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MECHANISM OF POLYMERIZATION OF METHYL METHACRYLATE BY TRIPHENYLPHOSPHINE AND Fe(III) COMPLEX IN DIMETHYL SULPHOXIDE

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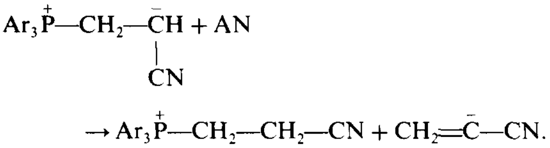
Abstract—The triphenylphosphine (TPP) initiated polymerization of methyl methacrylate (MMA) in dimethyl sulphoxide (DMSO) has been studied. The polymerization was found to be solvent-sensitive and could be accelerated by Lewis acids like Fe^{3+}. Kinetic studies showed that the propagation was free radical in nature. The charge transfer complex formed between MMA and TPP in DMSO was thought to be responsible for the initiation of polymerization. From spectrophotometric studies and also from studies of the molecular weights of polymers, it has been concluded that a transition metal ion-activated dipole interaction between carbonyl oxygen and the phosphorus atom is responsible for the accelerated rate of polymerization.

INTRODUCTION

It is well known that phosphine reacts with olefins either by free radical initiation or in the presence of catalysts. Polymerizations of acrylic monomers with trivalent phosphorus compounds have been studied by many workers [1–4]. Honer *et al.* [5] proposed the formation of a Zwitterion for the initiation of anionic polymerization of monomers in which double bonds are activated by strongly electron-withdrawing groups. However, the formation of the Zwitterion has not yet been confirmed by work with tertiary phosphines. Jaacks *et al.* [6] suggested reaction (1) for the initiation of polymerization of acrylic monomers by triaryl phosphines;



$$Ar_3\overset{+}{P}—CH_2—\underset{\displaystyle CN}{\overset{-}{C}H} + AN \rightarrow Ar_3\overset{+}{P}—CH_2—CH_2—CN + CH_2{=}\overset{-}{C}—CN. \quad (1)$$

Reaction (1) however is unlikely [7]. Similarly, Ogawa and Quintana [7] studied the polymerization of acrylic monomers catalysed by triethyl phosphite. They reported that the electron-donating ability of the phosphite is important for initiation. Mao and Eldred [8] studied the photopolymerization of acrylic monomers initiated by triphenyl derivatives of phosphorus, antimony, arsenic and bismuth. They reported that these compounds did not all initiate the photopolymerization by the same mechanism. For example, the bismuthine, stibine and arsine initiated the photopolymerization of monomers that normally could be polymerized by a free radical mechanism induced by peroxide or azo type of catalyst. Triphenyl phosphine (TPP), on the other hand, initiated the photopolymerization only of acrylic types of monomer, styrene being completely unaffected. Thus, TPP was quite selective. It has been reported [9] that a mixture of TPP and Fe(III) could initiate the charge transfer polymerization of acrylonitrile in dimethyl sulphoxide (DMSO). However, polymerization of acrylic monomers initiated thermally by TPP alone has not been reported so far. Here, we attempt to elucidate the mechanism of initiation of polymerization of methyl methacrylate (MMA) by TPP in the presence or absence of Fe(III) in DMSO.

EXPERIMENTAL PROCEDURES

Materials

MMA [10] and DMSO [11] were purified by standard procedures. TPP (BDH) was recrystallized to constant melting point (m.p. 79.5–80°C). The complex, hexakis (dimethyl sulphoxide) Fe(III) perchlorate $[Fe(DMSO)_6](ClO_4)_3$ (A) was prepared as previously [12].

Polymerization

Polymerizations were conducted in dilatometers under vacuum ($10^{-3} \sim 10^{-4}$ mm of Hg); the rates were obtained by the usual procedures [13]. Polymers were dried under vacuum after precipitation in excess methanol containing a trace of hydroquinone. Values of molecular weight, $\bar{M}_n$, of polymers in chloroform (AR) were obtained viscometrically at 30° from the relation [14],

$$[\eta] = 4.3 \times 10^{-5} \bar{M}_n^{0.8}. \quad (2)$$

Molecular weights were also determined osmometrically using a vapour-pressure osmometer (WESCAN 232A).

