows}} \text{PDP-H}_2\text{A Complex } \mathrm{C_1}$$

$$\mathrm{C_1 + PET} \overset{K_3}{\rightleftarrows} \text{PDP-H}_2\text{A-PET Complex } \mathrm{C_2}$$

$$\mathrm{C_2} \xrightarrow{k_1} \mathrm{PET^{\cdot} + HPO_4^{-} + PO_4^{\cdot -} + H^{+} + H_2O}$$

$$\mathrm{PO_4^{\cdot -} + H_2O} \xrightarrow{k_3} \mathrm{HPO_4^{-}} + \dot{\mathrm{O}}\mathrm{H}$$

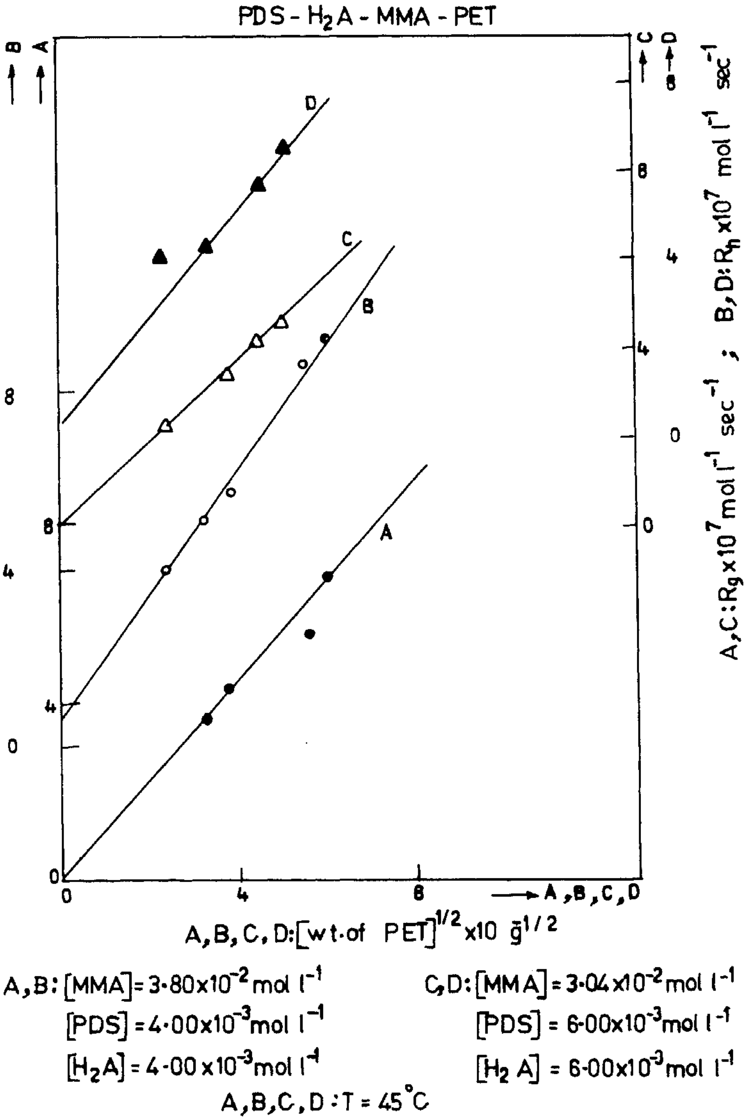


FIGURE 19 Effect of Weight of PET on R_g and R_h.

