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

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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°.

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Purification of initiator

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

Preparation of the polymers:

Pβ-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 *β-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% *β-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; *Pβ-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% *β-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 $CHCl_3$ 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 CCl_4. 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, $10 \times 5 \times 2.5$ 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).

Results and discussion

DTA traces of the homopolymers and copolymers are illustrated in Fig. 1. Two endothermic peaks are clearly visible, their relative importance being dependent upon the copolymer composition. The T_{max} for each peak is shown on the traces, which are comparable to those of the corresponding polymers.

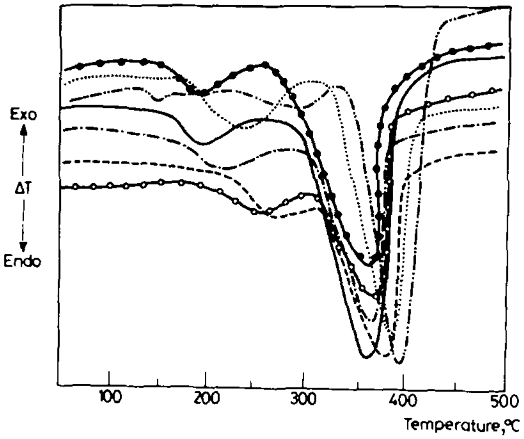


Fig. 1 DTA traces of *Pβ-BS, PMMA* and *β-BS-MMH* copolymers

——— *PB-BS*
–.·.–. 85% *B-BS*
· – – 62% *B-BS*
-0-0-0 50% *B-BS*
–•–•– 30% *B-BS*
– – – 10% *B-BS*
–..–..– *PMMA*

TG curves of *Pβ-BS, MMA* homopolymers and *β-BS-MMA* copolymers are shown in Fig. 2. The degradation starts at ~100° for *Pβ-BS* and ~200° for *PMMA*. Table 1 presents the percentage weight losses for each polymer and the maximum rate of weight loss shown by the derivative equipment associated with the TG apparatus. All the curves exhibit two-stage degradation behaviour. The TG curves reveal that the stabilities of the copolymers are intermediate between those of the two homopolymers.

Variation of stability with composition

To illustrate the initial stages of brakdown more clearly, the degradation was studied at the lower heating rate of 5 deg/min to give a clear picture of relative

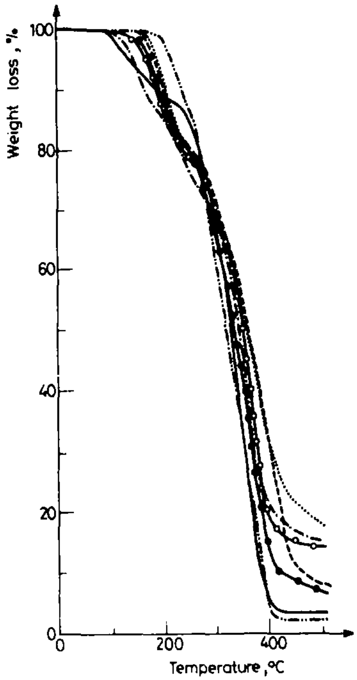


Fig. 2 TG curves for *Pβ-BS*, *PMMA* and *β-BS-MMA* copolymers

——— *Pβ-BS*
-.-.-. 85%*β-BS*
- - - 62% *β-BS*
-0-0-0 50% *β-BS*
-●-●-● 30% *β-BS*
- - - 10% *β-BS*
-..-..-..- *PMMA*

Table 1 Weight loss percentage for the homopolymers of *Pβ-BS* and *PMMA* and *β-BS-MMA* copolymers

