

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Mechanism of Charge Transfer Initiation by the Dimethyl Phenyl Phosphine/Fe(III) Catalyst System

A. Dutta<sup>a</sup>; P. K. Mahato<sup>a</sup>; N. N. Dass<sup>a</sup>

<sup>a</sup> Department of Chemistry Dibrugarh, University Dibrugarh, Assam, India

**To cite this Article** Dutta, A. , Mahato, P. K. and Dass, N. N.(1991) 'Mechanism of Charge Transfer Initiation by the Dimethyl Phenyl Phosphine/Fe(III) Catalyst System', Journal of Macromolecular Science, Part A, 28: 10, 1001 – 1008

**To link to this Article:** DOI: 10.1080/00222339108054080

**URL:** <http://dx.doi.org/10.1080/00222339108054080>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## **MECHANISM OF CHARGE TRANSFER INITIATION BY THE DIMETHYL PHENYL PHOSPHINE/Fe(III) CATALYST SYSTEM**

A. DUTTA, P. K. MAHATO, and N. N. DASS\*

Department of Chemistry  
Dibrugarh University  
Dibrugarh 786004, Assam, India

### **ABSTRACT**

The dimethyl phenyl phosphine (DMPP) initiated polymerization of methyl methacrylate (MMA) in dimethylsulfoxide was studied. Polymerization of MMA in this system required the presence of transition metal ions like  $\text{Fe}^{3+}$  or  $\text{Cu}^{2+}$ . Kinetic studies showed that the propagation was free radical in nature. An interaction between DMPP and MMA was detected spectrophotometrically. A proposed mechanism involves a transition metal ion-activated dipole interaction between the carbonyl oxygen and the phosphorus atom with the ultimate formation of a methyl methacrylate type of free radical.

### **INTRODUCTION**

The effect of transition metal ions on polymerizations has been studied by many workers [1–3]. Bamford [4] and Bengough [5] reported that ferric chloride acts as an electron transfer agent. The role of ferric ion in the polymerization of acrylamide initiated by ceric salt was studied by Narita et al. [6]. The radical polymerization is generally considered to be inhibited by ferric salt.

However, charge-transfer polymerizations initiated by compounds containing donor nitrogen atoms were found to be largely enhanced by transition metal ions [7-11]. These polymerizations required the presence of  $\text{CCl}_4$  in the system. The catalytic action of the transition metal ions is believed to be due to the complex formation between the metal ion and the various donor compounds used [12].

Polymerization of acrylic monomers initiated thermally in the presence of transition metal ions alone, in the absence of light, has not been reported so far. In the present investigation the polymerization of methyl methacrylate (MMA) initiated by dimethyl phenyl phosphine (DMPP) in the presence of  $\text{Fe}^{3+}$  was studied. The formation of a complex of MMA with DMPP was confirmed. Ferric ion at lower concentrations (below  $7.0 \times 10^{-2}$  mol/L) was found to catalyze the reaction. At comparatively higher concentrations, it acted as an electron transfer agent, and the rate of polymerization decreased with increasing concentration. Here, we attempt to elucidate the mechanism of initiation of polymerization of MMA by DMPP in the presence of  $\text{Fe}^{3+}$  at  $60^\circ\text{C}$  in dimethylsulfoxide (DMSO).

## EXPERIMENTAL

### Materials

MMA [4] and DMSO [13] were purified by published methods. DMPP (Fluka AG) was used without further purification. The complex hexakisdimethylsulfoxide Fe(III) perchlorate  $[\text{Fe}(\text{DMSO})_6](\text{ClO}_4)_3$ , A, was prepared as before [14].

### Polymerization

Polymerization with dry reagents was done at  $60^\circ\text{C}$  under vacuum in a three-limbed vessel. The first limb was filled with MMA in DMSO and the second with DMPP and complex A in DMSO. The vessel was completely evacuated [15], and then the contents of the two limbs were thoroughly mixed and transferred to the third limb, the dilatometer. The sealed dilatometer was then immediately introduced into a thermostat at  $60 \pm 0.01^\circ\text{C}$ . The reaction was followed dilatometrically. Gravimetric experiments were carried out in an evacuated H-tube. Polymers were

dried under vacuum after precipitation from an excess of methanol containing traces of hydroquinone.

The number-average molecular weights,  $\bar{M}_n$ , of PMMA samples were determined osmotically by using a vapor-pressure osmometer (WESCAN 232A). Ultraviolet spectra were obtained on a Shimadzu UV-240 spectrophotometer. Infrared spectra were obtained on a Perkin-Elmer 983 dual beam grating infrared spectrophotometer.

