Synthesis, Properties, and Comparative Analyses on the Chain Flexibility of an Ultrastable Vinyl Polyperoxide

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ABSTRACT: The most stable vinyl polyperoxide, namely, poly(indene peroxide) (PINDP), an alternating copolymer of indene and oxygen, was synthesized by the oxidative polymerization of indene. It was characterized by ^{1}H-NMR and ^{13}C-NMR, Fourier transform infrared, differential scanning calorimetry, direct pyrolysis mass spectrometry, and gas chromatography mass spectrometry studies. The overall activation energy for the degradation and the glass-transition temperature of PINDP were 47 kcal/mol and 327 K respectively, which were very high compared to those of other vinyl polyperoxides. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2108–2114, 2002

Key words: synthesis; NMR; glass transition; mass spectrometry

INTRODUCTION

Unlike simple organic peroxides, polymeric peroxides,[1–4] although long known, have not been studied extensively with regard to their stability and chain flexibility in vinyl polymerization. Compared to conventional peroxides, polyperoxides have been shown to produce comb-like polymers[5] and interpenetrating networks.[6] Vinyl polyperoxides,[4,7] which are alternating copolymers of oxygen and vinyl monomers, are of current interest not only due to their wide range of applications but also because they posses special features such as a high exothermic degradation,[8] because they exhibit the unusual phenomena of autopyrolysis and autocombustion[9] and because of their role in explaining the paradoxical effect of oxygen in vinyl polymerization[10] and their use in the development of novel fuels,[11] curatives in coating and molding applications[12] and potential initiators for the synthesis of homopolymers, active polymers, and block copolymers.[13–18]

The polyperoxides reported on earlier are gummy liquids in nature, which are difficult to handle quantitatively, and they also undergo slow degradation at room temperature. It is very difficult to store polyperoxides for long periods of time. It would be, therefore, desirable to synthesize a stable polyperoxide that could be stored for a long period and then used.

Poly(indene peroxide) (PINDP), which is a solid polymer, indeed has all of these characteristics.

Although PINDP was reported on earlier by Staudinger,[19] no analyses regarding the synthesis, characterization, and chain flexibility have been reported. We present here for the first time a detailed study of the synthesis, stability, and chain flexibility characteristics of PINDP, an alternating copolymer of indene (IND) and oxygen. Comparative studies on the chain flexibility of polyperoxides were also carried out from their glass-transition temperatures (T_g's).

EXPERIMENTAL

Materials

IND (97%; Aldrich, Bangalore, India), styrene (STY), α-methyl styrene (AMS), and methyl methacrylate (MMA) were freed from inhibitor and distilled under reduced pressure. α-Phenyl styrene (APS, 97%; Aldrich) was used as received. 2,2'-Azobis(isobutyronitrile) (AIBN; Koch Light, England) was recrystallized three times from methanol. Methanol, chloroform, and chlorobenzene were purified before use.

Synthesis of polyperoxides

We oxidatively polymerized IND by charging a solution of IND (3.2 mol/L) and AIBN (0.01 mol/L) in chlorobenzene in a stirred Parr reactor (Parr Instrument Co., New Jersey), thermostated at 50°C for 2 h under 200 psi of oxygen pressure. PINDP was separated from the reaction mixture by precipitation with methanol and was purified by repeated precipitation followed by the removal of the solvent by vacuum drying. Similarly, poly(α-phenylstyrene peroxide) (PAPSP), poly(styrene peroxide) (PSP), poly(α-meth-

