Thermal Degradation of Polymers.   Part I. Thermogravimetric and Differential Thermal Analysis Studies of Atactic Poly-*m*-aminostyrene and Related Polymers*

R. H. STILL, *Department of Chemistry and Biology, Hatfield College of Technology, Hatfield, Hertfordshire*, and C. J. KEATTCH, *John Laing Research and Development Ltd., Boreham Wood, Hertfordshire, England*

Synopsis

Thermogravimetric and differential thermal analysis have been employed to study the thermal degradation patterns of poly-*m*-aminostyrenes and poly-*m*-acetamidostyrenes of different molecular weights and also the corresponding 2:1 copolymers with styrene. The thermal degradation routes have also been compared and contrasted with that of polystyrene. Experiments have been carried out in static air and dynamic nitrogen, and the different behavior exhibited by these polymers has been reconciled in terms of their differing structures and different mechanisms for pyrolytic degradation.

INTRODUCTION

Numerous inorganic[1,2] and some organic[2,3] reactions have been studied with the aid of thermogravimetric analysis (TGA) and differential thermal analysis (DTA). In this paper, both TGA and DTA have been employed to investigate the thermal degradation of polymeric species related to poly-*m*-aminostyrene. This study has been carried out in static air and dynamic nitrogen, and attempts have been made to distinguish between oxidative and pyrolytic degradation under these conditions.

EXPERIMENTAL

Materials

The monomer *m*-aminostyrene was synthesized as previously reported[4-6] and was homopolymerized by use of α,α'-azobisisobutyronitrile at two different initiator concentrations (0.2 and 0.5% on the monomer weight) to yield two poly-*m*-aminostyrenes, I and II, of different molecular weights. The polymers were essentially of atactic sterieochemical configuration as a result of their mode of preparation, i.e., free-radical polymerization.

Copolymerization of styrene (2 moles) with *m*-aminostyrene (1 mole) yielded the 2.35:1 copolymer, III.

* Paper presented at the International Symposium on Thermal Analysis, The Northern Polytechnic, London, April 1965.

Acetylation of poly-*m*-aminostyrenes I and II by using the method previously reported,[7] yielded poly-*m*-acetamidostyrenes, IV and V, of different molecular weights. The logarithmic viscosity number $(1/c) \ln (\eta_{soln.}/\eta_{soln.})$, where c is grams of solute in 100 ml. of solution, was determined for solutions of IV and V in benzyl alcohol at 25°C. The values for c thus obtained were 1.2, 0.8, 0.6, 0.4 and on extrapolation yielded a limiting intrinsic viscosity $[\eta]$, of 0.93 and 0.52, showing them to have sensibly different molecular weights.

The copolymer, III, similarly treated yielded the 2.35:1 styrene–*m*-acetamidostyrene copolymer VI, $[\eta] = 0.85$ in benzyl alcohol at 25°C. by extrapolation.

Styrene, similarly polymerized with the use of 0.5% α,α'-azobisisobutyronitrile yielded polystyrene, VII, which had a molecular weight of 210,000. This value was derived by calculation from viscometric measurements in toluene at 25°C. by use of the Mark-Houwink equation.[8,9]

$$[\eta] = KM^{\alpha}$$

where $[\eta] = 0.79$ and the values of K and α were those reported by Green[10] for polystyrene in toluene at 25°C., viz., $K = 1.16 \times 10^{-4}$, $\alpha = 0.72$.

Apparatus and Procedure

Thermogravimetric Analysis Studies. A Stanton thermobalance (Model HT-SM) was used, programmed for a linear heating rate of 3°C./min. (nominal) in both static air and dynamic nitrogen. Approximately 100 mg. of material was employed in each experiment, and the samples were contained in preignited, recrystallized alumina crucibles (Royal Worcester, Size WA2). In the case of experiments carried out in a dynamic gas atmosphere, pure (White Spot) nitrogen was employed at a flow rate of 400 ml./min. All subsequent temperatures quoted for TGA experiments are furnace wall temperatures.

Differential Thermal Analysis Studies. This work was carried out on a Stanton thermobalance (Model HT-D) modified to perform simultaneous TGA and DTA.[11] A heating rate of 6°C./min. (nominal) was employed; platinum pieces were used as the inert reference material, and thermograms were obtained in static air and dynamic nitrogen atmospheres.

