Table II. NMR and IR Spectra for 2,4,6-Triaryl-Substituted Pyridine

	NMR data ($CDCl_3$),[a] δ		IR data (KBr), cm^{-1}		
compd	aliphatic H	aromatic H	CH strech vibrations	C=C vibrations	C=N vibrations
4a			3150	1595	1465
4b					
4c	5.90 s, $-OCH_2O$	7.12–8.24 m			
4d	6.04 s, $-OCH_2O$	6.85–8.20 m			
4e	5.97 s, $-OCH_2O$	6.80–8.10 m	3003	1600	1546
4f	2.35 s, $-CH_3$ 3.85–3.90 d, $-OCH_3$ ($J = 4$ Hz)	6.93–8.13 m			
4g			3157	1610	1475
4h	3.90 s, $-OCH_3$	7.50–8.41 m	3007	1608	1546
4i			3115	1605	1500
4j	3.83 s, $-OCH_3$	6.90–8.30 m			
4k	6.00 s, $-OCH_2O$	6.96–8.10 m			
4l	2.39 s, $-CH_3$	6.78–7.73 m			
4m	2.40 s, $-CH_3$	7.20–8.16 m			
4n	3.76 s, $-OCH_3$	6.80–8.00 m			
4o	3.70–3.75 d, $-OCH_3$ ($J = 5$ Hz)	6.70–7.80 m			
4p	2.40 s, $-CH_3$ 3.85–3.90 d, $-OCH_3$ ($J = 5$ Hz)	7.03–8.20 m			
4q			3000	1590	1570
4r	2.40 s, $-CH_3$	7.16–8.30 m			
4s	2.41 s, $-CH_3$	7.20–8.30 m			
4t	2.47 s, $-CH_3$ 3.85–3.90 d, $-OCH_3$ ($J = 4$ Hz)	7.00–8.40 m			

[a] Key: s = singlet, d = doublet, m = multiplet.

pyridines in general showed a characteristic absorption band in the region 3077–3000 cm^{-1} which is assigned to the C–H stretching mode of pyridine rings. The bands in the region between 1600 and 1500 cm^{-1} are assigned to the interaction between C=C and C=N vibrations of the pyridine rings.[7] The former band, appearing as a double absorption maxima near 1600 cm^{-1} appears to be a general characteristic of trisubstitution at the pyridine nucleus.[8] The chemical shift in the NMR spectra of 2,4,6-triaryl-substituted pyridines exhibits two pyridyl protons (singlet) in the range δ 7.00 to 7.45 and an aromatic multiplet in the range δ 7.50 to 8.45.

Experimental Section

Melting points were determined on a Gallenkamp apparatus and are uncorrected. The IR spectra were recorded on a Perkin-Elmer infracord spectrophotometer using KBr. The NMR spectra ($CDCl_3$) were run on a Varian A-60 spectrometer with tetramethylsilane as internal standard. Analytical samples were purified by column chromatography over neutral alumina, and purity was checked by thin-layer chromatography (TLC).

Isoquinolinium salts were prepared by treatment of α-bromo ketones with isoquinoline in dry benzene at reflux temperature.

Preparation of 2,4,6-Triaryl-Substituted Pyridines

To a stirred solution of 3 mmol of isoquinolinium salts (**1a–c**) in 10 mL of glacial acetic acid was added gradually a solution of α,β-unsaturated ketones (**2a–t**, 3 mmol) in 30 mL of glacial acetic acid in the presence of ammonium acetate under an inert atmosphere of nitrogen at reflux temperature for 3 h. The reaction mixture was then kept overnight at room temperature. It was then washed with ice cold water and the precipitated product so obtained was washed twice with methanol and was crystallized by the appropriate solvent mentioned in Table I.

Acknowledgment

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Spectral and Thermal Data on Poly(styrene peroxide)

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Poly(styrene peroxide) has been prepared and characterized. Nuclear magnetic resonance (NMR) spectra of the polymer show the shift of aliphatic protons. Differential scanning calorimetric (DSC) and differential thermal analysis (DTA) results show an exothermic peak around 110 °C which is characteristic of peroxide decomposition.

