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Kinetics of poly(styrene peroxide) initiated photopolymerization of methyl methacrylate

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This is a first comprehensive study on the photoinitiating capability of a vinyl polyperoxide. Polymerization of methyl methacrylate photoinitiated by poly(styrene peroxide) (PSP) at 30°C has been shown to follow the usual kinetic behaviour with respect to the initiator, monomer and light intensity for a PSP concentration of 0.0021–0.034 mol-equiv l^{-1}. At higher concentrations of PSP (0.046–0.31 mol-equiv l^{-1}) although kinetic order with respect to the monomer and light intensity follows usual kinetics the order with respect to PSP was found to be very low (0.21), which has been attributed to the occurrence of primary radical termination which has been quantified in terms of the primary radical termination parameter (δ/Σ). The initiator efficiency was found to be very low (0.06–0.07), it has been attributed to the competing unimolecular decomposition of alkoxy radicals with primary radical initiation. The presence of PSP segments in the poly(methyl methacrylate) backbone was confirmed by ^{1}H nuclear magnetic resonance. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: poly(styrene peroxide); photopolymerization; primary radical termination)

INTRODUCTION

In the last two decades efforts have been directed towards pollution free coatings, as a result of which ultraviolet (u.v.) initiated polymerization has gained significant importance in u.v. curable coating applications[1]. Low molecular weight conventional peroxides have been used as photoinitiators, however, there are hardly any reports on the use of polymeric peroxides as photoinitiators for vinyl polymerization.

Unlike simple low molecular weight peroxides their polymeric counterparts, although long known, have not been sufficiently studied with respect to their initiating characteristics[2,3]. Most of the studies reported to date deal only with the radical initiated thermal polymerization of vinyl monomers[3–7] except for a brief mention on the use of poly(methacrylonitrile peroxide)[8] and polymeric peroxides of dibasic organic acids[9] as photoinitiators for the polymerization of acrylonitrile and oligoester acrylate respectively. Vinyl polyperoxides[2] are attractive candidates as initiators and curatives over acid polyperoxides[3] on the basis of their high solubility in vinyl monomers, safety in handling, economy and simplicity of synthesis. The use of polymeric peroxides as initiators results in the formation of polymers containing peroxy segments in the main chain which may be used to obtain block copolymers.

Here we investigate the use of poly(styrene peroxide) (PSP), an alternating copolymer of styrene and oxygen, as a photoinitiator for methyl methacrylate (MMA) polymerization, the main emphasis being on the kinetics of this process.

EXPERIMENTAL

Materials

Styrene and MMA were freed of inhibitor by washing with 10% NaOH, and they were distilled under vacuum. Di-*tert*-butylperoxide (DTBP) was vacuum distilled. 1,10-Phenanthroline was used as such. Potassium ferrioxalate $K_3Fe(C_2O_4)_3.3H_2O$ was prepared as reported earlier[10]. PSP was prepared as described elsewhere[11]. The solvents used were purified as per standard procedures.

Techniques

Molecular weight of PSP was estimated at 25°C by gel permeation chromatography (g.p.c., Waters ALC/GPC-244, equipped with an RI detector) with THF as mobile phase using polystyrene standards. The number average molecular weight (M_n) of PMMA was obtained using Ubblehode viscometer (in benzene at 30°C) employing the following equation[12]

$$[\eta] = 8.69 \times 10^{-5}\ M_n^{0.76} \qquad (1)$$

The u.v. spectra were recorded on a Hitachi-3400 UV spectrophotometer. ^{1}H nuclear magnetic resonance (n.m.r.) spectra, in $CDCl_3$, were recorded on a Bruker 400 MHz AMX-400 spectrometer with TMS as internal standard. Thermogravimetric analysis (t.g.a.) was done

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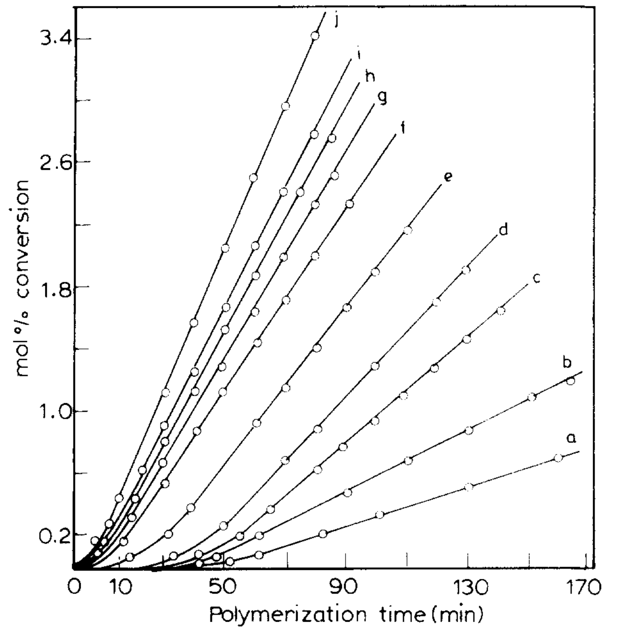