$$\dot{O}H + H_2A \xrightarrow{k_4} H_2O + A^{\cdot} + H +$$

$$C_1 + A^{\cdot} \xrightarrow{k_3} HPO_4^- + PO_4^- + H^+ + PET + H_2O$$

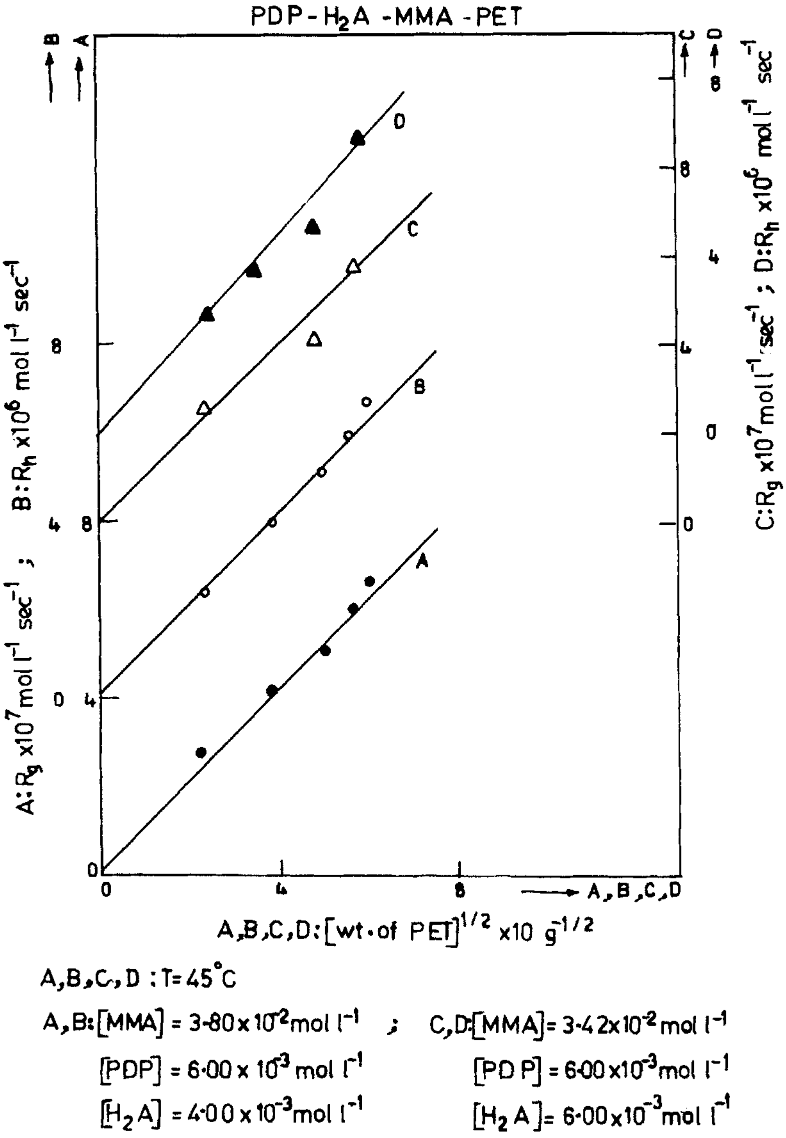


FIGURE 20 Effect of Weight of PET on R_g and R_h.

$$C_2 + M \xrightarrow{k_4} M_1 + PO_4^{-} + H_+^{+} + PET$$

$$M + A^{-} \xrightarrow{k_6} M_1^{\cdot}$$

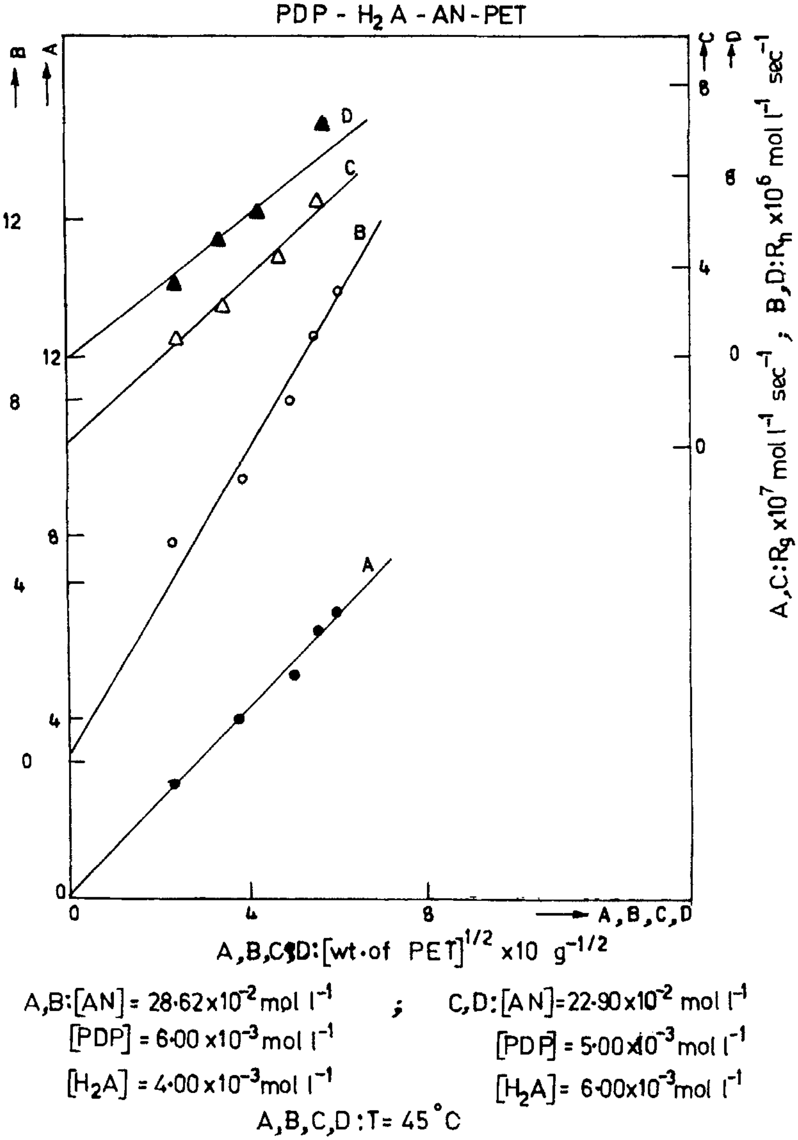


FIGURE 21 Effect of Weight of PET on R_g and R_h.