Introduction

Polymeric peroxides are generally formed by the reaction of monomer with O_2.[1] Many of the polymeric peroxides are explosive materials. These polymeric peroxides have been used as initiators in polymerization reactions. They have also the potential for use in propellants[2,3] and explosives. The synthesis of poly(styrene peroxide) (PSP) has been reported earlier[5–7] and has been characterized by infrared (IR) spectra iodometric

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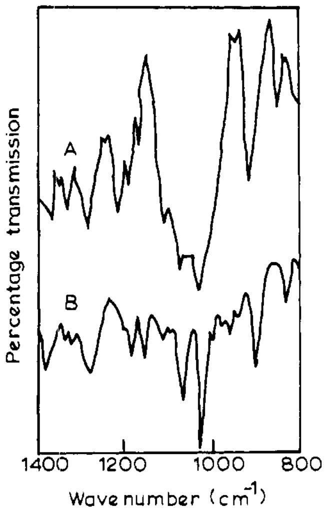

Figure 1. IR spectra of (A) poly(styrene peroxide) and (B) polystyrene.

estimation and microanalysis. In the present work PSP has been synthesized and the data on NMR, DTA, and DSC have been collected and analyzed.

Experimental Section

The PSP was synthesized on similar lines to that described earlier.[5] The material was purified by dissolving and precipitating from methanal several times and was then dried under vacuum at 25 °C. PSP was characterized by microanalysis and IR spectra. IR spectra are shown in Figure 1; a strong, broad absorption band at 1025 cm^{-1} characteristic of peroxide linkage[5] can be seen. PSP is quite safe to handle but should always be stored in a refrigerator in the dark.

NMR Studies

NMR spectra of PSP and polystyrene (PS) in CCl_4 (30 mg/mL) were recorded at 22 °C on a 100-MHz Varian Associates spectrometer; NMR spectra were also recorded in $CDBr_3$ at 80 °C. NMR spectra of PS and PSP are shown in Figure 2. The peaks in both PS and PSP are smooth and poorly resolved because the polymer is atactic, since they have been prepared by free radical bulk polymerization. Both the peaks corresponding to α and β backbone protons get completely shifted in PSP (α protons are shifted more compared to β protons) and there is no sign of any peak in the region of aliphatic protons corresponding to PS. This suggests that the -O-O- group gets attached to methylene carbon. The -O-O- group in PSP decreases the shielding effect of the phenyl group and makes the benzene ring rotate more freely, thus making PSP more atactic than PS. That is why downfield for PSP we get a single sharp peak compared to two peaks in PS.

DTA and DSC Studies

The DTA and DSC thermograms of PSP were obtained on an automatic Wagnomat DTA-02 Universal GDR instrument and Perkin-Elmer DSC IB instrument, respectively. In DTA runs, 50 mg of the sample and 2 °C min^{-1} of heating were used. The operation was done in air.

The calibration and operation of DSC instrument were done according to the manufacturer's instructions. Flowing dry N_2 was used as an inert atmosphere inside the calorimetric cell.

