Polymer Bulletin 2, 117-123 (1980)

Polymer Bulletin

Effects of Phosphorous Oxychloride, Phosphorous Trichloride and Dichlorophenylphosphine on the Radical Polymerisation of Acrylonitrile Under Heterogeneous Conditions

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SUMMARY

The effects of $C_6H_5PCl_2$, $POCl_3$ and PCl_3 on the free radical polymerisation of acrylonitrile initiated by *a,a'* -azobisisobutyronitrile were kinetically investigated in benzene and trichloroethylene solutions. With PCl_3 rates of polymerisation were unaffected but the degrees of polymerisation were found to decrease with increasing PCl_3 . With $C_6H_5PCl_2$ and $POCl_3$ however both rates and degrees of polymerisation were adversely affected. Thus PCl_3 acts as a chain transfer agent while the other two phosphorous compounds function as degradative chain transfer agents.

INTRODUCTION

The effect of chlorophosphines (PCl_3 , $C_6H_5PCl_2$ and $(C_6H_5)_2PCl$) on the homogeneous radical polymerisation of styrene (UEMURA et al. 1977) and methyl methacrylate (UEMURA et al. 1978) have been reported previously. With styrene they functioned as degradative chain transfer agents while with methyl methacrylate they accelerated the rates. The rate increase was found to be dependent on chlorine content of the phosphine and was attributed to the formation of an $n - \pi$ complex between chlorophosphine and the monomer. It has also been reported that $POCl_3$ and $C_6H_5POCl_2$ have similar acclerating effects on the radical polymerisation of both methyl methacrylate and styrene(TANINAKA et al. 1978 a) . With both monomers formation of weak complexes was substantiated by NMR data. While the formation of the complex was responsible for the increased rates with methyl methacrylate , concurrent cationic polymerisation was shown to occur with styrene. Besides the acceleration of rates normal chain transfer was also evident. In solvents of high dielectric constant both $POCl_3$ and PCl_3 have been shown to be cationic initiators for the polymerisation of styrene (TANINAKA et al.1977 1978 b).

In this paper we report some of our results on the effect of PCl_3 , $C_6H_5PCl_2$ and $POCl_3$ on the radical polymerisation of acrylonitrile under

0170-0839/80/0002/0117/$01.40

heterogeneous conditions in benzene and trichloro ethylene as solvents.

EXPERIMENTAL

Acrylonitrile (AN) was purified by standard methods. $C_6H_5PCl_2$ was synthesised by Friedel - Crafts reaction (BUCHNER and LOCKHART , 1951) and purified by vacuum distillation(B.P. 89-90°C/10 mm Hg). $POCl_3$ and PCl_3 were distilled under nitrogen . Azobisisobutyronitrile (AIBN) was synthesised and recrystallised from ethanol (OVERBERGER et al. 1949)

Polymerisations were carried out in thick walled glass tubes with ground joints fitted with N_2 gas inlet and outlet. Reaction mixtures were thoroughly deoxygenated by flushing with oxygen-free dry N_2 . Care was taken to protect the systems from being exposed to moisture. The reactions were carried out at a constant temperature in the range 60-75°C. Conversions were limited to 20 percent or less and polymers precipitated by addition of absolute methanol. Rates of polymerisation were followed gravimetrically. The polymer was purified further by solution in DMF and reprecipitation by methanol for viscosity measurements and estimation of phosphorous content. Viscosities of polymer solutions in DMF ($\approx$ 0.1 %) were determined at 25°C or 30°C using an Ubbelohde viscometer and average degrees of polymerisation calculated using the following relationships.

$$\eta = 2.43 \times 10^{-4} \ M^{0.75}$$ at 25°C (CLELAND and STOCKMEYER,1955)

$$\eta = 2.09 \times 10^{-4} \ M^{0.76}$$ at 30°C(INAGAKI et.al,1965)

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

RESULTS AND DISCUSSION

With $C_6H_5PCl_2$ and $POCl_3$ rates of polymerisation (R_p) were proportional to the square of the monomer concentration and the first power of the initiator concentration in both solvents (Fig.1). The average degrees of polymerisation were also directly proportional to $[AN]^2$ (Fig.1). Plots of R_p versus $[POCl_3]^{-1}$ or $[C_6H_5PCl_2]^{-1}$ were also linear(Fig.2). Average degrees of polymerisation were found to decrease with increasing concentration of either $C_6H_5PCl_2$ or $POCl_3$ (Fig.2). The second order in

