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Effect of 2-Chloro-1,3,2-Dioxaphospholane on the Radical Polymerisation of Acrylonitrile, Styrene and Methyl Methacrylate

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ABSTRACT

The effect of 2-Chloro-1,3,2-dioxaphospholane on the AIBN initiated polymerisation of acrylonitrile, methyl methacrylate and styrene was investigated kinetically in benzene at 60 – 80°C. With acrylonitrile normal kinetic orders with respect to monomer and AIBN could be observed with the phospholane behaving as a chain transfer agent. With methyl methacrylate and styrene it was observed that the phospholane causes enhancement of the rates due to concurrent radical and ionic polymerisation besides functioning as a chain transfer agent.

INTRODUCTION

We have previously reported the effects of $POCl_3$ PCl_3 and $C_6H_5PCl_2$ on the radical polymerisation of acrylonitrile in benzene (VARA PRASAD and MAHADEVAN 1980). $C_6H_5PCl_2$ and $POCl_3$ were shown to be degradative chain transfer agents while PCl_3 behaved as a normal chain transfer agent. Analysis of the phosphorous content of the polymers indicated that some copolymerisation also took place. In this paper we report the effects of addition of a heterocyclic phospholane on the radical polymerisation of acrylonitrile, methyl methacrylate and styrene in benzene solution.

EXPERIMENTAL

Acrylonitrile(AN), methyl methacrylate(MMA) and styrene(ST) were freed from inhibitors and purified by distillation under reduced pressure. 2-Chloro-1,3,2-dioxaphospholane (CDP) was synthesised from ethylene glycol and PCl_3 by a known procedure (LUCAS et.al. 1950) and purified by distillation (67-69°C, 45mm) . AIBN was prepared by literature method. Polymerisation was carried out in thick walled pyrex tubes under N_2 atmosphere and the conversions were limited to 10-20 percent. Rates

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of polymerisation($-d[M]/dt$) were obtained gravimetrically. Polymers were purified by solution in suitable solvents followed by reprecipitation in absolute methanol for viscometry. Average degrees of polymerisation were calculated using the following relationships.

(i) For polyacrylonitrile in DMF at 30°C

$$\log \bar{P}_n = 3.1176 + 1.3158 \log \eta_{int.}$$

(INAGAKI et.al., 1965)

(ii) For polymethyl methacrylate in benzene at 30°C

$$\log \bar{P}_n = 3.637 + 1.3158 \log \eta_{int.}$$

(COHN-GINSBERG et.al.,1962)

(iii) For polystyrene in benzene at 30°C

$$\log \bar{P}_n = 3.248 + \log \eta_{int.} \times 1.40$$

(JOHNSON and TOBOLSKY,1952)

The phosphorous content of the polymers was estimated by the molybdenum blue method (FISKE and SUBBA ROE, 1925).

RESULTS AND DISCUSSION

With AN rates were proportional to the first power of the monomer concentration and the square root of the initiator concentration (Fig.1). Rates were unaffected by addition of CDP (Table 1). With MMA and ST plots of $-d[M]/dt$ versus $[AIBN]^{\frac{1}{2}}$ were linear with intercepts on the rate axis (Fig.1).In addition plots of $-d[M]/dt$ versus [CDP] were also linear with intercepts(Fig.1) . At a fixed concentration of the initiator rates increased by 40 percent in the case of MMA and 20 percent in the case of ST for a seven fold increase in CDP (Table 1). With both MMA and ST monomer orders varied between 1.4 and 1.7