## RESULTS AND DISCUSSION

A series of experiments was done by adding different amounts of DMPP to a constant composition of MMA and complex A in DMSO at 60°C. Similar experiments were also done by adding different amounts of complex A to a constant composition of MMA and DMPP. The results indicated that the rate of polymerization decreases with increasing [DMPP], giving a maximum at an optimum concentration of  $7.0 \times 10^{-3}$  mol/L of DMPP, and the rate of polymerization increases with increasing [A] (up to a limiting concentration of  $7.0 \times 10^{-2}$  mol/L) at a fixed [MMA] and at an optimum [DMPP] in DMSO at 60°C. Some typical examples showing the effect of [A] on the polymerizations of MMA in this system at 60°C are shown in Fig. 1. The DMPP-initiated polymerization in the presence of complex A gave a linear rate curve up to at least 10% conversion. Under the experimental conditions used, no polymer was obtained even after 2 h when complex A was missing from the polymerizing system. The effect of temperature on the rate of polymerization indicated a positive temperature coefficient. The overall energy of activation was calculated to be 8.1 kcal/mol. The number-average degree of polymerization,  $\bar{P}_n$ , as determined osmotically, is shown in Table 1. The value of  $k_p/k_t^{1/2}$  was calculated by using the conventional relationship

$$-\bar{P}_n d[M]/dt = (k_p^2/k_t)[M]^2 \quad (1)$$

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 [16]. The polymerization initiated by the mixture of DMPP and complex A can be inhibited by hydroquinone, 1,1-diphenyl-2-picrylhydrazyl (DPPH), and oxygen. These results suggest a free-radical mechanism for the polymerization reaction.

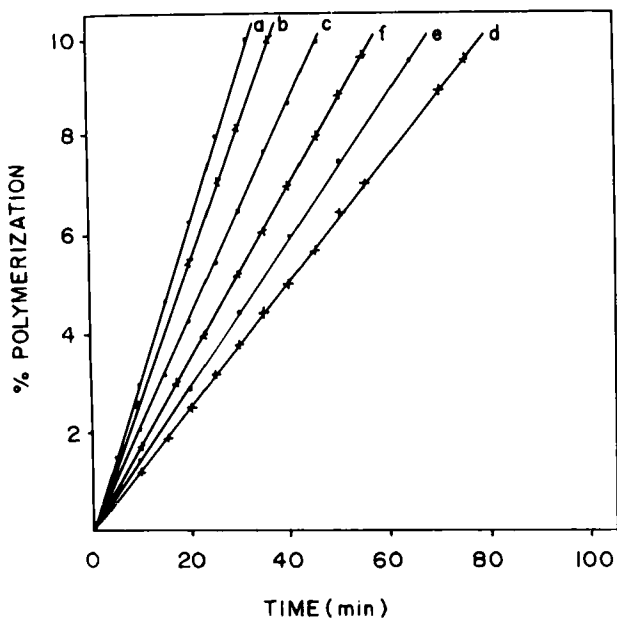


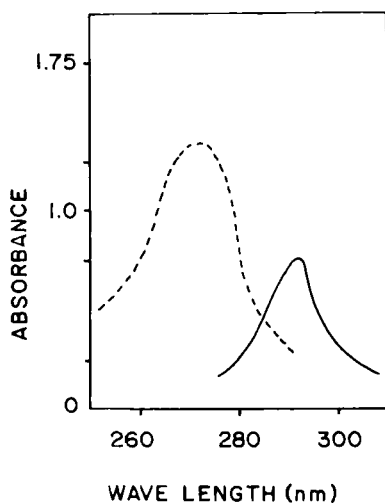
FIG. 1. Polymerization of MMA in DMSO at 60°C initiated by DMPP in the presence of the complex A: [MMA] = 1.88 mol/L, [DMSO] = 11.26 mol/L, [DMPP] =  $7.0 \times 10^{-3}$  mol/L. Curve (a), [A] =  $7.0 \times 10^{-2}$  mol/L; (b), [A] =  $7.0 \times 10^{-3}$  mol/L; (c), [A] =  $3.5 \times 10^{-3}$  mol/L; (d), [A] =  $7.0 \times 10^{-4}$  mol/L; (e), [A] =  $1.17 \times 10^{-3}$  mol/L; (f), [A] =  $2.34 \times 10^{-3}$  mol/L.

Figure 2 shows the experimental UV spectra of DMPP in DMSO and in MMA. The spectra of the MMA solution of DMPP showed the existence of 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 DMPP. Further, DMPP affected the C=O band rather than the C=C band in the IR spectra and caused the C=O band to shift to lower frequency. However, no polymerization of styrene took place under the experimental conditions, so it was concluded that DMPP coordinates to the oxygen of the carbonyl group of MMA and the structure of the complex is similar to that of the triphenyl phosphine reported earlier [17]. The complex, I, formed between DMPP and MMA would be weak. This is due to the electron-withdrawing inductive effect of the benzene ring.

