THERMAL STABILITY OF BROMOBENZYLATED POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)

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ABSTRACT

The thermal stability of bromobenzylated poly(2,6-dimethyl-1,4-phenylene oxide) (BrPPO) in a nitrogen atmosphere was studied by thermogravimetry. While PPO is thermally stable up to 673 K, BrPPO begins to degrade at 490–540 K, depending on the degree of bromination. The weight loss of BrPPO in the first degradation stage also depends on the degree of bromination. The activation energy for the first degradation stage is about 185 kJ mol^{-1} for BrPPO with a degree of bromination of 50% or less and about 110 kJ mol^{-1} for BrPPO with a higher degree of bromination.

INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a widely used engineering plastic. PPO can be brominated at either the benzene ring or the methyl group, depending on reaction conditions [1,2]. The thermal properties of ring-brominated PPO have been studied [3,4]. Both PPO and ring-brominated PPO undergo one-stage degradation in a nitrogen atmosphere, but the incorporation of bromine lowers the initial degradation temperature and increases the char yield [3]. Methyl-brominated PPO, also known as bromobenzylated PPO, is commonly used as a precursor polymer for further reactions to incorporate other functional groups into PPO [1,5–7]. Chander et al. [5] observed that a bromobenzylated PPO sample showed a two-stage degradation in a nitrogen atmosphere. In this paper, the effect of the degree of bromination on the thermal stability of bromobenzylated PPO will be reported.

EXPERIMENTAL

Materials

PPO was obtained from General Electric; its weight-average molecular weight was 40,700 as determined by intrinsic viscosity measurement.

Bromobenzylated PPO was prepared following the method of White and Orlando [2]. The degree of bromination was varied by adjusting the amount of N-bromosuccinimide used and reaction time. The degree of bromination was determined by ^{1}H-NMR based on the ratio of proton signal intensity of CH_2Br ($\delta = 4.3$) to that of CH_3 ($\delta = 2.1$). In the following discussion, the number after BrPPO (bromobenzylated PPO) denotes the mole percentage of PPO unit that has been brominated.

Equipment

The glass transition temperatures (T_g) of various BrPPO samples were measured using a Perkin-Elmer DSC-4 differential scanning calorimeter with a heating rate of 20 K min^{-1}. The initial onset of slope in the DSC curve was taken as T_g.

The TG curves of various samples in a nitrogen atmosphere were obtained using a Du Pont 9900 thermal analysis system fitted with a 951 thermogravimetric analyzer. The nitrogen flow rate was 75 ml min^{-1} and the heating rate was 20 K min^{-1}. The activation energy of degradation was calculated from the TG curve using the method of Coats and Redfern [8] and assuming first-order kinetics.

RESULTS AND DISCUSSION

The T_g value of ring-brominated PPO increases linearly with increasing degree of bromination [3,4]. Both White and Orlando [2] and Jauhiainen [4] observed a lower T_g value for bromobenzylated PPO than that of PPO, but there was a substantial difference in their T_g values. The present study shows that the T_g value of bromobenzylated PPO decreases linearly with increasing degree of bromination as shown in Fig. 1.

The TG curves of PPO and various BrPPO samples are shown in Figs. 2 and 3. While PPO is thermally stable up to 673 K, BrPPO begins to degrade at a lower temperature. In contrast to the one-stage degradation of ring-brominated PPO [3], BrPPO undergoes a two-stage degradation in agreement with that previously observed by Chander et al. [5]. The amount of weight loss of BrPPO in the first degradation stage depends on the degree of bromination as shown in Fig. 4. When the gas evolved by BrPPO upon heating was passed into a silver nitrate solution, silver bromide precipitate was formed. Thus the initial degradation of BrPPO involves the loss of hydrogen bromide. The curve in Fig. 4 shows the calculated weight loss based on dehydrobromination of BrPPO. The experimental weight loss agrees very well with the calculated weight loss.