Phosphorus analyses on low molecular weight polymer (mol. wt = 2900), precipitated several times for dimethyl formamide (DMF) solution, were made by the spectrophotometric Molybdenum Blue method [15]. A similarly treated physical mixture of polymer and TPP was used as a blank. u.v. Spectra were obtained on a Shimadzu UV-240 spectrophotometer. i.r. Spectra were obtained on a Perkin–Elmer 883 grating i.r. spectrophotometer.

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RESULTS AND DISCUSSION

TPP-initiated polymerization

TPP alone can initiate the polymerization of MMA in DMSO even at 40°. It was found that the polymerization of MMA with TPP alone was slow and dependent on the concentration of TPP present in a constant composition of MMA and DMSO. However, in the presence of a Lewis acid like Fe^{3+}, increased rates were observed. Experiments were done by adding various amounts of TPP to a constant composition of MMA and A in DMSO at 60°C. Similar experiments were also done by adding various amounts of the complex A to a constant composition of MMA and TPP. The results showed that the rate of polymerization decreased with increasing TPP, giving a maximum at a concentration of 2.2×10^{-3} mol l^{-1}. Ferric ion at lower concentrations ($<2.3 \times 10^{-2}$ mol l^{-1}) was found to catalyse the reaction; at comparatively higher concentrations, it acted as an electron-transfer agent and the rate of polymerization decreased with increasing concentrations at fixed [MMA] and at optimum [TPP] in DMSO at 60°C. Some typical examples showing the effect of Fe^{3+} concentrations on the polymerization of MMA initiated by TPP at 60° are shown in Fig. 1. The TPP-initiated polymerization in the presence of A gave a linear rate curve up to at least 10% conversion. The polymerization effected by TPP is inhibited by hydroquinone and by 1,1-diphenyl-2-picryhydrazyl, indicating a radical mechanism for the polymerization. The resulting poly MMA was found to contain phosphorus even after repeated reprecipitations. A physical mixture containing TPP and polyMMA, which had been initiated by α, α′-azobisisobutyronitrile showed no phosphorus after one reprecipitation.

Overall activation energy of polymerization

The effect of temperature on the rate of TPP initiated polymerization of MMA in the presence of Fe(III) indicated a positive temperature coefficient. The overall energy of activation was 33 kJ mol^{-1}.

Table 1. Values of $k_p/k_t^{1/2}$ obtained for various polymerization conditions at 60°. [TPP] = 2.2×10^{-3} mol l^{-1}

[M] mol l^{-1}	[A] mol l^{-1}	$\bar{P}_n$	-10^5 d[M]/dt (mol l^{-1} sec^{-1})	$k_p/k_t^{1/2}$ (l mol^{-1} sec^{-1})$^{1/2}$
1.88	Nil	1168	3.56	0.109
1.88	1.0×10^{-4}	1347	4.42	0.130
1.88	2.4×10^{-2}	1685	5.52	0.162
1.88	1.3×10^{-3}	1765	6.02	0.173
1.88	2.2×10^{-3}	2008	6.98	0.199
2.82	2.2×10^{-3}	3442	8.48	0.192
3.31	2.2×10^{-3}	4336	9.89	0.198
3.76	2.2×10^{-3}	4906	11.23	0.197
				Avg. 0.170

