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SHORT COMMUNICATION

Thermal Stability of Polystyrene Peroxide

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Polymeric peroxides are a very important class of compounds in polymer chemistry because they can be used as initiators for polymerization and because of their formation during the oxidation of polymers. In order to prevent polymer deterioration, the formation and degradation of polymeric peroxides should be controlled. Thus an in-depth understanding of the mechanism of decomposition of polymeric peroxides is essential. The present status of the field of polymeric peroxides has been reviewed recently [1]. Reference 1 also describes the large amount of work done by Mayo et al. several years ago. Generally, these polymeric peroxides can be classified into hydroperoxides, where the peroxide group is attached as a side chain to the main carbon skeleton of the polymer, and into in-chain peroxides, where the O–O bond is present in the main backbone. The present work deals with the in-chain peroxide of polystyrene.

No information is available on the effect of molecular weight on the thermal stability of polymeric peroxides. The present communication describes the effect of molecular weight on the thermal decomposition of poly(styrene peroxide).

Poly(styrene peroxide) (PSP) was synthesized by copolymerizing styrene with oxygen using AIBN as initiator. Fifty milliliters of styrene was taken in a 250-mL, three-necked, round-bottom flask fitted with two gas bubblers and a long Leibigs condenser. The condenser was made very long (~3 ft) to minimize the escape of styrene. The set up was kept at 50°C in a thermostat, and O_2 was bubbled through it at a rate of 1 L/min. Recrystallized AIBN was used as the initiator. Polymerization was done for 15 h. Samples of different molecular weight were prepared by changing the initiator

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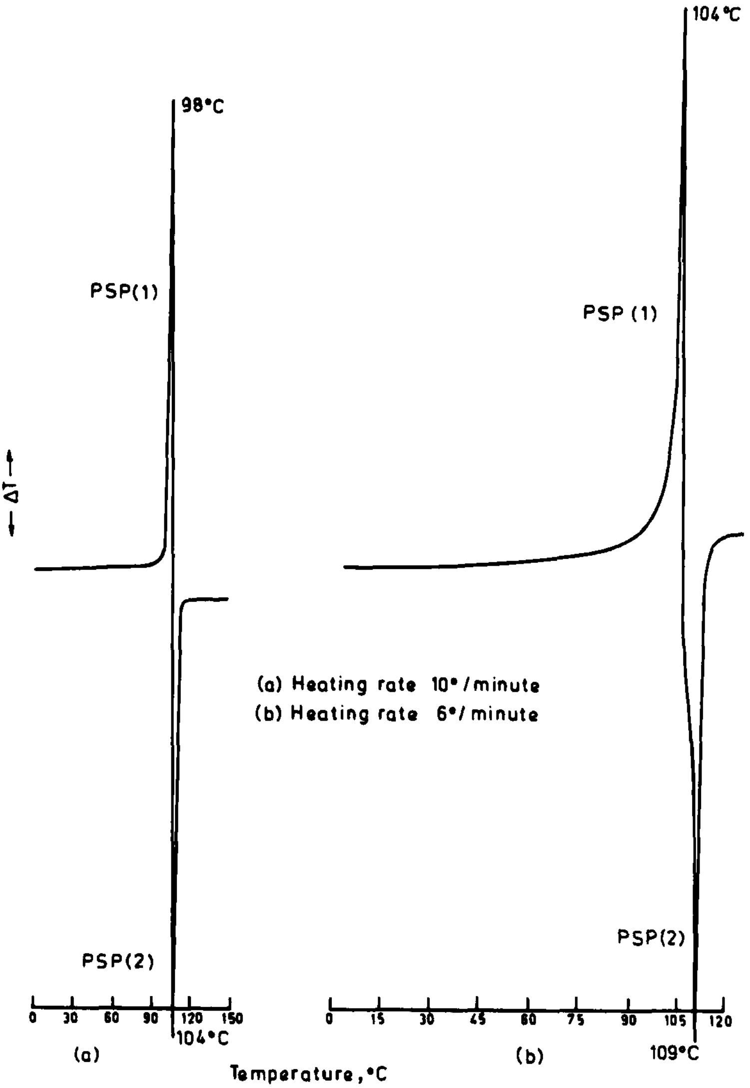

FIG. 1. Differential DTA thermogram of PSP(1) and PSP(2).

