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STUDY ON THE THERMAL BEHAVIOURS OF HOMO- AND COPOLYMERS OF STYRENE, MA AND AN BY THERMOGRAVIMETRY*

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The thermal behaviours of polystyrene (PS), polymethylacrylate (PMA), polyacrylonitrile (PAN), polystyrene-co-methylacrylate [P(S : MA)](alternate and random), polystyrene-co-acrylonitrile [P(S : AN)] (alternate) and a terpolymer of styrene, methylacrylate and acrylonitrile [P(S : MA : AN)] are discussed on the basis of non-isothermal thermogravimetric studies. The thermal stabilities of the copolymers have been found to be intermediate between of those of the individual homopolymers. The stability of the [P(S : AN)] copolymer is higher than those of the individual homopolymers. The activation energy values are also in accordance with the thermal behaviours of these polymers.

The use of polymers for high-temperature systems has made it imperative to study the thermal behaviours of different types of polymers and copolymers. Studies on the thermal behaviours of these polymers are helpful in increasing their applicability and also in modifying the molecular structure to improve the useful properties. The thermal degradation of vinyl homo- and copolymers has been studied by only a few workers [1—5] and the pyrolytic products of some polymers have also been identified [1—4]. In this investigation, the thermal behaviours of homo- and copolymers (binary and ternary) of vinyl monomers, i.e. methyl acrylate (MA), styrene (S) and acrylonitrile (AN) have been studied by thermogravimetry.

Experimental

Homo- and copolymers of S, MA and AN monomers were synthesized in the bulk phase by free radical polymerization, using $\alpha\ \alpha'$-azobisisobutyronitrile (AIBN) (Table 1). Binary and ternary alternate copolymers of S, AN and MA were prepared using $ZnCl_2$ as complexing agent.

The intrinsic viscosity, $(\eta)_{int}$, of the samples was measured by dilute solution viscometry, in benzene solution at 25°. The samples were characterized by infrared spectroscopy, using a Perkin-Elmer 599 B IR spectrophotometer to determine the molecular structure via the bands at 2952 cm^{-1} (aromatic), 2240 cm^{-1} ($-CN$), and 1730 cm^{-1} (ester). The NMR spectra were also recorded in deuterated chloro-

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Table 1

Data showing the conditions of preparation of polymers and copolymers of different compositions and the values of T_i and E

S. No.	Polymer	AIBN × 10^4, mole/l	$ZnCl_2 \times 10^3$ mole/l	Nature of polymer	$[\eta]_{int}$	T_i,K	E, kJ/mole
1	PS	5	—	Homopolymer	1.045	552	109
2	PMA	5	—	Homopolymer	3.13	598	133
3	PAN	5	—	Homopolymer	—	582	326*
4	P(S:AN)	5	4.5	Alternate copolymer (S:AN – 1:2)	0.68	596	142
5	P(S:MA)	5	5	Alternate copolymer (S:MA – 1:1)	1.00	550	113
6	P(S:MA)	—	5	Alternate copolymer (S:MA – 1:1)	0.88	554	121
7	P(S:MA)	5	—	Random copolymer	0.40	543	109
8	P(S:MA:AN)	5	5	Alternate terpolymer	0.21	554	121

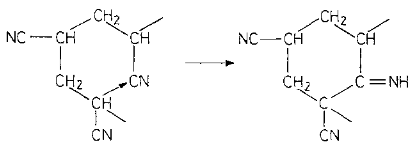
* Calculated by the method of Fuoss et al [9].

form ($CDCl_3$) solution, using TMS as an internal standard, with a Varian XL-100 NMR spectrometer, to determine the structural compositions of the copolymers.

The thermal evaluation of these samples was done by dynamic thermogravimetry, using a Stanton Redcroft (TG 750) thermobalance in nitrogen atmosphere (10 ml/min) at a heating rate of 10°/min. The activation energy, E, of degradation was calculated from the curves, using the Coats and Redfern [6] method, by plotting $\log\left(\frac{g(\alpha)}{T^2}\right)$ vs. $1/T$, the intercept giving the value of $E/2.3\ R$.

Results and discussion

The initial temperatures (T_i) of weight loss of PS and PMA are 552 and 598 K. but their weight loss behaviours have been found to be the same (Fig. 1) (Table 1), Madorsky [7] has reported that PS and PMA both produce monomer and small chain fragments during thermal degradation by depolymerization and random chain scission, which includes varying amounts of intra- and inter-chain transfer reactions, as indicated by their similar weight loss behaviours. The thermal stability of PS has also been reported to be dependent on the end-groups of the molecular chain formed during synthesis [2]. The weight loss of PAN has been found to be faster after the initiation temperature of 580 K (Table 1), and within 5° a 50%