RESULTS AND DISCUSSION

Thermogravimetric Analysis

TGA studies in static air and dynamic nitrogen showed that, under the experimental conditions employed, no stable intermediate compounds were formed as evidenced by the absence of any horizontal plateaux in the weight-loss curves.

Poly-*m*-aminostyrene and the related copolymers were compared with a similarly produced atactic polystyrene sample. The thermal stabilities of these polymers in air and nitrogen are summarized in Table I, the decom-

position temperatures quoted being the temperatures at which the first measurable weight losses occurred on the thermogravimetric curves.

TABLE I
Thermal Stability of Polymers in Air and Nitrogen

Polymer	Decomposition temperature, °C.	
	Air	Nitrogen
Poly-*m*-aminostyrene, I	360	360
Poly-*m*-aminostyrene, II	380	—
Styrene–*m*-aminostyrene copolymer, III	260	320
Poly-*m*-acetamidostyrene, IV	300	—
Poly-*m*-acetamidostyrene, V	310	300
Styrene–*m*-acetamidostyrene copolymer, VI	300	340
Polystyrene VII	260	350

Reference to Table I shows that polystyrene is the least thermally stable of the polymers studied. It is also apparent from these thermogravimetric analysis studies in static air that introduction of an amino group into the *meta* position in styrene increases the thermal stability of the resultant poly-*m*-aminostyrenes, I and II, but in contrast, the styrene–*m*-aminostyrene copolymer, III, shows no enhanced thermal stability.

The introduction of an acetamido grouping into the *meta* position in styrene increases the thermal stability of the resultant poly-*m*-acetamidostyrenes, IV and V, to a lesser degree than the amino group. This de-
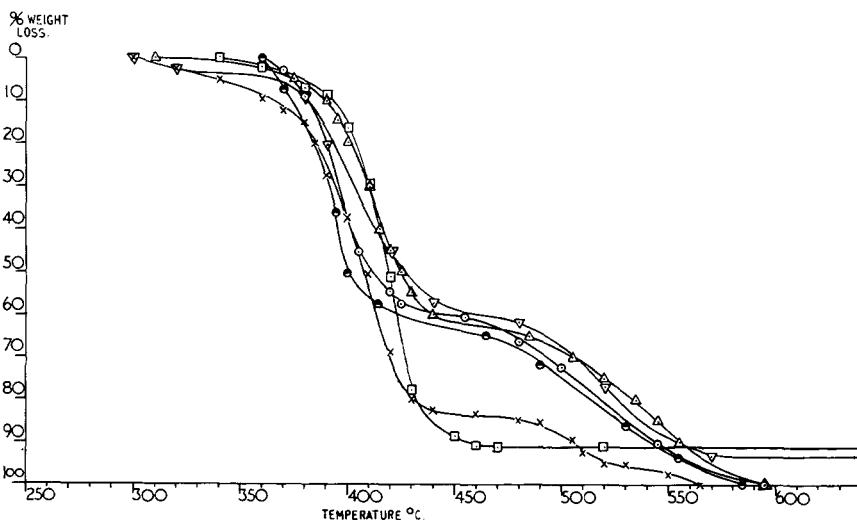