concentration while maintaining the other experimental condition constant. Two samples were prepared: PSP(1) with an initiator concentration of 50 mg/50 mL of styrene and PSP(2) with 200 mg of initiator in 50 mL of styrene. The purity of the PSP samples was determined by IR, NMR, and C and H analysis. Viscometry was used to

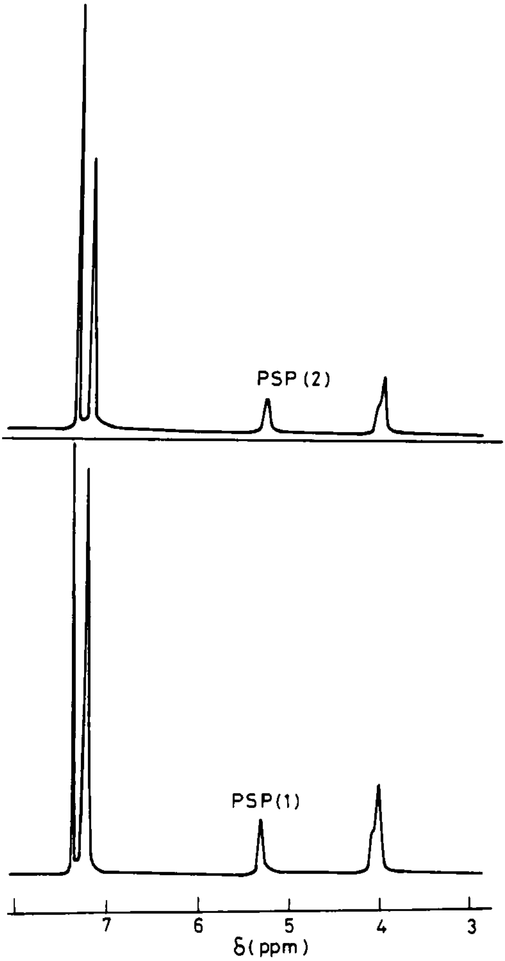

FIG. 2. FT NMR (270 MHz) ^{1}H spectra of PSP(1) and PSP(2) in $CDCl_3$ at room temperature.

determine the molecular weight of PSP(1) and PSP(2). The intrinsic viscosity was 0.028 for PSP(1) and 0.018 for PSP(2). DTA and dynamic TG studies were carried out on these samples. Homemade DTA and dynamic TG assemblies were used in the present work [2, 3]. In DTA, the T and ΔT were recorded on a strip chart recorder. In both experiments the reproducibility of temperature measurements were within 1°C. Differential DTA of the PSP samples was done in the following manner. PSP(1) was taken in one of the cups and PSP(2) was taken in the other DTA cup. DTA thermogram were recorded at two different heating rates, one at 6°/min and the other at 10°/min. The thermograms are shown in Fig. 1. In both cases a difference of about 6°C was recorded between the decomposition temperatures of PSP(1) and PSP(2). PSP(1) decomposes at a lower temperature than PSP(2), thereby showing that the sample with a high molecular weight is less stable than the one with the lower molecular weight. The temperature at which the sudden weight loss occurs was noted by dynamic TG. A difference of 11° was observed in the decomposition temperature of PSP(1) and PSP(2).

The observed difference in thermal stability can be explained in two ways. It may be due to the difference in O–O bond strength because of the change in molecular weight or due to the strain on the O–O bond because of the increase in polymer chain length. To confirm whether there is a change in O–O bond distance due to a change in molecular weight, FT NMR spectra of the PSP samples were taken using an instrument of 270 MHz frequency. The spectra are given in Fig. 2. It is evident that there is no change in chemical shift between PSP(1) and PSP(2). This suggests that the O–O bond distance does not change when the molecular weight is changed. Thus the change in thermal stability due to a change in molecular weight may be explained only on the basis of the strain on the O–O bond due to an increase in chain length. It is obvious that the peroxide having a higher molecular weight will produce more strain on the O–O bond and will therefore be less stable as compared to the one having a lower molecular weight.

SUMMARY

It has been observed that poly(styrene peroxide) with a high molecular weight is thermally less stable than the same polymer with a low molecular weight. This has been explained as being due to the strain on the O–O bond due to the greater polymer chain length.

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