edged. We also thank L. Brimacombe and V. Frantisak for synthesizing some of the samples investigated here.

Registry No. (NECMM)(DNBEM) (complex), 103515-28-2; NECMA, 122624-68-4; (NECMM)(DNBEM) (copolymer), 122624-70-8; DNBEA, 80880-32-6; DNBEM (homopolymer), 82008-07-9; NECMM (homopolymer), 67549-45-5; NECMA·DNBEA, 122624-69-5.

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Poly(vinylnaphthalene peroxide)s: Syntheses, Characterization, and Thermal Reactivity

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ABSTRACT: Three new polymeric peroxides based on vinyl and substituted vinylnaphthalenes have been synthesized and characterized. The thermal reactivity of these polymers was studied by DSC and PGC. The ΔH_d° values of these polymers are close to or slightly higher than the earlier reported PSP. They are also powdery materials and are superior autocombustible fuel.

Introduction

Not long ago, Cais and Bovey reported on the chain flexibility and molecular dynamics of poly(styrene peroxide) (PSP),[1] an effort undertaken for the first time to study the physicochemical properties of polymeric peroxides, which had thus far received attention[2,3] only in regard to their intermediacy in the inhibition by oxygen in vinyl polymerization. Recently, studies from our laboratory on polymeric peroxides have been of the former nature and were successful in providing a thermochemical explanation for the unusual, exothermic, thermal degradation of these polymers.[4,5] Application of this characteristic exothermic degradation of these polymers has resulted in detecting a unique phenomenon of autopyrolysis in PSP,[6a] which has caused it to be considered as a candidate for a specialized fuel of the future.[6b] The property of autopyrolysis exhibited by these polymers is due to their unusual, highly exothermic heats of degradation.

An evaluation of the heats of degradation of different polymeric peroxides is out of question for want of data. The number of polyperoxides reported so far is only about a dozen,[3] and even these, except for one or two, have hardly been characterized. Under the circumstances, it seemed desirable to prepare new polyperoxides in view of their potential as highly exothermically degrading materials. By a comparison of the available heats of degradation of PSP[4] and poly(methyl methacrylate peroxide) (PMMAP)[5] (the former being higher), it was thought best to try aromatic monomers for making new polyperoxides. Hence, vinyl and substituted vinylnaphthalenes were chosen. In this paper, we describe the syntheses, characterization, and thermal reactivity of three new polyperoxides. Conforming to expectations, all these polymers exhibited equal or slightly higher heats of degradation than PSP. They were powdery materials, thus affording easier handling and use compared to the earlier reported PSP, a sticky semisolid polymer under ambient conditions.

Experimental Section

Preparation of Monomers. 2-Vinylnaphthalene was prepared from 2-acetonaphthone (Fluka AG) by reduction with $NaBH_4$ followed by dehydration of the resulting secondary alcohol with iodine and benzene under reflux for 0.5 h. 1,α-1-(α-methylvinyl)naphthalene and 2-(α-methylvinyl)naphthalene were prepared from 1-acetonaphthone (Fluka AG) and 2-acetonaphthone, respectively. The naphthones were subjected to Grignard reaction with CH_3MgI, and the resulting tertiary alcohols were dehydrated by stirring benzene solutions of them with *p*-toluenesulfonic acid overnight. All the monomers were purified by column chromatography (silica gel; petroleum ether).

Polymerization. The polymeric peroxides were prepared by passing a copious flow of oxygen through benzene solutions of monomers in glass cells fitted with a sintered funnel at the bottom for passing gas and placed in a water bath at 50 °C. This cell assembly provides intimate mixing of oxygen with the monomers and also constant stirring. AIBN (0.02 mol %) was used as the initiator. The polyperoxide of 2-vinylnaphthalene was formed in 12% yield by passing in oxygen for 48 h; those of 1- and 2-(α-methylvinyl)naphthalenes were formed after 100 h each, in 15% yield. The polymers were precipitated by using petroleum ether and purified by several reprecipitations.