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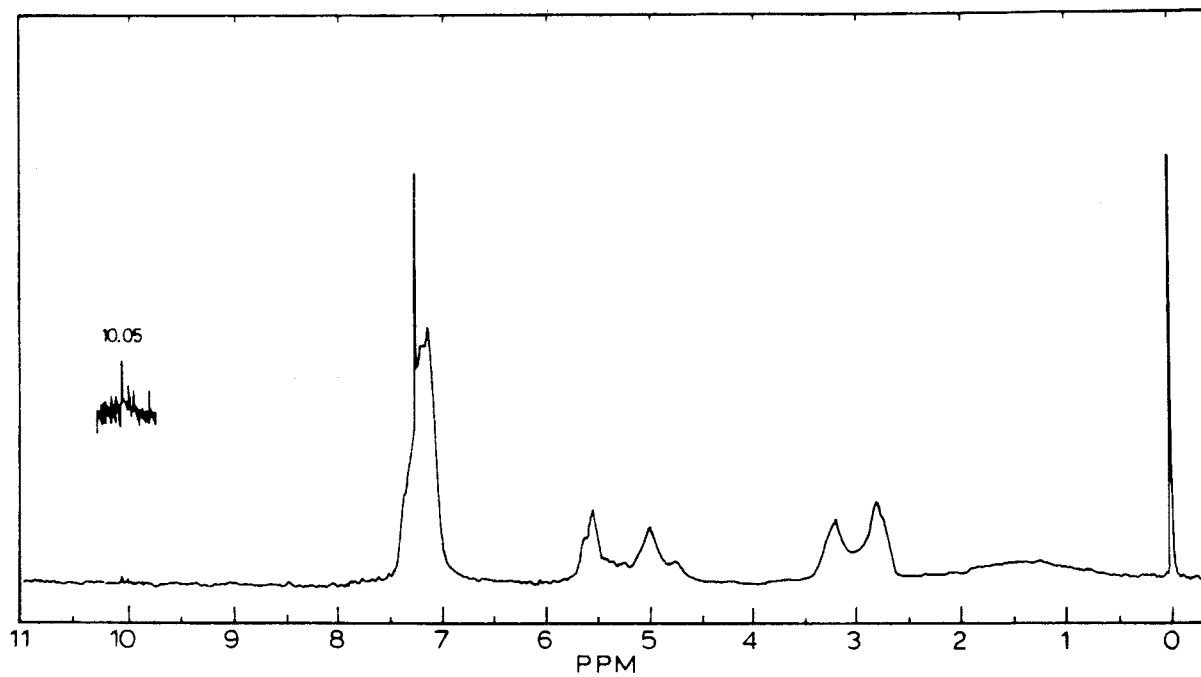
Figure 1 ^{1}H-NMR spectrum of PINDP.
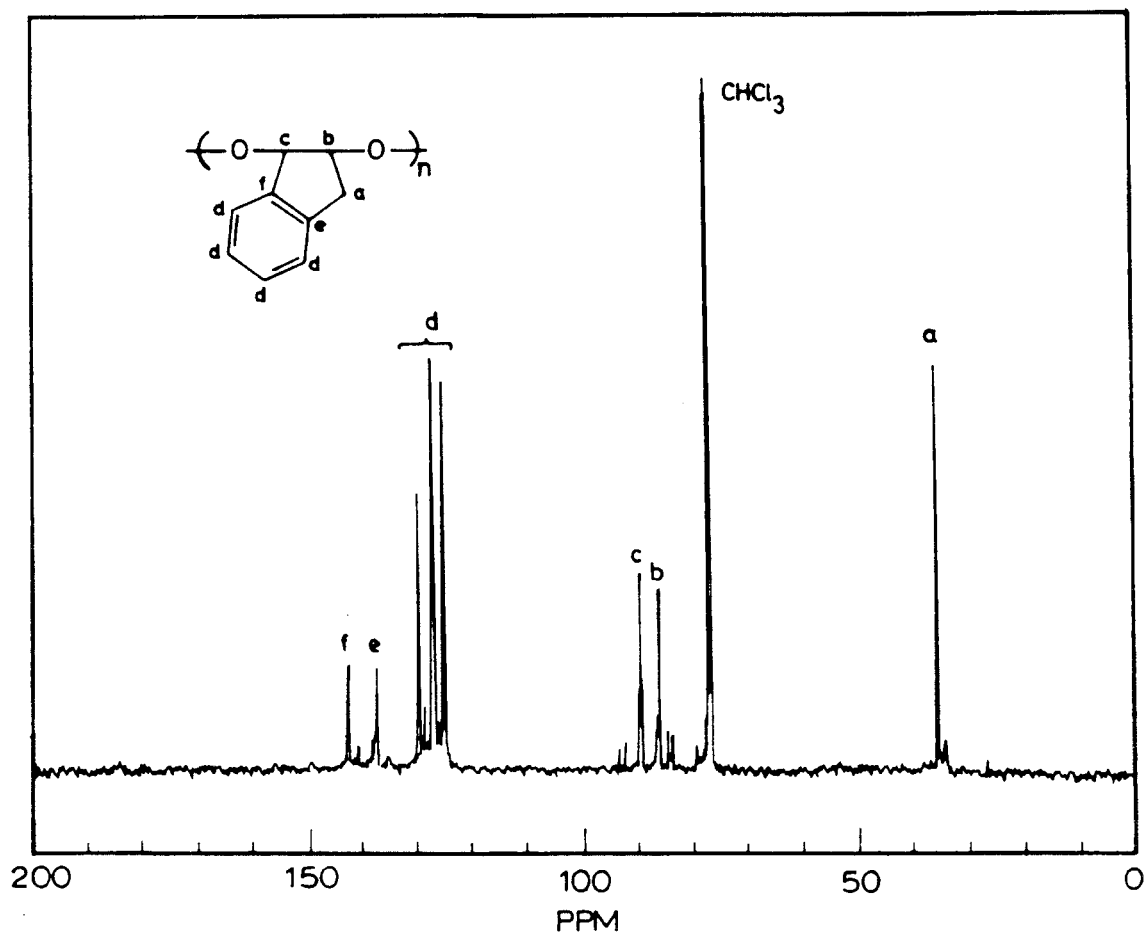
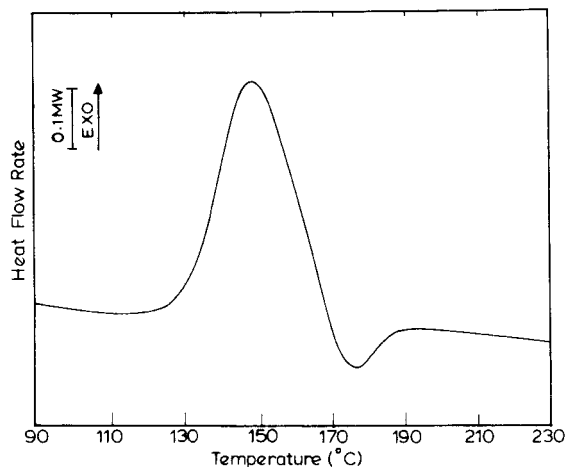
Figure 2 Broadband ^{13}C-NMR spectrum of PINDP.