Propagation

$$M_1^{\cdot} + M \xrightarrow{k_p} M_2^{\cdot}$$

$$M_{n-1}^{\cdot} + M \xrightarrow{k_p} M_n^{\cdot}$$

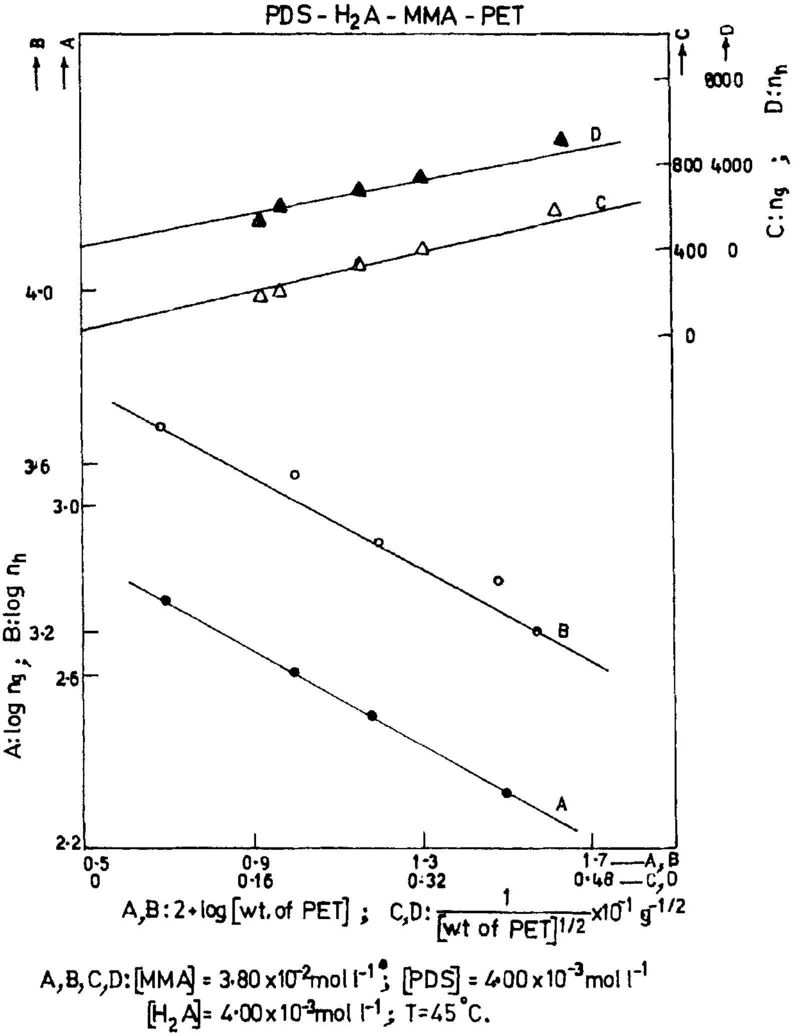


FIGURE 22 Effect of Weight of PET on n_g and n_h.

Termination

$$M_n^{\cdot} + M_n^{\cdot} \xrightarrow{k_{t4}} \text{Homopolymer}$$

For the above mechanism, the expressions for R_h and n_h would similarly taken from Refs. [14] and [15] and can be suitably written as

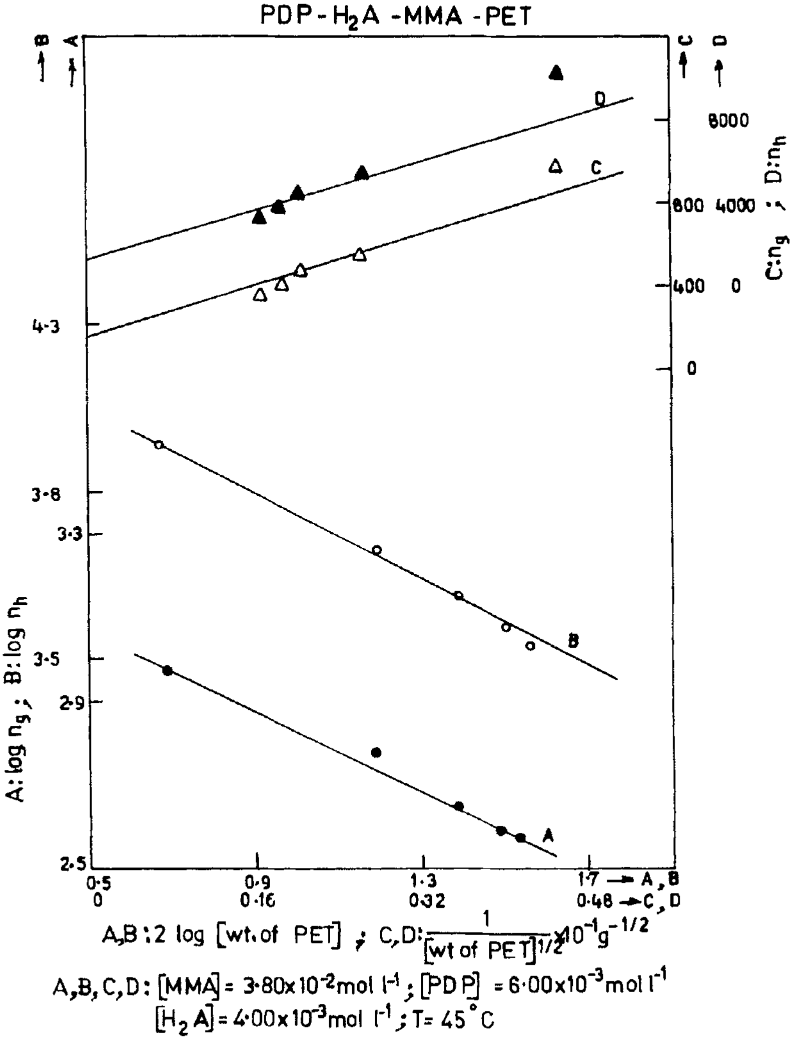


FIGURE 23 Effect of Weight of PET on n_g and n_h.

$$R_h = k_p \frac{k_3 K_1 K_2{}^{1/2}}{(k_{t4})^{1/2}} (\mathrm{PET})^{0.5}\, [\mathrm{H_2A}]^{0.5} [\mathrm{PDP}]^{0.5}\, [\mathrm{M}]^{1.5} \qquad \mathrm{E}_3$$

$$n_h = \frac{k_p [\mathrm{M}]^{0.5}}{(k_{t4})^{0.5} (2k_3 K_1 K_2)^{0.5}\, (\mathrm{PET})^{0.5}\, [\mathrm{H_2A}]^{0.5} [\mathrm{PDP}]^{0.5}} \qquad \mathrm{E}_4$$

