

NOTE

Synthesis, Spectral Characterization, and Thermochemical Studies of Poly(phenyl methacrylate peroxide)

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INTRODUCTION

Radical polymerization in the presence of oxygen known as oxidative polymerization results in the formation of low-molecular-weight products with oxygen-containing functional groups (aldehydes, ketones, etc.) in addition to copolymers with oxygen.¹ The features of the simultaneous occurrence of polymerization and oxidation have been the subject of numerous investigations, and it has led to the establishment of oxidative polymerization as an independent field of radical-chain polymerization.

Since the first report on polyperoxide by Staudinger² in 1925 only a small number of polymers belonging to this class have been characterized.^{3–6} Of these polymers, poly(styrene peroxide) (PSP), first reported by Bovey and Kolthoff,⁷ has received considerable attention.^{8–16} Polyperoxides find applications as polymeric initiators,^{16–18} in preference to conventional simple peroxides, to obtain homopolymers, block copolymers, and novel comb polymers and as curators in coating and molding.¹⁹ Recently, PSP has been shown to behave as a unique autocombustible polymer fuel, its combustion being controlled by degradation.¹⁵ The property of autopyrolysis by these polymers is a result of their unusual and highly exothermic heats of degradation.

Early work before the 1960s dealt with the mechanism and kinetics of the oxidative polymerization of vinyl monomers.^{3–6} The spectral characterization of polyperoxides was initiated by Cais and Bovey²⁰ in 1977. However, only a few polyperoxides have been spectroscopically characterized so far.²¹ Interestingly, poly(phenyl methacrylate peroxide) (PPMAP), another member of this class of polymers, reported by Razuvaev et al.,²² has not been characterized by spectroscopic methods. As an autocombustible polymer fuel, it is also of particular interest for studying the degradation behavior of polymeric peroxides. Hence, in the report on the present investigation, spectroscopic studies of the alternating copolymeric structure of PPMAP are discussed. Further, thermal degradation has been studied in detail. The study of

the mechanism of primary exothermic degradation was supplemented by thermochemical calculations.

EXPERIMENTAL

Materials

Phenyl methacrylate (PMA; Lancaster, England) was freed from inhibitor by washing it with 5% NaOH and then with water several times. After drying over anhydrous Na₂SO₄, it was distilled under reduced pressure. 2,2'-Azobis(isobutyronitrile) (AIBN; Koch-Light, England) was recrystallized twice from methanol. The oxygen used was of high purity. The solvents were purified by standard procedures.

Measurements

The FTIR spectrum was recorded on a Bruker Equinox 55 FTIR spectrometer. The polymer was taken as thin film cast from CHCl₃ solution on the KBr plates and the spectrum was recorded at room temperature. The 200-MHz ¹H-NMR spectrum was recorded on a Bruker AC-F 200 FT NMR spectrometer in CDCl₃. Chemical shifts were assigned with reference to tetramethylsilane (TMS). The ¹³C-NMR spectrum (50.12 MHz) was recorded in the same spectrometer using CH₂Cl₂ as solvent (D₂O external lock). The molecular weight of the polyperoxide was obtained using a Waters ALC/GPC 224 instrument with THF as a mobile phase at 30°C, using polystyrene as standard.

Thermal analysis was made using a Perkin-Elmer DSC-2C differential scanning calorimeter (DSC) under nitrogen atmosphere at heating rates of 5°C, 10°C, 20°C, 40°C, and 80°C/min with a sample size of 1–5 mg. Thermogravimetric analysis (TGA) was accomplished on a Mettler Toledo TGA 850 instrument under a nitrogen atmosphere at a heating rate of 10°C/min with a sample weight of 11.2 mg.

