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Similar products but different mechanisms in thermal and photodegradation of vinyl polyperoxides

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Abstract

Vinyl polyperoxides degrade through two competing reactions, they pyrolyze unimolecularly through a chain unzipping process but they photolyze mainly through a disproportionation mechanism involving hydrogen transfer process. Surprisingly, in dilute solutions, we have observed that vinyl polyperoxides such as poly(styreneperoxide), poly(methylmethacrylate peroxide), poly(α-methylstyreneperoxide) and poly(α-phenylstyrene peroxide) photolyze to give the same products which are obtained through the chain unzipping process. Still, the photodegradation mechanism seems to be different than the thermal degradation. While thermal degradation is controlled by the dissociation of the O–O bonds, the photodegradation depends upon the stability of the bialkoxy radicals. The poly(α-phenylstyrene peroxide), however, shows unusual thermal and photostability which has been explained from stable crystalline structure and retarding effect of the degradation product, respectively. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyperoxides; Thermal degradation; Photodegradation

1. Introduction

Vinyl polyperoxides are a unique class of polymers in the sense that they pyrolyze highly exothermally [1,2], in contrast to the common polymers which generally degrade endothermally. They are receiving rejuvenated attention in the wake of some inquiring studies regarding their physicochemical behavior such as, auto-pyrolyzability, auto-combustibility [3] and their role as thermal [4,5], photo [6], base catalyzed [7] initiators and exhibition of unusual auto-accelerating and auto-decelerating kinetics [8–10]. Polyperoxides pyrolyze unimolecularly, above 100°C, through a radical chain unzipping process giving aldehydes and ketones, and to glycols and hydroxy compounds, etc. through a disproportionation process involving hydrogen transfer reactions [11]. Photodegradation of neat polyperoxides occur mostly through the disproportionation mechanism [11]. Surprisingly, in solution photolysis of polyperoxides, mostly, unimolecular decomposition products are formed. In view of the fact that thermal and photodegradation products (in dilute solution) are similar, our aim here is to examine whether their mechanisms are the same or still different. Hitherto, this is the first report on a comparative study of the photo and thermal degradation of polyperoxides.

2. Experimental section

2.1. Materials

The α-methyl styrene (AMS), methyl methacrylate (MMA) and styrene (ST) were freed from the inhibitor and distilled under reduced pressure. The α-phenyl styrene (APS) (97%, Aldrich, USA) was used as received. The Azobis(isobutyronitrile) (AIBN) (Koch Light Laboratories, England) was recrystallised three times from methanol.

2.2. Polymerization and characterization

Poly(α-methyl styrene peroxide) (PMSP), poly(methyl methacrylate peroxide) (PMMAP), poly(styrene peroxide) (PSP) and poly(α-phenyl styrene peroxide) (PAPSP) were prepared by the oxidative polymerization of AMS, MMA, ST and APS, respectively. A typical procedure for the synthesis of PSP is given below. The styrene (25 ml) solution of AIBN (0.1 mol/l) was charged in a stirred Parr reactor (thermostated at 50°C) for 3 h under 100 psi of oxygen pressure. The PSP was precipitated from the reaction mixture, using methanol as a non-solvent. The polymer was purified by repeated precipitation from chloroform

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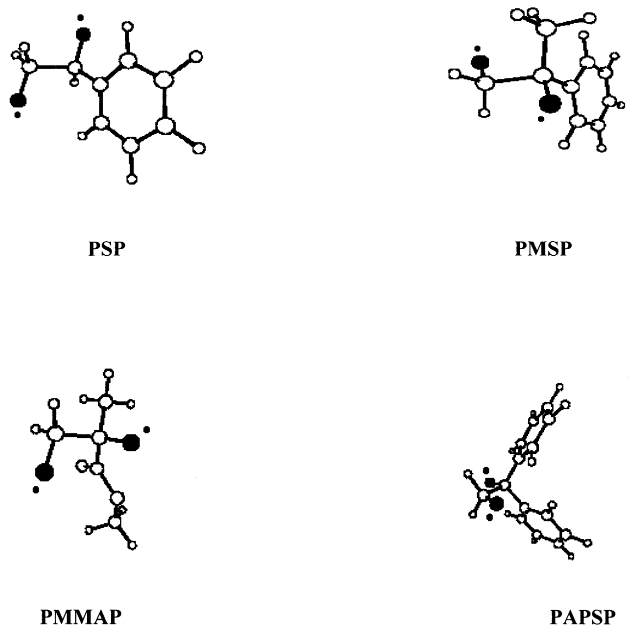


Fig. 1. Optimized structures of the bialkoxy radicals of polyperoxides.

solution and dried under vacuum. Similarly, the PMMAP, PMSP and PAPSP were also prepared.