Analysis. All NMR spectra were recorded in $CDCl_3$ at ambient temperature: ^1H NMR spectra on a Varian T-60 (60 MHz) or a Bruker FT-270 spectrometer (270 MHz) and ^{13}C NMR spectra on a Bruker FT-270 spectrometer (67.89 MHz) under broad-band

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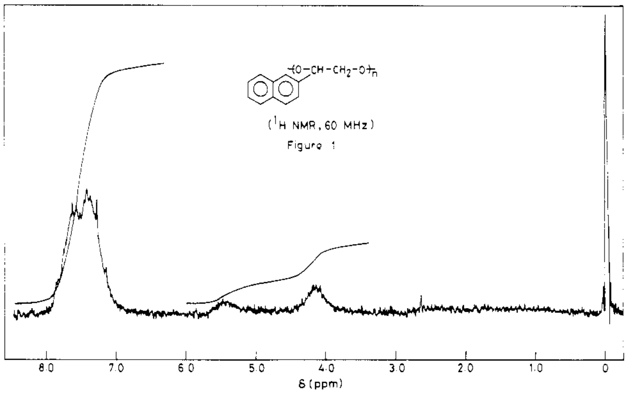
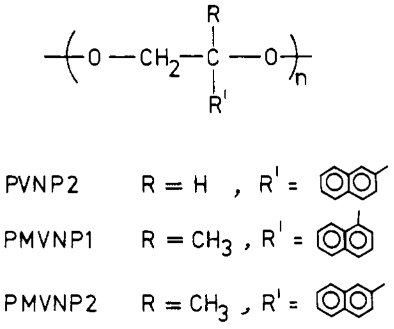


Figure 1. ^{1}H NMR spectrum of PVNP2.

Chart I
Structure of the Polyperoxides



^{1}H decoupled, off-resonance ^{1}H decoupled, and spin–echo Fourier transform (SEFT) modes. Differential scanning calorimeter (DSC) measurements were performed on a Du Pont 990 instrument, at heating rates of 1, 2, 5, 10, 20, and 50 °C min^{-1} using sample weights of 1.5–3.5 mg. Pyrolysis gas chromatographic (PGC) studies were conducted with a Shimadzu gas chromatograph Model GC-4C PF equipped with a pyrolyzer unit (PYR-1A) and a recorder (C-RIA chromatograph) and employing a flame ionization detector. Stainless steel columns of 3-mm inner diameter and 2-m length packed with 5% OV-17 on 80/100 mesh chromosorb silanized (Chromatopak Enterprises, Bombay) were used to separate compounds. Nitrogen at a 35 mL min^{-1} flow rate was used as the carrier gas. The pyrolysis temperature range studied was 150–350 °C. The products were identified by comparing their retention times with those of pure compounds.

Results and Discussion

Poly(2-vinylnaphthalene peroxide) (PVNP2) Characterization. PVNP2 was characterized spectroscopically. The IR spectrum showed a weak characteristic O–O absorption at 890 cm^{-1}. The 60-MHz ^{1}H NMR spectrum of PVNP2 shows signals at δ 4.2 (2 H, br d), 5.5 (1 H, br t), and 7.0–7.9 (7 H, br m) corresponding to OCH$_2$, OCH, and Ar–*H*, respectively (Figure 1). The 67.89-MHz ^{13}C NMR spectrum shows signals corresponding to all carbon atoms of the repeat unit of the polymer (Chart I). The signals at δ 75.84 and 76.09 (each s), 82.86 and 83.15 (each s), and 124.01–140.01 correspond to CH$_2$–O, CH–O, and aromatic ring carbons, respectively (Figure 2a,b).