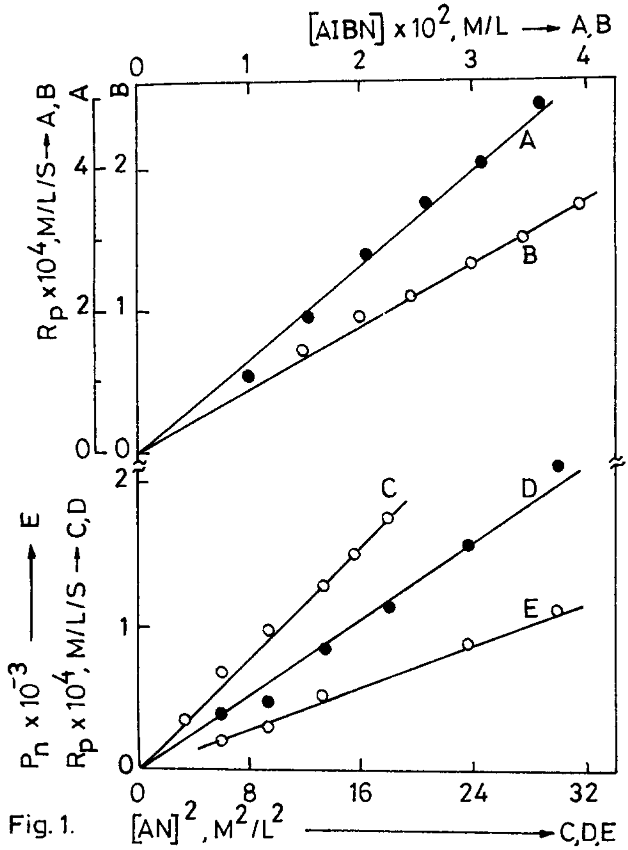

Fig. 1.

Variation of R_p and P_n with AIBN and $[AN]^2$.

Line A : [AN] = 4.56 M, [$POCl_3$] = 1.223 M, 70°C /C_6H_6

Line B : [AN] = 3.05 M, [$C_6H_5PCl_2$] = 0.442M, 65°C /C_6H_6

Line C : [AIBN] = 0.0247 M, [$C_6H_5PCl_2$] = 0.442 M, 65°C/C_6H_6

Line D : [AIBN] = 0.024 M, [$POCl_3$] = 0.917 M, 60°C /C_6H_6

Line E : [AIBN] = 0.0249 M, [$POCl_3$] = 1.22 M, 70°C/C_6H_6

monomer and first order in initiator can be explained on the basis of a complex formed between monomer and phosphorous compound coupled with degradative chain transfer. Formation of such complexes has already been substantiated by NMR in the case of triphenyl phosphite and AN (TANINAKA et al., 1975). We have also observed that the chemical shifts of the vinyl protons moved to higher magnetic fields in the presence of $C_6H_5PCl_2$ or $POCl_3$ relative to their position in pure AN.

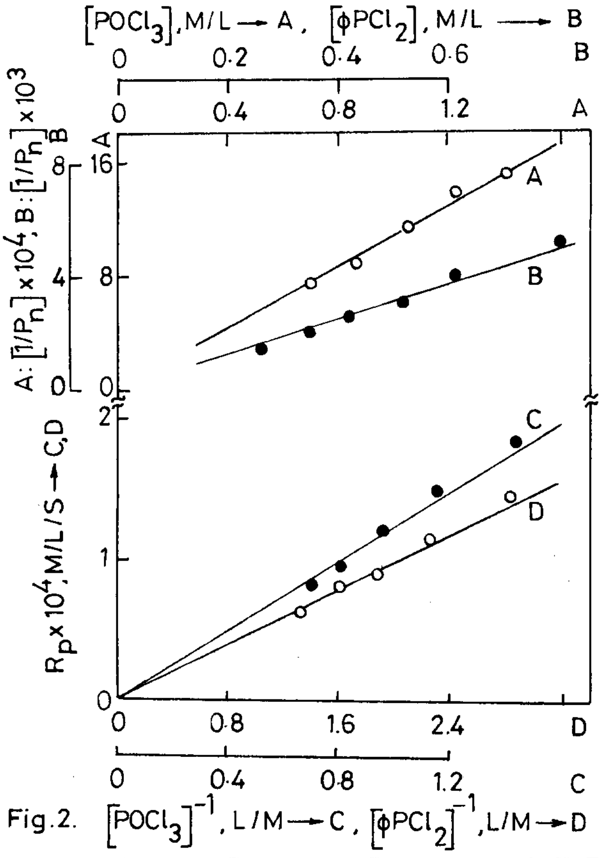

Fig.2.

