ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 127 (1999) 143–145

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

The effect of a cationic salt on the photoinitiated polymerization of methyl methacrylate

Nergis Arsu [*], Meral Aydin

Yildiz Technical University, Department of Chemistry, 80270 Sisli, Istanbul, Turkey

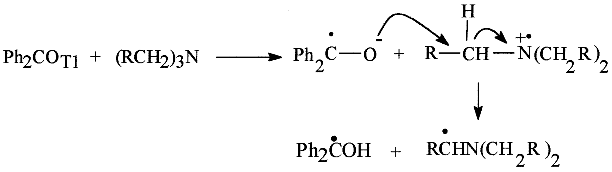
Received 23 March 1999; accepted 24 May 1999

Abstract

The photoinduced free radical polymerization of methyl methacrylate in the presence of benzophenone and thiophenoxyacetic acid were investigated. It has been observed that adding of diphenyliodoniumhexafluorophosphate ($Ph_2I^+PF_6$) salt increased the rate of polymerization and molecular weight of polymer. ©1999 Elsevier Science S.A. All rights reserved.

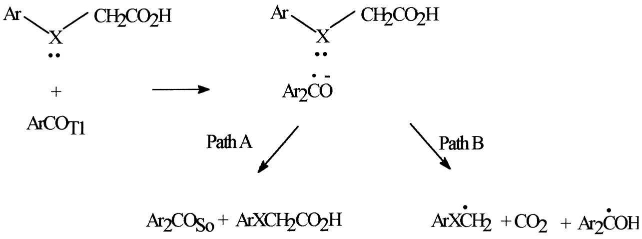
1. Introduction

Many aromatic ketones possess long lived n → π* triplet states (~10^{-6} s) which abstract hydrogen atoms from suitable C–H bonds (e.g. those in alkanes, ethers and alcohols) [1–4]. The n → π* and π → π* triplet states of aromatic ketones also undergo electron transfer reactions with donors such as tertiary amines (Scheme 1).



Scheme 1.

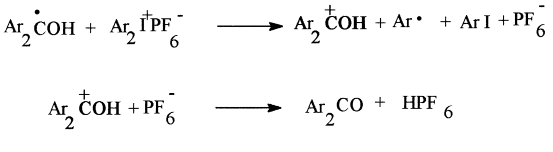
This reaction can lead to the production of α-aminoalkyl radicals as shown in Scheme 1. These radicals are most effective at initiating the polymerization of acrylates and methacrylates. Recognition that triplet ketones react as shown in Scheme 1, led to the finding that other electron donors such as β-aminoalcohols and α-aminoacids could be used [5]. The range of donors was further extended by using other carboxylic acids of the type $RXCH_2CO_2H$ where X = O, S. Reactions of these acids is thought to proceed via the mechanism as shown in Scheme 2 although it should be pointed out that Baum and Norman [6] proposed an alternative mechanism not involving electron transfer.



Scheme 2.

The generation of radicals of the type $RX\dot{C}H_2$ (where X = O, S or NH) in these reactions suggests that such reactions may be of value as initiating reactions for the radical mediated polymerisation of acrylate and methacrylates. Ketyl radicals ($Ar\dot{C}OH_2$) are also generated in these reactions and there is evidence to support the view that such radicals are inefficient initiators of acrylate and methacrylate polymerization reactions [7,8].

Ketyl radicals can be used with benefit in cationic polymerisation processes due to the fact that they are potent reducing agents. Typical photoinitiator for cationic polymerisation reactions are iodonium and sulphonium salts having non-nucleophilic counterions. Ketyl radicals ($Ar\dot{C}OH_2$) will reduce iodonium salts generating an acid and a free radical (Scheme 3) [9,10].



Scheme 3.

---

[*] Corresponding author.

1010-6030/99/$ – see front matter ©1999 Elsevier Science S.A. All rights reserved.
PII: S1010-6030(99)00118-5

Table 1
Photoinduced free radical polymerisation of methyl methacrylate [4.68 mol l^{-1}] in the presence of benzophenone with thiophenoxyacetic acid under nitrogen

Run	Benzophenone (mol l^{-1})	Thiophenoxy acetic acid (mol l^{-1})	Time (h)	The amount of polymer (g)	Conversion %	$R_p \times 10^5$ (mol l^{-1} s^{-1})
1	4.132×10^{-2}	1.32×10^{-1}	1	0.0172	3.675	4.778
2	4.132×10^{-2}	1.32×10^{-1}	2	0.0360	7.692	5.000
3	4.132×10^{-2}	2.64×10^{-1}	1	0.0194	4.145	5.389
4	4.132×10^{-2}	2.64×10^{-1}	2	0.0560	11.966	7.778
5	6.02×10^{-2}	1.32×10^{-1}	1	0.0166	3.547	4.611
6	6.02×10^{-2}	1.32×10^{-1}	2	0.0342	7.308	4.750
7	6.02×10^{-2}	2.64×10^{-1}	1	0.0202	4.316	5.611
8	6.02×10^{-2}	2.64×10^{-1}	2	0.0565	12.073	7.847
9	8.264×10^{-2}	1.32×10^{-1}	1	0.0174	3.718	4.833
10	8.264×10^{-2}	1.32×10^{-1}	2	0.0397	8.483	5.514
11	8.264×10^{-2}	2.64×10^{-1}	1	0.0207	4.423	5.750
12	8.264×10^{-2}	2.64×10^{-1}	2	0.0511	10.919	7.097