Polymer mole, % *β-BS*	Volatilization Temperature, °C	First stage T_{max}, °C	Weight loss, %	Second stage T_{max}, °C	Weight loss, %	Wt.% remaining at 500°C
PB-BS	100	205	12	363	83	5
85	108	215	15	371	68	17
62	195	250	19	405	62	19
50	130	220	20	380	65	15
30	135	230	19	395	73	8
10	165	335	19	400	72	9
PMMA	200	270	12	400	58	3

stability for the entire composition range. The stability increases toward *PMMA*, and the copolymer with 62 mole percent *β-BS* is more stable than the other copolymers. The smooth change in stability with composition is well demonstrated in Fig. 3, in which the weight loss percentage at a selected temperature (200°) in the programmed degradation using the data in Fig. 2 is plotted against composition. The most clearly defined feature of the reaction is the existence of a single stability maximum in the curve of stability versus copolymer composition, occurring in the region of 62 mole percent *β-BS* copolymer. The ir spectra of the degradation products of *β-BS-MMA* copolymers show the formation of an anhydride structure, which has characteristic bands at 1800 and 1740 cm^{-1} (Fig. 4). The quantitative measurements on the anhydride structure, by means of ir spectroscopy, are detailed in Table 2. These data show that the highest value for this structure is 18.6% for the copolymer with 62% *β-BS*; this displays greater stability than the other copolymers. It seems that the formation of the anhydride structure is a direct function of the proportion of adjacent *β-BS-MMA* units in the copolymers. The

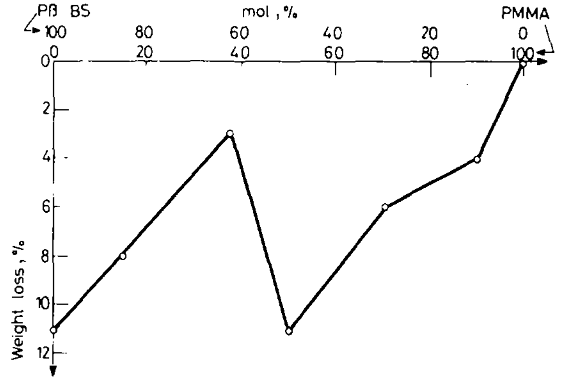


Fig. 3 Comparison of weight loss percentage at 200°C with copolymer composition for heating rate 5 deg/min

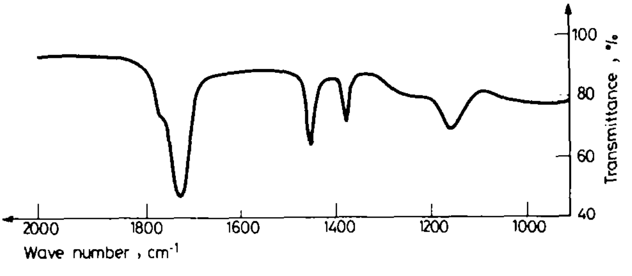
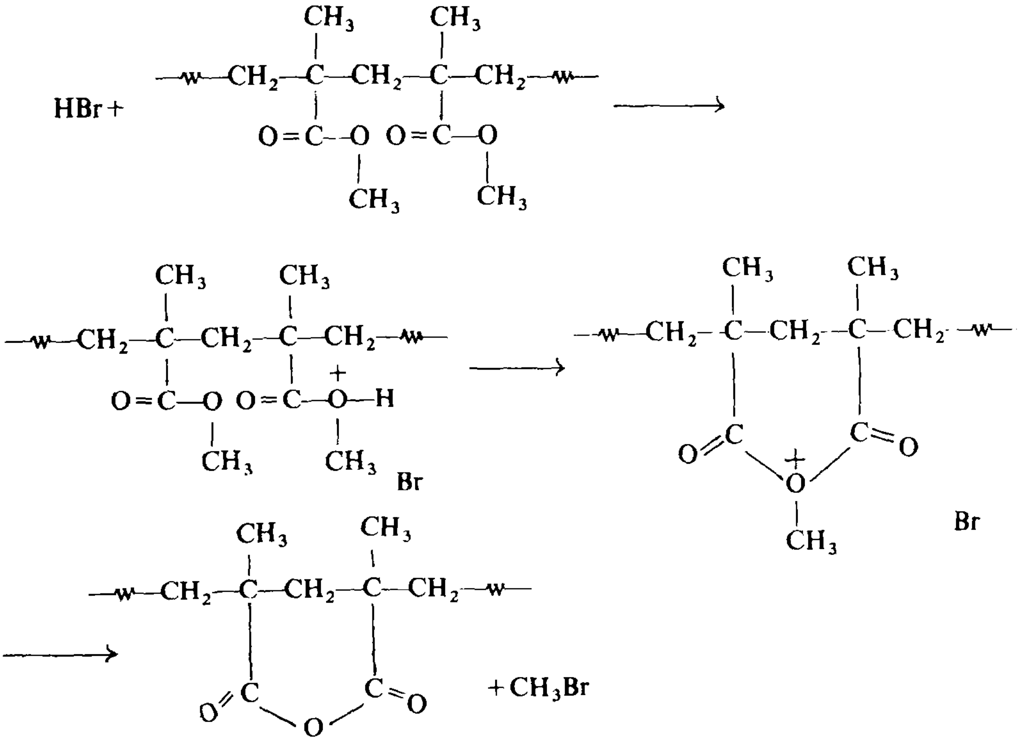


