ELSEVIER Thermochimica Acta 275 (1996) 225–233

thermochimica
acta

On the thermal decomposition of copolymers of maleic anhydride with styrene

C.N. Cascaval *, G. Chitanu, A. Carpov

"Petru Poni" Institute of Macromolecular Chemistry, Aleea Gr. Ghica Voda, 41 A, Iasi 6600, Romania

Received 28 March 1995; accepted 7 August 1995

Abstract

The thermal degradation behaviour of copolymers of maleic anhydride and styrene was studied by pyrolysis–gas chromatography and thermogravimetry. The main decomposition products analysed in the temperature range 200–600°C are styrene, benzene, toluene and ethylbenzene, the proportions of which vary with temperature and the nature of the copolymer. The experimental techniques used allowed a differentiation to be made between the copolymers analyzed. The apparent thermal stability of maleic anhydride–styrene copolymers is lower than that of polystyrene and decreases in the order: alternating, random and block.

Keywords: Decomposition; Gas chromatography; Maleic anhydride copolymers; Pyrolysis; Thermogravimetry

1. Introduction

Maleic anhydride (MA)–styrene (S) copolymers have been synthesized for use as emulsifiers, auxiliary agents in the paper and textile industry, plastic additives, pigment dispersions and coatings, adhesives, printing inks, etc. [1–3]. Studies of the synthesis of MA copolymers have been carried out with special emphasis on polymerization kinetics and mechanisms [4], the determination of reactivity ratios [5], the interpretation of solvent effects on the microstructure of copolymers [6] and the realization of a high conversion [7].

---

* Corresponding author.

SSDI 0040-6031(95)02698-3

MA can initiate the change-transfer polymerization of S in the presence of various solvents. Polymerization proceeds through both the change-transfer complex and the free monomer. An alternating copolymer is synthesized from an equimolecular mixture of monomers at moderate temperatures (below 90°C) [8]. At temperatures higher than 90°C, when the charge-transfer complex does not form, a copolymer of random structure is obtained [9]. Polymerization with an excess of S monomer leads to the formation of S blocks in the polymer chain [10].

The characterization of MA–S copolymers has been investigated by several authors for evaluation of composition [11], the distribution of monomer sequences along the chain [12] and the study of the thermal behaviour [9,13,14]. Since there are few data published regarding the influence of the structure of MA–S copolymers upon the thermal decomposition, the present paper reports the study of some MA–S random, alternating and block copolymers. The techniques employed, namely, pyrolysis–gas chromatography (P–GC), thermogravimetry (TG) and derivative thermogravimetry (DTG) give information not only on the distribution of the decomposition products and the relative thermal stability, but also show how it is possible to distinguish between the various types of MA–S copolymers.

2. Experimental

2.1. Materials

Analytical reagent-grade chemicals were used throughout. The monomers MA (purity 99.9%) and S (99.9%) were commercial products that were carefully purified prior to use. Thus, MA was twice recrystallized from chloroform to remove the maleic acid developed by storage; S was distilled under reduced pressure. Benzene, toluene, and xylene used as solvents were dried with Na for 48 h and then distilled. Benzoyl peroxide (78.91% active content) used as the free radical initiator was recrystallized from dry methanol.

2.2. Synthesis

Copolymerizations were carried out in solution-suspension and alternating and random copolymers were obtained by filtration. The experimental conditions used and some characteristics of the copolymers obtained are listed in Table 1.

The alternating copolymer was synthesized at 80°C by a charge-transfer mechanism [8,13], while at 145°C a random copolymer was obtained [8,15]. The polymerizations were allowed to reach high conversions (80–90 %) so as to have a more realistic approach on the copolymer behaviour [16]. The alternating and random copolymers were extracted for 24 h with dry benzene in a Soxhlet apparatus to remove the unreacted monomers, then dried at 40°C and reduced pressure for 3–4 days.