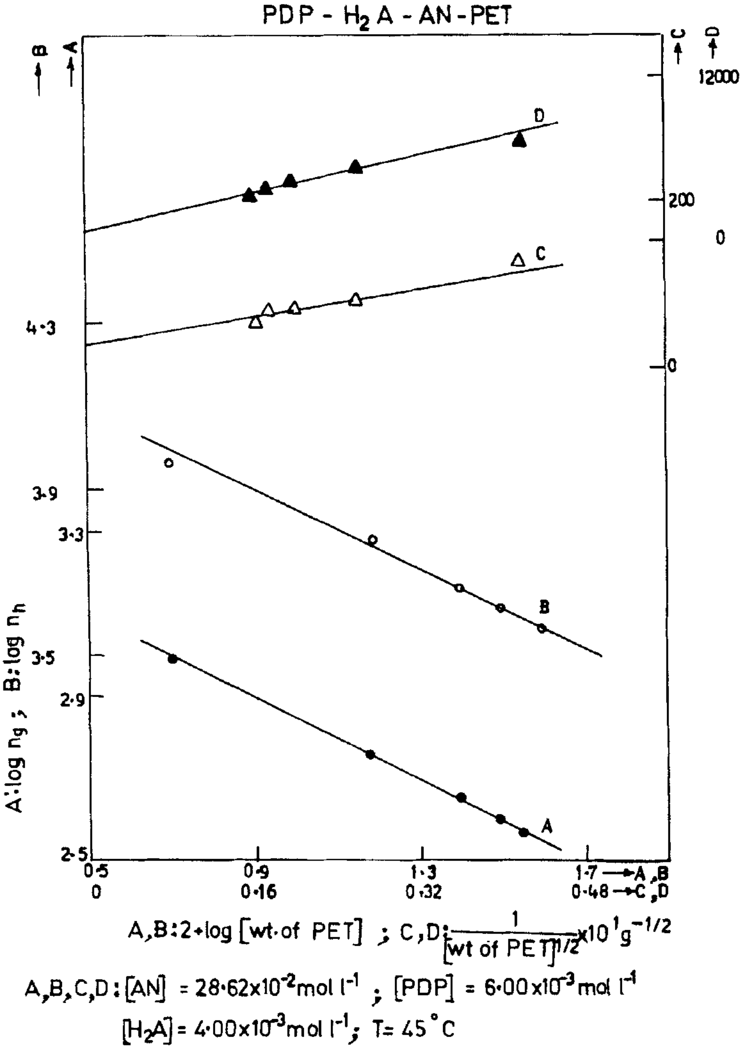


FIGURE 24 Effect of Weight of PET on n_g and n_h.

All the experimental results such as three halfth order dependence on [AN], square root order dependences on $(PET)^{0.5}$, $[PDP]^{0.5}$ and $[H_2A]^{0.5}$ can be seen in E3. In E_4, all the experimental observations related to n_h could be seen.

Evaluation of Composite Rate Constants for the Systems and Test their Invariance

From the slope of the plots R_g *vs* [AN] (Fig. 5A), R_g *vs* $[\mathrm{PDP}]^{0.5}$ (Fig. 9A), R_g *vs* $[\mathrm{H_2A}]^{0.5}$ (Fig. 15A), R_g *vs* $(\text{weight of PET})^{0.5}$ (Fig. 21A) and using the conditions, the average value of the composite rate constant in E_1 (Tab. VI)

$$k_g \frac{(k_1K_1K_2)^{1/2}}{(k_{t1})^{1/2}}$$

was obtained as $4.38 \times 10^{-4}\,\mathrm{mol^{-1}\,l\,g^{0.5}\,sec^{-1}}$.

That the rate expression as given by E_2 as the right choice for n_g is further confirmed by the fact that the composite rate constants

$$\frac{k_g}{(k_{t1})^{1/2}(2k_1K_1K_2)^{0.5}}$$

remains invariant for all the variations of [AN], [PDP], $[\mathrm{H_2A}]$ and [PET]. The values so obtained are given in Table VI.

This composite rate constant was evaluated from the slopes of the plots n_g *vs* [AN] (Fig. 16C), n_g *vs* [PDP]−0.5 (Fig. 12C), n_g *vs* $[\mathrm{H_2A}]$−0.5 (Fig. 18C) and n_g *vs* (PET)−0.5 (Fig. 24C). The average value was calculated to be 21.2 g−0.5.

Multiplying the composite rate constant values from R_g and n_g, kg/ kt 0.5 value was obtained for PAN grafting onto PET as $0.096\,\mathrm{mol^{-0.5}\,l^{0.5}\,sec^{-0.5}}$, It is interesting to note that this value is close to the value determined in PMS-$\mathrm{H_2A}$-AN-PET system. $(0.117\,\mathrm{mol^{-0.5}\,l^{0.5}\,sec^{-0.5}})$ [14, 15].

Taking the ratio of the composite rate constants values obtained from R_g and n_g the value $k_1K_1K_2$ was calculated to be $2.07 \times 10^{-5}\,\mathrm{mol^{-1}\,l\,sec^{-1}}$.