The 200 MHz ^{1}H NMR spectra were recorded on Bruker AC-F 200 FT NMR spectrometer in $CDCl_3$. The chemical shifts were assigned with respect to tetramethylsilane. The ^{1}H NMR spectrum revealed the formation of an alternating copolymer (i.e.1:1 stoichiometry) of vinyl monomer unit and oxygen [4,12–15]. No homopolymer impurities were detected within the accuracy of the NMR instrument.

2.3. Glass transition temperatures

Glass transition temperatures (T_gs) were determined using Rheometric scientific DSC + instrument. The instrument was calibrated with Indium, Tin and Lead standards. 3 ml/min nitrogen purged was maintained during measurements. An amount of 10 mg of each sample was loaded, and rapidly cooled to −80°C then it was heated at a heating rate of 10°C/min.

2.4. Thermal degradation

Thermal degradation studies were carried out on a Dupont differential scanning calorimeter (DSC) model 910, and Dupont thermogravimetric (TG) analyzer model 951. In dynamic DSC, polyperoxide samples of 1–2 mg were heated at a rate of 10°C/min in open aluminum pans under nitrogen atmosphere. The temperature axis was calibrated using indium. Dynamic TG (3°C/min) and isothermal TG thermograms are obtained with a 10 mg sample.

2.5. Photodegradation

For photolysis, a 400 W quartz high pressure mercury lamp, with forced air cooling, was used. Since O–O chromophore absorbs in the region 280–310 nm [16], ultra violet (UV) radiation was used for photodegradation. The polyperoxide sample in neat form as well as in $CDCl_3$ solution (0.1 mol/l) were taken in 5 mm quartz NMR tubes which were irradiated by keeping the tube at a distance of 20 cm, away from the center of the mercury lamp. The photolysis was carried out at room temperature (30°C). The NMR tubes were removed at regular intervals of time and ^{1}H NMR spectra recorded. The concentrations of the degradation products were obtained from the peak area of the selected signals.

3. Computational methods

The geometry of the bialkoxy radicals were fully optimized using AM1 Hamiltonian and PECI = 8 formalism [17–19]. The optimized structures were used in configuration interaction calculations that included single and pair excitations involving eight molecular orbitals spanning the frontier orbitals. The degenerate sets of molecular orbitals were fully included in each bialkoxy radical. Heat of formations (ΔH_f^0) of the bialkoxy radicals of polyperoxides, in their optimized structures, are listed in Table 3 and their optimized structures are given in Fig. 1.

Table 1
Thermal degradation data and glass transition temperatures (T_gs) of vinyl polyperoxides

Polyperoxide	E_d (kcal/mol)	E_a (kcal/mol)	Temperature ($T_{1/2}$, (K)) at 50% weight loss	Isothermal degradation rate at 85°C (wt.%/min)	T_g (K)
PMSP	33 ± 2	35.0 (Ref. [4])	374.7	0.48	264.4
PMMAP	38 ± 2	38.0 (Ref. [14])	403.5	0.20	228.9
PSP	41 ± 2	38.2 (Ref. [23])	420.7	0.16	278.9
PAPSP	45 ± 2	45.0 (this work)	444.0	0.09	312.8