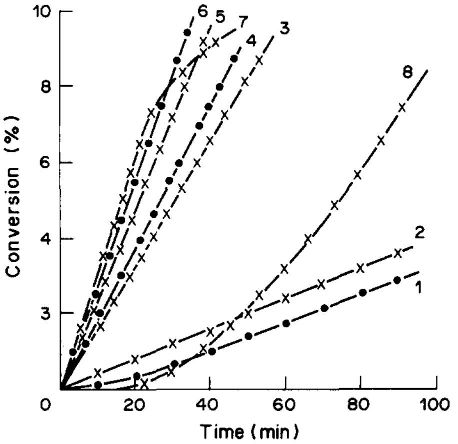


Fig. 1. Effects of Fe(III) complex concentrations on the polymerization of MMA initiated by TPP in DMSO at 60°. [MMA] = 1.88 mol l^{-1}; curve (1) [TPP] = 1.0×10^{-3} mol l^{-1}, [A] = nil; curve (2) [TPP] = 2.2×10^{-3} mol l^{-1}, [A] = nil. Curves (3)–(8) [TPP] = 2.2×10^{-3} mol l^{-1}; curve (3) [A] = 4.25×10^{-4} mol l^{-1}; (4) [A] = 8.8×10^{-4} mol l^{-1}; (5) [A] = 1.4×10^{-3} mol l^{-1}; (6) [A] = 2.2×10^{-3} mol l^{-1}; (7) [A] = 8.5×10^{-3} mol l^{-1}; (8) [A] = 2.6×10^{-2} mol l^{-1}.

Number-average degree of polymerization

The number-average degree of polymerization, $\bar{P}_n$, as determined by osmometric and viscometric methods is shown in Table 1. The values of $k_p/k_t^{1/2}$ were calculated by using the conventional relationship

$$-\bar{P}_n \mathrm{d}[M]/\mathrm{d}t = (k_p^2/k_t)\,[M]^2 \qquad (3)$$

where k_p and k_t represent the rate constants of propagation and termination respectively. The values of $k_p/k_t^{1/2}$ obtained here agree satisfactorily with the literature value, i.e. 0.197 (l/mol sec)$^{1/2}$ at 60° [16] so supporting a radical polymerization.

Activation energy of the initiation

The Arrhenius plot of $k_p/k_t^{1/2}$ for temperatures between 30 and 70° is shown in Fig. 2. The apparent activation energy $E_a(=E_p - E_t/2)$ for the TPP-initiated polymerization of MMA in presence of Fe^{3+}, from data for 40°, 45° and 50°, was 14.7 kJ mol^{-1}, E_p and E_t being the activation energies of propagation and termination respectively. It follows that the activation energy of initiation is 37 kJ mol^{-1}.

Selectivity of dimethyl sulphoxide

The polymerization did not occur in solvents such as DMF, acetonitrile (CH_3CN), heptane, C_6H_6,

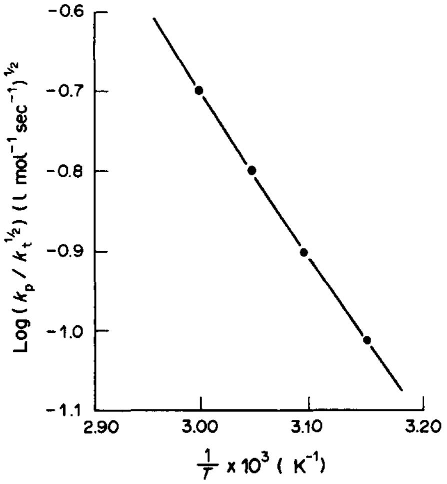


Fig. 2. Arrhenius plot for $k_p/k_t^{1/2}$.

Table 2. Spectral data for TPP in various solvents

Solvent	[TPP] (mol l^{-1})	λ_{max}	ϵ_{max}
DMSO	4.60×10^{-4}	280	9000
DMF	1.50×10^{-4}	262	8400
CH_3CN	1.80×10^{-4}	262	11,600
$CHCl_3$	1.25×10^{-4}	262	9500
CCl_4	1.15×10^{-4}	262	11,700
Heptane	1.0×10^{-4}	262	10,860

CCl_4, $CHCl_3$ under the experimental conditions (at 60° for 2 hr). However, *ca* 3% conversion/hr was noted when DMSO was used as a solvent. Thus, DMSO was quite selective. Further, a long induction period was observed when the reaction was conducted in the presence of a co-solvent. To understand the selective nature of DMSO for the polymerization initiated by TPP, spectrophotometric studies were made with TPP in various solvents. Table 2 shows some of the spectral data for TPP in various solvents; it can be seen that the absorption at 262 nm is shifted to longer wave lengths in DMSO. This effect may be due to the fact that TPP is oxophilic in character and becomes more polar in the excited state [17], the non-bonding electrons of the excited state are stabilized (relative to the ground state) by electrostatic interaction with a polar solvent of high dielectric constant such as DMSO. Hence, in DMSO the n-electrons of the P-atom become available for interaction with the monomer. Because of the presence of benzene nuclei in TPP, the n-electrons of the P-atom (in the ground state) are less available for interaction with the monomer, so explaining the absence of polymerization in solvents other than DMSO. The large dielectric constant of DMSO probably helps to stabilize the n-electrons of the P-atom because, when the dielectric constant of the medium was lowered by adding CCl_4, no polymer was obtained under the experimental conditions. Thus the dielectric constant of the medium also plays an important role and the exact nature of the interaction remains obscure.