Computational methods

The well-documented commercial software packages Insight II[®] and the semiempirical program package Ampac/Mopac (version 6.0) from Biosym Technologies,²³ were used for the calculation of heats of formation (ΔH_f°). The Insight II[®] code assigns an empirical potential energy function to each atom from the central valence force field (cvff) depend-

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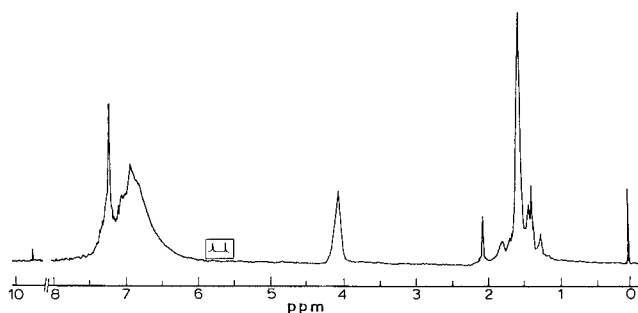


Figure 1 $^1\text{H-NMR}$ spectrum of PPMAP in CDCl_3 (inset: peak at 5.86 ppm are expanded 10 times).

ing on the element type and the nature of the chemical bond. Further, this code has been benchmarked for numerous other molecular systems and its accuracy documented in the literature. The geometry of all the compounds was fully optimized using AM1 Hamiltonian.^{24,25}

Polymerization

PMA was oxidatively polymerized by charging a solution of 2.78×10^{-3} mol/L PMA and AIBN (0.02 mol/L) in benzene in a Parr reactor equipped with stirrer (Parr Instrument Co., Moline, IL) and thermostated at $50 \pm 0.5^\circ\text{C}$ for 72 h under oxygen pressure of 200 psi using a procedure described elsewhere.¹⁹ PPMAP was separated from the reaction mixture by precipitating it with petroleum ether and purified by repeated precipitation followed by removal of the solvent by vacuum-drying. PPMAP was obtained as a white sticky material. The yield of PPMAP was found to be 16%.

RESULTS AND DISCUSSION

Molecular weight

The number-average (\bar{M}_n) and weight-average (\bar{M}_w) molecular weights of PPMAP were found to be 1743 and 2170, respectively. Generally, vinyl polyperoxides have a low molecular weight²⁶ ($\bar{M}_n = 300\text{--}5000$) because of various chain transfer reactions occurring during oxygen copolymerization. A detailed examination of the mechanism of formation revealed that this category of polymers undergo facile degradation during polymerization, generating chain transfer agents such as aldehydes, which react with macro growing radicals, resulting in a low molecular weight.

$^1\text{H-NMR}$ spectra

The $^1\text{H-NMR}$ spectrum of PPMAP is given in Figure 1. The signals at δ 1.48, 4.15, and 6.4–7.4 ppm are assigned to the methyl, methylene, and aromatic protons, respectively. The methyl signal is not shifted, whereas the methylene signal is shifted considerably downfield because of the two oxygen atoms directly attached to it. No homopolymer impurities can be detected from the NMR spectrum. All the groups present simple first-order spectra. The methyl and methylene protons constitute the A_3 and A_2 spin systems, respectively. As in the case of other vinyl polyperoxides, here, too,

the molecular weight and the end groups are determined by chain transfer reactions. In PPMAP, as in poly(methyl methacrylate peroxide),²⁷ the chain begins with $\text{HO}_2\text{—CH}_2\text{—C}(\text{CH}_3)(\text{COOC}_6\text{H}_5)=$ and $\text{O=CH—O—O—C}(\text{CH}_3)(\text{COOC}_6\text{H}_5)\text{—}$ groups and terminates with $\text{—CH=C}(\text{CH}_3)(\text{COOC}_6\text{H}_5)$ groups. Thus, the major terminating group in PPMAP is the unsaturated chain end. This is clearly reflected in the $^1\text{H-NMR}$ spectrum of PPMAP. The peak at δ 5.86 ppm (doublet) corresponds to the $\text{O}_2\text{—CH}^*=\text{C}(\text{CH}_3)(\text{COOC}_6\text{H}_5)$ proton and the peak at δ 9.8 ppm to the $\text{O=CH}^*\text{—O—O—C}(\text{CH}_3)(\text{COOC}_6\text{H}_5)\text{—}$ proton.