MA does not undergo homopolymerization by normal free-radical initiation [17] so that it is impossible to obtain a true MA–S block copolymer. A mechanical mixture of

Table 1
MA–S alternating and random copolymers analyzed by thermal degradation

Type of copolymer	Monomer ratio in feed (mol)	Solvent	Monomer/ solvent ratio ($\mathrm{g\,ml^{-1}}$)	Benzoyl peroxide[a] (%)	Temperature of reaction T (°C)	Acid number (I_a)	Monomer ratio in copolymer[b] (mol)
Alternating	1:1	Toluene	1:4	0.5	80	393	1:1.02
Random	1:1	Xylene	1:10	0.3	145	324	1:1.43

[a] Gram per 100 gram monomer.

[b] Calculated as $x:y$, where $x = 1.25 \times 10^{-5} \times I_a$ mol MA and $y = (1 - 1.225 \times 10^{-3} \times I_a)/104$ mol S.

polystyrene (PST) and MA monomer (1:1 molar ratio) as fine powder was obtained, followed by co-precipitation from a benzene solution. This mixture was used to simulate a block copolymer, as was done before for S-methyl methacrylate copolymer [18].

2.3. Techniques

The MA content of the alternating and random copolymers was determined conductometrically as the acid number I_a in an acetone/water mixture (1:1 vol) with aqueous 0.1 N NaOH, using a Radiometer AB Copenhagen CDM 2d conductivity meter and a CDC 114 cell. The I_a was calculated as follows

$$I_a = \frac{V \times n \times 40}{a}\ (\text{mg NaOH})/(\text{g copolymer}),$$

where V is the consumption (ml) of NaOH solution, n the normality of the NaOH solution, and a the sample weight (g).

The monomer ratio of the copolymers was confirmed by means of ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectra of the copolymers were obtained in deuterated acetone as solvent and tetramethylsilane as internal standard using JEOL-JNMC 60-HL equipment at 55°C.

The copolymer samples were pyrolysed in the temperature range 200–600°C by means of a filament-type pyrolysis unit described elsewhere [19]. The separation and analysis of the thermal decomposition products were carried out with a Siemens L-400 gas chromatograph provided with a flame ionization detector, operating under the following conditions: the chromatographic column (2 × 3 mm i.d.) was packed with acid-washed Chromosorb W (60–80 mesh) coated with 5% carbowax 20M; the column temperature was programmed from 60 to 200°C at a heating rate of 280 K min^{-1}; argon was used as carrier at a flow rate of 24 ml min^{-1}.

TG and DTG experiments were carried out on a MOM-Budapest derivatograph under the following operational conditions: sample weight, 50 mg; heating rate, 285 K min^{-1} in atmospheric air; reference material, α-Al_2O_3.

3. Results and discussion

3.1. Pyrolysis–gas chromatography

Typical P–GC curves for MA–S copolymers at 580°C are shown in Figs. 1–3. Identification of the pyrolysis products (Table 2) was carried out by using the relative retention times of various reference substances. The main pyrolysis products are benzene, toluene, ethylbenzene and styrene. These products result from S units. Visual inspection of the pyrolytic chromatograms shown in Figs. 1–3, led to the empirical observation that the same degradation products are formed for all the copolymers analysed. In contrast, the content of the main pyrolysis products differs markedly as a function of the nature of the copolymer.

Starting from the experimental observation that the copolymers analyzed yield only hydrocarbons on pyrolysis in inert media, we have assumed the relative weight of each component to be an integer, as was done elsewhere [20] for copolymers of vinyltoluene and divinylbenzene. Thus, a semi-quantitative determination of the pyrolysis products of MA–S copolymers was accomplished and the results are summarized in Table 2.

