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EFFECT OF IODINATION ON THE THERMAL PROPERTIES OF POLYSTYRENE

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ABSTRACT

The effect of iodination on the glass-transition behaviour and thermal stability of polystyrene was studied by differential scanning calorimetry and thermogravimetry. The glass-transition temperature T_g of polystyrene increases linearly with increasing degree of iodination, but the heat capacity change at T_g decreases with the degree of iodination. Iodination was found to reduce the thermal stability of polystyrene, probably due to the incorporation of weak links during the iodination process.

INTRODUCTION

The properties and applications of poly(*p*-iodostyrene) (PIS) have been the subject of several investigations. Mishra reported that the stability of PIS as an electret was poorer than those of polystyrene (PS), poly(*p*-bromostyrene) and poly(*p*-chlorostyrene) [1]. Russell and Stein studied the miscibility of PIS with PS and with polycaprolactone [2]. We have recently studied the effect of iodination of PS on its miscibility with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [3]. While PS is miscible with PPO, the incorporation of iodine in PS reduces its miscibility with PPO. In this communication, we report the effect of iodination on the glass-transition behaviour and the thermal stability of PS.

EXPERIMENTAL

Materials

PS with a weight-average molecular weight of 150,000 was obtained from BDH Chemicals Ltd. PS was iodinated by reaction with iodine/iodic acid in nitrobenzene [4,5]. The extent of iodination was adjusted by varying the reaction time. The degree of iodination, in terms of mole percentage of

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iodinated PS units, was determined by elemental analysis for iodine. Iodination has been found to occur in the *para* position of the benzene ring [4,5].

Equipment

The glass-transition temperatures T_g of various samples were measured with a Du Pont 910 differential scanning calorimeter using a heating rate of 20 K min^{-1}. Each sample was scanned several times to check the reproducibility of the T_g values. T_g was taken as the initial onset of the change of slope in the DSC curves.

The TG and DTG curves of various samples in a nitrogen atmosphere were obtained with a Du Pont 951 thermogravimetric analyser. The nitrogen flow rate was 75 ml min^{-1} and the heating rate was 20 K min^{-1}.

RESULTS AND DISCUSSION

Glass-transition behaviour

The T_g value of iodinated PS was found to increase linearly with increasing degree of iodination as shown in Fig. 1. Regression analysis of the results leads to the equation

$$T_g\ (\mathrm{K}) = 373.3 + 0.577x$$

where x is the degree of iodination. From the equation, the T_g value for a 100% iodinated PS sample is calculated to be 431 K which is in good agreement with the reported value of 429 K for poly(*p*-iodostyrene) [1,6].

The heat capacity change at T_g (ΔC_p) was found to decrease with increasing degree of iodination as shown in Fig. 2. Extrapolation of the results gives a value of 0.19 J K^{-1} g^{-1} for a 100% iodinated PS sample.

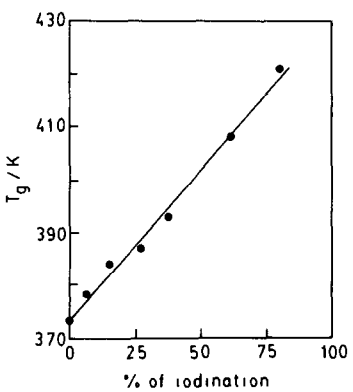

Fig. 1. T_g of iodinated polystyrene.

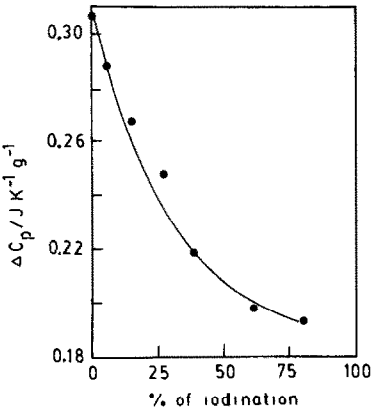

Fig. 2. ΔC_p of iodinated polystyrene.