Variation of R_p and P_n with $POCl_3$ and $C_6H_5PCl_2$

Line A : [AN] = 4.56 M , [AIBN] = 0.025 M, 70°C/C_6H_6
Line B : [AN] = 3.04 M , [AIBN] = 0.024 M, 75°C/C_6H_6
Line C : [AN] = 4.56 M , [AIBN] = 0.0254 M, 60°C/C_6H_6
Line D : [AN] = 3.04 M , [AIBN] = 0.0247 M, 65°C /C_6H_6

The scheme given below would account for the observed kinetics , with P representing the phosphorous compound and M the monomer

$$\mathrm{P} + \mathrm{M} \underset{}{\overset{K}{\rightleftharpoons}} \text{Complex}$$

$$\text{AIBN} \xrightarrow{k_d} 2\,\mathrm{R}^{\bullet}$$

$$\begin{aligned}
&R^{\bullet} + M \xrightarrow{k_i} R\text{-}M^{\bullet} \\
&R\text{-}M^{\bullet} + M \xrightarrow{k_p} R\text{-}M\text{-}M^{\bullet} \quad \text{etc.} \\
&R\text{-}M_n^{\bullet} + P \xrightarrow{k_t} \text{Polymer} + X^{\bullet} \\
&R\text{-}M_n^{\bullet} + X^{\bullet} \xrightarrow{k_t'} \text{Polymer}
\end{aligned}$$

Application of the steady state approximation to the species $R^{\bullet}$, $X^{\bullet}$ and $R\text{-}M_n^{\bullet}$ leads to the following rate law :

$$R_p = k_p\, k_d\, [M]\, [AIBN] \,/\, k_t\, [P]_{eq.}$$

If we assume that the complex cannot participate in the degradative chain transfer step and since monomer is in excess the expression for the rate of polymerisation becomes

$$R_p = k_p\, k_d [AIBN][M]\ (\ 1 + K[M])\ /\ k_t [P]_{Total}.$$

Under conditions such that $K[M] \gg 1$, this rate expression is in agreement with the data. In the absence of significant mutual termination , chain transfer to initiator , monomer and solvent the average degrees of polymerisation are given by

$$P_n = k_p\, K\ [M]^2 \,/\, 2\, k_t\, [P]_{Total} \ .$$

The values of the composite constant $k_p\, k_d\, K / k_t$ calculated from rate data appear in Table 1 . The values are slightly larger for $POCl_3$ compared to $C_6H_5PCl_2$ in benzene . Even if k_d is assumed to be indepedent of the medium , K as well as k_t are dependent on the type of phosphorous compound. Also the values are very much lower in trichloroethylene compared to benzene.

In contrast to $C_6H_5PCl_2$ and $POCl_3$ addition of PCl_3 had no effect on the rates of polymerisation , the order with respect to monomer and initiator being 1 and ½ respectively. However plots of $(P_n)^{-1}$ versus $[PCl_3]/[AN]$ were linear with intercepts on the P_n axis indicating conventional chain transfer. The chain transfer constants are also listed in Table 1 . The values are of the same order as reported earlier for 1,1 - dichloroethylene but lower than those reported for styrene (LITTLE and HARTMANN, 1966).

TABLE 1

Mean values of rate parameters and chain transfer constant

System	Temp. °C	k_pk_d K $/k_t$ (L/M/sec.)	k_{tr}/k_p
$C_6H_5PCl_2$ - Benzene/AN	65	1.97×10^{-4}	-
	75	6.95×10^{-4}	-
$POCl_3$ - Benzene/AN	60	2.15×10^{-4}	-
	70	8.02×10^{-4}	-
$C_6H_5PCl_2$ - C_2HCl_3/AN	65	0.82×10^{-4}	-
	75	3.07×10^{-4}	-
PCl_3 - Benzene/AN	65	-	1×10^{-3}
	75	-	1.81×10^{-3}

The data on phosphorous content of the unfractionated polymers indicate that there is some copolymerisation also taking place. The ratio P_n / Number of P atoms per mole of polymer varies from 60 to 110 with $C_6H_5PCl_2$, 110 to 160 with $POCl_3$ and from 110 to 150 with PCl_3 . Mere chain transfer , degradative or otherwise would lead to very much lower values for the phosphorous content. Rigorous fractionation of polymers followed by estimation of phosphorous content is required to establish reactivity ratios.

Acknowledgement

Financial assistance by the C.S.I.R., New Delhi is gratefully acknowledged.

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Received November 27, 1979