From the slope of the plots R_h *vs* [AN]1.5 (Fig. 5B), R_h *vs* [PDP]0.5 (Fig. 9B), R_h *vs* $[\mathrm{H_2A}]$0.5 (Fig. 15B), R_h *vs* [PET]0.5 (Fig. 21B) and the conditions used, the average value of the composite rate constant in E3

$$k_p \frac{(k_3K_1K_2)^{1/2}}{(k_{t4})^{1/2}}$$

was calculated to be $1.46 \times 10^{-2}\,\mathrm{mol^{-0.5}}\ 11.5\,\mathrm{g^{-0.5}\ sec^{-1}}$.

TABLE VI PDP-H_2A-AN-PET. Evaluation of rate constants using R_g and n_g. $T = 45°C$; $\mu = 0.24\,mol\,l^{-1}$; $[H^+] = 8.00 \times 10^{-2}\,mol\,l^{-1}$

Variation and range	*Figure*	*Composite rate constants from grafting studies* from R_g		n_g	
		Slope	$k^{\#}$ $mol^{-1}\,l\,g^{-1/2}\,sec^{-1}$	*Slope*	K^* $mol^{-1}\,l\,sec^{-1}$
$[AN] \times 10$ $mol\,l^{-1}$		$\frac{\#k_g(k'_1K'_1K'_2)^{1/2}}{k_{t1}^{1/2}}$		$^*k'_g/(k'_t)^{1/2}$	$(2k'_1K'_1K'_2)^{1/2}$
1.431 to 7.155	5A	0.94×10^{-6} sec^{-1}	0.43×10^{-3}	–	–
2.862 to 7.155	16 C	–	–	0.06×10^5 $mol^{-1/2}l^{-1/2}$	18.4
$[PDP]\,mol\,l^{-1}$	9A	5.71×10^{-6}	0.69×10^{-3}	–	–
10.0 to 80.0	12C	$mol^{1/2}l^{-1/2}\,sec^{-1}$	–	15.2×10 $mol^{1/2}l^{-1/2}$	21.2
$[H_2A]\,mol\,l^{-1}$	15A	3.77×10^{-6}	0.391×10^{-3}	–	–
10.0 to 80.0		$mol^{1/2}\,l^{-1/2}\,sec^{-1}$	–	12.2×10 $mol^{1/2}\,l^{-1/2}$	20.9
	18C	–	–		
(Wt. of PET)g	21A	1.09×10^{-6}	0.79×10^{-3}	–	–
0.05 to 0.35		$mol\,l^{-1}g^{-1/2}$ sec^{-1}	–	11.3×10^2 $g^{-1/2}$	24.3
0.05 to 0.35	24C	–	–	–	–

TABLE VI (Continued). PDP-H_2A-AN-PET. Evaluation of rate constants using R_h and n_h. $T = 45°C$; $\mu = 0.24\,mol\,l^{-1}$; $[H^+] = 8.00 \times 10^{-2}\,mol\,l^{-1}$

Variation and range	*Figure*	*Composite rate constants from grafting studies*			
		from R_h			n_h
		Slope	$k^{\#}$ $mol^{-1/2}l^{3/2}g^{-1/2}sec^{-1}$	*Slope*	K^* $mol^{-1/2}l^{1/2}g^{-1/2}$
$[AN] \times mol\,l^{-1}$		$\frac{\#k_p(k'_3K'_1K'_2)^{1/2}}{k_{t6}^{1/2}}$		$*k'_p/(k'_{t4})^{1/2}$	$(2k'_3K'_1K'_4)^{1/2}$
1.431 to 7.155	5B	1.09×10^{-5} $mol^{-1/2}\,l^{1/2}\,sec^{-1}$	0.50×10^{-2}	–	–
2.862 to 7.155	16D	–	–	0.46×10^{5} $mol^{-1}l$	142
$[PDP]\,mol\,l^{-1}$	9B	10.6×10^{-5}	2.44×10^{-2}	–	–
10.0 to 80.0		$mol^{1/2}\,l^{-1/2}\,sec^{-1}$	–	29.6×10^{2}	220
10.0 to 80.00	12D			$mol^{1/2}\,l^{-1/2}$	
$[H_2A]\,mol\,l^{-1}$	15B	11.7×10^{-5}	2.20×10^{-2}	–	–
10.0 to 80.0		$mol^{1/2}\,l^{-1/2}\,sec^{-1}$	–	21.4×10^{2}	196
10.0 to 80.0	18D	–	–	$mol^{1/2}\,l^{-1/2}$	
(Wt. of PET)g	21B	1.70×10^{-5}	2.27×10^{-2}	–	–
0.05 to 0.35		$mol\,l^{-1}g^{-1/2}$ sec^{-1}	–	16.5×10^{3} $g^{1/2}$	214
0.05 to 0.35	24D	–	–	–	–

The choice for n_h is confirmed by the fact that the composite rate constants

$$\frac{k_p}{(k_{t4})^{0.5}(2k_3K_1K_2)^{1/2}}$$

remains invariant for all the variations. The values so obtained are given in Table VII.

This composite rate constant was evaluated from the slope of the plots n_h *vs* [AN] (Fig. 16D), n_h *vs* $[\mathrm{PDP}]^{-0.5}$ (Fig. 12D), n_h *vs* $[\mathrm{H_2A}]^{-0.5}$ (Fig. 18D) and n_h *vs* $(\text{weight of PET})^{-0.5}$ (Fig. 24D) and the average value was calculated to be $193\,\mathrm{mol^{-1}\,l\,Sec^{-1}}$.