DSC Studies. The DSC studies of PVNP2 were carried out at heating rates of 1, 5, 10, 20, and 50 °C min^{-1}. It was found that PVNP2 degrades highly exothermically, the products of the degradation completely vaporizing during the process. The apparent enthalpy change of degradation and peak temperatures of degradation were determined from the DSC thermograms. Corrections for the heats of vaporizations (ΔH_v°) of the degradation products, viz., 2-naphthaldehyde and formaldehyde, had to be made before the actual heat of degradation of PVNP2 could be arrived at. The ΔH_v° of 2-naphthaldehyde could not be obtained from the literature, nor could it be computed by the group additivity method[5] for want of group values. However, the ΔH_v° of 2-acetonaphthone[1] (Table I) has been used as an approximation, in place of the ΔH_v° of 2-naphthaldehyde (it is found that the ΔH_v° values of benzaldehyde and acetophenone are almost equal[1]). The data obtained from DSC runs are summarized in Table I. The average heat of degradation (ΔH_d°) of PNVP2 was found to be 205 ± 4 kJ mol^{-1}.

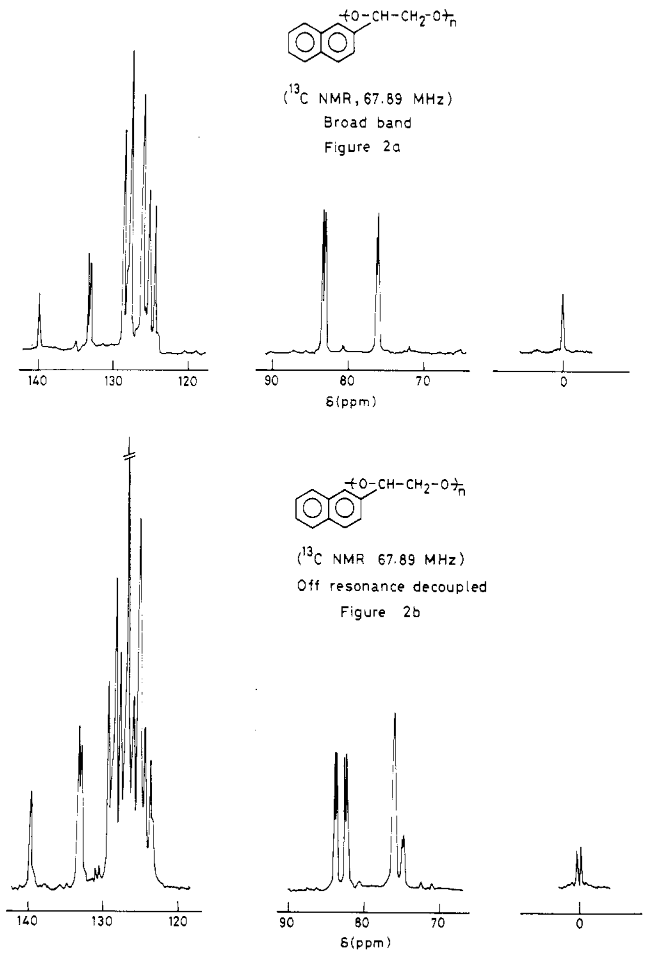


Figure 2. ^{13}C NMR spectrum of PVNP2.

Table I
DSC Analysis of the Polyperoxides[a]

	heating rate, °C min^{-1}	peak temp, °C	ΔH_d°, kJ mol^{-1}	average ΔH_d°, kJ mol^{-1}
PVNP2	1	90.4 ± 1.0	208	206 ± 4
	5	105.4 ± 1.0	203	
	10	112.9 ± 1.0	207	
	20	122.9 ± 1.0	202	
	50	132.9 ± 1.0	210	
PMVNP1	2	121.6 ± 1.0	230	222 ± 8
	5	130.4 ± 1.0	222	
	10	135.4 ± 1.0	215	
	20	141.6 ± 1.0	218	
	50	144.1 ± 1.0	221	
PMVNP2	2	122.2 ± 1.0	215	222 ± 10
	5	129.7 ± 1.0	232	
	10	135.2 ± 1.0	221	
	20	140.8 ± 1.0	212	
	50	145.1 ± 1.0	219	

[a] ΔH_v° of 2-naphthaldehyde and of 2-acetonaphthone[9] = 69 kJ mol^{-1} has been used to obtain the corrected value of ΔH_d°. ΔH_d° values are in kJ mol^{-1} of the repeat unit of the polymer. ΔH_v° of 1-acetonaphthone[9] = 67.4 kJ mol^{-1} has been used to obtain the corrected value of ΔH_d° of PMVNP1.

