Journal of Thermal Analysis, Vol. 45 (1995) 1239-1243

INVESTIGATION OF THE THERMAL DEGRADATION PROCESS OF POLYSTYRENE BROMINATED ON THE RING

K. Pielichowski[1] *and L. Stoch*[2]

[1]Institute of Organic Chemistry and Technology, Technical University, ul. Warszawska 24, 31–155 Cracow
[2]Academy of Mining and Metallurgy, 30–059 Cracow, Poland

Abstract

The results of investigation of the degradation process of polystyrene brominated on the ring via an ionic route have been presented. Using thermogravimetric (TG) and differential thermal analysis (DTA) methods, the course of degradation of polymer samples with different bromine content has been described. Introducing of bromine on the aromatic ring influenced the initial decomposition temperature (IDT) and the temperature corresponding to the maximum of decomposition rate (T_m).

The samples have been pyrolyzed at 300°C and some pyrolysis products were identified by means of gas chromatography/mass spectrometry. Finally, the possible mechanism of degradation was presented.

Keywords: brominated polystyrene, TG, thermal degradation

Introduction

Halogenation of polymers remains one of the most important reactions since it makes possible determination of the global reactivity of investigated structures, as well as description of novel processes and materials. The gradual replacement of traditional materials by synthetic polymers in many applications has brought with a number of problems, not the least of which is the high inflammability of the polymers and their tendency to produce highly toxic fumes during the course of thermal decomposition [1]. The presence of bromine in the polymer, either as an integral part of its chemical structure or in additive materials, can often have a fire retarding effect [2, 3]. Hence, bromination of polystyrene (PS) is variously carried out to obtain graft polymers and high-reactive modifications which can also serve as potentially fire-resistant materials [4]. Depending on the reaction conditions bromination may lead to the introduction of different amounts of bromine solely into the ring or chain or into both areas of the PS structure [5]. In the case of bromination supported by Lewis acid,

0368–4466/95/ $ 4.00

John Wiley & Sons, Limited
Chichester

bromination occurs on the aromatic rings, preferably at the para position [6, 7]. Formed structures are characterised by different values of the degradation parameters proving that localisation and amount of bromine play a dominant role during thermal decomposition.

This paper attempts to show the thermal degradation behaviour of the brominated polystyrene, synthetised via an ionic route, by means of thermogravimetry and differential thermal analysis, Complementary, preliminary analysis of volatile degradation products was conducted.

Experimental

Materials

PS-samples, brominated on the ring, were synthetised and characterised as described previously [5].

A slight change in reaction conditions enabled us to obtain polymers with different bromine content as shown in Table 1.

Table 1 Characteristics of the samples

No. of sample	Br content / wt%
1	0
2	3
3	36
4	45

Techniques

TG and DTA analysis were performed using a Derivatograph-C thermal analyser (MOM, Hungary). The conditions were: heating rate of 10 deg·min^{-1}; sample mass of 10±1 mg; gas flow of 50 cm^3/min and Al_2O_3 as an inert material. The experiments have been carried out both in argon and air.

The pyrolyses were carried out using a quartz tube with a weighed amount of polymer (0.5 g) inserted through an interface into the glass reactor with silicon oil. The temperature was continuously monitored by a suitably temperature programmer. The pyrolysis temperature was set at 300°C; the pyrolysis time was 60 min. Argon as the carrier/inert gas was used. Gas samples were transferred to the chromatograph using a dedicated gas syringe.

The identification of the pyrolysis products was performed on a Hewlett-Packard 5890 II GC-MS operating in electron impact mode, under the standard conditions.

Results and discussion

Initially, the thermal analysis studies were conducted in air–Table 2. Sample 2 turned out to be the most stable one, with an initial decomposition temperature (IDT) of 227°C. The TG profiles of degradation of samples 3 and 4 were similar, displaying an initial 40% mass loss sup to a temperature of 380°C. Generally, one stage of degradation was observed. Temperatures of the maximum degradation rate lay in the range of 320–395°C, having the highest value for the sample 2. Results of the differential thermal analysis reveal the occurrence of an endothermic heat effect with maximum at temperatures of 300–390°C.