As can be seen in Table 2, the concentration of the main pyrolysis products is a function of the type of copolymer analysed. Thus, there is a pronounced increase in

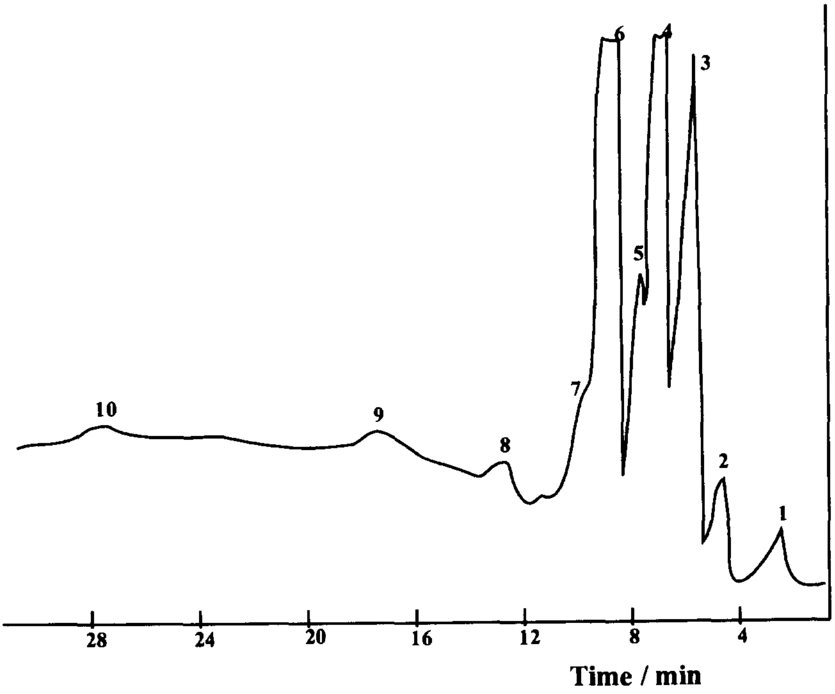

Fig. 1. Typical pyrolytic chromatogram of random MA–S copolymer recorded at 580°C. Peaks 1–10 as in Table 2.

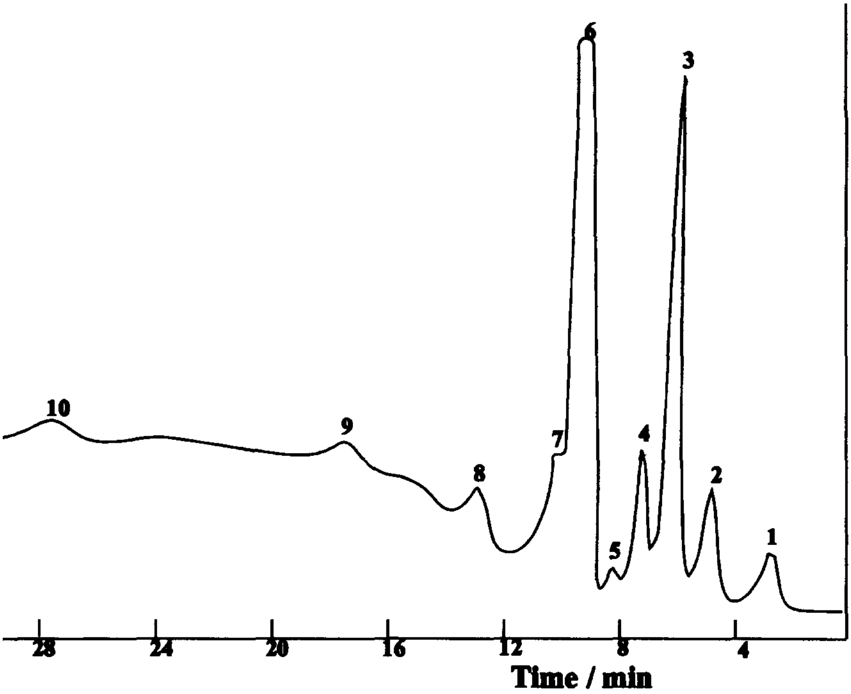

Fig. 2. Typical pyrolytic chromatogram of alternating copolymer recorded at 580°C.

