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Structure and Pyrolysis of Poly(methyl methacrylate peroxide): A Thermochemical Approach

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ABSTRACT: The structure of poly(methyl methacrylate peroxide) (PMMAP) has been confirmed by using IR and NMR. The degradation of PMMAP has been studied by using differential scanning calorimetry, thermogravimetry, and pyrolysis gas chromatography. The degradation products were identified as methyl pyruvate and formaldehyde, accounting for more than 95% of the total degradation products. The measured heat of degradation of PMMAP was found to be -44 ± 2 kcal mol^{-1}. The mechanism of the primary exothermic degradation leading to the above products has been substantiated by thermochemical calculations.

Introduction

Polymeric peroxides are an important class of compounds. Since the first report of its kind in 1925 by Staudinger,[1] only a small number of polymers belonging to this class have been studied.[2-18] Of these, poly(styrene peroxide) (PSP), first reported by Bovey and Kolthoff[19] has received considerable attention.[20-29] They have been used as initiators,[30,31] in preference to conventional simple peroxides, in a search to obtain novel polymers such as comb polymers.[32] Recently, PSP has been shown to behave as a unique autocombustible polymer fuel, its combustion being controlled by degradation.[29] Poly(methyl methacrylate peroxide) (PMMAP) is another member of this class of polymers. Its formation and structure are reported along with its degradation products.[33-36] In view of their potential as initiators and, as autocombustible polymer fuels, it is of general interest to study the degradation behavior of polymeric peroxides. Hence, in the present investigation, in which a spectroscopic confirmation of the alternating copolymeric structure of PMMAP is provided, its degradation has been studied in detail and has been supplemented by thermochemical calculations.

Experimental Section

PMMAP was prepared by reacting freshly distilled methyl methacrylate (MMA) in a current of oxygen for 24 h at 50 °C in the presence of azobisisobutyronitrile initiator (0.02 M % of monomer).[33] The polymer was purified by repeated precipitation using methanol.

The IR spectrum was recorded in CCl_4 on a Perkin-Elmer Spectrophotometer, Model 597. All NMR spectra were recorded at ambient temperature in $CDCl_3$ containing tetramethylsilane. The 60-MHz ^1H NMR spectrum was recorded on a Varian T-60 spectrometer, the 270-MHz ^1H NMR spectrum on a Bruker WH270 FT NMR spectrometer, and the 25-MHz ^{13}C NMR spectrum on a JEOL FX 90Q FT NMR spectrometer.

Pyrolysis gas chromatographic (PGC) studies were carried out as described elsewhere[37] by using an OV-17 column, in the pyrolysis temperature range 150–350 °C at intervals of 50 deg. The degradation products were also identified by IR and NMR.

The thermal analysis was done using a du Pont 990 differential scanning calorimeter (DSC) at heating rates of 2, 5, 10, 20, and 50 °C/min. The sample weight was ca. 2.5 mg. The temperature axis and the measured enthalpy were calibrated by using pure indium. The thermogravimetric analysis (TGA) was done with a ULVAC SINKU-RIKO simultaneous DTA-TGA instrument at a heating rate of 10 °C/min with a sample weight of 3 mg.

Results and Discussion

The 1:1 copolymeric structure of PMMAP, shown below, was confirmed by the spectroscopic data presented in Table I. A 1:1 structure and molecular dynamics of an earlier parallel example, viz., PSP, have been studied in great detail by Cais and Bovey.[38]

$$-(O-CH_2-C(COOCH_3)CH_3-O)_n-$$

The IR spectrum (Table I) shows all absorptions characteristic of the above repeat unit of the polymer. The ^1H NMR spectrum (Figure 1a, Table I) shows signals corresponding to the CCH_3, $C(O)CH_3$, and OCH_2 protons. The ^{13}C NMR (Figure 1b,c, Table I) also shows signals corresponding to the five C atoms present in the repeat unit, with the expected off-resonance splitting patterns.