Figure 3 DSC thermogram of PINDP.

ylstyrene peroxide) (PAMSP), and poly(methyl-methacrylate peroxide) (PMMAP) were synthesized from the oxidative polymerization of APS, STY, AMS, and MMA, respectively, as described elsewhere.[20,21]

Techniques

Fourier transform infrared spectra were recorded on a Fourier transform Bio-Rad (FTS7) spectrometer. ^{1}H-NMR spectra in CDCl$_3$ were recorded on a Brucker ACF 200-MHz spectrometer (USA). ^{13}C-NMR spectra in CHCl$_3$ were recorded on a Brucker AMX 400-MHz spectrometer (USA). Chemical shifts were assigned with reference to tetramethylsilane. Thermal analysis was done on a PerkinElmer DSC-7 differential scanning calorimeter (USA) at heating rates of 5, 10, 15, 20, and 25°C/min in flowing nitrogen (30 cm^3/min). T_g's were also measured with differential scanning calorimetry (DSC) at a heating rate of 10°C/min under a nitrogen atmosphere.

TABLE I
E_d of the Degradation Values for the Polyperoxides Investigated

Polyperoxide	E_d (kcal/mol)
PINDP	47
PAPSP	45
PSP	38
PMMAP	38
PAMSP	33

Molecular weights were estimated by gel permeation chromatography (GPC; Waters HCL/GPC 244, with a refractive index detector) with tetrahydrofuran as the solvent. The GPC instrument was calibrated with polystyrene as a standard. Direct pyrolysis mass spectrometry (DP-MS) analysis (70 eV) was carried out with a Schimadzu QP 1100EX mass spectrometer (USA). Gas chromatography (GC-MS) analysis was carried out with a JEOL JMX-DX-303-GC mass spectrometer (USA). For GC-MS analysis, a chloroform solution of the polymer was injected at 250°C, as described elsewhere.[22]