Figure 1 Plot of conversion vs time for the photopolymerization of MMA initiated by PSP, at 30°C; [PSP] = (mol-equiv l^{-1}). (a) = 0.0021; (b) = 0.0054; (c) = 0.0136; (d) = 0.0232; (e) = 0.0335; (f) = 0.0462; (g) = 0.0824; (h) = 0.1220; (i) = 0.1583; (j) = 0.3095

on a Dupont 951 t.g.a. with Dupont TA2000 analyser under nitrogen atmosphere. The gas chromatography-mass spectrometry (g.c.-m.s.). analysis was done on a JEOL JMS-DX mass spectrometer equipped with SE-30 high resolution fused silica capillary column.

Low conversion MMA polymerization

Polymerization kinetics was followed by dilatometric technique[13,14]. For u.v. irradiation a 400 W quartz high pressure mercury vapour lamp (HPMVL) was used with forced air cooling arrangement. The incident light intensity (I_0), in the 300–400 nm region falling on the dilatometer kept at a distance of 17.2 cm from the lamp, was 4.284×10^{-8} einstein l^{-1} s^{-1} as determined by ferrioxalate actinometry[10]. Polymerization was carried out in a constant temperature bath maintained at 30°C. The PMMA was precipitated in hexane and purified by repeated precipitation from acetone/cyclohexane (5/8) mixture and finally dried under vacuum to constant weight. Conversions were kept below 5%. The rate of polymerization (R_p) was determined from the slope (S) of the mole percent conversion (in terms of mm fall in the meniscus height in the dilatometer) vs irradiation time using the following equation[14]

$$R_p = \frac{S \times W \times 1000}{100 \times V \times M} (\text{mol}\, l^{-1}\, s^{-1}) \qquad (2)$$

where V, M and W are, respectively, the volume of the dilatometer in ml (8.65 ml), molecular weight of the monomer and weight of the monomer taken.

The mean polychromatic quantum yield of PSP decomposition (ϕ) in the 300–400 nm wavelength region was determined at 30°C by potassium ferrioxalate actinometry[10].

Table 1 Bulk polymerization of MMA photoinitiated by PSP at 30°C

No.	[PSP] $\times 10^2$ (mol-equiv l^{-1})[a]	$R_p \times 10^5$ (mol l^{-1} s^{-1})	$1/DP_n \times 10^4$	Initiator exponent
1	0.21	1.00	0.66	
2	0.54	1.62	0.90	
3	1.36	2.61	1.29	0.49
4	2.32	3.28	1.62	
5	3.35	4.17	2.00	
6	4.62	4.58	2.08	
7	8.24	5.40	2.24	
8	12.20	5.64	2.26	0.21
9	15.83	5.82	2.28	
10	30.95	7.14	2.89	

[a] 1 mol-equiv is the weight of PSP repeat unit expressed in grams

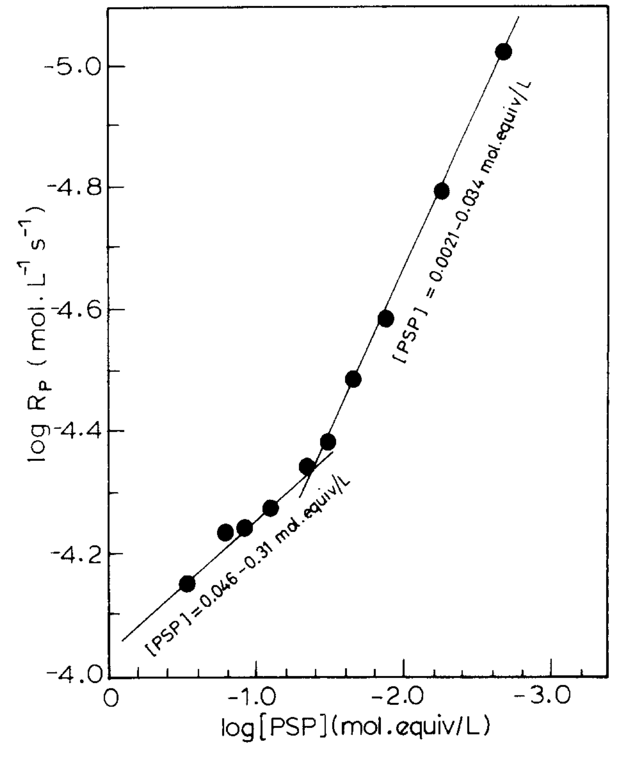

Figure 2 Dependence of R_p on PSP concentration for the photopolymerization of MMA initiated by MMA, at 30°C