Multiplying the composite rate constants from R_h and n_h the value $k_p/(k_t)^{0.5}$ was calculated to be $1.68\,\mathrm{mol^{-0.75}\,l^{-0.75}\,g^{-0.5}\,Sec^{-0.5}}$.

Taking the ratio of the composite rate constant values obtained from R_h and n_h, the value $k_3K_1K_2$ was calculated to be $7.56 \times 10^{-5}\,\mathrm{mol^{-1.5}\,l^{-1.5}\,Sec^{-1}}$.

Knowing $k_1K_1K_2$ from R_g and n_g measurements as $2.07 \times 10^{-5}\,\mathrm{mol^{-1}\,l\,Sec^{-1}}$ and $k_3K_1k_2$ value from R_h and n_h measurement as $7.56 \times 10^{-5}\,\mathrm{mol^{-1.5}\,l^{1.5}\,Sec^{-1}}$, the ratio k_1/k_3 was obtained as $0.273\,\mathrm{mol^{0.5}\,l^{-1.5}}$, The very low value predicts the predominance of homopolymerization over grafting than in PMS-$\mathrm{H_2A}$-AN-PET system.

The values obtained for $k_1K_1K_2$ and $k_3K_1K_2$ from the slopes of the plots $-R_{\mathrm{PDP}}$ *vs* [PDP] are $3.44 \times 10^{-4}\,\mathrm{mol^{-1}\,l\,g^{-1}\,sec^{-1}}$ and $3.00 \times 10^{-4}\,\mathrm{l\,g^{-1}\,Sec^{-1}}$ respectively for two different [M]. The ratio k_1/k_3 was calculated to be 0.162. This again supports $k_1 \ll k_3$ as it was inferred through grafting.

In the case of PDP-$\mathrm{H_2A}$ redox initiated graft co-polymerization of PMMA onto PET, a different observation with respect to monomer dependence was noted. The three halfth order dependence with PAN case was not observed and a first order dependence was noted instead.

This requires the possible change in the mechanism especially in the initiation step. With the inclusion of a new iteration step the graft co-polymerization mechanism can now be proposed for PDS-$\mathrm{H_2A}$-MMA-PET system.

TABLE VII PDS-H_2A-MMA-PET. Evaluation of rate constants using R_g and n_g. $T = 45°C$; $\mu = 0.24\,mol\,l^{-1}$; $[H^+] = 8.00 \times 10^{-2}\,mol\,l^{-1}$

Variation and range	*Figure*	*Composite rate constants from grafting studies*			
		from R_g			n_g
		Slope	$k^{\#}$ $mol^{-1}\,l\,g^{-1/2}\,sec^{-1}$	*Slope*	K^* $mol^{-1}\,l\,sec^{-1}$
[MMA] $mol\,l^{-1}$		$\frac{\#k_g(k'_7K'_3K'_4)^{1/2}}{k_{t5}^{1/2}}$		$*k'_g/(k_t^5)^{1/2}$	$(2k'_7K'_3K'_4)^{1/2}$
7.6 to 76.0	3A	4.23×10^{-6} sec^{-1}	2.37×10^{-3}	–	–
7.6 to 76.0	4C	–	–	6.96×10^{-3} $mol^{-1/2}\,l^{-1/2}$	17.5
$[PDS] \times 10^{-2}$ $mol\,l^{-1}$	7A	6.40×10^{-6}	5.96×10^{-3}	–	–
10.0 to 80.0		$mol^{1/2}\,l^{-1/2}\,sec^{-1}$	–	14.8×10	15.6
10.0 to 80.0	10C			$mol^{1/2}\,l^{-1/2}$	
$[H_2A] \times 10^{-2}$ $mol\,l^{-1}$	14A	6.50×10^{-6}	6.05×10^{-3}	–	–
10.0 to 80.0		$mol^{1/2}\,l^{-1/2}\,sec^{-1}$	–	14.7×10	16.3
20.0 to 80.0	6C	–	–	$mol^{1/2}\,l^{-1/2}$	
(Wt. of PET)g	19A	0.93×10^{-6}	6.14×10^{-3}	–	–
0.05 to 0.35		$mol\,l^{-1}\,g^{-1/2}$ sec^{-1}	–	10.0×10^2 $g^{-1/2}$	14.8
0.05 to 0.35	22C	–	–	–	–

TABLE VII (Continued). PDS-H_2A-MMA-PET. Evaluation of rate constants using R_h and n_h. $T = 45°C$; $\mu = 0.24\,mol\,l^{-1}$; $[H^+] = 8.00 \times 10^{-2}\,mol\,l^{-1}$

Variation and range	*Figure*	*Composite rate constants from grafting studies*			
		from R_h		*n_h*	
		Slope	*$k^{\#}$ $mol^{-1/2}\,l^{3/2}\,g^{-1/2}\,sec^{-1}$*	*Slope*	*K^* $mol^{-1/2}\,l^{1/2}\,g^{-1/2}$*
$[MMA] \times mol\,l^{-1}$		$\frac{\#k_p(k'_7K'_3K'_4)^{1/2}}{k_{t6}1/2}$		$*k'_p/(k'_{t6})^{1/2}$	$(2k'_7K'_3K'_4)^{1/2}$
7.60 to 76.0	3B	5.76×10^{-5} sec^{-1}	2.28×10^{-2}	–	–
1.90 to 76.0	4D	–	–	0.062×10^{-5} $mol^{-1/2}\,l^{-1/2}$	158
$[PDS] \times 10^{-2}$ $mol\,l^{-1}$	7B	8.95×10^{-5}	5.89×10^{-2}	–	–
10.0 to 80.0		$mol^{1/2}\,l^{-1/2}\,sec^{-1}$	–	13.5×10	144
10.0 to 80.0	10D			$mol^{1/2}\,l^{-1/2}$	
$[H_2A] \times 10^{-2}$ $mol\,l^{-1}$	14B	9.00×10^{-5}	6.05×10^{-2}	–	–
10.0 to 80.0		$mol^{1/2}\,l^{-1/2}\,sec^{-1}$	–	14.3×10	152
20.0 to 80.0	6D	–	–	$mol^{1/2}\,l^{-1/2}$	
(Wt. of PET)g	19B	1.27×10^{-6}	5.92×10^{-2}	–	–
0.05 to 0.35		$mol\,l^{-1}\,g^{-1/2}$ sec^{-1}	–	11.0 $g^{1/2}$	161
0.05 to 0.35	22D	–	–	–	–