Fig. 1. TGA curves: (●) poly-*m*-aminostyrene (II) in air; (○) poly-*m*-aminostyrene (II) in nitrogen; (△) poly-*m*-acetamidostyrene (IV) in air; (▽) poly-*m*-acetamidostyrene (IV) in nitrogen; (✕) styrene–*m*-acetamidostyrene copolymer (VI) in air; (▢) styrene–*m*-acetamidostyrene copolymer (VI) in nitrogen.
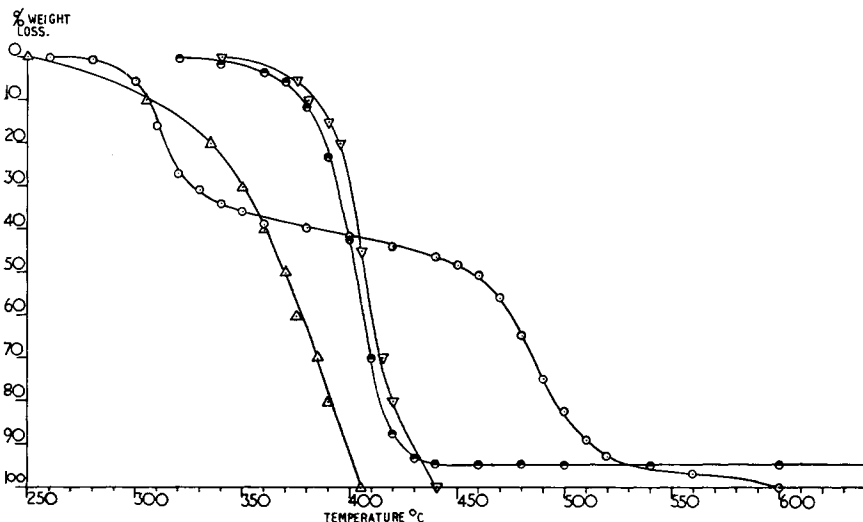
Fig. 2. TGA curves: (⊙) styrene–*m*-aminostyrene copolymer in air; (⊜) styrene–*m*-aminostyrene copolymer in nitrogen; (△) polystyrene in air; (▽) polystyrene in nitrogen.
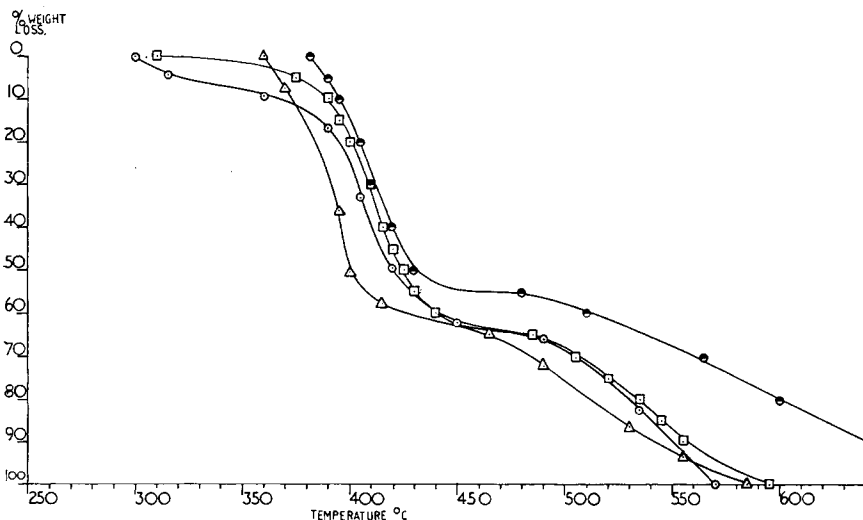

Fig. 3. TGA curves: (⊜) poly-*m*-aminostyrene (I) in air; (△) poly-*m*-aminosty-rene (II) in air; (⊙) poly-*m*-acetamidostyrene (IV) in air; (▯) poly-*m*-acetamidostyrene (V) in air.

crease in thermal stability may be due to the breakage of the side chain unit, i.e., —NHCOCH₃ from the macromolecule followed by thermal de-polymerization of the resultant product.

The styrene–*m*-acetamidostyrene copolymer, VI, where *m*-acetamido-styrene units have been introduced into a polystyrene chain, has a similar thermal stability to the poly-*m*-acetamidostyrene homopolymers, which indicates an increase in thermal stability over the amino copolymer.

A comparison of the thermogravimetric curves in static air and dynamic nitrogen (Fig. 1) shows little or no difference in the case of poly-*m*-aminostyrene, poly-*m*-acetamidostyrene, and the styrene–*m*-acetamidostyrene copolymer. There is, however, a marked difference in behavior of polystyrene and the styrene–*m*-aminostyrene copolymer as is shown in Figure 2. This different behavior has been resolved by DTA studies which show variations in the degradation mechanism of these materials and also of the polymers shown in Figure 1. These results are discussed in detail later in this section.

It is also apparent from the thermogravimetric curves (Fig. 3), that molecular weight has no significant effect on the thermal degradation in static air of poly-*m*-aminostyrenes (I and II) or poly-*m*-acetamidostyrenes (IV and V).