The DTG curves show that the rate of weight loss in the first degradation stage of BrPPO reaches a maximum at 605 K, independent of the degree of
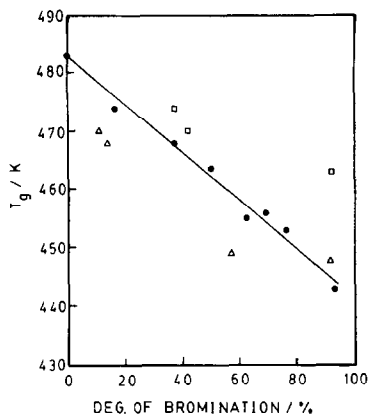
Fig. 1. T_g for BrPPO: ●, this work; □, ref. 2; △, ref. 4.

bromination. However, the initial degradation temperature (T_i) depends on the degree of bromination as shown in Fig. 5. For ring-brominated PPO, a decrease in T_i as a function of the degree of bromination has also been observed [3].

The Coats–Redfern plots for three BrPPO samples are shown in Fig. 6. Figure 7 shows the effect of the degree of bromination of BrPPO on the activation energy (E_a) of the first degradation stage: E_a is about 185 kJ mol^{-1} for BrPPO with a degree of bromination of 50% or less and about 110 kJ mol^{-1} for BrPPO with a higher degree of bromination.
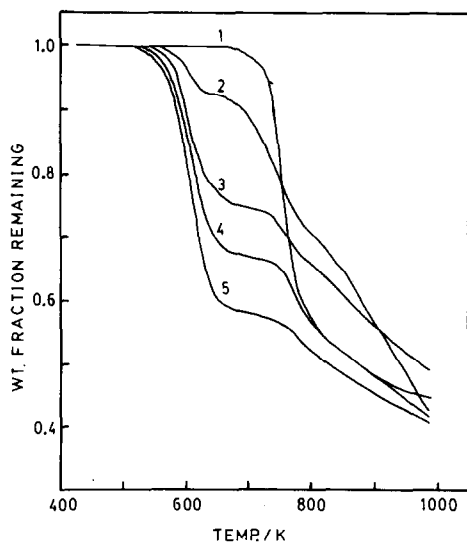
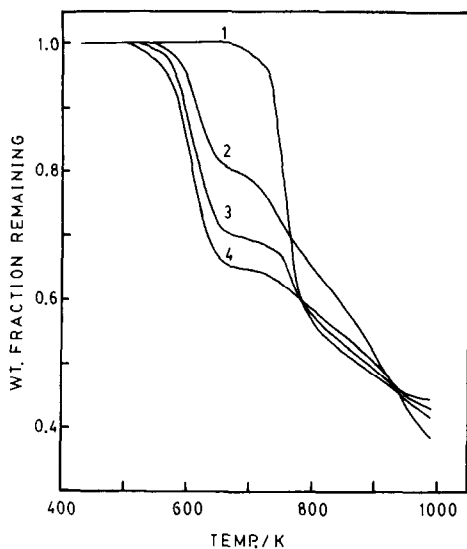Fig. 2. TG curves for various polymers: 1, PPO; 2, BrPPO16; 3, BrPPO50; 4, BrPPO69; 5, BrPPO92.

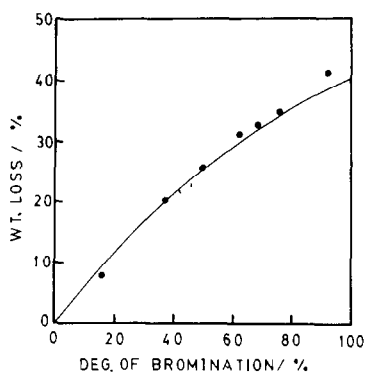Fig. 3. TG curves for various polymers: 1, PPO; 2, BrPPO37; 3, BrPPO62; 4, BrPPO76.