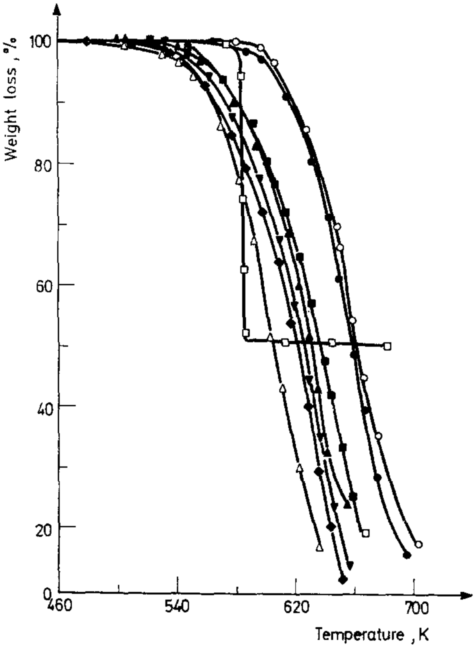
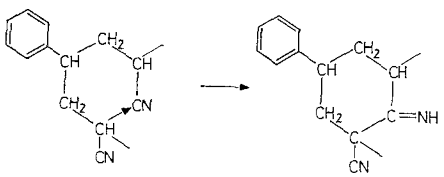


Fig. 1. TG of homo- and copolymers of styrene, MA and AN (10deg/min) ○ PMA, △ PS, □ PAN, ● P(S : AN), ■ P(S : MA), without AIBN, ▲ P(S : MA : AN), ▼ P(S : MA), (Without $ZnCl_2$), ♦ P(S : MA)

weight loss takes place (Fig. 1). Kaesche-Krische [8] has reported that the steep weight loss from PAN is associated with the formation of unsaturated liquid nitrile, which is followed by cyclization of the AN unit, making the resultant product more thermally stable (reaction 1), which causes the appearance of a plateau after 585 K (after 50% weight loss) (Fig. 1).

The thermal stabilities of [P(S : MA)] copolymers (alternate and random) have been found to be intermediate between those of the individual homopolymers of S and MA (Fig. 1). The terpolymer, i.e. [P(S : MA : AN)], has also been found to exhibit intermediate thermal behaviour between those of PS and PMA. The intermediate thermal stabilities of the binary copolymers of MA and S clearly show that depolymerization and random chain scission are similar to those of PS and PMA. The possibility of cyclization or crosslinking in the alternate terpolymer [P(S : MA : AN)] is less compared to pure PAN, and hence its thermal behaviour has not been found to be affected by introduction of AN units in the molecular chain, and the pattern of weight loss is same as for PS, PMA and [P(S : MA)]. The high thermal stability of the [P(S : AN)] copolymer (Fig. 1) may be due to the intramolecular cyclization of AN units, as the alternating sequence of AN and S displays a ratio of 2 : 1. Barton and Werner [10] have also reported the formation of this type of sequence in copolymer under similar conditions. The possible cyclic structure formation may take place by reaction 1 (reaction 2).



The activation energy, E, calculated by the Coats and Redfern method [6], where $g(\alpha) = [-\log(1-\alpha)]^{1/n}$, has also been found to be in accordance with the thermal behaviour of homo- and copolymers (Table 1). The activation energies of alternate and random copolymers of S and MA are intermediate between those of PS and PMA, while with the introduction of AN as alternating units with S and MA, the value of E for the terpolymer remains at 121 kJ/mole, i.e., intermediate between the values for PS and PMA. The E value of PAN is high, i.e. 326 kJ/mole, possibly due to simultaneous chain scission, cyclization and crosslinking. Assuming the same possible cyclization (reaction 2) in the [P(S : AN)] copolymer, this can be interpreted in that the activation energy of degradation becomes high, i.e. 142 kcal/mole.

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Zusammenfassung — Basierend auf nicht-isotherme thermogravimetrische Untersuchungen wurde das thermische Verhalten von Polystyrol [PS], Polymethacrylat [PMA], Polyacrylnitril [PAN], Polystyrol-co-methacrylat [P(S : MA)] (alternierend und random), Polystyrol-co-acrylnitril [P(S : AN)] (alternierend) sowie eines Mischpolymeren von Styrol, Methacrylat und Acrylnitril [P(S : MA : AN)] untersucht. Die thermische Stabilität der Kopolymeren liegt zwischen denen der individuellen Homopolymeren. Die thermische Stabilität des Kopolymeren [P(S : AN)] ist höher als die der individuellen Homopolymeren. Die Werte der Aktivierungsenergie sind ebenfalls in Übereinstimmung mit dem thermischen Verhalten dieser Polymere.

Резюме — На основе неизотермических термогравиметрических исследований, обсуждено термическое поведение полистирола, полиметилакрилата, полиакриронитрила, кополимера полистирола и метилакрилата (чередующегося и произвольного), кополимера полистирола (чередующе- гося), и трехзвенного полимера стирол-метилакрилат-акрилонитрил. Найдено, что термическая устойчивость кополимеров является промежуточной среди индивидуальных гомополимеров. Устойчивость трехзвенного полимера стирол-метилакрилатакрилонитрил является наиболее высокой по сравнению с отдельными гомополимерами. Значения энергии активации согласуются с термическим поведением исследованных полимеров.