Differential Thermal Analysis

Reference to Figure 1 shows that poly-*m*-aminostyrenes (I, II), poly-*m*-acetamidostyrenes (IV, V) and the styrene–*m*-acetamidostyrene copolymer (VI) all have similar weight loss curves in static air and dynamic nitrogen. However, the DTA thermograms of the above polymers obtained in the same gas atmospheres (Fig. 4) demonstrate that the thermal degradative character differs in the different pyrolysis atmospheres. Poly-*m*-acetamidostyrene (Fig. 4a), in static air shows an endothermic degradation at 440°C., followed by exothermic degradation at 600°C. In dynamic nitrogen, however, the degradation mechanism differs in that only an endothermic degradation at 440°C. is manifest. This behavior is probably due to the fact that, in air, pyrolysis occurs, followed by oxidation; in nitrogen, however the oxidative degradation stage is absent. The anomalous 16°C. exotherm observed in static air is reproducible for both the same sample and for the other poly-*m*-acetamidostyrene of different molecular weight. No explanation, however, can be offered for its magnitude.

Poly-*m*-aminostyrene (Fig. 4b) shows an exothermic degradation at 380°C., followed by an endothermic degradation at 440°C., whereas in dynamic nitrogen, only an endothermic degradation at 440°C. is observed. Thus, in static air, oxidative degradation is followed by pyrolysis, whereas only pyrolysis occurs in a nitrogen atmosphere.

The styrene–*m*-acetamidostyrene copolymer (Fig. 4c) in static air shows an endothermic degradation at 440°C. followed by an exothermic degradation at 560°C. In dynamic nitrogen, only an endothermic degradation at 450°C. is apparent. Thus, again, the presence of a nitrogen atmosphere suppresses the oxidative degradation.

It appears, therefore, that the thermal degradation of poly-*m*-aminostyrene in static air depends upon an oxidative initiation of degradation at a given temperature, while that of poly-*m*-acetamidostyrene is dependent on the thermal rupturing of weak bonds, possibly in the acetamido side chain, which is then followed by oxidative degradation of the residue.

The increased thermal stability of the styrene–*m*-acetamidostyrene co-polymer in static air, compared with both polystyrene and the styrene–*m*-aminostyrene copolymer, may be ascribed to the acetyl group of the acetamido unit which appears to inhibit the initial oxidative degradation
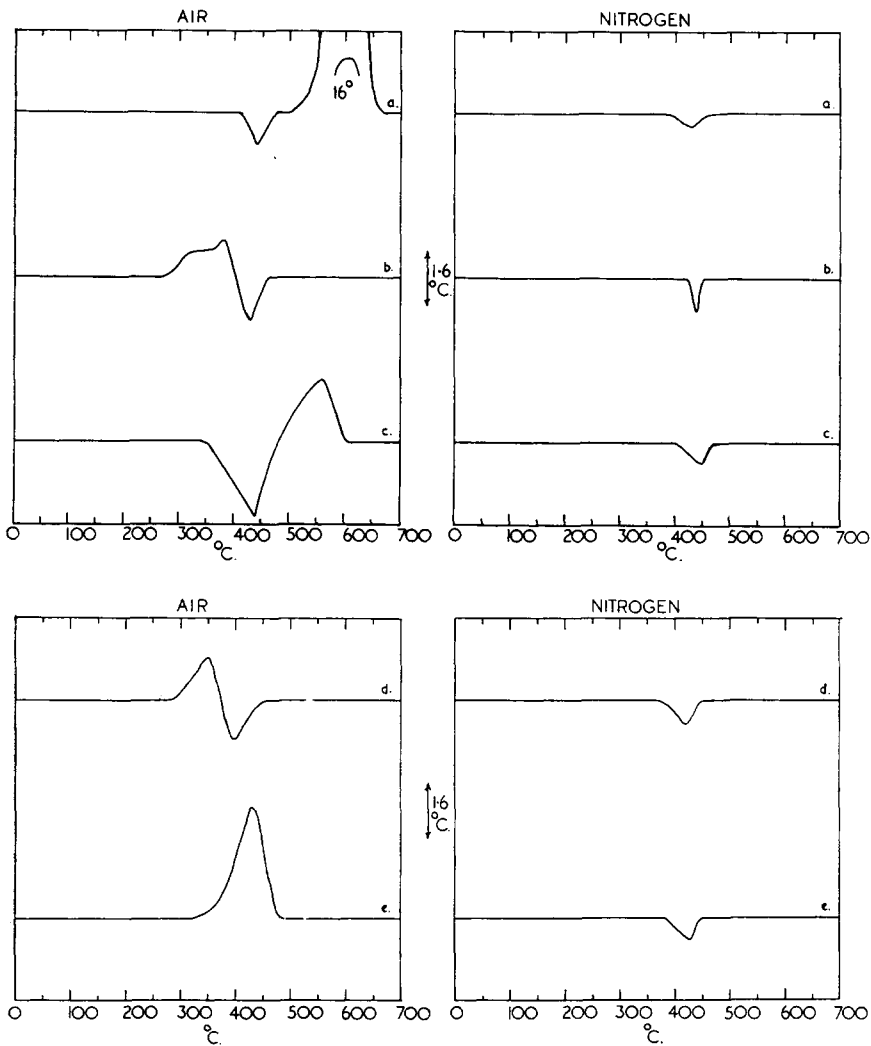