Iodinated PS can be considered as a copolymer of styrene and *p*-iodostyrene. There are several equations relating T_g and the composition of a copolymer. Two widely used equations are the Fox equation [7]

$$1/T_g = w_1/T_{g1} + w_2/T_{g2}$$

and the Couchman equation [8]

$$T_g = (w_1\ \Delta C_{p1}\ \ln\ T_{g1} + w_2\ \Delta C_{p2}\ \ln\ T_{g2})/(w_1\ \Delta C_{p1} + w_2\ \Delta C_{p2})$$

where w_i is the weight fraction of component i in the copolymer, and ΔC_{pi} and T_{gi} are the heat capacity change at glass transition and the glass-transition temperature of homopolymer i, respectively. Figure 3 shows the T_g–composition curves predicted by the two equations. The calculations were based on T_g values of 373 and 429 K, and ΔC_p values of 0.306 and 0.19 J K^{-1} g^{-1} for PS and PIS, respectively. The Couchman equation gives a reasonably good fit of the T_g values.

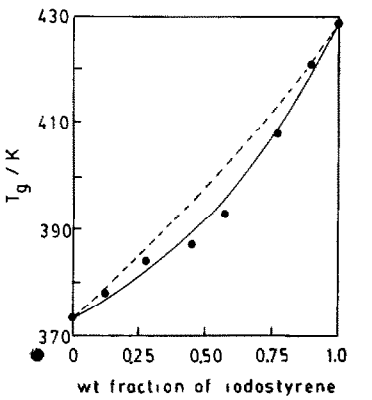

Fig. 3. T_g–composition curves of iodinated polystyrene predicted by the Couchman equation (———) and by the Fox equation (— — —); ● denotes experimental T_g values.

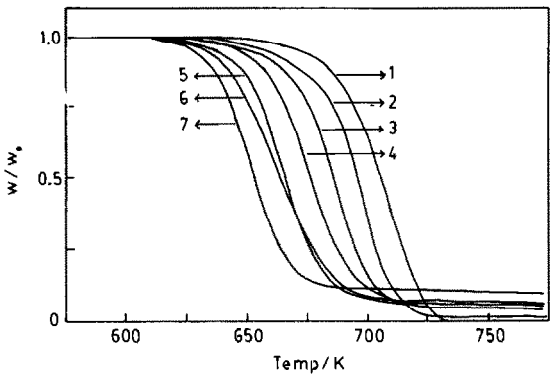

Fig. 4. TG curves of polystyrene (1) and iodinated polystyrene with differing degrees of iodination: (2) 6%; (3) 15%; (4) 27%; (5) 38%; (6) 61%; and (7) 80%.

Thermal stability

The TG curves of PS and various iodinated PS are shown in Fig. 4. Both PS and iodinated PS undergo a one-stage degradation. The thermal stability of PS decreases with increasing degree of iodination. The effect of iodination on the initial degradation temperature T_i and the temperature at which the sample loses half of its initial weight (T_{50}) is shown in Figs. 5 and 6, respectively. Compared to PS, the T_i value for an 80% iodinated PS is 30 K lower. The effect of iodination on T_{50} values is more drastic. The T_{50} value for an 80% iodinated PS is 55 K lower than that of PS.

PS degrades thermally in a single stage and monomeric styrene is the main volatile product [9]. The initial decrease in the molecular weight of PS has been attributed to the weak links incorporated in PS during its formation [9]. Crivello and Lee [5] reported that the number-average molecular

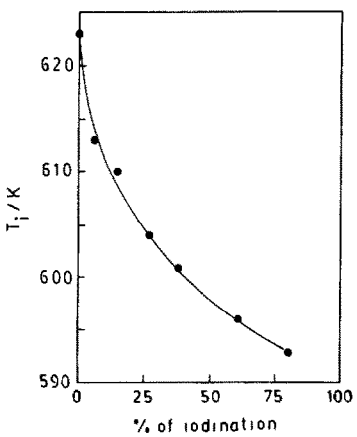

Fig. 5. T_i of iodinated polystyrene.

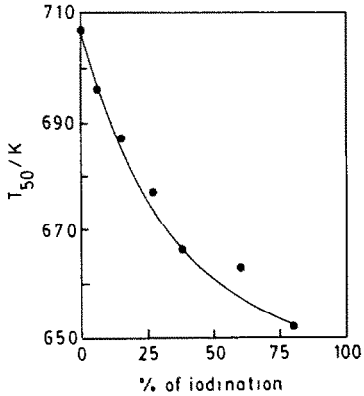

Fig. 6. T_{50} of iodinated polystyrene.

weight of PS remained practically unchanged upon iodination to an extent of 82%. If there are no chain scissions during the iodination process, the molecular weight of an 82% iodinated PS should be about twice that of PS. Apparently, chain scissions do occur. The poorer thermal stability of iodinated PS is probably a result of additional weak links introduced by the chain scissions during iodination.

ACKNOWLEDGEMENTS

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