$^{13}\text{C-NMR}$ spectra

The $^{13}\text{C-NMR}$ spectrum (Fig. 2) exhibits signals corresponding to the four carbon atoms present in the repeat unit. The signals at δ 18.5, 76.1, and 82.9 ppm are assigned to the methyl, methylene, and quaternary carbon atoms, respectively. The aromatic carbon atom bonded to oxygen gives a signal at 151.4 ppm, whereas the ortho, para, and meta carbons resonate at 121.7, 125.7, and 129.4 ppm, respectively. A considerable downfield shift of the methylene and the quaternary carbon results from the two electronegative oxygen atoms bonded to it. The peak at 166.6 ppm is assigned to the carbonyl groups present in the repeating unit.

FT-IR spectra

The FT-IR spectrum of PPMAP is shown in Figure 3. The strong band near 1047 cm^{-1} is assigned to the peroxide (—O—O—) bond stretching. The intense band at 1128 cm^{-1} results from the C—O stretch. The bands appearing in the region, $2925\text{--}3030\text{ cm}^{-1}$ are assigned to the aliphatic and aromatic C—H stretching modes. The broad absorption centered at 3500 cm^{-1} is attributed to the hydroxyl and hydroperoxide end groups. The formation of these end groups via various chain transfer mechanism is known.²⁷ The very intense band appearing at 1744 cm^{-1} is assigned to the carbonyl groups present in the repeat unit. Other carbonyl groups present in the different end groups also show infrared absorption in this region, and hence they are not distinguishable. The weak absorption band at 1600 cm^{-1} is a result of the stretching of the C=C group present in the terminating group. The major terminating group is

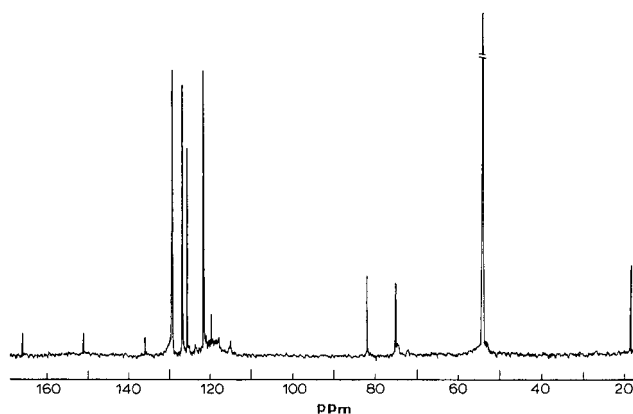


Figure 2 $^{13}\text{C-NMR}$ spectrum of PPMAP in CH_2Cl_2 .

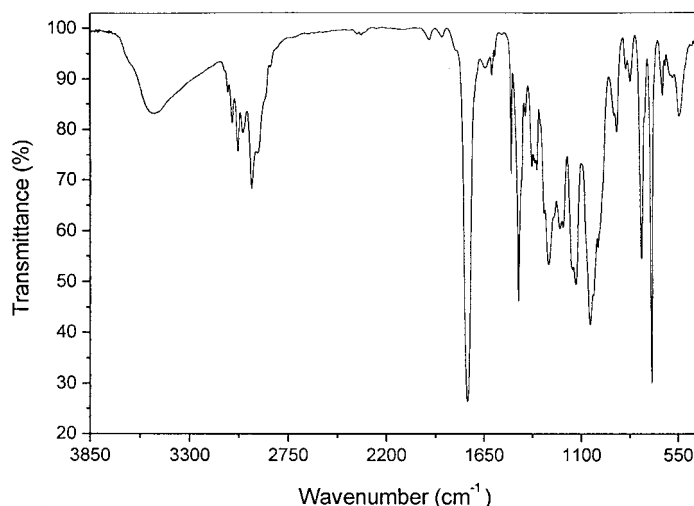
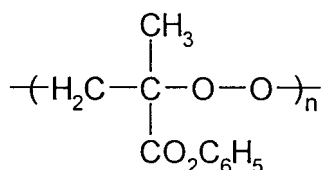


Figure 3 FT-IR spectra of PPMAP.