Fig. 4. DTA curves in air or nitrogen: (*a*) poly-*m*-acetamidostyrene; (*b*) poly-*m*-aminostyrene; (*c*) styrene–*m*-acetamidostyrene copolymer; (*d*) styrene–*m*-amino-styrene copolymer; (*e*) polystyrene.

observed in the thermal degradation in static air of these latter two polymers (Fig. 4).

TGA of polystyrene (VII) and of the styrene–*m*-aminostyrene copolymer (III) yields different weight loss curves in static air and dynamic nitrogen,

and DTA confirms a different mechanism of thermal degradation in these different pyrolysis atmospheres.   The styrene–*m*-aminostyrene copolymer (Fig. 4*d*) in static air shows an exothermic degradation at 350°C., followed by an endothermic degradation at 400°C.   In dynamic nitrogen, only an endothermic degradation at 420°C. is manifest.

Similarly, polystyrene (Fig. 4*e*) in static air shows only an exothermic degradation at 430°C. and an endothermic degradation at 430°C. in dynamic nitrogen.

Thus, in the case of the styrene–*m*-aminostyrene copolymer in static air, oxidative degradation is followed by pyrolysis, whereas in dynamic nitrogen, only pyrolysis occurs.

Polystyrene shows simply oxidative degradation in static air and pyrolysis in nitrogen.   This behavior is similar to that observed by Danusso and Polizzotti[12,13] for a sample of atactic polystyrene.

Additional DTA results in static air were obtained on a DuPont 900 differential thermal analyzer.   These thermograms gave the same general pattern shown in the above figures and differed only in one respect, namely a small, reproducible endotherm, 0.1°C. in magnitude, in the range 120–150°C.   This could be ascribed to changes in the thermal conductivity of the polymers resulting in a contraction in volume.   This contraction has been observed visually in a conventional melting point apparatus.   In order to obtain a fuller understanding of the mechanism of thermal degradation of these and other polymers, work is currently proceeding on the analysis of the volatile products, and the results will form the subject of a future communication.

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Résumé

L'analyse thermogravimétrique et thermique différentielle a été appliquée à l'étude de la dégradation thermique de poly-*m*-aminostyrène et de poly-*m*-acétamidostyrène de différents poids moléculaire de même que des copolymères 2:1 correspondant avec le styrène. Les voies de dégradation thermique ont également été comparées et mises en contraste avec celles du polystyrène. Les expériences ont été effectuées soit à l'air soit dans du l'arote et le comportement différent manifesté par ces polymères peut être expliqué sur la base de différences de structures et d'un mécanisme différent de dégradation pyrolytique.

Zusammenfassung

Thermogravimetrische und Differentialthermoanalysen wurden zur Untersuchung des Verhaltens von Poly-*m*-aminostyrolen und Poly-*m*-acetamidostyrolen von verschiedenem Molekulargewicht und ebenso der entsprechenden 2:1-Copolymeren mit Styrol beim thermischen Abbau verwendet. Die thermischen Abbauwege wurden ebenfalls verglichen und denjenigen von Polystyrol entgegengestellt. Die Versuche wurden statisch unter Luft und dynamisch unter Stickstoff ausgeführt und das verschiedene Verhalten dieser Polymeren aufgrund ihrer verschiedenen Strukturen und des verschiedenen Mechanismus des pyrolytischen Abbaus erklärt.