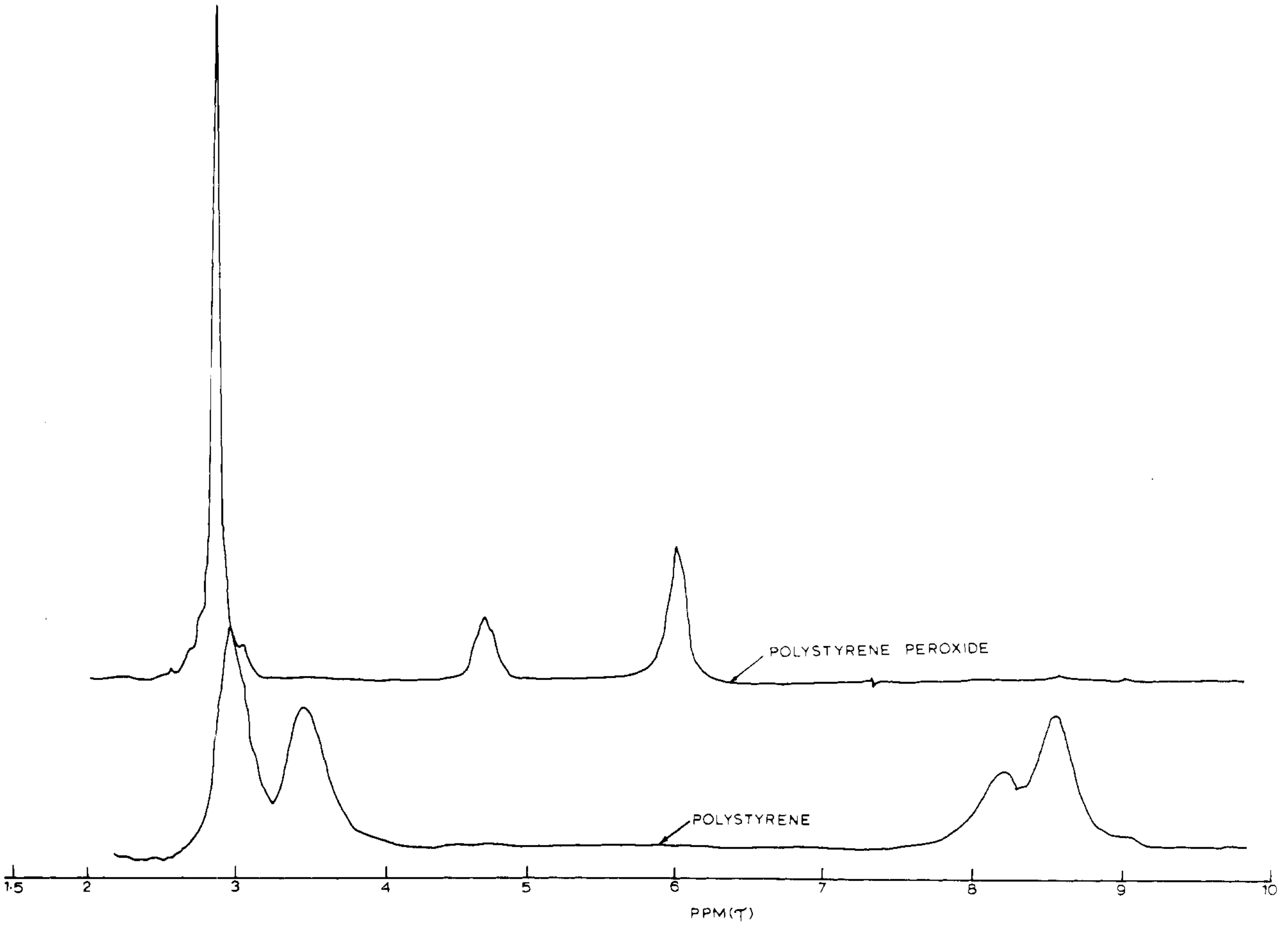

Figure 2. NMR spectra of poly(styrene peroxide) and polystyrene.

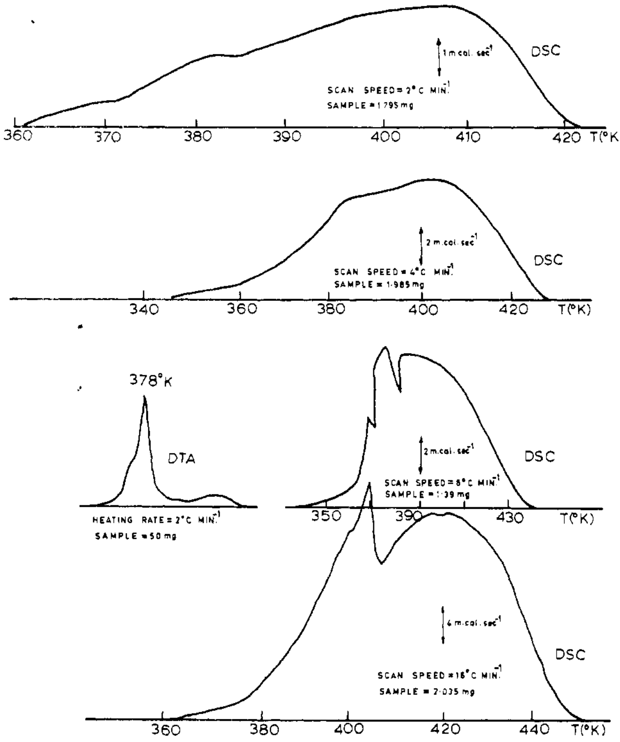

Figure 3. DTA and DSC thermograms (exothermic) in scanning mode for poly(styrene peroxide) decomposition.

Sealed pans were used during the operation which contained about 2 mg of the sample. Scanning rates of 2, 4, 8, and 16 °C min^{-1} and range settings of 2, 4, and 8 mcal s^{-1} for 10-in. deflection were employed.

The DSC/DTA thermograms of PSP up to a limited temperature of interest are shown in Figure 3. For pure PS the DTA and DSC both exhibit endotherms around 450 °C which is characteristic of its degradation. The PSP shows exothermic decomposition around 110 °C in addition to the endothermic degradation around 450 °C. The exothermic decomposition of PSP around 100 °C is characteristic of peroxide bond breakage. Many of organic peroxides are known to decompose violently around this temperature. The DSC thermograms show that exothermic peak temperature shifts ahead as the heating rate is increased. The shift of peak temperature with the change in heating rate is quite well-known in literature.

It has been reported earlier that PSP explodes above 100 °C. The present thermal studies have shown that cause of explosion may be the highly exothermic reactions of the peroxides which start occurring around 100 °C. It may be possible to determine the concentration of PSP in a PS + PSP mixture by estimating the enthalpy of the exothermic DSC peak around 100 °C.

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Correction

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