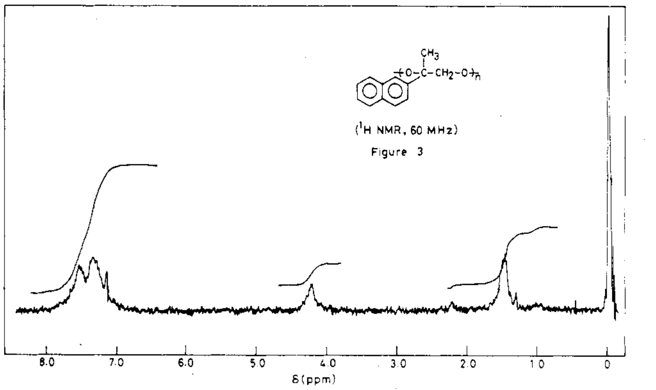


Figure 3. ^{1}H NMR spectrum of PMVNP2.

The activation energy for the degradation process of PVNP2 has been determined by a Kissinger plot of ln ϕ/T_m^2 against $1/T_m$, where ϕ is the heating rate and T_m (K) the peak temperature in the DSC thermogram, as described earlier.[5] The E value is found to be 155 ± 8 kJ mol^{-1}, comparable to the O–O bond dissociation energy.[5]

PGC Studies. The pyrolysis products of PVNP2 were analyzed by PGC. It was found that when pyrolyzed at 90 °C PVNP2 gives 2-naphthaldehyde and formaldehyde nearly quantitatively (both products together amount to 98%). However, at higher pyrolysis temperatures secondary degradation seems to set in, and the pyrogram contains more peaks than those corresponding to naphthaldehyde and formaldehyde. The identification of these peaks was not attempted. However, the fact that at 90 °C pyrolysis temperature only two products are detected points to O–O bond scission as the primary degradation step. A representative pyrogram of the PGC studies of all the polymers is given in Figure 5. The concentration of the two products at the pyrolysis temperature of 90 °C was 83% for 2-naphthaldehyde and 15% for formaldehyde.

2-Naphthaldehyde was also detected by separately pyrolyzing the polymer: IR (neat) ν_{max} 1690 cm^{-1} (C=O).

Polymeric Peroxides of 1-(α-Methylvinyl)naphthalene and 2-(α-Methylvinyl)naphthalene (PMVNP1 and PMVNP2). Characterization. Both PMVNP1 and PMVNP2 were characterized spectroscopically. Their IR spectra show absorptions characteristic of the 1:1 copolymeric nature of these polymers. The characteristic weak O–O absorption is observed at 860 cm^{-1}. The 60-MHz ^{1}H NMR spectra of PMVNP1 and PMVNP2 are nearly the same. Each one shows signals at δ 1.6 (3 H, br s), 4.4 (2 H, br s), and 7.2–8.2 (7 H, br m) corresponding to CCH_3, OCH_2, and Ar–*H*, respectively (Figure 3). The 67.89-MHz ^{13}C NMR spectrum of PMVNP2 shows signals corresponding to all carbon atoms of the repeat unit of the polymer (Chart I). The signals at δ 22.26 (q), 58.49 (t), 85.63 (s), and 124.06–139.63 (m) correspond to CH_3–C, CH_2–O, C–O, and aromatic ring carbon atoms, respectively. The 67.89-MHz ^{13}C NMR spectrum of PMVNP1 is similar. Here, the assignments are confirmed by a ^{13}C SEFT spectrum instead of the off-resonance decoupled spectrum used in the former case. The signals at δ 22.68, 58.49, 87.2, and 124.79–137.27 correspond to CH_3–C, CH_2–O, C–O, and aromatic ring carbon atoms (Figure 4a,b).