TABLE 1

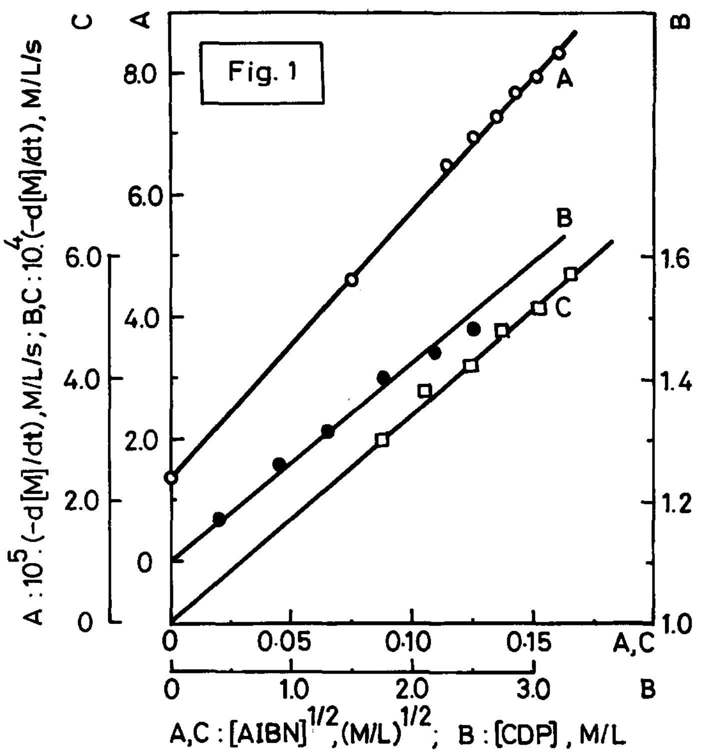
Variation of $-d[M]/dt$ with [CDP]

CDP M / L	$-d[MMA]/dt^{(a)}$ 10^4 M/L/sec	$-d[ST]/dt^{(b)}$ 10^5 M/L/sec	$-d[AN]/dt^{(c)}$ 10^4 M/L/sec.
nil	1.10	5.50	3.08
0.4439	1.17	5.75	3.06
0.8878	1.26	5.89	3.15
1.332	1.38	6.21	3.08
1.7757	1.40	6.47	3.19
2.2196	1.43	6.67	3.12
2.6635	1.50	6.82	3.17
3.1210	1.66	6.95	3.15

(a) [MMA] = 1.88 M , [AIBN] = 0.02 M , 65°C .

(b) [ST] = 2.62 M , [AIBN] = 0.015 M , 70°C .

(c) [AN] = 3.04 M , [AIBN] = 0.025 M , 65°C .



Line A : [ST] = 2.62 M/L; [CDP] = 1.11 M/L, 70°
Line B : [MMA] = 1.88 M/L ; [AIBN] = 1.99×10^{-2} M/L, 65°
Line C : [AN] = 3.04 M/L; [CDP] = 1.11 M/L, 75°

The accelerating effect of CDP on the rates observed with MMA and ST can be attributed to concurrent radical and ionic initiation of polymerisation. Such initiation of polymerisation by PCl_3 in the case of styrene in nitrobenzene solution has been reported earlier(TANINAKA and MINOURA, 1977) The following mechanism would account for the kinetics

$$2\ \text{CDP} \ \overset{K}{\rightleftharpoons} \left[{}^{O}_{O}{>}P{<}^{Cl}_{Cl}{}^{-} + P{<}^{O}_{O}\right] \ \text{or} \ X^-R^+$$

Initiation: $X^-R^+ + M \xrightarrow{k_i} R\text{-}M^+\ X^-$

Propogation: $R\text{-}M^+X^- + M \xrightarrow{k_p} R\text{-}M\text{-}M^+X^-$ etc.