To substantiate the point that the complex formed between DMPP

TABLE 1. Values of  $k_p/k_t^{1/2}$  Obtained at Various Polymerization Conditions at 60°C.  $[DMPP] = 7.0 \times 10^{-3}$  mol/L

[M], mol/L	[A], mol/L	$\bar{P}_n$	$-10^5 \frac{d[M]}{dt}$ , mol·L <sup>-1</sup> ·s <sup>-1</sup>	$k_p/k_t^{1/2}$ , (L·mol <sup>-1</sup> ·s <sup>-1</sup> ) <sup>1/2</sup>
1.88	$7.0 \times 10^{-3}$	1889	6.88	0.192
1.88	$7.0 \times 10^{-2}$	1932	7.06	0.196
1.88	$3.5 \times 10^{-3}$	1795	5.02	0.160
2.82	$7.0 \times 10^{-3}$	3394	8.84	0.194
3.31	$7.0 \times 10^{-3}$	4205	9.75	0.193
3.76	$7.0 \times 10^{-3}$	4840	10.95	0.194
			Av	0.188

FIG. 2. Ultraviolet spectra: (--)  $7.0 \times 10^{-3}$  mol/L of dimethyl phenyl phosphine in DMSO (ref.: DMSO); (—)  $7.0 \times 10^{-3}$  mol/L of dimethyl phenyl phosphine in MMA (ref.: MMA).

and MMA was a rather weak one, the following experiments were performed. At a constant DMPP concentration the UV spectra of successive dilutions of the DMPP-monomer mixture were obtained. The absorption maxima and the molar extinction coefficients were determined after each dilution. Figure 3 shows the change in wavelength of the complex peak of DMPP ( $7.0 \times 10^{-3}$  mol/L) in MMA upon dilution with a solution of  $7.0 \times 10^{-3}$  mol/L of DMPP in DMSO; as the monomer concentration is reduced to about 0.1%, the absorption maximum shifted toward 273 nm. Figure 3 actually represents a composite of the complexed and noncomplexed DMPP, which has an area of overlap as seen in Fig. 2, thereby giving the impression of a shift in the wavelength. This equilibrium behavior is quite typical of weak complexes [18] and suggests that the complex is solvent sensitive.

Metal ions like  $\text{Ag}^+$  or  $\text{Hg}^{2+}$  are known [19] to affect the C=C bond center of MMA. Similarly, in the charge transfer polymerization of MMA in the presence of transition metal ions, it is believed that the back-donation of electrons from the filled molecular orbital of the metal occurs at the C=C bond center [20, 21]. The interaction between complex A and the monomer or between complex A and DMPP could not

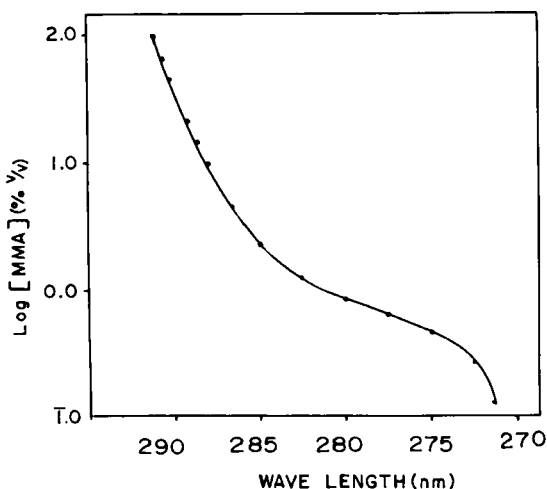


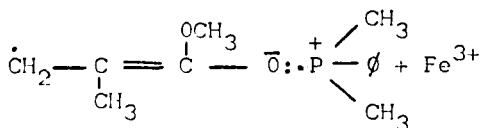
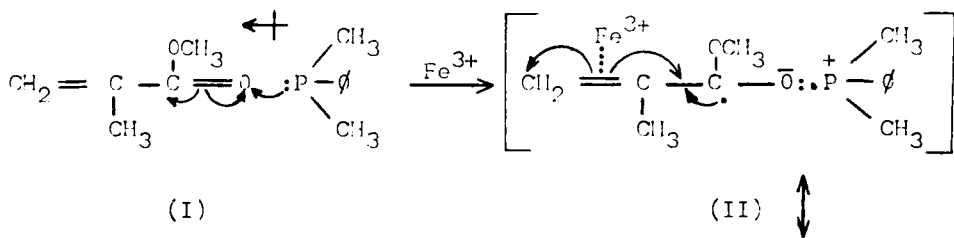
FIG. 3. Change in wavelength of complex peak of dimethyl phenyl phosphine ( $7.0 \times 10^{-3}$  mol/L) in MMA upon dilution with a solution of  $7.0 \times 10^{-3}$  mol/L of dimethyl phenyl phosphine in DMSO.