—CH=C(CH₃)(COOC₆H₅), as in poly(α -methylstyrene peroxide).^{27,28}

Based on the above discussion, the general structure of PPMAP can be given as



Thermal degradation

The DSC studies were carried out at heating rates of 5°C, 10°C, 20°C, 40°C, and 80°C min⁻¹. A typical thermogram is given in Figure 4. The studies reveal a highly exothermic degradation of PPMAP. The ΔH_f^0 of the compounds studied here in their optimized structure are listed in Table I. The

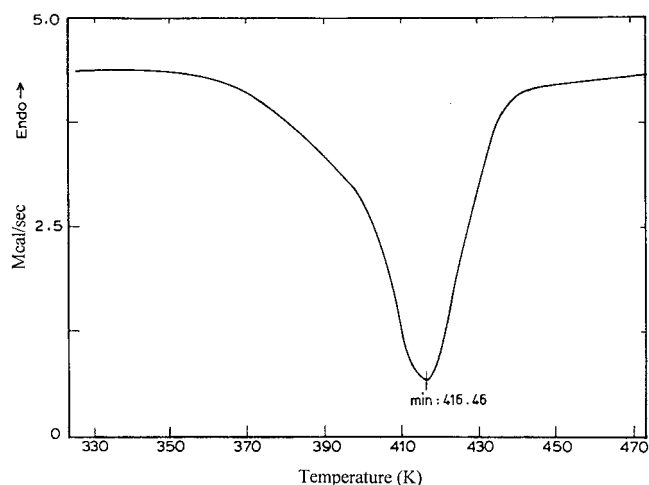


Figure 4 DSC thermogram of PPMAP at a heating rate of 10°C/min.

enthalpy of degradation, ΔH_d^0 (the mean area under the exotherm at various heating rates), was calculated using the data given in Table I and was found to be -48.6 ± 2 kcal mol⁻¹, after applying a correction for the heat of vaporization (ΔH_v^0) of formaldehyde. The ΔH_v^0 for formaldehyde has been reported²⁹ as 5.90 kcal mol⁻¹. Because of the similarities between PPMAP and PSP in the heat of degradation, it is likely that PPMAP also shows auto-pyrolyzability and auto-combustibility, although no studies in this regard have been reported.

A Kissinger's plot³⁰ of $\ln \phi/T_m^2$ versus $1/T_m$, where ϕ denotes the heating rate and T_m the peak temperature in the DSC thermogram, is given in Figure 5. The slope of this straight-line plot yields the activation energy (E_d) for the degradation process. The value of E_d was found to be 39.44 ± 2 kcal mol⁻¹, which is comparable to the dissociation energy of the O—O bond (Table II). This, as well as the symmetrical nature of the DSC thermogram (Fig. 4), suggests that the degradation of PPMAP is a single-step process and is initiated by the scission of the O—O bond. Thermogravimetric analysis (Fig. 6) of the polymer was carried out under a nitrogen atmosphere at a heating rate of 10°C min⁻¹. Weight loss occurred in a single step beginning at 90°C and ending at 150°C, where the weight loss was almost complete.