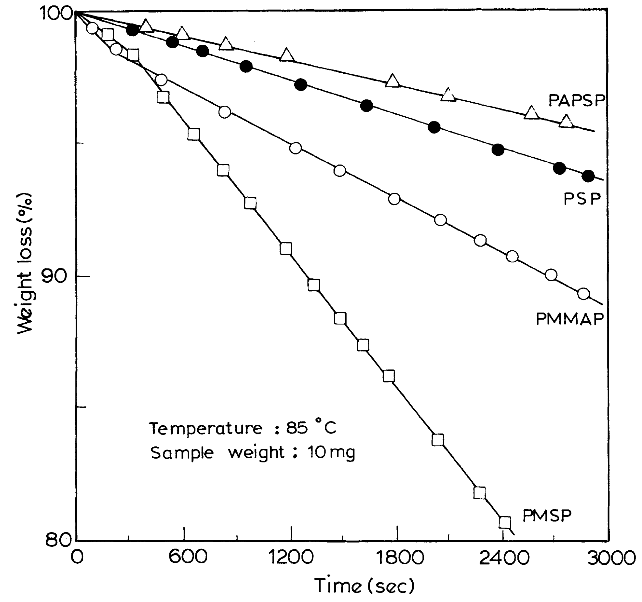


Fig. 2. Isothermal TG thermograms of PAPSP, PMSP, PMMAP and PSP at 85°C.

4. Results and discussion

4.1. Properties of polyperoxides

4.1.1. Alternating nature and molecular weights

The polyperoxides are alternating copolymers of vinyl monomers and oxygen [4,12–15]. Typically, their molecular weight are low (4000–8000) [4,15,20], due to facile degradation and chain transfer reactions [20,21].

4.1.2. Glass transition temperatures and peak temperatures

Glass transition temperature is the characteristic property of an amorphous polymer. The T_gs for various polyperoxides are given in Table 1. We did not notice melting temperatures (T_m) of the polyperoxides. It has been well established from this laboratory that degradation of polymers take place at their peak temperatures (T_m) [3,4,14,15]. So, all the polyperoxides discussed here are amorphous in nature except PAPSP, which is a semicrystalline powder as confirmed by X-ray diffraction analysis [15].

4.2. Thermal degradation

Thermal degradation of various polyperoxides has been studied in this laboratory from DSC. The DSC thermograms of the polyperoxides show a very neat and smooth exotherms, which suggest that the mechanism of degradation is unique and it is devoid of any side reactions. From the data collected on the peak temperatures at various heating rates activation energy (E_a) for the thermal degradation of various polyperoxides were calculated using Kissinger's method [22]. The results are summarized in Table 1.

The E_a values in all these polyperoxides were assigned to O–O bond dissociation energy. Thermal stability of various polyperoxides could be compared from E_a. Lower the E_a values, higher would be the rate of thermal degradation. Since Kissinger's method involves multiple dynamic thermograms, it was thought to verify the thermal degradation mechanism from a more reliable isothermal degradation mode. The polyperoxides, under isothermal conditions, show a continuous weight loss with time, without any steps, suggesting a unique mechanism without any side reactions. Fig. 2 shows the isothermal TG thermograms of various of vinyl monomer unit and oxygen, which is in time. The rates of isothermal degradation and the E_a values both follow the following trend for the thermal stability of various polyperoxides:

$$\text{PAPSP} > \text{PSP} > \text{PMMAP} > \text{PMSP} \qquad (1)$$

This suggests that the results obtained from dynamic and isothermal thermal analyses are concordant.

Since thermal degradation involves O–O bond dissociation as the rate controlling step, it was thought to verify the same by calculating bond dissociation energy from the thermal data. From the dynamic TG runs, temperatures corresponding to 50% degradation ($T_{1/2}$, in °C) were obtained. By using the following empirical relationship [24] the bond dissociation energies (E_d) for polyperoxides were calculated

$$T_{1/2} = 5.75E_d + 185 \qquad (2)$$

The $T_{1/2}$ and the E_d values are given in Table 1. Small differences in the E_d values in polyperoxides may be due to the structural factors. It is expected that lower the E_d, faster would be the rate of thermal degradation. It may be seen that E_d values (Table 1), correspond to the O–O bond dissociation energies of the polyperoxides, and these values are quite comparable with the E_a obtained from the Kissinger's method. This reassures that the activation barrier in the thermal degradation of the polyperoxide is the O–O bond dissociation energy. Obviously, higher the O–O bond dissociation energy more stable would be the polyperoxide. The relative stability of the polyperoxides, based on E_d values, was also found to follow sequence (1). The E_d and E_a values of PAPSP are very high suggesting that PAPSP is highly thermally stable compared to other polyperoxides.