RESULTS AND DISCUSSION

The bulk polymerization of MMA using PSP (M_n = 4570) as photoinitiator was carried out at 30°C for various concentrations of PSP (0.0021–0.31 mol-equiv l^{-1}). The mol% conversion–irradiation time plots for MMA polymerization for various concentrations of PSP are given in *Figure 1*. The conversions in the absence of PSP were very low indicating that PSP is the main photoinitiator. The R_p values (after the induction period) were calculated from the initial slopes of *Figure 1*, the results are presented in *Table 1*.

The dependence of R_p on the order of PSP concentration was found to be 0.49 and 0.21 at a PSP concentration of 0.0021–0.034 and 0.046–0.31 mol-equiv l^{-1} respectively. A plot of log R_p *versus* log[I] is given in *Figure 2*. The effect of varying MMA concentration on the R_p at [PSP] of 0.0136, 0.0462 and 0.0824 mol-equiv l^{-1} is given in *Figure 3*. The order with respect to monomer was found to be between 0.95–0.97. The order with respect to the light intensity (I_0) varied between 0.46–0.48 for a [PSP] of 0.0136, 0.0462 and 0.0824 mol-equiv l^{-1} (*Figure 4*).

The kinetic order with respect to MMA and I_0 follows classical photopolymerization kinetics in the

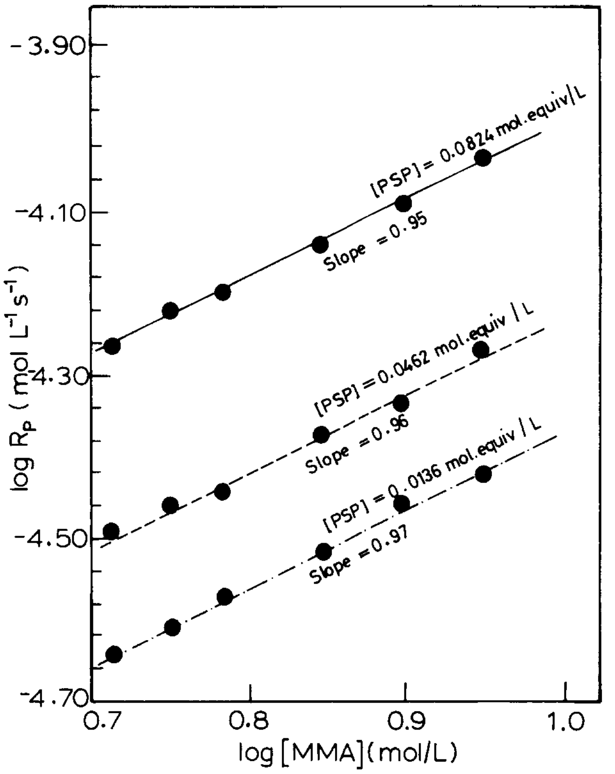

Figure 3 Dependence of R_p on monomer concentration for the photopolymerization of MMA initiated by PSP, at 30°C

concentration range of PSP studied whereas the kinetic order with respect to [PSP] deviates from the normal kinetics at higher concentration of PSP(> 0.046 mol-equiv l^{-1}). From *Figure 2* one can distinguish two regions of PSP concentrations and the corresponding R_p can be written as follows

Case I :

[PSP] = 0.0021–0.034 mol-equiv l^{-1};

$$R_p \propto [I_0]^{0.5}\,[\mathrm{MMA}]^{1.0}\,[\mathrm{PSP}]^{0.49} \qquad (3)$$

In this PSP concentration, the rate equation follows classical kinetics. *Figure 5* shows a linear relationship when the reciprocal degree of polymerization (DP_n) is plotted against $(\mathrm{PSP})^{0.5}$. The global rate constant $k_p/(k_t)^{0.5}$ is obtained from the Mayo plot (*Figure 6*) using the following equation[1,15,16]

$$\frac{1}{DP_n} = \frac{(2-x)k_t R_p}{k_p^2\,[\mathrm{M}]^2} + C_\mathrm{M} + C_\mathrm{I}\frac{[\mathrm{PSP}]}{[\mathrm{M}]} \qquad (4)$$

where x is the ratio of termination by combination to overall termination and has the value of 0.3 for MMA photopolymerization at 30°C[17,18]; the DP_n, [M], C_I and C_M are the degree of polymerization, monomer concentration, chain transfer to initiator and chain transfer to monomer respectively. The value of $k_p/(k_t)^{0.5}$ obtained was 0.0681 $(\mathrm{l\,mol^{-1}\,s^{-1}})^{0.5}$ which compares well with the reported value (0.0658 $(\mathrm{l\,mol^{-1}\,s^{-1}})^{0.5}$) for the azo(bisisobutyronitrile) (AIBN) initiated photopolymerization of MMA at 30°C[1,19,20] where the chain transfer to initiator is negligible. The C_M value (2.2×10^{-5}) obtained from the intercept of *Figure 6* was found to be in good agreement with the reported literature values[1,15,16]. The C_I thus obtained using the modified equation (4), was 2.1×10^{-4}, which is low enough to show that chain transfer to PSP is insignificant.