RESULTS AND DISCUSSION

Characterization of PINDP

We synthesized PINDP, an alternating copolymer of IND and oxygen, by copolymerizing IND with oxygen (200 psi) in the presence of AIBN initiator at 50°C. We separated the PINDP from the reaction mixture by precipitating it from methanol as a white solid; The weight-average molecular weight (M_w) and number-average molecular weight were 2400 and 1600, respectively. The polydispersity index was 1.50. The rather low molecular weight of PINDP was very similar to that of its other vinyl counterparts[4] (M_w = 2000–5000), and a detailed examina-
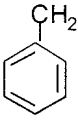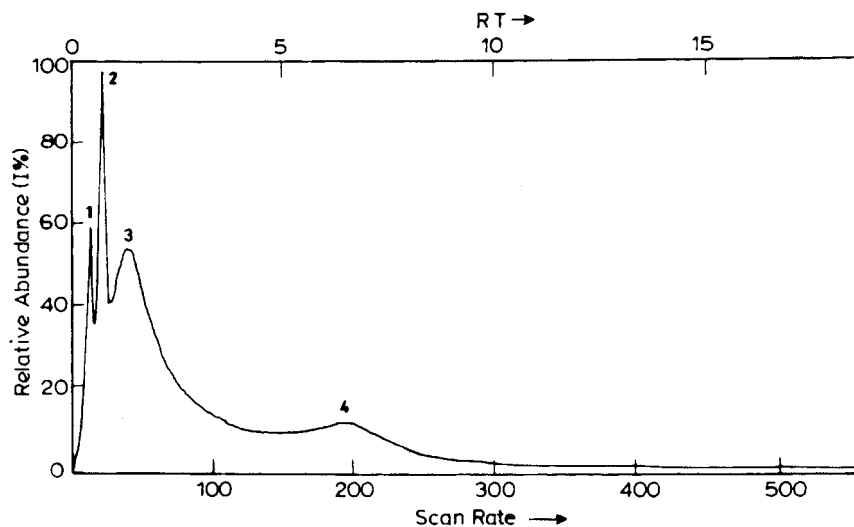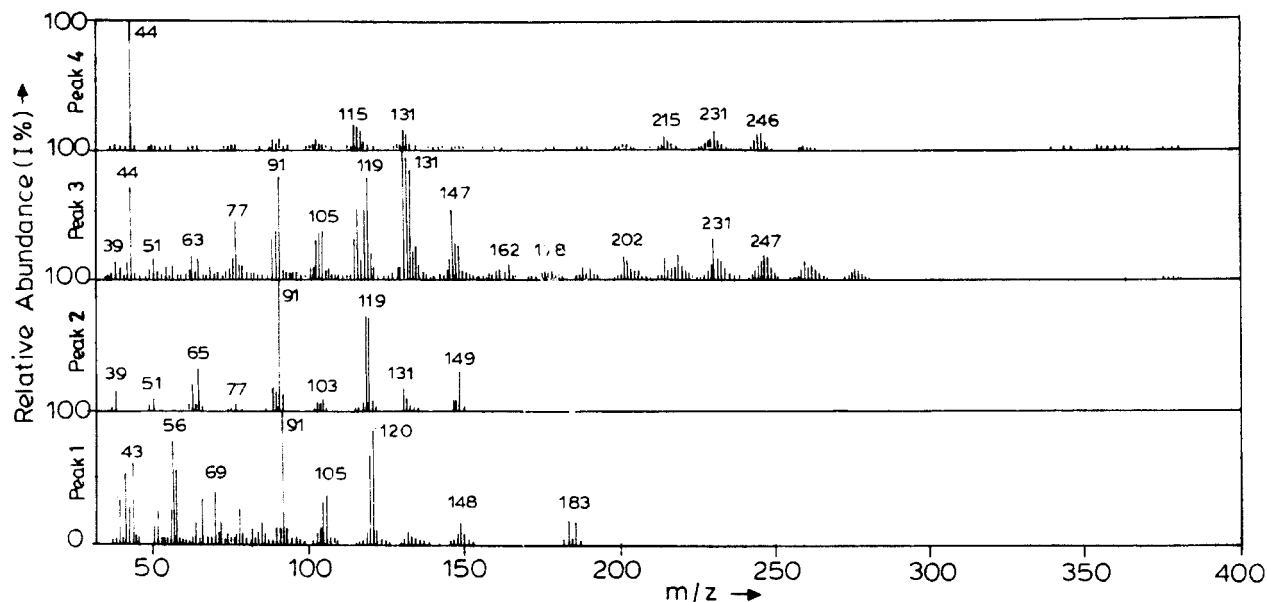