The degradation products of the polymer were analyzed by PGC. A typical pyrogram is given in Figure 2. Methyl pyruvate and formaldehyde were identified as the major products of degradation, accounting for about 95% in the temperature range 150–350 °C. Above 350 °C a greater number of peaks appeared in the pyrogram with lower retention times, probably due to secondary products. The composition of the products at the various pyrolysis temperatures was on an average 75% methyl pyruvate and 21% formaldehyde.

DSC studies revealed a highly exothermic degradation of PMMAP. A typical thermogram is given in Figure 3a. No residue was found in the pan after the degradation was over. The enthalpy of degradation, $\Delta H_d°$ calculated from the mean area under the exotherm at various heating rates, was found to be 44 ± 2 kcal mol^{-1}, after applying corrections for the heat of vaporization of methyl pyruvate and formaldehyde.

A Kissinger's plot[39] of $\ln \phi/T_m^2$ against $1/T_m$, where ϕ is the heating rate and T_m (K), the peak temperature in the DSC thermogram, is given in Figure 4. The slope of this plot gives the activation energy (E) for the process. The E value was found to be 38 ± 2 kcal mol^{-1}, which is comparable to the O–O bond dissociation energy (Table III). This, as well as the symmetry of the DSC thermo-

Table I
Spectroscopic Data for Poly(methyl methacrylate peroxide)

infrared spectra[a]					^{13}C NMR[b]	
vibration	wavenumber, cm^{-1}	assignments no. of protons	^1H NMR[b] δ 60 MHz	^1H NMR[b] δ 270 MHz	broad band, δ	off-resonance splitting
ν_{C-H}	2980–2920					
$\nu_{C=O}$	1730					
ν_{C-O} (—CH$_2$—O—)	1310–1260, 1040	—CCH$_3$—	1.41 (br s, 3 H)	1.44 (br s, 3 H)	171.03 (C=O), 84.78 (C—O)	s, s
ν_{C-O} (—C—O—)	1200	—OCH$_3$	3.76 (br s, 3 H)	3.76 (br s, 3 H)	75.79, 75.41 (CH$_2$—O)	s, s
δ_{C-H} (—CH$_2$—)	1440	—OCH$_2$	4.25 (br s, 2 H)	4.34 (br q, 2 H)	52.33 (CH$_3$—C=O), 18.47 (CH$_3$—C—)	q, q
δ_{C-H} (CH$_3$—)	1375–1360					
ν_{O-O}	880					

[a] CCl_4 solvent. [b] $CDCl_3$ solvent.

Table II
Thermochemical Data[a]

compound	$\Delta H_f°$, kcal mol^{-1} value	$\Delta H_f°$, kcal mol^{-1} ref	$\Delta H_c°$, kcal mol^{-1} value	$\Delta H_c°$, kcal mol^{-1} ref	$\Delta H_v°$, kcal mol^{-1} value	$\Delta H_v°$, kcal mol^{-1} ref
MMA	-85.4[b]	this work				
methyl pyruvate (l)	-134.6[b]	this work			12.6[b]	this work
formaldehyde (g)	-27.7	45, 46	136.4	47, 48	5.9	45
carbon dioxide (g)	-94.1	45, 46				
water (l)	-68.3	47				
PMMAP	-107.6	this work	626.6[c]	this work		

[a] $\Delta H_p°$ of PMMA = 13.6 kcal mol^{-1}.[49] [b] The values were calculated by group additivity method. [c] Derived from PMMA.[49]