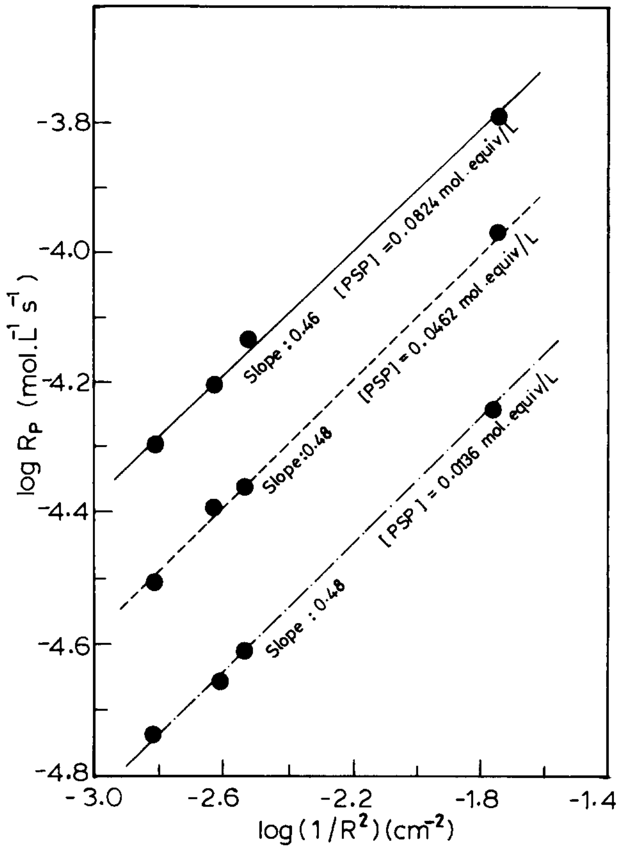

Figure 4 Plot of log R_p vs $1/R^2$ for the polymerization of MMA, at 30°C, using PSP as photoinitiator; R = distance between the lamp and the dilatometer

Case II :

[PSP] = 0.046–0.31 mol-equiv l^{-1};

$$R_p \propto [I_0]^{0.5}\,[MMA]^{1.0}\,[PSP]^{0.21} \qquad (5)$$

Figure 5 shows a linear relationship when the reciprocal of DP_n of PMMA polymers is plotted against $[\mathrm{PSP}]^{0.21}$. This is in good agreement with the R_p dependence on $[\mathrm{PSP}]^{0.21}$. At high concentration of PSP (> 0.046 mol-equiv l^{-1}) the Mayo plot (*Figure 6*) substantially deviates from the corresponding plot for the low [PSP] (case I). The considerable reduction in the initiator exponent indicates that the polymerization kinetics is complex. The plausible reasons for the low initiator exponent are: (i) primary radical decomposition (PRD); (ii) chain transfer to photodecomposition products of PSP; (iii) primary radical termination (PRT).

The occurrence of PRD, the unimolecular decomposition and disproportionation of β-peroxyalkoxy radicals formed by the random scission of the peroxide bond has been reported for PSP even at temperatures below 30°C[21]. In the present case, photodecomposition products namely benzaldehyde, formaldehyde, α-hydroxyacetophenone and phenylglycol[21] were found to form during the photopolymerization of MMA, which accounted for roughly 2% (estimated by the g.c.-m.s. analysis of methanol filtrate) of the PSP taken. The quantity of decomposition products is very low and hence the PRD may not influence the initiator exponent to a large extent. Also there is no variation in the order