Figure 4 TIC of PINDP.
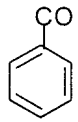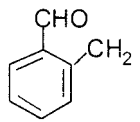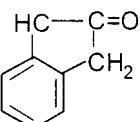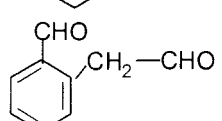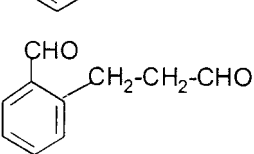
Figure 5 Mass spectra corresponding to the individual peak maxima observed in the TIC of PINDP.

tion of the mechanism of formation clearly reveals that this class of polymers undergoes facile degradation during polymerization itself, generating

TABLE II
Structural Assignments in the DP-MS of PINDP

Structure	m/z
CH$_2$—CHO	43
CH$_2$—CH$_2$—CHO	57
C$_6$H$_5$	77
(benzyl CH$_2$)	91
(benzoyl CO)	105
(CHO, CH$_2$ disubstituted benzene)	119
(HC—C=O, CH$_2$ ring)	131
(CHO, CH$_2$—CHO disubstituted benzene)	148
(CHO, CH$_2$-CH$_2$-CHO disubstituted benzene)	162

chain-transfer agents, such as aldehydes, which react with macro growing radicals, resulting in low molecular weights.

The IR spectrum of PINDP showed characteristic absorptions at 3050 and 2980 cm^{-1}, corresponding to aromatic C—H and methylene C—H stretching, respectively; the 1600, 1494, and 1452 cm^{-1} bands were assigned to ring carbon stretching modes. A band at 1002 cm^{-1} was found, which corresponded to the peroxy group (O—O) absorption. The broad absorption between 3450 and 3700 cm^{-1} was assigned to the stretching of both hydroxy (—OH) and hydroperoxy (—OOH) groups present at the chain ends. Similar end groups have been observed in PSP,[23,24] PAMSP,[25] and poly(vinylacetate peroxide).[26]

The ^{1}H-NMR spectrum of PINDP (Fig. 1) showed signals at 7.0–7.5, 5.5–5.8, and 4.6–5.2 ppm, corre-
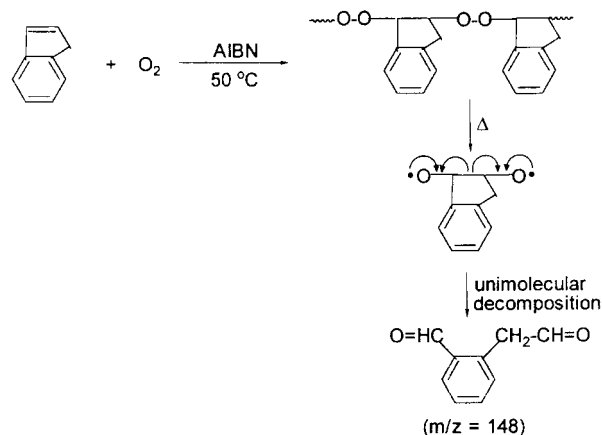
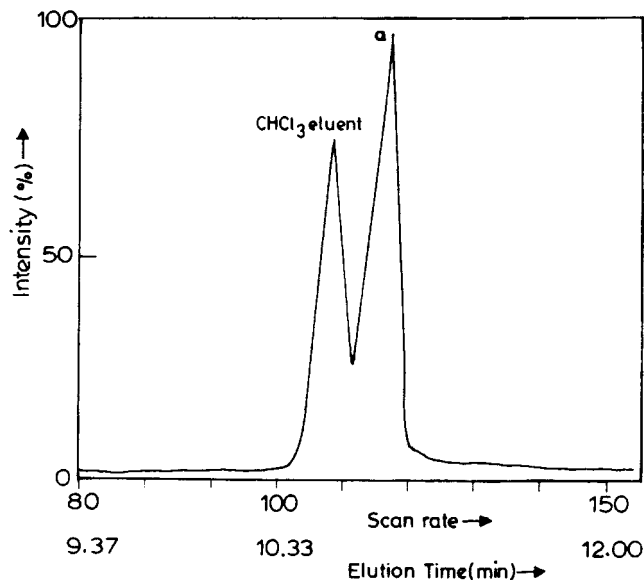**Scheme 1** Mechanism of formation of the molecular ion peak m/z = 148.