Initiation

$$\mathrm{PDS} + \mathrm{H_2A} \underset{\rule{3em}{0.4pt}}{\xrightarrow{K_3}} \mathrm{PDS\text{-}H_2A\ complex\ C_3}$$

$$\mathrm{C_3} + \mathrm{PET} \underset{\rule{3em}{0.4pt}}{\xrightarrow{K_4}} \mathrm{PDS\text{-}H_2A\text{-}PET\ complex\ C_4}$$

$$\mathrm{C_4} \xrightarrow{k_7} \mathrm{PET}\cdot + \mathrm{H_2O} + \mathrm{HSO_4^-} + \mathrm{H^+} + \mathrm{SO_4^{\cdot -}}$$

$$\mathrm{PET}\cdot + \mathrm{M} \xrightarrow{k_2} \mathrm{PETM}\cdot$$

$$\mathrm{SO_4^{\cdot -}} + \mathrm{H_2O} \xrightarrow{k_8} \mathrm{OH}\cdot + \mathrm{HSO_4^-}$$

$$\mathrm{OH}\cdot + \mathrm{H_2A} \xrightarrow{k_4} \mathrm{H_2O} + \mathrm{A^{\cdot -}} + \mathrm{H^+}$$

$$\mathrm{C_4} + \mathrm{A^{\cdot -}} \xrightarrow{k_9} \mathrm{SO_4^{\cdot -}} + 2\mathrm{HA^-} + \mathrm{HSO_4^-} + \mathrm{H^+}$$

Propagation

$$\mathrm{PETM}\cdot + \mathrm{M} \xrightarrow{k_g} \mathrm{PETM_2}\cdot$$

$$\mathrm{PETM}_{n-1}\cdot + \mathrm{M} \xrightarrow{k_g} \mathrm{PETM}_n\cdot$$

Termination

$$2\mathrm{PETM}_n\cdot \xrightarrow{k_{t5}} \text{graft copolymer}$$

For the above mechanism of grafting, the suitable expression for R_g and n_g can be obtained as

$$R_g = k_g \frac{(k_7 K_3 K_4)^{1/2}}{(k_{t5})^{1/2}} [\mathrm{M}](\mathrm{PET})^{0.5}[\mathrm{PDS}]^{0.5}[\mathrm{H_2A}]^{0.5} \quad \mathrm{E_5}$$

$$n_g = \frac{k_g[\mathrm{M}]}{(k_{t5})^{1/2}(2k_7 K_3 K_4)^{0.5}[\mathrm{PET}]^{0.5}[\mathrm{PDS}]^{0.5}[\mathrm{H_2A}]^{0.5}} \quad \mathrm{E_6}$$

In E_5 all the experimental observations such as first power dependence on [M], square root order dependences on [PDS], $[H_2A]$ and PET towards R_g can be seen. All the experimental observations made towards n_g are found in E_6.

The mechanism for the simultaneous homopolymerization can be written as

Initiation

$$\mathrm{PDS} + \mathrm{H_2A} \xrightleftharpoons{K_1} \mathrm{PDS\text{-}H_2A\ complex\ C_3}$$

$$\mathrm{C_3} + \mathrm{PET} \xrightarrow{k_4} \mathrm{PDS\text{-}H_2A\text{-}PET\ complex\ C_4}$$

$$\mathrm{C_4} \xrightarrow{k_7} \mathrm{PET}\cdot + \mathrm{H_2O} + \mathrm{HSO_4^-} + \mathrm{H^+} + \mathrm{SO_4^{-}}$$

$$\mathrm{SO_4^{-}} + \mathrm{H_2O} \xrightarrow{k_8} \mathrm{OH}\cdot + \mathrm{HSO_4^-}$$

$$\mathrm{OH}\cdot + \mathrm{H_2A} \xrightarrow{k_4} \mathrm{H_2O} + \mathrm{A^{-}} + \mathrm{H^+}$$

$$\mathrm{C_3} + \mathrm{A^{-}} \xrightarrow{k_{10}} \mathrm{SO_4^{-}} + 2\mathrm{HA^-} + \mathrm{HSO_4^-} + \mathrm{H^+}$$

$$\mathrm{C_4 + M \xrightarrow{k_{11}} M_1\cdot + SO_4^{\dot{-}} + H^+ + H_2O + PET\cdot}$$

$$\mathrm{M + A^{\dot{-}} \xrightarrow{k_6} M_1\cdot}$$

Propagation

$$\mathrm{M_1\cdot + M \xrightarrow{k_p} M_2\cdot}$$

$$\mathrm{M_{n-1}\cdot + M \xrightarrow{k_p} M_n\cdot}$$

Termination

$$\mathrm{2M_n\cdot \xrightarrow{k_{t6}} Homopolymer}$$

For the above mechanism of homopolymerization, the suitable expression for R_h and n_h would be written

$$R_h = k_p\frac{(k_7K_3K_4)^{1/2}}{(k_{t6})^{1/2}}[\mathrm{PET}]^{0.5}[\mathrm{H_2A}]^{0.5}[\mathrm{PDS}]^{0.5}[\mathrm{M}] \quad \mathrm{E_7}$$

$$n_h = \frac{k_p[\mathrm{M}]}{(k_{t6})^{0.5}\,k_7K_3K_4(\mathrm{PET})^{0.5}[\mathrm{H_2A}]^{0.5}[\mathrm{PDS}]^{0.5}} \quad \mathrm{E_8}$$