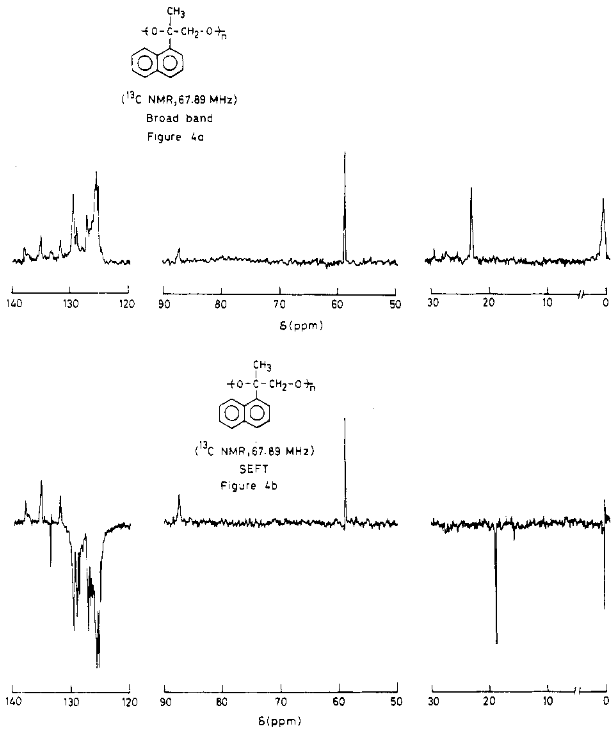


Figure 4. ^{13}C NMR spectrum of PMVNP1.

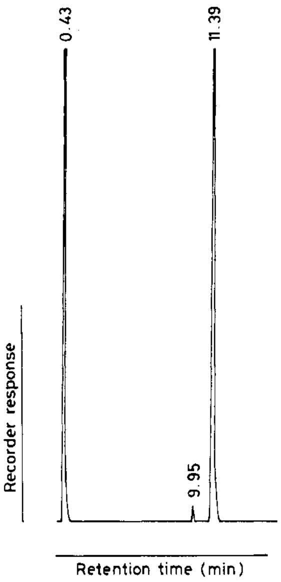


Figure 5. Pyrogram of PMVNP1.

DSC Studies. DSC analyses of the degradation of PMVNP1 and PMVNP2 have been carried out as in the case of previously mentioned polymers. The runs were carried out at heating rates of 2, 5, 10, 20, and 50 °C min^{-1}. The $\Delta H_d°$ of these two polymers were calculated by applying corrections for the $\Delta H_v°$ of 1-acetonaphthone or 2-acetonaphthone as the case may be.[1] It was found that in these two cases 50 wt % of the material taken was left behind in the DSC cups without vaporizing. This residue was identified as the corresponding ketone, 1-acetonaphthone or 2-acetonaphthone. This accounts for 59 mol % of the ketone. Hence, a $\Delta H_v°$ correction for 41 mol % of vaporized ketone was applied in the calculation of the actual $\Delta H_d°$ of these two polymers. The average $\Delta H_d°$ values of PMVNP1 and PMVNP2 were 222 ± 8 and 222 ± 10 kJ mol^{-1}, respectively. The data obtained from the DSC runs are presented in Table I.

The activation energies (E values) for the degradation processes of these two polymers were determined from Kissinger plots similar to that described already. The E values for both polymers were found to be 155 ± 8 kJ mol^{-1} each, in good agreement with the O–O bond dissociation energies. This is indicative of a chain mechanism of degradation for these polymers as well, as in the case of PMMAP.