Figure 6 Py-GC-MS spectrum of PINDP.

sponding to aromatic protons (4H), the methine proton (1H) bonded to the aromatic ring, and the methine proton (1H) connected to the methylene group, respectively. The two peaks observed at 2.8 and 3.2 ppm were attributed to the methylene group.

The ^{13}C-NMR spectrum of PINDP (Fig. 2) exhibited signals at 128–130, 138, 143, 90, 86, and 36 ppm; they were assigned to the aromatic ring [Fig. 2(d)], two aromatic ipsos [Fig. 2(e,f)], the methine carbon attached to the aromatic ring [Fig. 2(c)], the methine carbon adjacent to the methylene group [Fig. 2(b)], and the methylene carbon [Fig. 2(a)], respectively.

Thermal decomposition

The thermal stability of PINDP was studied with DSC recorded under a nitrogen atmosphere at heat-

ing rates of 5, 10, 15, 20, and 25°C/min. (Fig. 3) PINDP showed a broad exotherm between 132 and 170°C followed by a small endotherm between 170 and 190°C. The small endotherm may have been due to the melting of the degradation product. Exothermic degradation generally observed in all polyperoxide polymers, and it is due to the decomposition of the O—O bond followed by unzipping to form the degradation products, which have lower enthalpies of formation compared to the parent polymer. From the peak temperatures using Kissinger's plot,[27] we found the overall activation energy (E_d) for the decomposition to be 47 kcal/mol, corresponding to the peroxy bond dissociation. For comparison sake, we have also listed the E_d values of other vinyl polyperoxides (Table I). The E_d values for the degradation of PAPSP, PSP, PMMAP, and PAMSP were reported earlier.[21]

From the measurements of E_d (Table I), we found that the stability of the vinyl polyperoxides decreased in the order PINDP > PAPSP > PSP > PMMAP > PAMSP, showing that PINDP was the most stable initiator among the polyperoxide polymers.

DP-MS analysis

DP-MS technique involves the introduction of the polymer sample into the mass spectrometer through a direct insertion probe; the temperature is gradually increased until thermal degradation occurs. The primary products are then ionized and detected immediately. Figure 4 presents the total ion chromatogram (TIC) of PINDP, and the mass spectrum corresponding to the individual peak maxima of the TICs are presented in Figure 5. The products identified are given in Table II. The molecular ion peak ($m/z = 148$), based on the fragmentation pattern, was attributed to the formation of a substituted glyoxal, and its origin
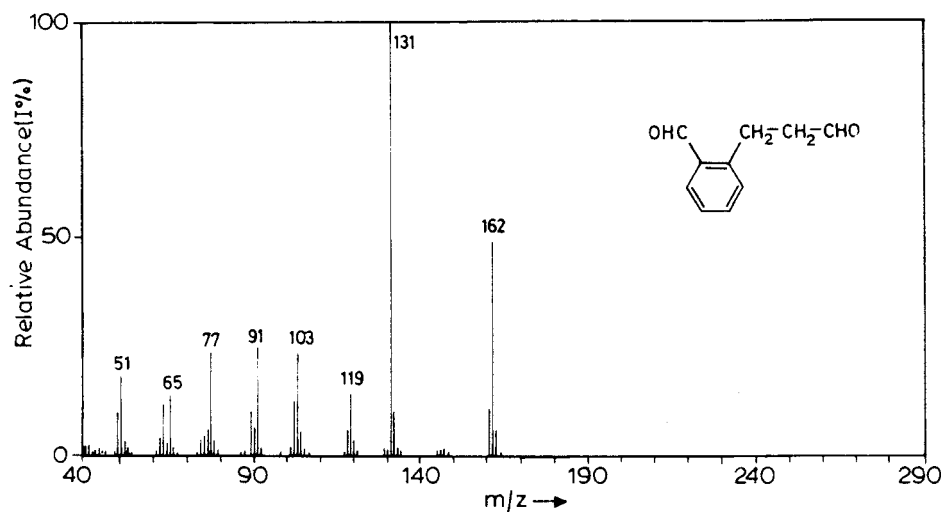