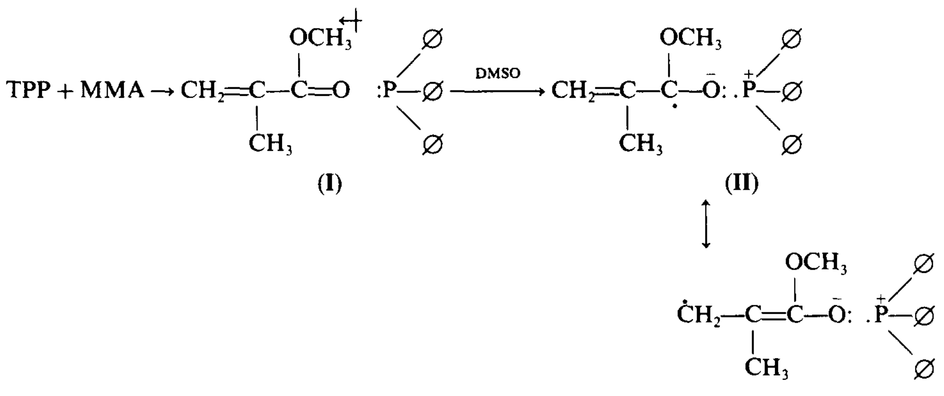
Complex formation

Figure 3 shows u.v. spectra of TPP in DMSO in the presence and absence of MMA. The spectrum of MMA solution of TPP showed a new peak at 292 nm and was found to follow Beer's law. This new peak is thought to be due to the formation of a complex between MMA and TPP. Further, TPP affected the C=O band rather than C=C band in the i.r. spectra and caused the C=O band to shift to lower frequency. Since, no polymerization of styrene took place under the experimental conditions, it was concluded that TPP co-ordinates to the oxygen of the carbonyl group of MMA and the structure of the complex is similar to that of the dimethyl phenyl phosphine reported earlier [18]. The complex, I, formed between TPP and MMA would be very weak because of electron-withdrawing inductive effect of benzene nuclei on TPP. To check that the complex formed between TPP and MMA was rather weak, the following experiments were performed. At a constant TPP concentration, the u.v. spectra of successive dilutions of the TPP monomer mixture were obtained. The absorption maxima and the molar extinction coefficients were determined after each dilution. The results showed that, as the concentration of the monomer was decreased (=0.1%) and replaced by DMSO, the λ_{max} approached the value (280 nm) for TPP in DMSO indicating the existence of complexed and non-complexed TPP. This equilibrium behaviour is quite typical of weak complexes [19] and suggests that the complex is solvent-sensitive.

The spectra of a typical reaction mixture containing TPP (1×10^{-3} mol l^{-1}) and MMA (3×10^{-2} mol l^{-1}) in DMSO at 20° showed different absorptions. The band at 292 nm disappeared and a new band of low intensity appeared at 346 ± 2 nm. The band at 346 ± 2 nm in DMSO may be attributed to the charge transfer (CT) interaction between TPP and MMA to produce free radicals responsible for the initiation of polymerization. The exact nature of the interaction must be quite complex. However, it is evident that the solvent, i.e. DMSO must have played a role in producing free radicals.

Mechanism of initiation

Since a solution of TPP in DMSO alone could not initiate the polymerization of acrylonitrile even at 60°, we propose the following scheme to explain the reaction:



(I)

(II)