Table 2 Temperatures (°C) at which mass loss reached the levels specified on heating in air measured by TG

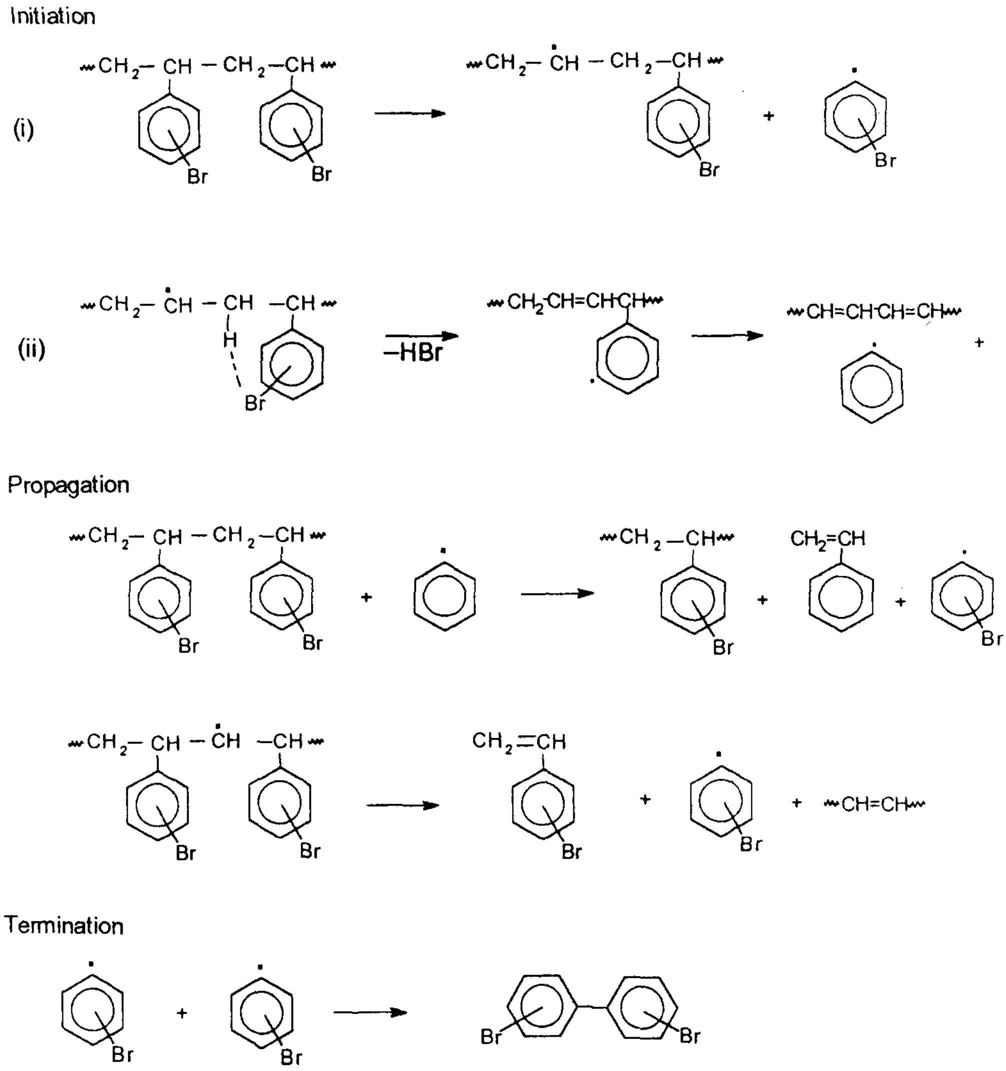
Sample	Mass loss / %						
	5	10	20	30	40	50	60
1	303	313	327	340	353	364	375
2	355	372	381	386	392	400	404
3	312	330	343	352	360	377	–
4	329	348	360	371	378	398	–

The results of measurements performed under the atmosphere of argon show that the samples 3 and 4 undergo a degradation in higher temperatures than sample 2, which possess less bromine atoms per PS repeat unit, respectively (Table 3). Maxima of the decomposition rate, on the basis of 1st derivative of the weight loss curve, were found at 375–410°C. Above this temperature range only a gradual reduction in mass was observed. When other heating rates were employed, it was found that the temperature at which the maximum rate of weight loss occurred was sensitive to this parameter [8].