Table 2
Photoinduced free radical polymerisation of methyl methacrylate for different concentration and irradiation

Run	Bezophenone (mol l^{-1})	Acid (mol l^{-1})	$Ph_2I^+PF_6^-$ (mol l^{-1})	The amount of polymer (g)	Conversion %	$R_p \times 10^5$ (mol l^{-1} s^{-1})
1[a]	4.132×10^{-2}	–	–	0.0045	0.962	1.250
2	4.132×10^{-2}	–	3.0×10^{-2}	–	–	–
3[a]	4.132×10^{-2}	–	3.0×10^{-2}	0.0015	0.321	0.417
4	4.132×10^{-2}	1.32×10^{-1}	–	0.0090	2.115	2.750
5[a]	4.132×10^{-2}	1.32×10^{-1}	–	0.0172	3.675	4.778
6[a]	4.132×10^{-2}	1.32×10^{-1}	3.0×10^{-2}	0.0334	7.137	9.278

[a] Experiments were carried out under nitrogen atmosphere. [MMA]: 4.68 mol l^{-1}; t : 60 min.

Previously, we investigated the effect of diphenyliodonium hexafluorophosphate salt on the photoinitated free radical polymerisation using polysilanes and it was found out that in the presence of the cationic salt the rate of polymerisation significantly increased [11].

In this paper we explain: (a) the use of thiophenoxyacetic acid/benzophenone reaction as an initiator system for methyl methacrylate, (b) the effect of using an iodonium salt in conjunction with the thiophenoxyacetic acid/benzophenone system as means of increasing the yield of initiating radical (i.e. by utilising the aryl radicals generated in the reduction reaction).

2. Experimental

2.1. Materials

Benzophenone, thiophenoxyacetic acid were obtained from Aldrich . Dichloromethane and methanol were bought from Merck. Diphenyliodoniumhexafluorophosphate salt were prepared as indicated in the literature [8] and methylmethacrylate was washed twice with 5% NaOH and distilled over CaH_2 under vacuum.

2.2. Irradiation

Methyl methacrylate [4.68 mol l^{-1}] in CH_2CI_2 and benzophenone as photoinitiator including thiophenoxyacetic acid in the presence and in the absence of iodonium salt were irradiated in a photoreactor equipped with 8 Philips lamps emitting nominally at $\lambda = 350$ nm for 60 and 120 min either in air or nitrogen atmosphere. Polymer were obtained after precipitation in methanol. Conversion % and Polymerization Rates were calculated for all samples gravimetrically. Light intensity was measured by using potassium ferrioxalate actinometer and was found to be 6.876×10^{13} photon s^{-1}.

2.3. Analysis

The M_n values were calculated from g.p.c chromatography according to standard polystyrene samples using a Knauer M-64 instrument and THF as the eluent at a flow rate of 1 ml min^{-1}.

3. Results and discussion

Table 1 shows the rates of polymerisation (R_P) for the polymerisation of methyl methacrylate using a benzophenone-thiophenoxyacetic acid initiating systems. In all cases the values of R_P are greater for the 2 h irradiation experiments when compared with the 1 h irradiation experiments. It is likely that this is due to residual oxygen in the solution giving rise to an induction period. For a fixed concentration of benzophenone at a fixed irradiation time the R_P is always higher for the solution containing the highest concentration of acid.

This is to be expected since increasing the concentration of the acid increases the rate of production of the initiating radicals $ArSCH_2$.

Table 3
Photoinduced free radical polymerization of methylmethacrylate in the presence of benzophenone and thiophenoxyaceticacid by adding of iodonium salt under nitrogen atmosphere[a]

Run	Benzophenone ($\mathrm{mol\,l^{-1}}$)	Thiophenoxy acetic acid ($\mathrm{mol\,l^{-1}}$)	Time (h)	The amount of polymer (g)	Conversion %	$R_p \times 10^5$ ($\mathrm{mol\,l^{-1}\,s^{-1}}$)
1	4.132×10^{-2}	1.32×10^{-1}	1	0.0334	7.137	9.278
2	4.132×10^{-2}	1.32×10^{-1}	2	0.0928	19.829	12.889
3	4.132×10^{-2}	2.64×10^{-1}	1	0.0568	12.137	15.778
4	4.132×10^{-2}	2.64×10^{-1}	2	0.1030	22.009	14.306
5	8.264×10^{-2}	1.32×10^{-1}	1	0.0435	9.295	12.083
6	8.264×10^{-2}	1.32×10^{-1}	2	0.0645	13.782	8.958
7	8.264×10^{-2}	2.64×10^{-1}	1	0.0362	7.735	10.056
8	8.264×10^{-2}	2.64×10^{-1}	2	0.1063	22.714	14.764

[a] [MMA]: $4.68\,\mathrm{mol\,l^{-1}}$; [$Ph_2I^+PF_6^-$] : $3 \times 10^{-2}\,\mathrm{mol\,l^{-1}}$.