Table II
Pyrolysis Gas Chromatography of the Polyperoxides

	aldehyde/ketone		formaldehyde	
pyrolysis temp, °C	retention time, min	concn, %	retention time, min	concn, %
		PVNP2[a]		
90		83.0		15.0
		PMVNP1		
150	11.13	83.0	0.37	12.9
200	11.16	82.8	0.39	13.0
250	11.17	83.2	0.40	12.7
300	11.19	83.1	0.41	13.0
350	11.18	83.0	0.40	13.0
		PMVNP2		
150	11.13	82.5	0.43	12.9
200	11.17	82.9	0.47	13.0
250	11.21	83.0	0.52	13.1
300	11.16	82.9	0.46	13.0
350	11.19	83.0	0.49	12.8

[a] This is a less stable polyperoxide and gives secondary degradation products above the pyrolysis temperature of 90 °C.

Table III
Comparative Study of Thermal Degradation of the Various Polyperoxides[a]

polyperoxide	DSC peak temp, °C	actual heat of degradation, kJ mol^{-1}
PSP	149.1 ± 1.0	−209 ± 8
PMMAP	145.4 ± 1.0	−184 ± 8
PVNP2	112.9 ± 1.0	−206 ± 4
PMVNP1	135.4 ± 1.0	−222 ± 8
PMVNP2	135.2 ± 1.0	−222 ± 10
PDVBP[b]	147.5 ± 1.5	

[a] A heating rate of 10 °C min^{-1} has been maintained in all cases. [b] Poly(1,4-divinylbenzene peroxide),[3] the polymer in this case was a cross-linked one, and, therefore, the exact structure and hence the $\Delta H_d°$ could not be determined.

PGC Studies. The pyrolysis products of PMVNP1 and PMVNP2 were analyzed by PGC in the pyrolysis temperature range 150–350 °C. The pyrolysis products were found to be formaldehyde and 1-acetonaphthone or 2-acetonaphthone (Figure 5). The small peak at a retention time of 9.95 min might arise by a disproportionation mechanisms such as is operative in PSP[7] and PMMAP.[5] Above 350 °C, it was found that secondary degradation sets in, and a greater number of peaks appear in the pyrogram. The two products in each case accounted for 96% of the total products. The average concentration of the two products remained at 83% ketone and 13% formaldehyde. The data derived from the PGC studies are presented in Table II.

The pyrolysis products were also analyzed and characterized separately. 2-Acetonaphthone: IR (neat) ν_{max} 1685 cm^{-1} (D=O); ^{1}H NMR (60 MHz) δ 2.6 (3 H, s, CO–CH$_3$), 7.2–8.4 (7 H, m, 7 Ar–*H*). 1-Acetonaphthone: IR (neat) ν_{max} 1675 cm^{-1} (C=O); ^{1}H NMR (60 MHz) δ 2.41 (3 H, s, CO–CH$_3$), 6.9–7.7 (7 H, m, 7 Ar–*H*) were thus characterized.

Conclusions

Three new polymeric peroxides have been synthesized from vinyl and substituted vinylnaphthalene monomers (aromatic monomers) and characterized. All these polymers degrade exclusively into formaldehyde and the corresponding aldehyde or ketones, similar to those of PSP and PMMAP. All of them possess extremely high heats of degradation. The heats of degradation of these three polyperoxides were found to be larger than that of the aliphatic polymer PMMAP (Table III) and slightly higher than PSP. PVNP2 was found to be less stable than PMVNP1 and PMVNP2, presumably due to the former being a secondary peroxide. Tertiary peroxides have been shown to be more stable.[8]

As expected, these polyperoxides also exhibit autopyrolysis and autocombustion, though no quantitative studies in this regard have been undertaken. A comparison of the various polyperoxides with respect to their degradation products, heats of degradation, etc., is given in Table III.

Registry No. 2-Vinylnaphthalene, 827-54-3; 2-acetonaphthone, 93-08-3; 1-(α-methylvinyl)naphthalene, 1855-47-6; 1-acetonaphthone, 941-98-0; 2-(α-methylvinyl)naphthalene, 3710-23-4.

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