4.3. Photodegradation

Photodegradation studies on polyperoxides are very few. In addition to a brief mention by Mayo et al. [11] some studies have been carried out in this laboratory [6]. Photodegradation studies in the present investigation were carried out in ^{1}H NMR quartz tube itself in $CDCl_3$ solvent by irradiating it with UV at room temperature (30°C). The ^{1}H NMR spectra of the photodegraded PSP in $CDCl_3$ at different times of UV irradiation are shown in Fig. 3, the assignments of the spectra are: undegraded PSP [4.0 ppm for $-CH_2-$, 5.3 for $\rangle CH-$ and 7.2 (multiplet) for aromatic

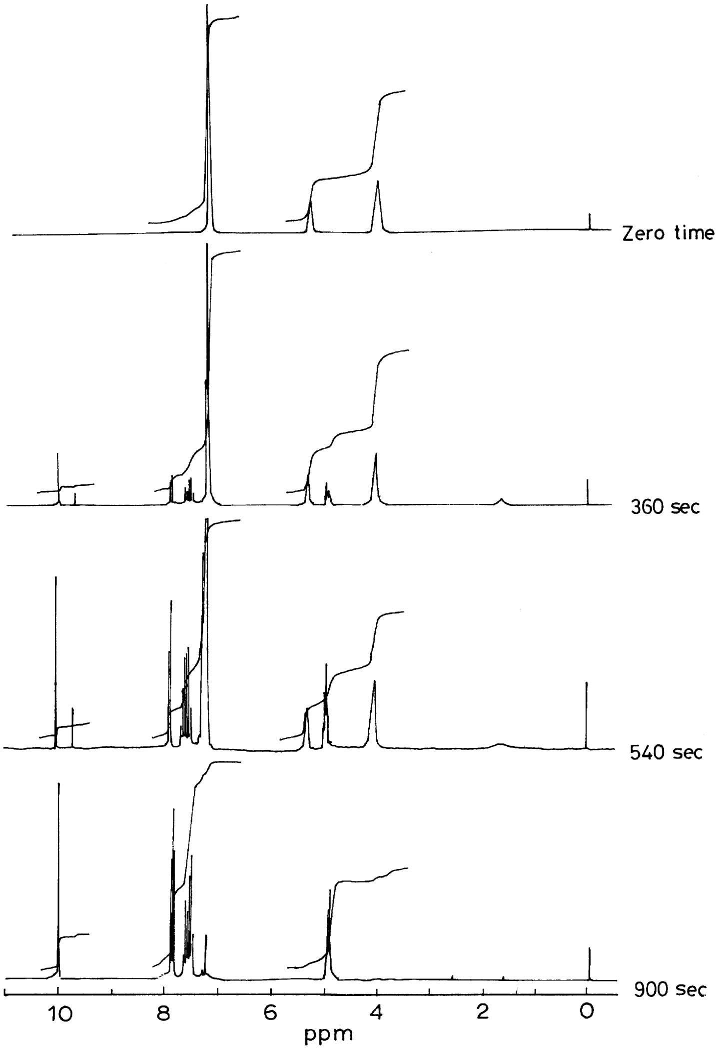
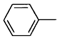


Fig. 3. ^{1}H NMR spectra of PSP in $CDCl_3$ at different times of UV irradiation.

protons]; benzaldehyde [10.0 ppm for –CHO and 7.6–7.9 (multiplet) for aromatic protons] and paraformaldehyde [4.9 ppm (multiplet)]. The ^{1}H NMR assignments of the photodegraded products of various polyperoxides are summarized in Table 2. Major photolysis products (>95%) of polyperoxides in a dilute solution, in the present investigation, were found to be the unimolecular decomposition species. In unimolecular decomposition, which is a

Table 2
The ^{1}H NMR assignments of the photodegradation products of polyperoxides

	NMR absorption[a], in ppm units					
	–CH_2–	⟩CH–	–	–CH_3	–$COOCH_3$	–CH=O
PSP	4.03 (s)	5.31 (s)	7.20–7.30 (m)			
PMSP	4.43 (s)		6.91–7.26 (m)	1.56 (s)		
PMMAP	4.35 (s)			1.46 (s)	3.76 (s)	
PAPSP	4.61 (s)		6.74–7.26 (m)			
Benzaldehyde			7.50–7.91 (m)			10.02 (s)
Acetophenone			7.43–7.99 (m)	2.62 (s)		
Methyl pyruate				2.49 (s)	3.88 (s)	
Benzophenone			7.45–7.83 (m)			
Paraformaldehyde	4.71–5.01 (m)					

[a] Multiplicity is indicated by s for singlet and m for multiplet.