Transfer: $R\text{-}M_n - M^+X^- + CDP \xrightarrow{k_{tr}}$ Polymer + R^+X^-

Termination: $R\text{-}M_n^+X^- \xrightarrow{k_t}$ Polymer + CDP

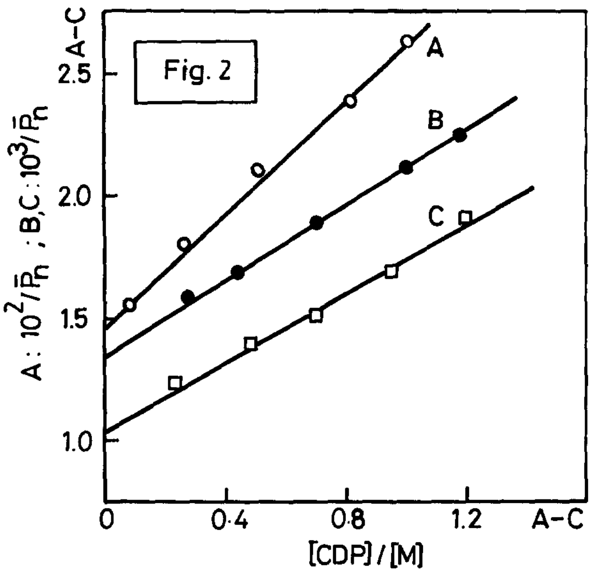


Fig. 2

Line A : [ST] = 2.62 M/L; [AIBN] = 2.369×10^{-2} M/L, 80°
Line B : [AN] = 3.04 M/L; [AIBN] = 2.49×10^{-2} M/L, 75°
Line C : [MMA] = 1.88 M/L; [AIBN] = 9.74×10^{-3} M/L, 75°

Under conditions such that there is negligible transfer to monomer and when k_{tr} [CDP] > k_t the rate law for ionic polymerisation would become

$$(-d\,[M]/dt)_{ionic} = (\,k_p\,k_i\,K\,[CDP]\,[M]^2)/\,k_{tr}$$

and for the total rate of polymerisation we can write

$$(-d\,[M]/dt)_{Total} = \frac{k_p'\,k_d^{\frac{1}{2}}\,[AIBN]^{\frac{1}{2}}\,[M]}{(\,k_t')^{\frac{1}{2}}} + \frac{k_p k_i\,K\,[CDP]\,[M]^2}{k_{tr}}$$

where the first term refers to the radical polymerisation with k_p', k_t' and k_d having the usual significance. This requires that in the radical polymerisation termination is predominantly mutual. Also chain transfer between macroradicals and CDP may involve >P-Cl or ⩾C-H bond rupture. For the reciprocal of the average degree of polymerisation we can derive the following expression.

$$(\bar{P}_n)^{-1} = \text{Constant} + \left[\frac{k_{tr}}{k_p} + \frac{k_{tr}'}{k_p'}\right]\frac{[CDP]}{[M]}$$

where k_{tr}' refers to the chain transfer constant for the radical polymerisation. Plots of $(\bar{P}_n)^{-1}$ versus [CDP] / [M] appear in Fig.2. From the slopes of these plots we can estimate a composite transfer constant for these polymerisations. The data appear in Table 2.

TABLE 2
Mean values of composite chain transfer constants

Monomer	Temp. °C	$\left[\frac{k_{tr}}{k_p} + \frac{k_{tr}'}{k_p'}\right] \times 10^3$
AN	65	0.225
AN	75	0.782
MMA	65	0.274
MMA	75	0.636
ST	70	9.09
ST	80	11.54

The composite constant has a very much larger value for styrene compared to the other two monomers. They are comparable to the values reported in the case of styrene polymerisation initiated by PCl_3 in nitrobenzene (TANINAKA and MINOURA ,1977).

Degrees of polymerisation were in the range 40-80 for polystyrene, 400-700 for polymethyl methacrylate and 400-600 for polyacrylonitrile. The analysis of phosphorous content of the polymers indicated that there was no copolymerisation when styrene was the monomer. The number of P atoms per chain varied from 0.35 to 0.90. With MMA however the number of P atoms per chain varied from 6 to 10 while with AN this number was between 7 and 11. In view of the fact that unfractionated polymers were analysed, apart from the occurance of copolymerisation no other conclusions can be drawn.

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