be detected spectrophotometrically. There was no experimental evidence [22] for the production of  $Fe^{2+}$  during the polymerization, so  $Fe^{3+}$  must activate the  $C=C$  bond and thereby facilitate the formation of free radicals. Scheme 1 might explain the reaction mechanism.

Therefore, in the presence of transition metal ions like  $Fe^{3+}$ , the phosphorus atom donates one of its unpaired electrons, resulting in an intermolecular charge transfer complex (II) too unstable to be detected spectrophotometrically. A rearrangement of electrons throughout the system, as shown in Scheme 1, produces a methyl methacrylate radical which can proceed to propagate the reaction. Experiments with other monomers like acrylonitrile, methyl acrylate, and vinyl acetate indicated similar results, and similar accelerative results with  $Cu^{2+}$  suggested that the presumption might be true.

CONCLUSION

The polymerization of MMA can be easily initiated by a mixture of DMPP and  $Fe^{3+}$  in DMSO. The addition of DPPH inhibits the reaction. An increase in the monomer concentration leads to a higher molecular weight of poly-MMA. The values of  $k_p/k_t^{1/2}$  obtained under various polymerization conditions are satisfactorily consistent with literature values,



SCHEME 1.



suggesting that the polymerization proceeds through free radical intermediates. The free radical responsible for initiation must be produced by the decomposition of the intermolecular charge-transfer complex involving the monomer, DMPP, and  $\text{Fe}^{3+}$  in DMSO.

### REFERENCES

- [1] N. N. Dass and M. H. George, *J. Polym. Sci., Part A-1*, **7**, 269 (1969).
- [2] M. M. Hussain and A. Gupta, *Makromol. Chem.*, **178**, 29 (1977).
- [3] S. R. Sen and N. N. Dass, *Eur. Polym. J.*, **18**, 477 (1982).
- [4] C. H. Bamford, A. D. Jenkins, and R. Johnstone, *Proc. R. Soc. (London), Ser. A*, **239**, 214 (1957).
- [5] W. I. Bengough and I. C. Ross, *Trans. Faraday. Soc.*, **62**, 2251 (1966).
- [6] H. Narita, S. Okamoto, and S. Machida, *Makromol. Chem.*, **111**, 14 (1968).
- [7] S. D. Baruah and N. N. Dass, *Ibid.*, **180**, 1351 (1979).
- [8] S. S. Begum and N. N. Dass, *J. Polym. Sci., Polym. Lett. Ed.*, **20**, 297 (1982).
- [9] S. S. Begum and N. N. Dass, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 2561 (1985).
- [10] S. S. Begum and N. N. Dass, *Polym. J.*, **19**, 1255 (1987).
- [11] S. K. Saha and A. K. Chaudhuri, *J. Polym. Sci., Polym. Chem., Ed.*, **25**, 519 (1987).
- [12] N. N. Dass, *Prog. Polym. Sci.*, **10**, 51 (1984).
- [13] R. S. Drago, D. M. Hart, and R. L. Carlson, *J. Am. Chem. Soc.*, **87**, 1900 (1965).
- [14] P. D. Chetia and N. N. Dass, *Indian J. Chem.*, **11**, 934 (1973).
- [15] M. H. George, *J. Polym. Sci., Part A-1*, **2**, 3169 (1964).
- [16] M. Matsuda and T. Hirayama, *Ibid.*, **5**, 2769 (1967).
- [17] T. J. Mao and R. J. Eldred, *Ibid.*, **5**, 1741 (1967).
- [18] A. S. Meyers and G. H. Ayres, *J. Am. Chem. Soc.*, **79**, 49 (1957).
- [19] H. Narita, Y. Sakamoto, and S. Machida, *Makromol. Chem.*, **152**, 143 (1972).
- [20] S. Hussain and N. N. Dass, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 3181 (1982).
- [21] S. Hussain and N. N. Dass, *Eur. Polym. J.*, **18**, 795 (1982).
- [22] B. M. Mandal, U. S. Nandi, and S. R. Palit, *J. Polym. Sci., Part A-1*, **7**, 1107 (1969).

Received May 4, 1990

Revision received April 5, 1991