From the results of the degradation product analysis²² and the measurement of E_d for the degradation process (corresponding to the scission of the O—O bond), a radical chain scission mechanism for the degradation of PPMAP, similar to that of PSP, could be proposed,⁹ as given below:

TABLE I
Thermochemical Data

Compound	ΔH_f^0 (kcal mol ⁻¹)	
	Value	Reference
PMA	-30.74	this work
Phenyl pyruvate	-76.63	this work
Formaldehyde (g)	-27.7	29, 33
PPMAP	-44.14	this work

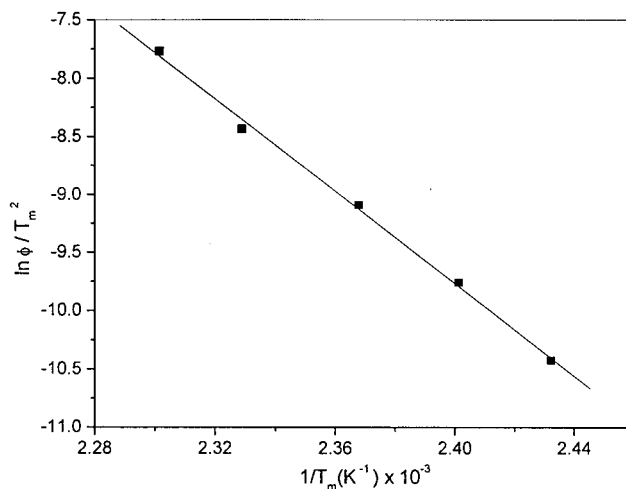
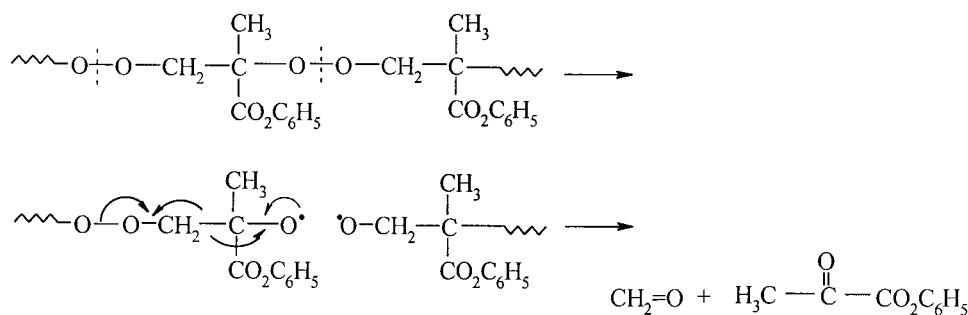


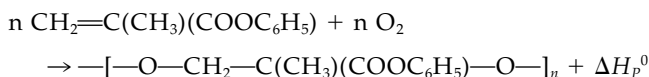
Figure 5 Kissinger's plot of $\ln \phi / T_m^2$ against $1/T_m$.



The above mechanism indicates that the exotherm observed in the DSC is a result of the primary degradation of PPMAP. This finds support from the thermochemical calculations.

To calculate the heat of degradation (ΔH_d^0) of PPMAP, its heat of formation (ΔH_f^0) is required. This was evaluated from the heat of polymerization (ΔH_p^0).

The reaction of O_2 with phenyl methacrylate leads to the formation of PPMAP,



In this process one $\text{C}=\text{C}$ bond and one $\text{O}=\text{O}$ bond are broken to form one $\text{O}-\text{O}$, one $\text{C}-\text{C}$, and two $\text{C}-\text{O}$ bonds. Using the bond energy data given in Table II, the value of

TABLE II
Bond Energy Data

Bond type	Bond energy (kcal mol ⁻¹)	Ref.
C=C	145.8	34, 35
C-C	82.8	35
C=O formaldehyde	166.0	34, 35
C=O ketones	179.0	34, 35
C-O	85.5	34, 35
O=O	119.1	34, 35
O-O	32.0	35

