*Short Communication*

# THERMAL STUDIES OF COPOLYMERS OF STYRENE AND MALEIC ANHYDRIDE

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Copolymers of styrene and maleic anhydride prepared by a charge transfer mechanism have been studied thermally by thermogravimetry and differential scanning calorimetry. The copolymers degrade in two stages; the first stage accounts for about 85% of the degradation. Incorporation of maleic anhydride to styrene decreases the thermal stability of the later. Differential scanning calorimetric studies show two exotherms between 300° to 500 °C. Glass-transition temperatures for the copolymers are lower than that of polystyrene.

Charge transfer copolymerization and thermal studies of the copolymers have been performed extensively in this laboratory [1–3]. Thermogravimetric (TG) studies of polystyrene (PSt) and its copolymers have been discussed by several workers [4–6]. Eisenberg et al. [7] showed that in PSt copolymers ionic groups were sometimes more effective in raising the glass-transition temperature than were hydrogen-bonding interactions.

We now report the thermal behaviour of some copolymers of St and maleic anhydride (MAn) with different compositions, prepared by a charge transfer-initiated mechanism.

## Experimental

Copolymers of St and MAn with different feed ratios were prepared by a charge transfer-initiated mechanism, using *n*-butylamine and carbon tetrachloride as initiators, in dimethyl sulphoxide in vacuum at 60°. The precipitated copolymers

were dissolved in an acetone-dioxan (1 : 1 v/v) mixture and reprecipitated from a mixture of petroleum ether and toluene (2 : 1 v/v). The copolymers were then filtered off, washed and dried in vacuum. The copolymer compositions were estimated by determining the anhydride content conductometrically [8]. Reactivity ratios ($r_1$ and $r_2$) were calculated from the data obtained for low conversions (usually less than 10%), via the Finemann–Ross (FR) and Kelen–Tüdős (KT) methods [9, 10]. The intrinsic viscosity [$\eta$] in chloroform at 30° was determined with an Ubbelohde viscometer.

$^{13}$C–NMR spectra were recorded on a Bruker WH–270 pulsed Fourier transform NMR spectrometer at 67.89 MHz, using broad band proton decoupling.

Thermogravimetric analysis was carried out with a Perkin–Elmer thermal analyser in air, at a heating rate of 10 deg/min $5 \pm 1$ mg of powdered sample was used.

Differential scanning calorimetric (DSC) data were obtained during first heating in air with a Mettler TA 3000 instrument employing standard laboratory practice at a heating rate of 10 deg/min $4 \pm 1$ mg of sample was used for each DSC experiment.

## Results and discussion

Table 1 shows the intrinsic viscosities and compositions of the copolymers. The graphically calculated values of $r_1$ and $r_2$ were:

$$\text{FR method:} \quad r_1 = 0.033 \pm 0.003 \quad r_2 = 0.004 \pm 0.002$$

$$\text{KT method;} \quad r_1 = 0.032 \pm 0.002 \quad r_2 = 0.003 \pm 0.002$$

The structural data calculated via the equations suggested by Ekpenyong [11] showed that the alternation St–MAn was more than 90%. The triad distributions

**Table 1** Intrinsic viscosities [$\eta$] and compositions of St/MAn copolymers prepared by charge transfer mechanism

| Feed ratio [St]/[MAn] | [$\eta$] dl g$^{-1}$ | Copolymer composition [St]/[MAn] |
|---|---|---|
| 0.50 | 0.69 | 1.01 |
| 1.02 | 0.72 | 1.03 |
| 2.04 | 0.79 | 1.07 |
| 2.98 | 0.85 | 1.10 |
| 5.50 | 0.91 | 1.18 |
| 9.00 | 0.98 | 1.40 |
| 23.11 | 1.02 | 2.12 |

for the copolymers (up to a feed ratio of 5.5), obtained from the $^{13}C$–NMR study, were MSM $\approx$ 89%, SSM $\approx$ 4%, MSS $\approx$ 4% and SSS $\approx$ 2%. Peak assignments were made and triad distributions were established as described elsewhere [12]. Thus the copolymers formed have an alternating tendency, irrespective of the feed ratio used. However, when the feed ratio [St]/[MAn] is very high (23:1), the copolymer composition is approximately 2:1; the high St content might be due to the formation of homopolymer PSt together with the copolymer. This is confirmed by the fact that such samples are insoluble in dilute alkali and swell in acetone [13].

The [$\eta$] values of the copolymers increase with increase of the St content in the feed.