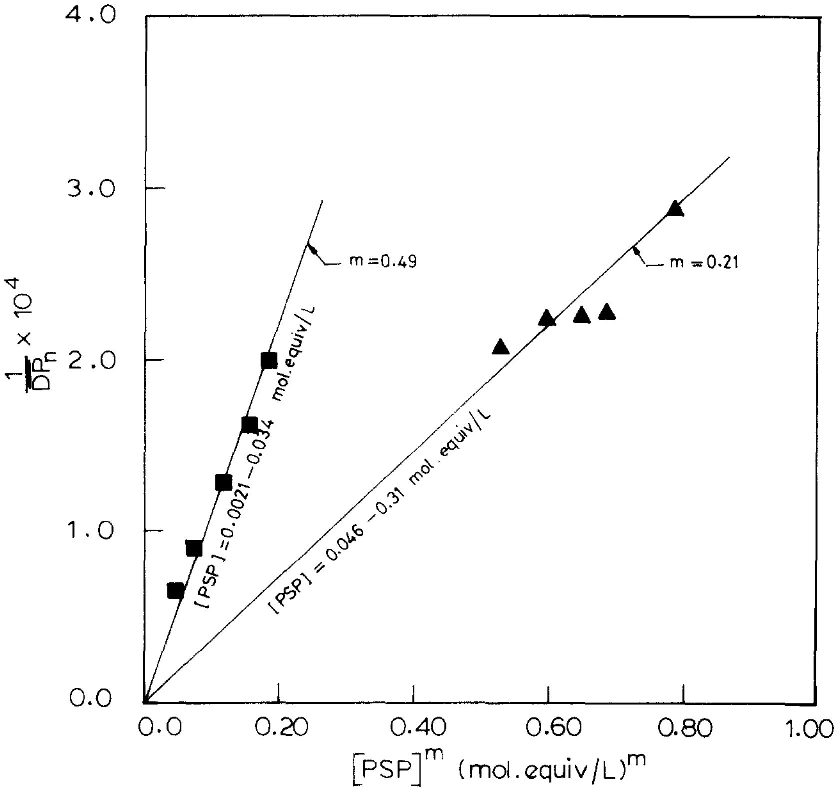

Figure 5 Plot of reciprocal degree of polymerization vs $[PSP]^{0.5}$ and $[PSP]^{0.21}$

with respect to the light intensity in the entire range of [PSP] studied indicating that there is no screening effects due to the formed photodecomposition products. To further check whether the chain transfer involving the photodecomposition products of PSP occurs or not, separate photopolymerization experiments, using PSP as photoinitiator, were carried out in the presence of photodecomposition products. No observable effect of these decomposition products on the R_p and M_n of the resulting polymer was noticed, indicating that the chain transfer to the photodecomposition products is negligible.

Based on the foregoing discussion it therefore appears that PRT plays a major role at high concentration of

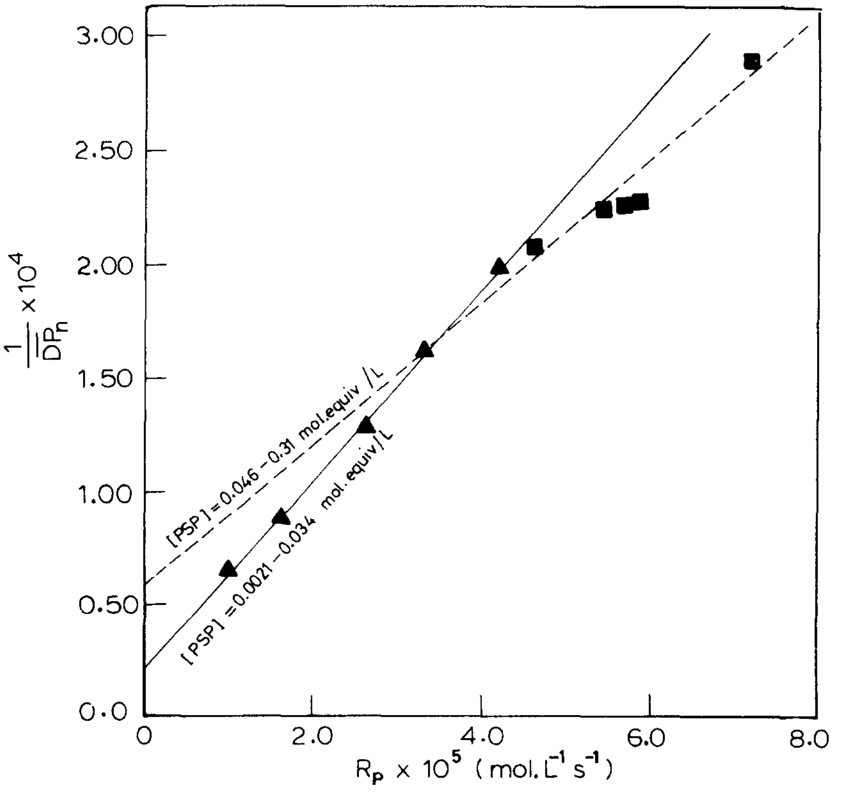

Figure 6 Plot of $1/DP_n$ vs R_p for the polymerization of MMA photoinitiated by PSP, at 30°C