Fig. 4 The 1000–2000 cm^{-1} region of the ir of degradation products of *β-BS-MMA* copolymers

Table 2 Mole percentage of anhydride structure in the degradation of *β-BS-MMA* copolymers at 10 deg/min to 500°C

Degradation products, Mole %	Copolymer composition, Mole % *β-BS*						
	Pβ-BS	85	62	50	30	10	*PMMA*
Anhydride structure	—	7.2	18.6	9.1	8.2	3.2	—

same conclusion was reached for *VB-MA* copolymers [4] and *VB-MVK* copolymers [5]. The sequence distribution of monomer units in the copolymers according to a method developed by Harwood [8], which requires monomer mixture, copolymer composition and reactivity ratios, which were measured by using an nmr technique [9] and found to be $r_1(\beta\text{-}BS) = 0.32 \pm 0.02$ and $r_2(MMA) = 2.72 \pm 0.2$, shows that the maximum number of adjacent *β-BS-MMA* units occurs for the copolymer with 62 mole percent *β-BS*. A possible mechanism for formation of the anhydride structure is:



Formation of the anhydride structure has a stabilizing effect. The copolymer with 62 mole percent *β-BS* is more stable than the other copolymers, but the stabilities of the copolymers are intermediate between those of the *Pβ-BS* and *PMMA* homopolymers. It is clear that, even when the stabilizing anhydride linkage has formed in the degrading copolymers, the effect is still not strong enough to provide a stability comparable to that of *PMMA* itself.

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Zusammenfassung — Die thermische Stabilität von β-Bromstyrol- und Methylmethacrylat-Homopolymeren sowie von sich über den ganzen Zusammensetzungsbereich erstreckenden β-Bromstyrol/Methylmethacrylat-Kopolymeren wurde thermogravimetrisch untersucht. An beiden Enden des Zusammensetzungsbereichs führt der Einbau von Komonomereinheiten zu einem Kopolymer, das stabiler als das bromierte Homopolymer ist. Maximale Stabilität wird bei einem Gehalt von etwa 62 Mol-% β-Bromstyrol erreicht. Die Bildung der Anhydridstruktur führt zur Stabilität des Kopolymers.

Резюме — Методом ТГ изучена термоустойчивость поли/β-бромстирола, полиметилакрилата и сополимеров β-бромстирола и метилметакрилата во всей области их состава. Соединение комономерных звеньев в сополимере для каждой экстремальной области состава, приводит к его большей термоустойчивости по сравнению с бромированным гомополимером. Максимальная термоустойчивость достигается для составов с содержанием β-бромстирола приблизительно равным 62%. Образование среди продуктов разложения ангидридной структуры способствует устойчивости сополимера.