TG traces for PSt and for the copolymers of St and MAn with varying compositions, obtained by heating the samples in air, are shown in Fig. 1. PSt was· observed to suffer a sharp weight loss in the temperature range 300–420°. The copolymers undergo a two-stage weight loss. Th first stage corresponds to about 85% when the composition is approximately 1:1. This first stage weight loss is in the same range as for the first stage degradation of PSt. With higher St content, the first stage weight loss and the decomposition temperature increase. The copolymers degrade at a lower temperature than that for PSt; thus, the incorporation of MAn into PSt decreases the thermal stability of the latter. The temperature of maximum rate of weight loss was at around 330°, whereas for PSt it was 380°. Since the compositions of the copolymers do not differ much, the thermal stabilities of the copolymers do not vary appreciably either. It is known that PSt decomposes mainly
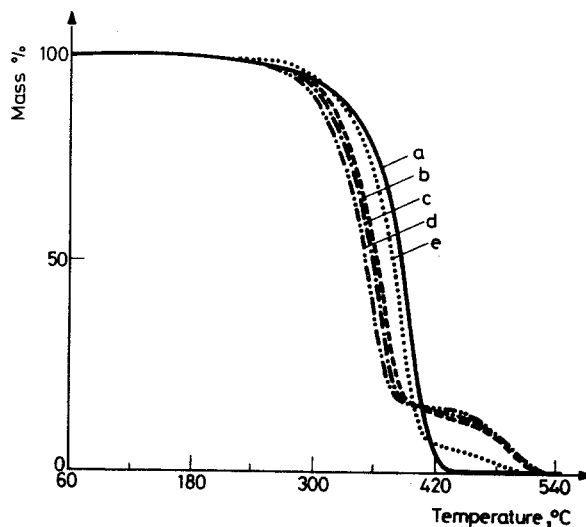


Fig. 1 TG traces in air at a heating rate of 10 deg/min for PSt and St co MAn with varying compositions: (a) PSt; (b) St co MAn (1.18:1); (c) St co MAn (1.10:1); (d) St co MAn (1.01:1); (e) St co MAn (2.12:1)
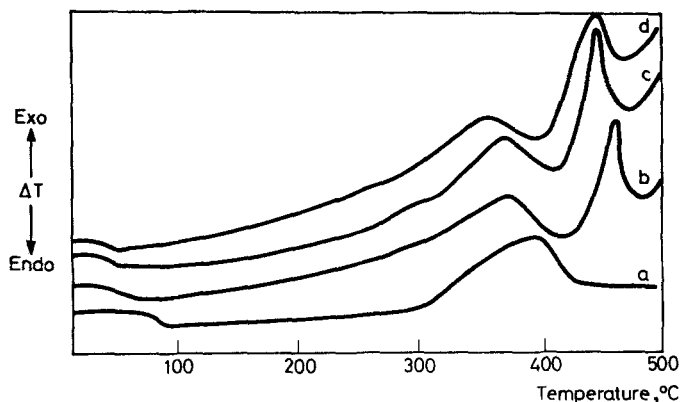
**Fig. 2** DSC traces in air at a heating rate of 10 deg/min for PSt and St co MAn with varying
compositions: (a) PSt; (b) St co MAn (2.12 : 1); (c) St co MAn (1.18 : 1); (d) St co MAn (1.01 : 1)

by depropagation and that the controlling factor in the mechanism of the
degradation is the nature of the side groups attached to the carbon atom at which
the chain scission occurs [14]. Thus, the anhydride units of MAn might be
responsible for the early degradation of the copolymers. For the copolymers, about
15% residue is left after 400°, and the maxima for the second stage degradation
occur at around 450°.

The DSC curves recorded in air at a heating rate of 10 deg/min, in the
temperature range 20–500°, for PSt and copolymers of St and MAn, are shown in
Fig. 2. For PSt, the DSC curve shows an endothermic transition at 98° and an
exothermic transition at 380°. The DSC traces for the copolymers indicate an
endothermic transition at around 50°, which may correspond to the glass transition
temperature $(T_g)$ of the copolymers. There are two exothermic peaks at around 360°
and 435°, the former having a lower enthalpy of transition ($\approx 120$ J $g^{-1}$) than the
latter ($\approx 200$ J $g^{-1}$). In both transition, the order of reaction (determined from the
Arrhenius plot) approximates to unity, showing that the decomposition process is
not too complex. The first exotherm is in the weight loss region, as shown by the TG
traces, and this is the main degradation stage, accounting for about 85% of the
degradation. The 15% remaining after the first stage causes the second exothermic
decomposition peak. The broadening of the first exotherm with increase of the
MAn content of the copolymer shows that, although the MAn units cause an early
start of degradation, they also introduce a slow step in the decomposition process.
Peak integration over the whole first stage exotherm gives a high value of enthalpy
of transition, because chain scission takes place in this stage. Since the copolymers
underwent degradation on heating, the reserve run did not reproduce the heating
curves.

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