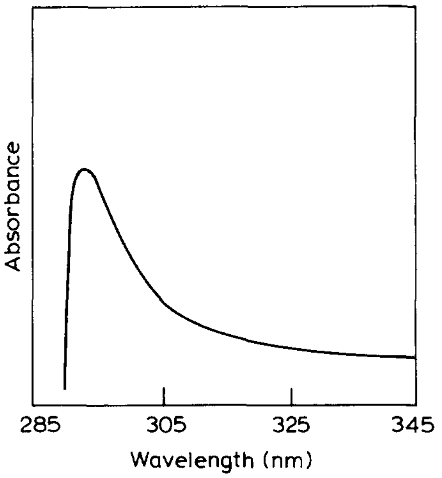

Figure 7 U.v. spectrum of PSP in MMA; [PSP] = 0.016 mol-equiv l^{-1}

Table 2 Absorption characteristics of PSP (in MMA)

Wavelength[a] (nm)	% Transmission	ϵ PSP
300	40	9.50
313	75	5.55
325	87	1.34
365	90	0.05

[a] In a HPMVL the approximate ratio of the intensities of four radiations (300, 313, 325 and 365 nm) is 0.4/0.8/0.5/1.5 (ref. 28); [PSP] = 0.016 mol-equiv l^{-1}

Table 3 Initiator efficiency for the photopolymerization of MMA initiated by PSP

[PSP] × 10^2 mol-equiv l^{-1}	f
0.21	0.061
0.54	0.062
1.36	0.064
2.32	0.060
3.35	0.067

PSP. Currently also it is in vogue that PRT is the main reason for low initiator exponent, and complex kinetics observed at higher initiator concentrations[1,22–27]. It is also likely that PRT is enhanced due to high viscosity encountered at higher [PSP] as normal biradical termination is rendered difficult due to the lower probability of the growing PMMA macroradicals approaching closer to each other. The suppression of bimolecular termination of the growing PMMA radicals is also supported by ^{1}H n.m.r. and t.g. studies, which are discussed under separate headings.

Initiator efficiency

The initiator efficiency (f) of PSP in the concentration range of 0.0021–0.034 mol-equiv l^{-1} was calculated using the following equation

$$2\phi\epsilon lI_0 = \frac{R_p^2 k_t}{[\mathrm{MMA}]^2[\mathrm{PSP}]k_p^2} \qquad (6)$$

where ϕ, ϵ and l are the quantum yield (4.2) for PSP decomposition, molar extinction coefficient and path length (2.5 cm), respectively.

The majority of radiations in the 300–400 nm u.v. region in a HPMVL are 300, 313, 325 and 365 nm[28]. The radiations below 300 nm were cut off by using a pyrex tube and also PSP absorbs negligibly above 365 nm (*Figure 7*). The $I_0\epsilon$ value for PSP in the 300–400 nm region was obtained by considering the percentage transmission and ϵ values for PSP in MMA and from the intensities of these four radiations from the HPMVL lamp[28] (*Table 2*). The efficiency of PSP calculated as above is low and is in the range 0.060–0.067 (*Table 3*). The very low efficiency of PSP is due to the competing unimolecular decomposition involving facile unzipping of the β-peroxyalkoxy radicals[21] with the primary radical initiation in PSP resulting in the decreased rate of initiation (R_i). The initiator efficiency does not vary much with the [PSP] in the concentration range 0.0021–0.034 mol-equiv l^{-1}. At [PSP] > 0.046 mol-equiv l^{-1}, further decrease in the f values is anticipated, due to PRT. It is to be noted that the molecular weight of PSP used is low ($M_n = 4570$) hence invoking the concept of microviscosity[29,30] considered in some polyperoxides to explain the low f values can be ruled out for PSP on energetic grounds[7].

Quantification of primary radical termination

The conventional kinetic scheme excluding chain transfer reactions for the polymerization of MMA using PSP as photoinitiator is given below:

$$\begin{array}{llll}
\mathrm{PSP} & \xrightarrow{h\omega} & \mathrm{RO}^\circ & k_i \\
\mathrm{RO}^\circ + \mathrm{M}^\circ & \longrightarrow & \mathrm{M_1}^\circ & k_i' \\
\mathrm{M_r}^\circ + \mathrm{M}^\circ & \longrightarrow & \mathrm{M_{r+1}}^\circ & k_p \\
\mathrm{M_r}^\circ + \mathrm{M_s}^\circ & \longrightarrow & \mathrm{P_r} + \mathrm{P_s} \text{ or } \mathrm{P_{r+s}} & k_t \\
\mathrm{M_r}^\circ + \mathrm{RO}^\circ & \longrightarrow & \mathrm{P_r} & k_{prt} \\
\mathrm{RO}^\circ + \mathrm{RO}^\circ & \longrightarrow & \text{decomposition products} & k_t'
\end{array}$$