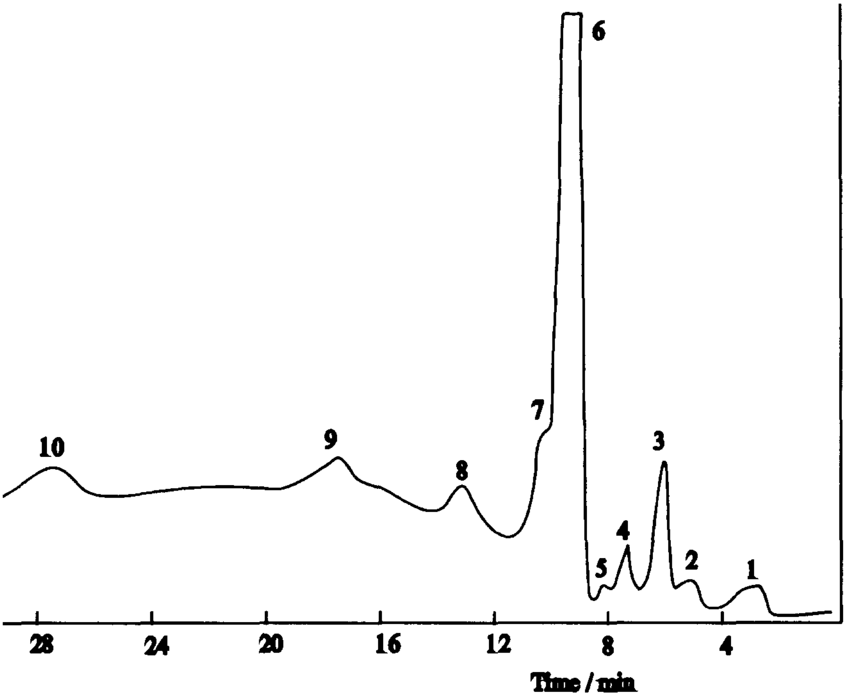

Fig. 3. Typical pyrolytic chromatogram of block copolymer recorded at 580°C.

Table 2
Composition of the pyrolysis products of MA–S copolymers at 580 °C

Peak No.[a]	Decomposition products	Copolymer sample content (in %)		
		Random	Alternating	Block
1	$C_1 - C_4$ high-volatile hydrocarbons	3.37	3.28	2.56
2	Benzene	4.65	5.44	3.23
3	Toluene	20.38	22.15	6.64
4	Ethylbenzene	21.68	5.89	3.56
5	Xylenes	0.94	1.26	Trace
6	Styrene	39.36	58.31	66.53
7	Unknown	0.35	0.74	1.13
8	α-Methylstyrene	0.72	0.55	5.16
9	1,3-Diphenylpropane	1.89	1.03	5.39
10	Dimer of styrene	6.62	1.28	5.72

[a] As in Figs. 1–3.

the amount of S in the order: random, alternating and block. Following the same order, there are decreases in the amounts of toluene and ethylbenzene. A gentle increase in the contents of α-methylstyrene and 1,3-diphenylpropane is noticed for the block copolymer towards the contents of the same products found for both the random and alternating copolymers. This behaviour is a consequence of the structure of the copolymers, i.e. insertion of cyclic, polar anhydride units between the substituted vinylaromatic units in the main chain.

There is a preponderance of S and S-related compounds in the degradation products because the anhydride groups in the copolymer easily hydrolyse even at moderate temperatures and are converted to maleic acid [14] which is decomposed to water and CO_2 as the main volatile products [15]. The hydrocarbon chain radicals that remain lead to S and products related to S.

Temperature influences the thermal decomposition of MA–S copolymers considerably. The single decomposition products evolved at temperatures up to 300°C were S (8–10% from the crude copolymer weight), toluene (0.5 up to 1.5%) and ethylbenzene (trace). The increase of the temperature led to an increase in the content of these products, especially the S content, which reaches a maximum at temperatures in the range 550–600°C. It was also observed that at temperatures higher than 400°C, an increase in the high volatile hydrocarbons takes place.