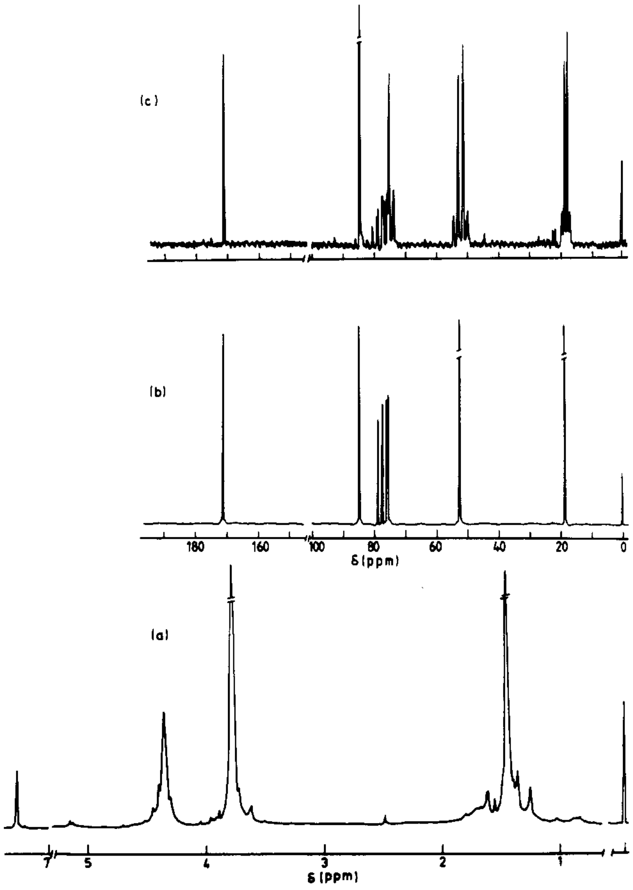


Figure 1. (a) ^1H NMR spectrum, (b) ^{13}C broad-band spectrum, and (c) ^{13}C off-resonance decoupled spectrum of PMMAP.

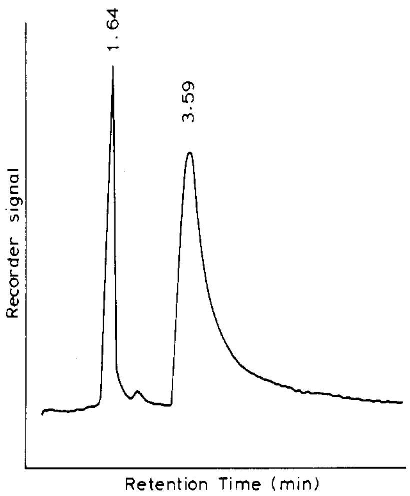
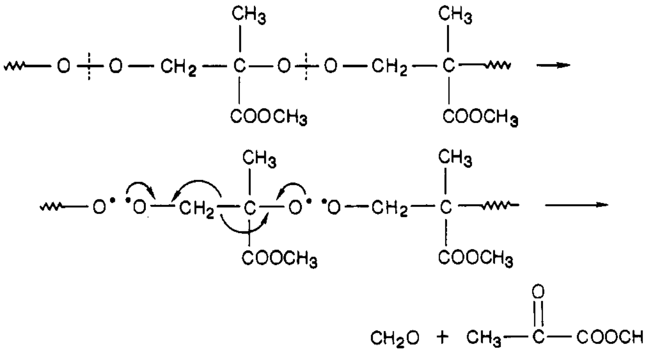


Figure 2. PGC pyrogram of PMMAP.

gram (Figure 3a), suggests that the degradation of PMMAP is a single-step process and is initiated by the scission of the O–O bond. A single-step weight loss in the TG (Figure 3b) also supports this observation.

Combining the results of the degradation product analysis and the measurement of *E* for the degradation process (corresponds to the scission of the O–O bond) a radical chain scission mechanism, for the degradation of PMMAP, similar to that of PSP,[40] could be proposed:



Small amounts of other products (other than 95% obtained in PGC) could also originate, via disproportionation mechanisms, as is operative in PSP.[40]

The above mechanism is indicative of the fact that the exotherm observed in the DSC is due to the primary degradation of PMMAP. This has been verified in the