Fig. 4. Dependence of first-stage weight loss on the degree of bromination of BrPPO: experimental value; ————, expected value.
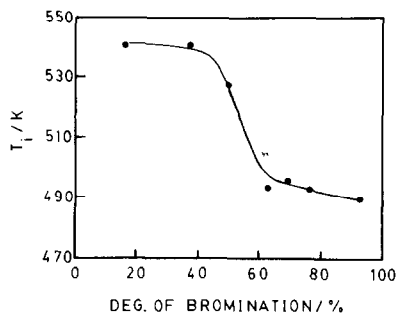

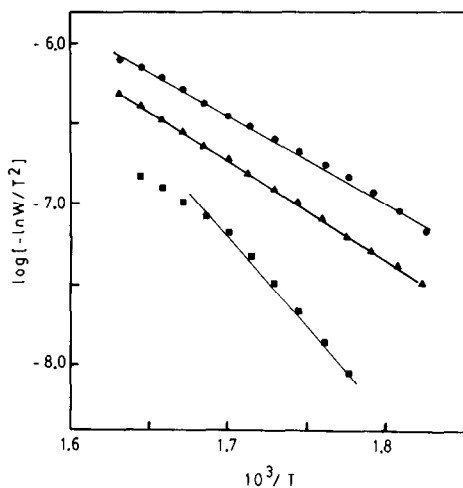Fig. 5. Dependence of initial degradation temperature (T_i) on the degree of bromination of BrPPO.

Fig. 6. Coats–Redfern plots for various polymers: ■, BrPPO16; ▲, BrPPO62; ●, BrPPO76.

The thermal degradation of PPO has been reviewed by Kryszewski and Jachowicz [9]. PPO first undergoes rearrangement as shown in Scheme 1. This is followed by random scission of the benzyl bonds leading to the formation of various products including 2-methylphenol, 2,6-dimethylphenol, 2,4-dimethylphenol and 2,4,6-trimethylphenol.

The initial degradation of BrPPO is likely to involve the homolytic scission of the C–Br bond to form a bromine atom and a benzylic radical, in
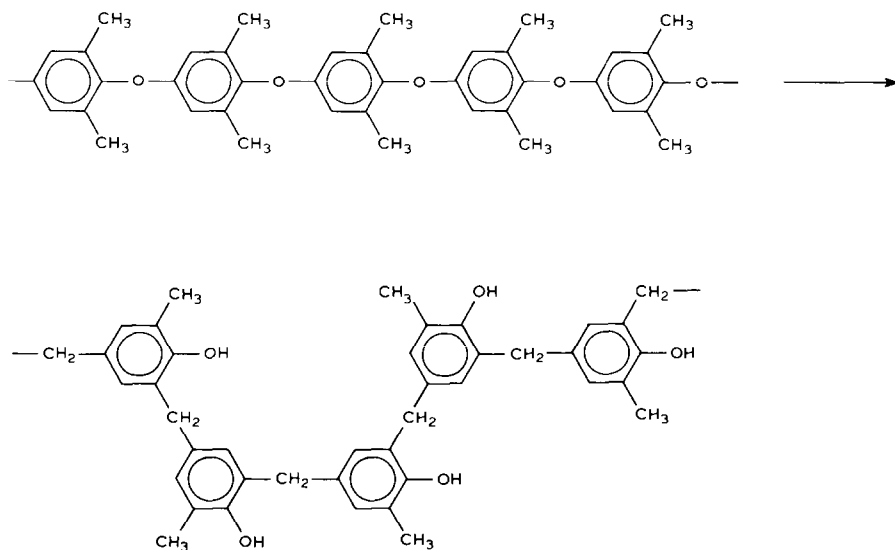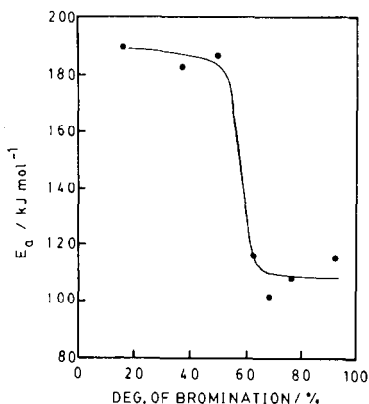

Scheme 1

Fig. 7. Dependence of activation energy (E_a) on the degree of bromination of BrPPO.

view of the low enthalpy of the C–Br bond. Hydrogen bromide is formed through hydrogen abstraction of a methyl group by the bromine atom. The benzylic radicals can rearrange to give a structure similar to that of the rearranged PPO. The final degradation can then proceed through benzylic scission in a similar manner to that shown by PPO.

ACKNOWLEDGMENTS

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