3.2. Thermogravimetric analysis

In the range of temperatures 20–600°C, the copolymers analysed show a characteristic thermal behaviour, which, as in the P–GC study, allows differentiation between the MA–S alternating, random and block copolymers. TG and DTG curves recorded for PST, MA (TG only) and for the copolymers analysed, are shown in Figs. 4 and 5. MA monomer degrades totally and at a very high rate at temperatures above 100°C, while

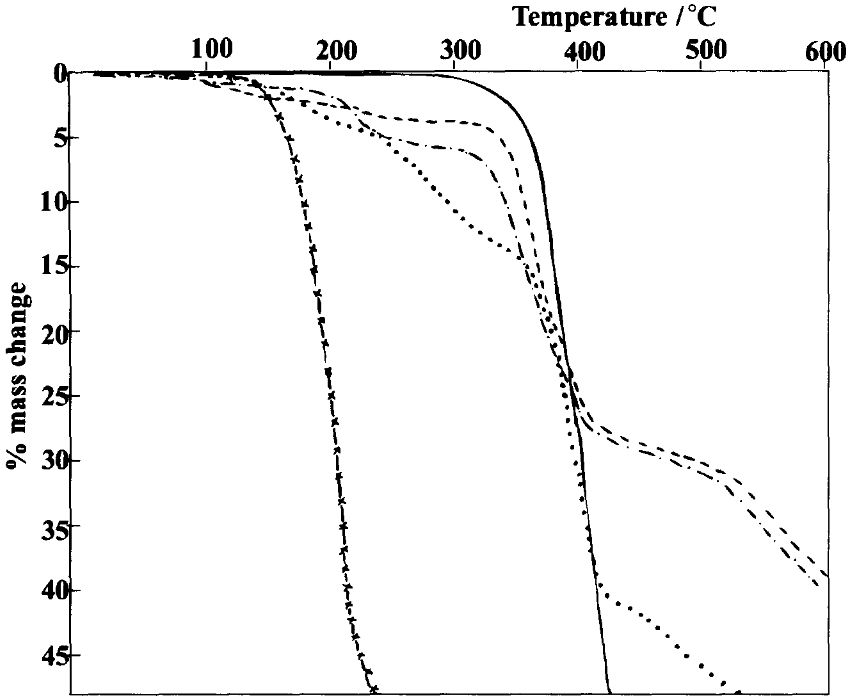

Fig. 4. TG curves for PST (——), MA monomer (×–×–×) and MA–S copolymers: alternating (- - -), random (–·–·–) and block (···).

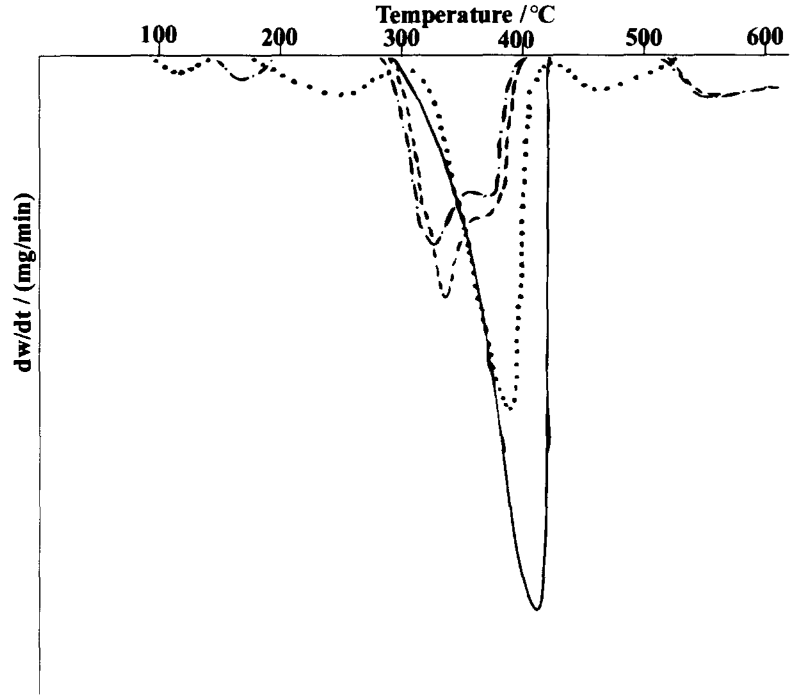

Fig. 5. DTG curves for PST (——) and MA–S copolymers: alternating (- - -), random (–·–·–) and block (···).

PST shows a sharp mass loss in a single decomposition stage in the temperature range 290–430°C.