$(R_1^{\bullet})$

$R_1^{\bullet} + M \rightarrow R_2^{\bullet}$

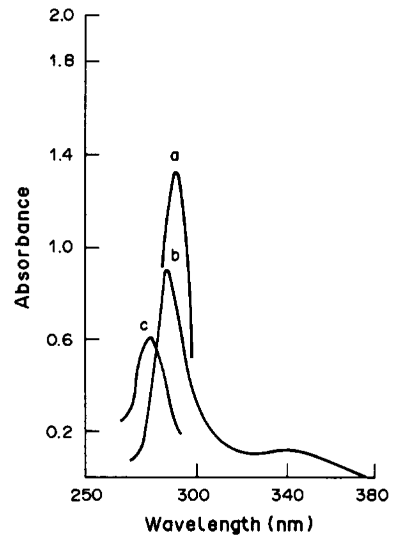
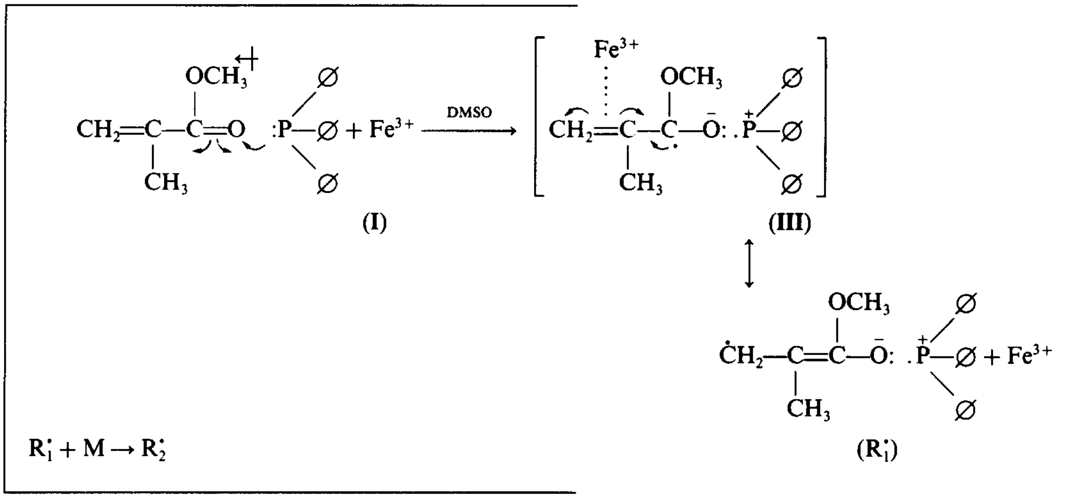


Fig. 3. u.v. Spectra: (a) TPP in MMA; (b) TPP and MMA in DMSO; (c) TPP in DMSO.

Thus, under the influence of DMSO, the phosphorus atom donates one of its unpaired electrons to the oxygen, resulting in an intermolecular charge transfer complex, **II**. A re-arrangement of electrons throughout the system, as shown in the scheme, produces a methyl methacrylate radical, which can proceed to propagate the reaction. The polymerization due to the charge transfer complex **II** was slow because the complex was weak. The non-occurrence of the above reaction in CH_3CN may be due to its competition with the monomer for complexing TPP. Similarly the inactivity of DMF may be attributed to its high complexing power. On the other hand, the solvents heptane, CCl_4, $CHCl_3$ and C_6H_6 are non-polar and so they do not allow the formation of the charged species shown in the mechanism.

Accelerated rates of polymerization

The rates of the TPP-initiated polymerization of MMA in DMSO could be greatly increased by the addition of Lewis acids like Fe^{3+}. Metal ions like Ag^+ or Hg^{2+} are known [20] to affect the α, β-double bond of vinyl monomers. Similarly, in the charge transfer polymerization of vinyl monomers, transition metal ions are also found to co-ordinate to the α, β-double bond [21, 22]. The interaction between A and the monomer or between A and TPP could not be detected spectrophotometrically at the levels of initiator and the Lewis acid employed. There was no experimental evidence [23] for the production of Fe^{2+} during the polymerization. So, Fe^{3+} must activate the α, β-double bond and thereby facilitate the formation of free radicals. The following scheme might explain the enhanced rate of formation of free radicals:



$R_1^\bullet + M \rightarrow R_2^\bullet$

Therefore, in the presence of the transition metal ions, the phosphorus atom donates one of its unpaired electrons at a greater rate, resulting in the intermolecular charge transfer complex, III, too unstable to be detected spectrophotometrically. Experiments with methyl acrylate indicated similar results and similar catalytic results with Cu^{2+} suggested that the assumption might be true.

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