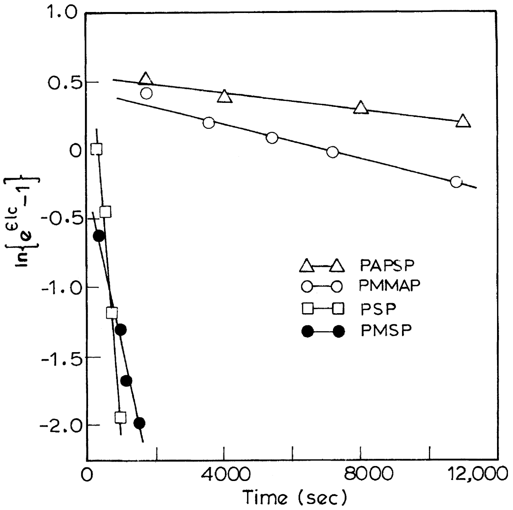


Fig. 4. The plot of $\ln(e^{\varepsilon lc} - 1)$ against time (t) for PAPSP, PMMAP, PMSP and PSP.

chain unzipping process, the macro alkoxy radicals undergo scission at a bond β to the radical center forming carbonyl compounds and formaldehyde. The carbonyl compounds of PSP, PMSP, PMMAP and PAPSP are benzaldehyde, acetophenone, methylpyruvate and benzophenone, respectively. Disproportionation products (glycols, hydroxy compounds, etc.) were not observed, probably their concentrations were too low to be detected within the sensitivity of the NMR instrument.

4.4. Photodegradation rate and quantum yield

The rate of photolysis [25,26] of O–O bonds can be represented as

$$\frac{dc}{dt} = \phi I_0(1 - e^{\varepsilon lc}) \tag{3}$$

where c is the concentration of the O–O chromophore, ϕ the quantum yield of photodegradation, I_0 the incident UV intensity, ε the absorption co-efficient of the O–O chromophore and l is the effective path length of the UV in the reaction vessel. Eq. (3) was simplified to obtain ϕ, it was integrated by taking $\varepsilon l = a$, $\phi I_0 = A$ and $y = e^{-ac}$, we get

$$\frac{y}{1-y} = B\,e^{aAt}; \qquad B = \frac{e^{-ac_0}}{1 - e^{-ac_0}} \tag{4}$$

where c_0 is the initial concentration of the O–O chromophore. Eq. (4) was further simplified in the following form

$$\ln(e^{ac} - 1) = -Ata - \ln B \tag{5}$$

By plotting $\ln(e^{ac} - 1)$ against time (t), one could obtain ϕ from the slope. The plots are shown in Fig. 4. Here I_0 was obtained by using potassium ferric oxalate actinometry [16], its value was 2×10^{16} quanta per second.

The ϕ values for all the polyperoxides are given in Table 3. From I_0 and ϕ values, the rate of photodegradation from Eq. (3) could also be obtained. The rate of photodegradation is proportional to ϕ. The ϕ values and the rates of photodegradation for various polyperoxides follow the following order:

$$\mathrm{PSP} > \mathrm{PMSP} > \mathrm{PMMAP} > \mathrm{PAPSP} \tag{6}$$

The unusually high value of ϕ (>1) for the PSP and PMSP photolyses is due to the fast unimolecular dissociation of the corresponding bialkoxy radicals. The higher ϕ-value of PSP shows that the dissociation reaction of PSP is faster than PMSP. Since ϕ is less than unity for PMMAP and PAPSP it shows that there is very slow dissociation of PMMAP and PAPSP alkoxy radicals and that these two polyperoxides are highly stable photolytically compared to PSP and PMSP.

To further quantify the relative stability of polyperoxides, the heat of formation ΔH_f^0 of the bialkoxy radicals of the polyperoxides were calculated. The results are shown in Table 3. The stability of the alkoxy radicals follow the following order:

$$\mathrm{PMMAP} > \mathrm{PMSP} > \mathrm{PSP} > \mathrm{PAPSP} \tag{7}$$

The quantum yields and the rates of photodegradation are consistent with the stability of the bialkoxy radicals only for three polyperoxides: PMMAP,PMSP and PSP. In PAPSP the bialkoxy radical is highly unstable and yet PAPSP is highly photostable amongst other polyperoxides. The unusual photostability of PAPSP is discussed below.