In E_7, all the experimental observations such as first power dependence on [MMA], square root order dependences on [PDS], $[H_2A]$ and PET related to R_h could be seen. All the experimental observations such as first power dependence on [MMA], inverse square root order dependences on (PET), $[H_2A]$ and [PDS] with regard to n_h could be accounted for in E_8.

Hence E_5, E_6, E_7 and E_8 are the most suitable expressions for R_g, n_g, R_h and n_h respectively.

From the slope of the plots R_g *vs* [MMA] (Fig. 3A), R_g *vs* $[PDS]^{0.5}$ (Fig. 7A), R_g *vs* $[H_2A]$ (Fig. 14A), R_g *vs* (weight of $PET^{0.5}$) (Fig. 19A) and using the conditions, the average value of the composite rate constant in E_5

$$k_g \frac{(k_7 K_3 K_4)^{1/2}}{(k_{t5})^{1/2}}$$

was calculated to be $3.58 \times 10^{-3}\,\mathrm{mol}^{-1}\,\mathrm{g}^{-0.5}\,\mathrm{Sec}^{-1}$.

E_6 becomes the right choice for n_g which is confirmed by the evaluation of the composite rate constant

$$\frac{k_g}{(k_{t5})^{1/2}(2k_7 K_3 K_4)^{0.5}}$$

for all the variations of MMA, PDS, H_2A and PET. The constancy in the values augment this view. The values thus obtained are given in Table VII.

This composite rate constant was evaluated from the slopes of the plots n_g *vs* [MMA] (Fig. 4C), n_g *vs* $[\mathrm{PDS}]^{-0.5}$ (Fig. 10C), n_g *vs* $[\mathrm{H_2A}]^{-0.5}$ (Fig. 6C) and n_g *vs* $(\mathrm{PET})^{-0.5}$ (Fig. 22C). The average value was calculated to be $15.8\,\mathrm{mol}^{-1}\,\mathrm{l}\,\mathrm{sec}^{-1}$.

Multiplying the composite rate constant values from R_g and n_g measurements, $k_g/(k_t)^{0.5}$ value was obtained as $0.238\,\mathrm{mol}^{-0.5}\,\mathrm{l}^{0.5}\,\mathrm{sec}^{-1}$.

Taking the ratio of the composite rate constant values obtained from R_g and n_g measurements the values $(k_7 K_3 K_4)$ was obtained as $2.26 \times 10^{-4}\,\mathrm{mol}^{-1}\,\mathrm{l}\,\mathrm{sec}^{-1}$.

From the slope of the plots R_h *vs* [MMA] (Fig. 3B), R_h *vs* $[\mathrm{PDS}]^{0.5}$ (Fig. 7B), R_h *vs* $[\mathrm{H_2A}]^{0.5}$ (Fig. 14B) and R_h *vs* $(\mathrm{PET})^{0.5}$ (Fig. 19B) and the conditions used the average value of the composite rate constant in E_7 is

$$k_p \frac{(k_7 K_3 K_4)^{1/2}}{(k_{t6})^{1/2}}$$

was calculated to be $4.55 \times 10^{-2}\,\mathrm{mol}^{-1}\,\mathrm{l}^{-0.5}\,\mathrm{sec}^{-1}$.

The suitability of E_8 for n_h is verified by the calculation of the composite rate constant

$$\frac{k_p}{(k_{t6})^{0.5}(k_7 K_3 K_4)}$$

for all the variation. The value so obtained are given in Table VII.

The close to constancy in the calculated values reveals the suitability of the selection of E_8 for n_h.

This composite rate constant was evaluated from the slope of the plots n_h *vs* [MMA] (Fig. 4D), n_h *vs* $[PDS]^{-0.5}$ (Fig. 10D), n_h *vs* $[H_2A]^{-0.5}$ (Fig. 6D) and n_h *vs* (weight of PET)$^{-0.5}$ (Fig. 22D) and the average value was calculated to be $145\,g^{-0.5}$.

Multiplying the composite rate constant values from R_h and n_h, the value $k_p/(k_t)^{0.5}$ was calculated to be $2.68\,mol^{-0.5}\,l^{0.5}\,g^{-1}\,sec^{-1}$.

Taking the ratio of the composite rate constant values obtained from R_h and n_h measurements the value $k_7 K_3 K_4$ was calculated to be $2.95 \times 10^{-4}\,mol^{-1}\,l\,sec^{-1}$.

It is significant to note the following interesting observations from the critical comparison of the three systems studied. The homopolymerization is predominantly occuring over grafting while using PMS or PDS as oxidant than PDP and suggesting PDP as better oxidant for grafting. Under identical conditions PMMA can be grafted efficiently on PET than PAN (Tabs. II and V).

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