Bamford *et al.*[31] have derived the following rate equation from the above kinetic scheme

$$\frac{1}{R_p} = \frac{\delta}{[\mathrm{M}]^2\Sigma} + \frac{\delta}{(2\phi\epsilon lI_0)^{0.5}}\,\frac{1}{[\mathrm{PSP}]^{0.5}[\mathrm{M}]} \qquad (7)$$

where $\delta = (k_t)^{0.5}/k_p$; $\Sigma = k_i'/\sigma(k_t)^{0.5}$ $\sigma = k_{prt}/k_t$; and δ/Σ is the primary radical termination parameter and is a measure of PRT[31]. The values of δ/Σ and $2\phi\epsilon lI_0$ obtained from the plot of $1/R_p$ *versus* $1/(\mathrm{PSP})^{0.5}$ (*Figure 8*), for a PSP concentration of 0.046–0.31 mol-equiv l^{-1}, using equation (7) are 8.8×10^5 mol s l^{-1} and 3.83×10^{-7} einstein $\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$, respectively. The positive value for the intercept (*Figure 8*) at higher PSP concentrations indicate the occurrence of PRT. The δ/Σ value obtained as above is two orders of magnitude greater than the calculated value (3.537×10^3 mol s l^{-1}) for the photopolymerization of MMA[27] initiated by AIBN, at 30°C, where PRT is almost negligible. A similar plot, for low initiator concentration of PSP (0.0021–0.034 mol-equiv l^{-1}), gave the intercept value as zero indicating the absence of PRT. The δ/Σ and $2\phi\epsilon lI_0$ values obtained as above are in close agreement with the δ/Σ (1.75×10^6 mol s l^{-1}) and $2\phi\epsilon lI_0$ (7.167×10^{-7} einstein $\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$) obtained from the plot of ln $R_p^2/[\mathrm{PSP}][\mathrm{MMA}]^2$ vs $R_p/[\mathrm{MMA}]^2$ as per the Deb and Meyerhoff equation[23].

Characterization of PMMA polymer

The 400 MHz ^{1}H n.m.r. spectrum of PMMA prepared using a PSP concentration of 0.502 mol-equiv l^{-1} is given in *Figure 9*. The weak signals at 7.2, 5.3 and 4.03 ppm, corresponding to the PSP segments[32], were assigned to the aromatic, methine and methylene protons. A weak

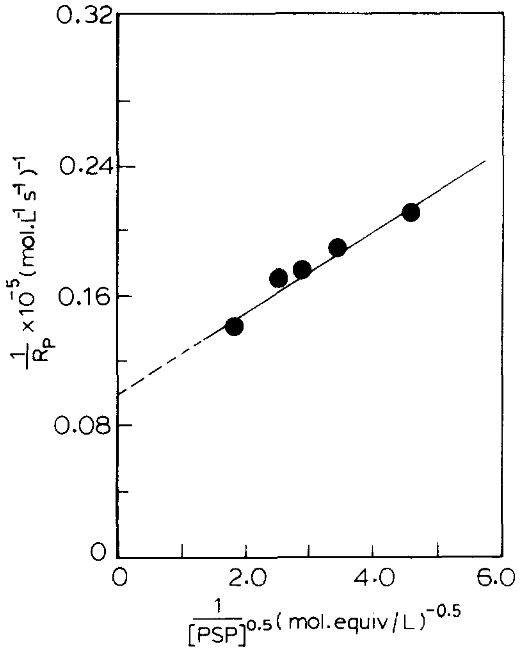

Figure 8 Plot of $1/R_p$ vs $1/[PSP]^{0.5}$ for the polymerization of MMA initiated by PSP, at 30°C

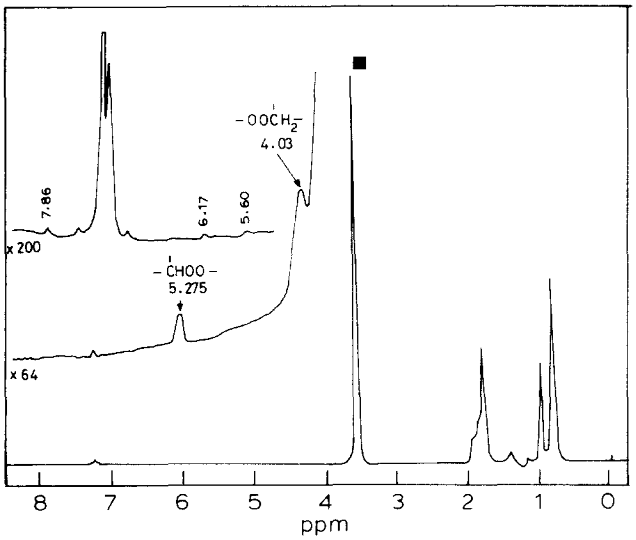

Figure 9 The 400 MHz ^{1}H n.m.r. spectrum of PMMA prepared using a PSP concentration of 0.502 mol-equiv l^{-1}