Table 3 Temperatures (°C) at which mass loss reached the levels specified on heating in argon measured by TG

Sample	Mass loss / %						
	5	10	20	30	40	50	60
1	370	378	385	390	395	400	405
2	360	375	393	400	405	410	418
3	371	378	389	397	402	404	411
4	374	382	393	400	404	406	412

Pyrolysis of the sample 3 yields mainly *p*-bromostyrene and styrene; hydrogen bromide, benzene, light hydrocarbons are the other degradation products observed. It is in agreement with the results already presented [9].



Scheme 1

The free radical mechanism, often postulated [10, 11] for PS degradation, consist of three steps: initiation, propagation and termination. For the ring-brominated PS, on the basis of pyrolysis results and TG data, the following mechanism can be proposed (Scheme 1).

The step (ii) in the initiation process was also partially proposed for the degradation route of PS with Br-content of more than 50% [12]. The radical depolymerization process presented in Scheme 1 describes the formation of bromobenzene and benzene which are the main decomposition products.

It seems logically to extend these studies for the quantitative analysis of the degradation products in relation to the amount and localisation of bromine in polymer structure.

Conclusion

The results described in this paper confirmed the earlier conclusion that PS containing bromine on the ring is described by the thermal parameters which values are generally similar to those of pure PS. Degradation of different chemical structures leads to the formation of the whole range of products; their influence on the global decomposition process is still the subject of investigation. The main question to be answered concerns the determination of the possibility of changing the main degradation mechanism by introducting of bromine in polymer.

References

1 N. Grassie, A. Johnston and A. Scotney, Eur. Polym. J., 17 (1981) 589.
2 J. W. Lyons, The Chemistry and Uses of Fire Retardants, Wiley Interscience, New York 1970.
3 M. Levin, S. M. Atlas and E. M. Pearce (Eds.), Flame-Retardant Polymeric Materials, Planum Press, New York 1975.
4 P. Hodge and D. C. Sherington, Polymer Supported Reactions in Organic Syntheses, Wiley Interscience, New York 1980.
5 K. Pielichowski, A. Puszynski and J. Pielichowski, Polym. J., 26 (1994) 822.
6 M. Camps, J. P. Montheard and F. Benrokia, Eur. Polym. J., 27 (1991) 389.
7 M. Camps, A. Jebri, P. Verlaque, A. Archavlis and R. Faure, Eur. Polym. J., 29 (1993) 99.
8 K. Pielichowski and L. Stoch, to be published.
9 I. C. McNeill and M. Coskun, Poly. Deg. and Stab., 23 (1989) 175.
10 M. T. Sousa Pessoa de Amorim, C. Bouster, P. Vermande and J. Veron, J. Anal. Appl. Pyrolysis, 3 (1981) 19.
11 G. Audisio and F. Bertini, J. Anal. Appl. Pyrolysis, 24 (1992) 61.
12 A. V. Antonov, R. M. Gitina, Y. D. Rogozhkina, A. L. Izyumnikov, I. L. Zhuravleva, Y. S. Bogachev and S. N. Novikov, Vysokomol. Soedin. (A), 32 (1990) 860.

Zusammenfassung — Vorliegend wurden die Ergebnisse einer Untersuchung des Abbauprozesses von ringbromiertem Polystyrol dargelegt. Mit Hilfe von Thermogravimetrie (TG) und Differentialthermoanalyse (DTA) wurde der Weg des Abbaues der Polymerproben mit unterschiedlichem Bromgehalt beschrieben. Die Einführung von Brom am aromatischen Ring beeinflußt die anfängliche Zersetzungstemperatur (IDT) und auch die Temperatur für die maximale Zersetzungsgeschwindigkeit (T_m).

Die Proben wurden bei 300°C pyrolysiert und einige Pyrolyseprodukte wurden mittels Gaschromatografie/Massenspektrometrie bestimmt. Abschließend wird ein möglicher Mechanismus für den Zersetzungsprozeß dargelegt.