The degradation of MA–S copolymers proceeds in several stages that depend on the type of copolymer. Important mass losses are observed between 270 and 430°C. The first decomposition stage, with mass losses of between 2 and 8% and at temperatures up to 270°C for alternating and random copolymers, and 320°C for the block copolymer, might be due to volatile matter and entrapped solvent present in the starting materials, releasing small molecules (CO_2) and moisture incorporated in the copolymers.

In contrast with the block copolymer, which in the range 270–420°C shows a single stage of degradation, both alternating and random copolymers degrade in two main stages with mass losses of up to 60%. The block copolymer shows a new decomposition stage starting at 420°C in a process which leads to the formation of tar by depolymerization, thermal cracking, cyclization reactions, etc. This process is over at 540°C, with mass losses of up to 10%.

The random and alternating copolymers show a carbonization zone at temperatures higher than 520°C, when fusion, disproportionation reactions and gasification processes occur. At 600°C, the decomposition of both random and alternating copolymers is not generally complete.

4. Conclusions

The data obtained by both P–GC and TG analysis show important differences regarding the thermal behaviour of MA–S block, random and alternating copolymers. The main decomposition products identified by P–GC are S, benzene, toluene and ethylbenzene. The yield of these products varies greatly with the type of copolymer and the temperature.

The MA–S copolymers analysed show a complex degradation mechanism with several stages of degradation and mass loss which are characteristic for each copolymer. The copolymers tested show a lower apparent thermal stability compared with PST (incorporation of MA units in PST decreases the thermal stability). The apparent thermal stability of MA–S copolymers decreases in the order: alternating, random and block.

References

[1] B.C. Trivedi and B.M. Culbertson, Maleic Anhydride, Plenum Press, New York, 1982.
[2] S.R. Ebdon and C.R. Towns, J. Macromol. Sci. Rev., Macromol. Chem. Phys., C26 (1986) 523.
[3] H. Maeda, Adv. Drug Delivery Rev., 6 (1991) 181.
[4] S. Belkhiria, T. Meyer and A. Renken, Chem. Ing.-Tech., 66 (1994) 513.
[5] B. Klumperman and G. Vonk, Eur. Polym. J., 30 (1994) 995.
[6] B. Klumperman and P.G. Brown, Macromolecules, 27 (1994) 6100.
[7] R. de Santos, B.G. Soares and A.S. Gomes, Macromol. Chem. Phys., 195 (1994) 2517.
[8] R.B. Seymour and D.P. Garner, J. Paint Technol., 48 (1976) 41.

[9] R.B. Seymour, D.P. Garner, G.A. Stahl and L.J. Sanders, Polym. Prepr., 17 (1976) 660.
[10] B.E. Buchak and K.C. Ramey, Polym. Lett. Ed., 14 (1976) 401.
[11] Y. Sigehiko, J. Hirano and Y. Isoda, J. Anal. Appl. Pyrol., 16 (1989) 159.
[12] S. Yamaguchi, J. Hirano and Y. Isoda, J. Anal. Appl. Pyrol., 12 (1987) 293.
[13] K. Bhuyan and N.N. Dass, J. Therm. Anal., 35 (1989) 2529.
[14] V. Jarm and G. Bogdanic, Thermochim. Acta, 171 (1990) 39.
[15] R.B. Seymour, D.P. Garner and L.J. Sanders, J. Macromol. Sci.,-Chem., A13 (1979) 173.
[16] C.E.R. Jones and G.E.J. Reynolds, Br. Polym. J., 1 (1969) 197.
[17] J.L. Lang, W.A. Pavelich and H.D. Clarey, J. Polym. Sci. A-1, (1963) 1123.
[18] N. Hurduc, C.N. Cascaval, I.A. Schneider and G. Riess, Eur. Polym. J., 11 (1975) 429.
[19] C.N. Cascaval, H. Oleinek, I. Zugrăvescu and I.A. Schneider, Makromol. Chem., 169 (1973) 129.
[20] C.N. Cascaval and V. Neagu, Polym. Degrad. Stab., (1994) 423.