Table 4
M_n value of some samples

Benzophenone ($\mathrm{mol\,l^{-1}}$)	Thiophenoxyaceticacid ($\mathrm{mol\,l^{-1}}$)	$Ph_2I^+PF_6^-$ ($\mathrm{mol\,l^{-1}}$)	M_n ($\mathrm{g\,mol^{-1}}$)	M_w/M_n
4.132×10^{-2}	1.32×10^{-1}	–	23000	2.458
4.132×10^{-2}	1.32×10^{-1}	3.0×10^{-2}	51000	1.923

Increasing the concentration of benzophenone and maintaining a constant concentration of acid does not lead to a very marked increase in R_P which probably reflects and the fact that even at the lowest concentration of benzophenone, most of the light necessary for exciting the ketone is fully absorbed.

Given that the results shown in Table 1 confirm that a mixture of benzophenone and thiophenoxyacetic acid can be used to initiate the polymerisation of methyl methacrylate, the effect of added iodonium salt on the initiating efficiency was explored. Table 2 shows the $R_P$values for the initiated polymerisation of methyl methacrylate containing added iodonium salt. Run 1, 2 and 3 are necessary 'blanks' which demonstrate that it is essential to have either benzophenone or thiophenoxyacetic acid and benzophenone, thiophenoxyacetic acid to initiate polymerisation.

Oxygen reduces the efficiency of the benzophenone, thiophenoxy acetic acid system (Runs 4 and 5) and Runs 5 and 6 demonstrate the beneficial effects of having added iodonium salts. Theses effects were explained in more detail and the results are shown in Table 3. If R_P values are considered for 1 h of irradiation using 4.132×10^{-2} M benzophenone and 1.32×10^{-1} M thiophenoxy acetic acid it can be seen that by comparing the values in Tables 1 and 3, the presence of the iodonium salt has increased the R_P value most significantly. Similarly if other concentrations of benzophenone or if the acid are considered, adding iodonium salt increase the R_P. Some preliminary experiments were carried out to see how the addition of iodonium salt affected the molecular weight of the polymer formed. The results are shown in Table 4 where it can be seen that the addition leads to an increase in molecular weight. If the concentration of radicals decrease, the molecular weight of polymer increase, probably M_n was affected by the addition of salt because it removes the ketyl radicals. The lower value of polydispersity was obtained.

4. Conclusion

The results presented demonstrate that benzophenone when used in conjunction with thiophenoxy acetic acid can initiate the polymerisation of methyl methacrylate i.e. an electron transfer induced fragmentation reaction has been used to generate initiating radicals. Other papers will describe the use of the electron transfer induced fragmentation of β-aminoalcohols to initiate polymerisation. The results also confirm the idea that ketyl radicals can be used to generate useful initiating radicals for the polymerisation of methacrylates.

Acknowledgements

We would sincerely thank Prof. R. Stephen Davidson for his most valuable contributions.

We would also like to thank Prof. Yusuf Yagci for supplying us iodonium salt and his valuable ideas and also we are grateful to Tübitak (Research Grant No. TBGA-AY/96) for financial support of GPC column.

References

[1] E.J. Baum, R.O.C. Norman, J. Chem. Soc. (B) 227 (1968).
[2] R.S. Davidson, P.S. Steiner, J. Chem. Soc. (C) 1682 (1971).
[3] R.S. Davidson, K. Harrison, P.R. Steiner, J. Chem. Soc.(C) 3480 (1971).
[4] R.S. Davidson, S. Korkut, P.R. Steiner, Chem. Comm. 1052 (1971).
[5] R.S. Davidson, P.R. Steiner, J.C.S. Perkin II 1357 (1972).
[6] R.O.C. Norman, R.J. Pritchett, J. Chem. Soc. (B) 926 (1967).
[7] Y. Yagci, A.C. Aydogan, A.E. Sizgek, J. Polym. Sci. Polym. Lett. Ed. 22 (1984) 103–106.
[8] Y. Yagci, J. Radiation Curing (1989) 5–15.
[9] J.V. Crivello, J.H.W. Lam, Macromolecules 10 (1977) 1307.
[10] S.P. Pappas, UV Curing Science and Technology, Technology Marketing Corporation, Stanford, CA,Vol I, 1978.
[11] N. Arsu, G. Hizal, Y. Yagci, Macromolecular Reports A32 (1995) 1257.