signal at 7.8–7.9 ppm was assigned to the *ortho* protons of benzoyl (C_6H_5CO) group[32] which is either present in the PSP block in PMMA or formed via the initiation of benzoyl radical formed due to the chain transfer of the growing PMMA radicals to benzaldehyde which is one of the major photodecomposition products.

An interesting observation seen in ^{1}H n.m.r. (*Figure 9*) is that PMMA obtained using PSP photoinitiator showed signals at 5.6 and 6.2 ppm corresponding to terminal vinylic protons[33]. These vinylic protons are as a result of termination of the growing PMMA chains by disproportionation. With decrease in the concentration of PSP from 0.502 mol-equiv l^{-1} to 0.0462 mol-equiv l^{-1} the signal due to the terminal vinylic protons in PMMA increases, the number of vinylidene ends determined from ^{1}H n.m.r. for 1000 MMA units are 0.34 and 0.07 for a PSP concentration of 0.0462 and 0.502 mol-equiv l^{-1} respectively. It seems the proportion of the growing PMMA radicals getting terminated by disproportionation mechanism decreases with increase in the concentration of PSP.

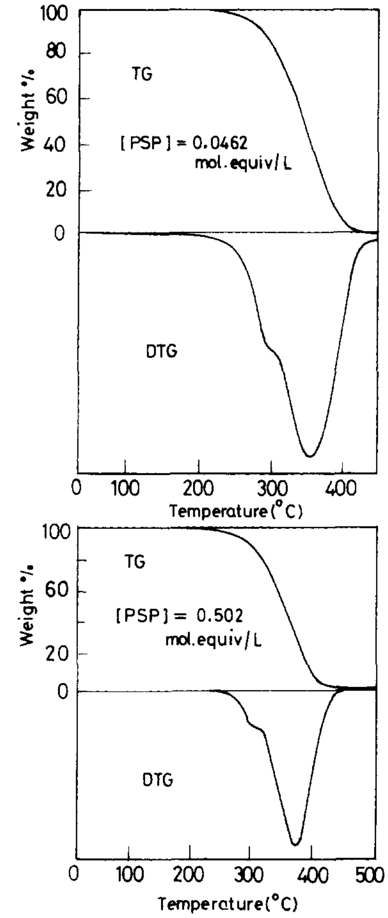

Figure 10 T.g. (thermogravimetric) and d.t.g. (differential thermogravimetric) traces of PMMA, prepared using PSP as photoinitiator, under nitrogen atmosphere (heating rate: 10°C min^{-1})

T.g.a. of PMMA prepared by radical method generally shows a three step degradation[34,35]. The first step occurs at 180°C due to the breakage of the weak head–head link in PMMA formed as a result of termination by combination. The second step at around 275°C is due to the initiation by the vinylic chain end, and the last step around 350°C is due to random scission. T.g. traces of PMMA prepared using two different concentrations of PSP are given in *Figure 10*. We did not see any weight loss due to head–head link in PMMA. Both the samples showed a two step degradation due to vinylic chain end initiation and random scission. However, the ratio of weight loss due to these two steps was found to vary for PMMA prepared using different concentrations of PSP. Further, the ratios were 1/1, 1/3 and 1/8 for PMMA prepared from DTBP, [PSP] = 0.0462 mol-equiv l^{-1} and [PSP] = 0.502 mol-equiv l^{-1}. These ratios substantiate the fact that in the case of PSP initiated photopolymerization of MMA, the termination by disproportonation mechanism is reduced significantly with increase in the [PSP] indicating the occurrence of termination of the growing PMMA radicals with the primary radicals.

CONCLUSION

The polymerization of MMA photoinitiated by PSP follows usual kinetics below a PSP concentration of 0.034 mol-equiv l^{-1}. However at higher PSP concentration (> 0.046 mol-equiv l^{-1}) the initiator exponent reduces drastically (0.21), which has been attributed to primary radical termination. The low efficiency of PSP has been attributed to the competing unimolecular decomposition of β-peroxyalkoxy radicals to non-radical products with the primary radical initiation. The presence of peroxy segments in PMMA, prepared using PSP as photoinitiator, has been confirmed by spectroscopic studies. This 'active' polymer containing peroxy segments can be conveniently used for synthesizing block copolymers.

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