Figure 7 Mass spectrum of peak a obtained by Py-GC-MS of-PINDP.

from the polymer backbone is presented in Scheme 1. Like all other vinyl polyperoxides, for PINDP the initiation of degradation occurred at the weak O—O bond. By the chain unzipping mechanism, the primary product ($m/z = 148$) was formed. Further, molecular ion peaks at 231, 247, and so on were also observed, which could have been due to a secondary reaction of the primary product.

Pyrolysis gas chromatography mass spectroscopy (Py-GC-MS) analysis

To probe the thermal degradation mechanism further, we carried out Py-GC-MS of PINDP at 250°C (Fig. 6). The mass spectrum corresponding to peak a is shown in Figure 7, and the structure corresponding to the molecular ion peak ($m/z = 162$) is shown in Scheme 2. The absence of the primary degradation product under Py-GC-MS conditions could have been attributed to its thermal instability. We arrived at the possible structure reported for $m/z = 162$ using the mass spectral database.[28]

Comparison of the flexibility of PINDP with that of other vinyl polyperoxides

T_g

T_g is the most significant secondary thermodynamic transition, which is related to the flexibility of a polymer. We determined the T_g of PINDP and compared it with that of other vinyl counterparts (Table III). From Table III, it is evident that T_g increased due to the presence of stiffer functional groups in the polymer backbone.[29] PINDP possessed a high T_g compared to

TABLE III
T_g Values for the Polyperoxides Investigated

Polyperoxide	T_g (K)
PMMAP	229
PAMSP	265
PSP	279
PAPSP	305
PINDP	327

other vinyl counter parts, indicating the more rigid nature of the polymer.

From the values of the T_g, it is clear that flexibility of the polyperoxides decreased in the following order: PMMAP > PAMSP> PSP > PAPSP > PINDP, showing that PINDP was the most rigid polymer among the polyperoxide polymers.
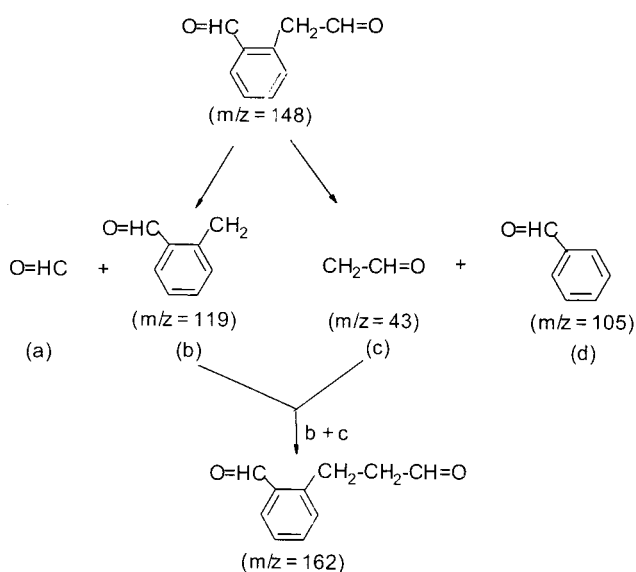
CONCLUSIONS

The relative thermal stability of PINDP, PAPSP, PSP, PMMAP, and PAMSP were compared from their E_d values. PINDP was found to be highly stable thermally compared to other polyperoxides. PINDP is much less hazardous than simple organic peroxides. Unlike other polyperoxides, which are gummy liquids (and difficult to handle quantitatively) and are generally stored in the cold, PINDP, which is a solid polymer (and easy to handle quantitatively), can safely be stored at room temperature. The T_g values showed that PINDP is more rigid compared to other polyperoxides.

Scheme 2 Mechanism of formation of molecular ion leak $m/z = 162$.

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