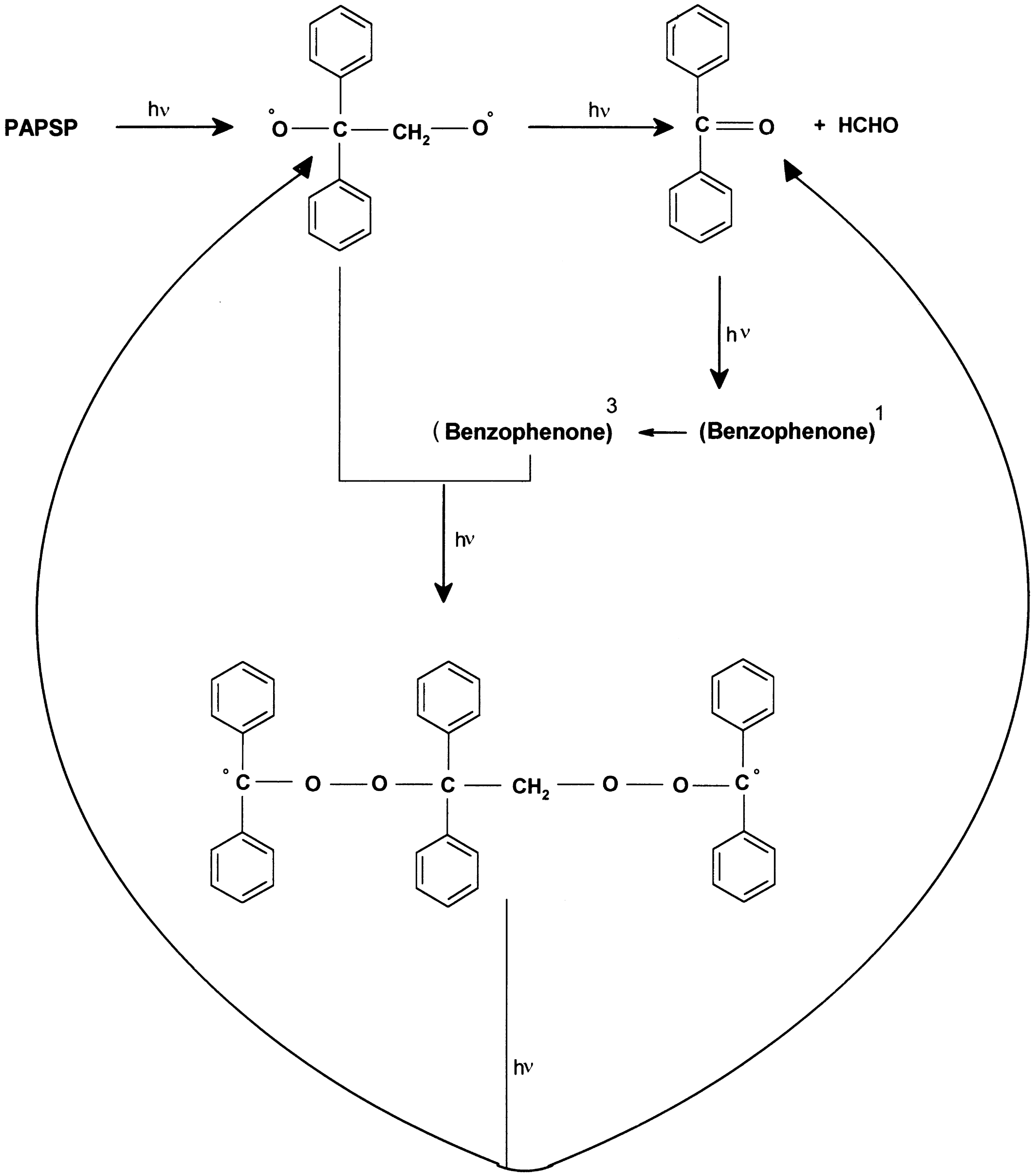
Table 3
Photodegradation data of vinylpolyperoxides

Polyperoxide	ε (in $CHCl_3$ at 300 nm) (l/mol cm)	ϕ	ΔH_f^0 (kcal/mol)	Rate of photodegradation at 30°C (mol/l/min)
PAPSP	10.0	0.12	+ 72.0	1.1×10^{-5}
PMMAP	12.2	0.17	− 72.5	9.2×10^{-5}
PMSP	8.5	3.50	+ 28.0	4.2×10^{-3}
PSP	9.5	9.20	+ 32.0	1.2×10^{-2}