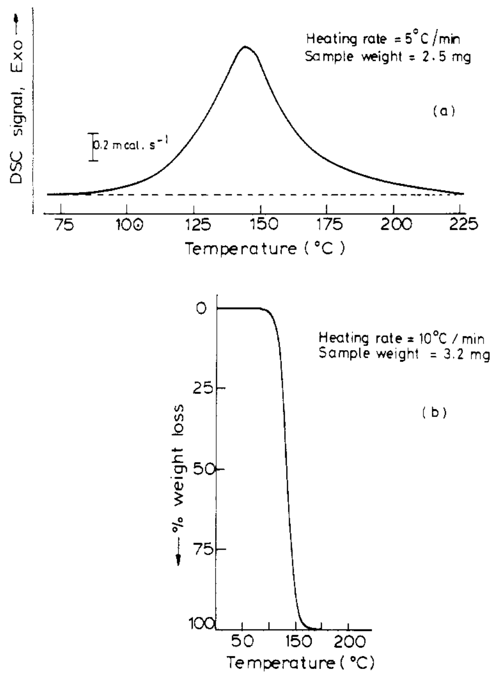


Figure 3. (a) DSC thermogram and (b) TG trace of PMMAP.

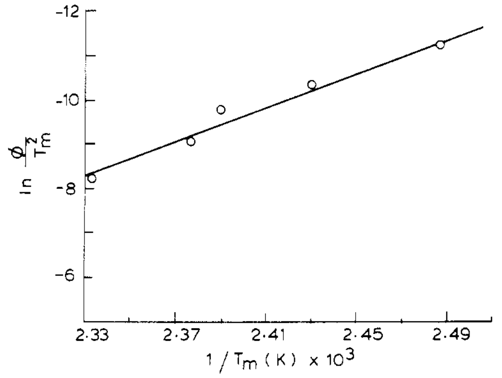


Figure 4. Kissinger's plot of ln ϕ/T_m^2 against $1/T_m$.

Table III
Bond Energy Data

bond type	bond energy, kcal mol^{-1}	ref
C=C	145.8	47, 50, 51
C—C	82.8	47, 50, 51
C=O formaldehyde	166.01	51
C=O ketones	179.0	47, 50, 51
C—O	85.5	47, 50, 51
O=O	119.1	51
O—O	35.0	51

following way, with the help of thermochemical calculations.[41]

The degradation of PMMAP can be represented as

$$\text{-O-(O-CH}_2\text{-C(COOCH}_3\text{)CH}_3\text{-O)}_n\text{-O-} \rightarrow n\text{-CH}_3\text{-C(=O)-COOCH}_3 + n\text{-CH}_2\text{O} + \Delta H_d° \quad (1)$$

$\Delta H_d°$ of PMMAP for the above reaction can be calculated from the heats of formation ($\Delta H_f°$'s) of PMMAP, methyl pyruvate, and formaldehyde. The necessary thermochemical data are presented in Table II. The $\Delta H_f°$'s of methyl pyruvate and methyl methacrylate and the heat of vaporization, $\Delta H_v°$, of methyl pyruvate have been calculated by the group additivity method;[42] the group values were taken from ref 43 and 44. The $\Delta H_f°$ of PMMAP could be calculated from (i) the heat of polymerization, $\Delta H_p°$, and (ii) the heat of combustion, $\Delta H_c°$, of PMMAP as follows.

(i) PMMAP is formed as

$$\text{MMA} + \text{O}_2 \rightarrow \text{PMMAP} + \Delta H_p° \quad (2)$$

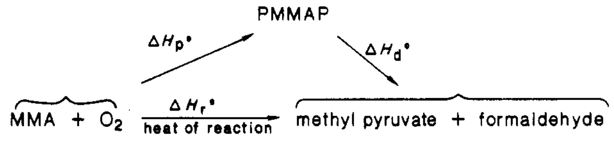
This process involves the scission of a C=C bond and an O=O bond and the formation of one O—O bond, one C—C bond, and two C—O bonds. From Table III, the value of $\Delta H_p°$ of PMMAP is calculated to be 20.9 kcal mol^{-1}. The $\Delta H_p°$ also depends on structural factors. For instance, the observed $\Delta H_p°$ of poly(methyl methacrylate) (PMMA) is 13.6 kcal mol^{-1}, while that of any vinyl polymerization is 19.8 kcal mol^{-1}.[41] Taking into consideration the structural factors, we therefore take the actual value of $\Delta H_p°$ of PMMAP to be 15 kcal mol^{-1}. Subsequently, using the value of $\Delta H_f°$ of MMA, the $\Delta H_f°$ of PMMAP is calculated to be −100.4 kcal mol^{-1}.