ΔH_p^0 for PPMAP was calculated to be 20.9 kcal mol⁻¹. However, ΔH_p^0 also depends on structural factors. For example, in vinyl polymerization the cleavage of one $\text{C}=\text{C}$ bond in the monomer gives rise to two $\text{C}-\text{C}$ bonds in the polymer, and the heat evolved in the process is 19.8 kcal mol⁻¹, compared with the experimental value ΔH_p^0 of 12.3 kcal mol⁻¹ for poly(phenyl methacrylate).³¹ Taking into account the structural factors,³² we therefore can take the

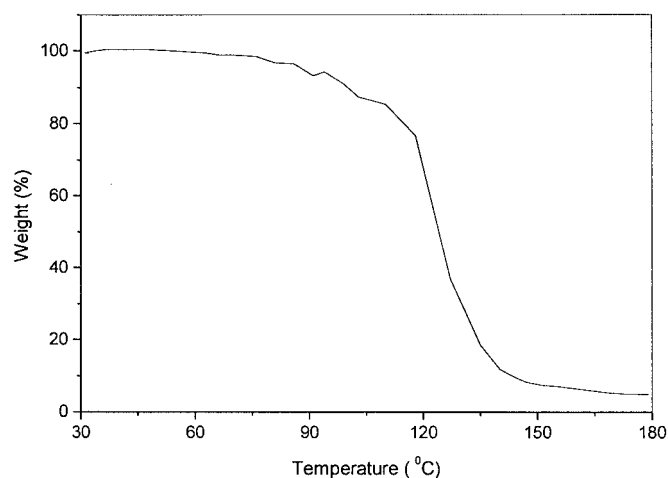
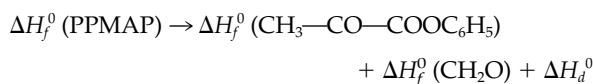


Figure 6 TGA curve of PPMAP at a heating rate of 10°C/min.

actual value of ΔH_p^0 for PPMAP to be 13.4 kcal mol⁻¹. Using this value and the ΔH_f^0 for PMA (Table I), we obtain for PPMAP the ΔH_f^0 as -44.14 kcal mol⁻¹.

The value of ΔH_d^0 for PPMAP was calculated by two different procedures.

- Using ΔH_f^0 , from the degradation scheme the heat change during the degradation of PPMAP is obtained theoretically to give formaldehyde (vapor) and phenyl pyruvate.



It was found to be -54.29 kcal mol⁻¹ after incorporating the correction for the heat of vaporization of formaldehyde.

- The ΔH_d^0 was also calculated from the bond dissociation energies. During the process of degradation of PPMAP, one C—C and one O—O bonds are broken, while two C—O bonds are converted to two C=O bonds and formaldehyde is vaporized. The calculated enthalpy change (ΔH_d^0) for this process is -53.3 kcal mol⁻¹.

A mean value of -53.8 kcal mol⁻¹ was taken for ΔH_d^0 of PPMAP from the values of ΔH_d^0 obtained by the two methods (-54.29 and -53.3 kcal mol⁻¹). The small difference between the experimental and theoretical values of ΔH_d^0 may arise from: (a) the approximation involved in the thermochemical input data, (b) the occurrence of minor side reactions during the degradation of PPMAP, and (c) the lower yields of aldehydes under the experimental conditions. The value of ΔH_d^0 of PPMAP suggests that the process should be exothermic. The good agreement between the experimentally measured and thermodynamically calculated values of ΔH_d^0 clearly demonstrates that the proposed mechanism of degradation should be acceptable.

CONCLUSIONS

The 1:1 copolymeric structure of PPMAP was confirmed spectroscopically for the first time. A radical chain-scission mechanism for the degradation of PPMAP has been proposed based on the analysis of its degradation products and kinetic studies by DSC. PPMAP shows a highly exothermic heat of degradation, and degradation is controlled by the dissociation of the peroxide (—O—O—) bond in the polymer backbone. The mechanism of the primary exothermic degradation has been substantiated by thermochemical calculations.

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