4.5. Unusual photostability of PAPSP

The unusual photostability of PAPSP could arise on account of the retarding effect of the degradation products which gets accumulated during the photodegradation process. On photodegradation PAPSP forms benzophenone as the major product. The benzophenone absorbs light in the same region as that of the peroxide group. Besides, the extinction co-efficient of the benzophenone is much higher than the peroxide group. Since benzophenone is a UV filter, it preferentially absorbs more UV light than the peroxide groups, consequently it retards the photodegradation of PAPSP. For further quantification, the photodegradation of PAPSP was also carried out in the presence of benzophenone.

An amount of 9.16 mmol/l of benzophenone was added in the $CDCl_3$ solution of PAPSP (0.14 mol/l). The photodegradation was carried out at room temperature (27°C) for 9 h.



Scheme 1.

The rate of photodegradation in absence and presence of benzophenone were found to be 3.5×10^{-4} mol/l and 2.3×10^{-4} mol/l, respectively. It shows that benzophenone retards the photodegradation of PAPSP. Under photo-conditions all the peroxide bonds in PAPSP degrade instantaneously forming the bialkoxy radicals that further dissociate to benzophenone and formaldehyde. The retarding action of benzophenone on the photodegradation of PAPSP can be explained in yet another way.

The benzophenone is a well-known photosensitizer and it would instantaneously form the corresponding biradical as shown in Scheme 1 (photodegradation of PAPSP). The reaction of benzophenone biradical with the bialkoxy radical is a relatively low energy process. The radical recombination product is a macro carbon centered biradical as shown in Scheme 1. This carbon-centered biradicals would be relatively more stable than the bialkoxy radicals because they are tertiary radicals and also they are stabilized by resonance due to the presence of adjacent aromatic rings. Besides, these carbon-centered radicals are far separated from each other. These carbon centered radicals would eventually dissociate to give the bialkoxy radicals but this would be a slow process and that is why the photodegradation of PAPSP is slowed down in the presence of benzophenone.

4.6. Comparison of thermal and photostabilities of various polyperoxides

The inequalities in the relative stability of polyperoxides under thermal and photo-conditions are shown in Tables 1 and 3. The thermal and photostability follow different trends which indicates that the thermal and photodegradation mechanisms are different in polyperoxides. Interestingly, photodegradation in solution as well as thermal degradation in bulk or neat form give the same products. Whereas thermal degradation is controlled by the O–O bond dissociation as the rate controlling step as discussed above, the photodegradation on the other hand would not involve O–O bond dissociation as the rate controlling step simply because all the O–O bonds will be instantaneously degraded in the presence of UV light. Hence, the stability of the resulting bialkoxy radicals, which further dissociate to stable products like aldehyde/ketones, would become the rate-controlling step. The stability of the corresponding bialkoxy radicals of various polyperoxides in terms of ΔH_f^0 (Table 3) follow the same trend as the photostability of the polyperoxides except for PAPSP. The unusual photostability of PAPSP has been discussed in the previous section.

4.7. Unusual thermal stability of PAPSP

The unusual thermal stability of PAPSP is rather surprising because the corresponding bialkoxy radical is highly unstable and one ought to get the fastest thermal degradation for PAPSP as compared to other polyperoxides. But PAPSP is highly thermally stable. It may also be noted that PAPSP is the only polyperoxide that is crystalline and the rest are amorphous. The high crystallinity of PAPSP perhaps imparts unusual thermal stability to PAPSP.

5. Conclusions

Thermal degradation in bulk, and photodegradation of polyperoxides in solution, produce the same products but they give a different order in the rate of thermal and photodegradation suggesting that the rate controlling processes are different in these two modes of degradation. While thermal degradation basically depends upon the dissociation of O–O bond, the photodegradation in solution is controlled by the stability of the bialkoxy radicals. Presence of crystalline domains, and influence of its own degradation products on the thermal and photodegradation, respectively, seems to be significant in imparting unusual thermal and photostability to PAPSP. Polyperoxides are perhaps the unusual and rare class of polymers where such a behavior is observed, i.e. in spite of products of thermal and photodegradation being same their mechanisms are still very different.

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