(ii) From the heat of combustion data for PMMAP, and $\Delta H_f°$'s of CO_2 and H_2O, the $\Delta H_f°$ of PMMAP is calculated to be −114.7 kcal mol^{-1}. The molar heat of combustion of PMMAP was taken to be the same as that of PMMA, since the carbon and hydrogen content in the repeat unit in both cases is the same. It has been shown[41] that the heats of combusion of polystyrene and PSP are equal.

An average value of −107.6 kcal mol^{-1} was then taken to be the $\Delta H_f°$ of PMMAP. From this value and the $\Delta H_f°$'s of methyl pyruvate and formaldehyde, the $\Delta H_d°$ of PMMAP was calculated from eq 1 to be −42.2 kcal mol^{-1}.

The $\Delta H_d°$ of PMMAP was calculated by other methods as well, as follows.

(1) During the degradation of PMMAP, on average one O—O bond and one C—C bond are broken, while two C—O bonds are converted to two C=O bonds and both methyl pyruvate and formaldehyde are evolved from the system. The enthalpy change for this process is −41.2 kcal mol^{-1}. (2) From the following Hess cycle,



the $\Delta H_d°$ is calculated to be −42.2 kcal mol^{-1}; $\Delta H_r°$ was calculated from $\Delta H_f°$ data (Table II).

An average value of −42 ± 1 kcal mol^{-1} can thus be taken as the calculated $\Delta H_d°$ of PMMAP. This is in good agreement with the experimentally measured $\Delta H_d°$ (−44 ± 2 kcal mol^{-1} by DSC) of PMMAP, showing that the primary degradation of PMMAP itself is exothermic. That the experimentally measured and thermochemically calculated values of $\Delta H_d°$ are equal also shows that the proposed mechanism of degradation (on which are the calculations based) is valid.

Conclusion

The 1:1 copolymeric structure of PMMAP was confirmed spectroscopically. A radical chain-scission mechanism for the degradation of PMMAP has been proposed based on the analysis of its degradation products and kinetic studies by DSC. This and the high exothermicity of the degradation are corroborated by thermochemical calculations.

Registry No. PMMAP (copolymer), 31095-12-2; CH_2O, 50-00-0; $H_3CCOCO_2CH_3$, 600-22-6.

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Monte Carlo Calculations for Linear Chains and Star Polymers with Intramolecular Interactions. 4. Dimensions and Hydrodynamic Properties below the Θ State

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ABSTRACT: Calculations on the radius of gyration and hydrodynamic properties of linear and several types of uniform star polymers of different lengths (the latter properties obtained in a nonpreaveraged way) have been performed in order to reproduce solvent conditions below the unperturbed state (previous simulations in this region only cover the radius of gyration of linear chains). The model used for these calculations considers Gaussian distances between neighboring units and also a Lennard-Jones (LJ) potential to describe interactions between nonneighboring units. This model has been already used in previous work to study the Θ and good solvent regions by setting the appropiate values of the LJ energetic parameters. The results and their combinations in terms of ratios g, h, and g' of the properties of the star polymers to those of the linear chains and in terms of the hydrodynamic molecular parameters P, Φ, and β for each given chain are reported and discussed. The decrease of the contraction (or expansion) for chains with an increasing number of arms and the slower changes in the hydrodynamic properties with varying solvent power with respect to the changes in the radius of gyration are the main conclusions of the study.

Introduction

In previous work,[1-3] we have numerically investigated the solution properties of linear and starlike polymers described through a molecular model with intramolecular interactions by means of Monte Carlo conformational simulations. The model consists of $N + 1$ units whose intramolecular distances to their nearest neighbors follow a Gaussian distribution with root mean squared (rms) deviation, b, equivalent to the familiar statistical length of a Gaussian subchain. The nonneighboring units interact through an effective Lennard-Jones (LJ) potential

$$V_{ij} = 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^{6}] \qquad (1)$$

where r_{ij} is the distance between the interacting units i and