THERMAL STABILITY OF POLY(β-BROMOSTYRENE) AND COPOLYMERS OF β-BROMOSTYRENE WITH METHYL METHACRYLATE*

A. A. El-Agamey and M. A. Diab

CHEMISTRY DEPARTMENT, FACULTY OF EDUCATION, MANSOURA UNIVERSITY, DEMIATTA, EGYPT

(Received March 14, 1985)

The thermal stabilities of poly(β-bromostyrene), poly-(methyl methacrylate) homopolymers and copolymers of β-bromostyrene-methyl methacrylate covering the entire composition range were studied using TG analysis. At each extreme of the composition range, incorporation of comonomer units results in a copolymer more stable than the brominated homopolymer. Maximum stability occurs for compositions of approximately 62 mole percent β-bromostyrene. The formation of the anhydride structure among the degradation products leads to the stability of the copolymers.

The poor thermal stability of brominated polymers, due to the weak character of the C—Br bond, has received much attention [1, 2]. Blauer and Goldstein [3] reasoned that interposing other monomer units in the poly(vinyl bromide) (PVB) chain would lend stability to the polymer. The copolymerization of methyl methacrylate (MMA) [2], methyl acrylate (MA) [4], methyl vinyl ketone (MVK) [5] and vinyl acetate (VA) [6] with VB is also clearly an effective means of stabilization. The objective of the present investigation was to examine the stability of poly(β-bromostyrene) (β-BS) homopolymer and copolymers of β-BS-MMA.

Experimental

Purification of monomers

β-BS (Aldrich Chemical Company, Inc.) and MMA (BDH Chemicals Ltd.) were degassed and twice distilled on a vacuum line, dried over calcium hydride and kept below −18°.

* Presented at the World Conference of Thermal Analysis, held in Bad Hofgastein (Austria), 1985.
Purification of initiator

2,2'-Azobisobutyronitrile (AIBN) (Eastman Kodak), used as initiator (0.1 w/v), was purified by dissolving in hot ethanol and filtering [7].

Preparation of the polymers:

$P\beta$-BS was prepared by bulk polymerization of a 25 ml sample at 60° with 0.1 w/v benzyl peroxide as initiator. The polymer was precipitated in petroleum ether (b.p. 40–60°), purified by reprecipitation from benzene solution and dried under vacuum. $PMMA$ and $\beta$-BS-MMA copolymers were prepared using AIBN as radical initiator and methyl acetate (50/50% v/v) a solvent. Five different compositions of the copolymers, with 85, 62, 50, 30 and 10 mole% $\beta$-BS units, were prepared to determine the reactivity ratios. The polymerizations were carried out in a thermostat at 60° to about 5% conversion. They were then precipitated in petroleum ether (b.p. 40–60°), reprecipitated in methanol from benzene solution, and dried under vacuum. Molecular weights were determined by osmometry with toluene or cyclohexane as solvent; $P\beta$-BS and $PMMA$ had $\bar{M}_n$ values of 75,000 and 133 000, respectively, and those of the copolymers were 63 000, 55 000, 69 000, 56 000 and 77 000 for 85, 62, 50, 30 and 10% $\beta$-BS, respectively.

Analytical techniques:

Infrared spectroscopy

Spectra were recorded on a Perkin–Elmer 257 grating spectrometer for qualitative or quantitative measurements of the anhydride structure of the degradation products with CHCl₃ as solvent.

Nuclear magnetic resonance spectroscopy

Spectra were obtained with a Perkin-Elmer R 32, 90 MHz spectrometer equipped with an integrator, with a 20 mg sample of copolymer. The polymers were dissolved in 10 ml of CCl₄. Five integrals were obtained for each sample and an average was used for determination of the polymer composition.

Thermal methods of analysis:

Thermogravimetry (TG) was carried out on a Du Pont 950 thermobalance. 10 mg samples were heated at 10 deg/min in a dynamic nitrogen atmosphere (70 ml/min); the sample holder was boat-shaped, 10 × 5 × 2.5 mm deep; the temperature-measuring thermocouple was placed 1 mm from the sample holder.

A Du Pont 900 instrument was used to obtain differential thermal analysis (DTA) curves, with small glass beads as reference. The sample was heated at 10 deg/min from ambient temperature to 500° in a nitrogen flow (80 ml/min).