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Simultaneous TA and MS analysis of alternating styrene–maleic anhydride and styrene–maleimide copolymers[☆]

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Abstract

The thermal behaviours of alternating styrene–maleic anhydride copolymer (St/MAn), styrene–methyl maleimide copolymer (St/MMI) and copolymers with different contents of MMI were studied by means of a simultaneous thermal analyser and quadrupole mass spectrometer system (STA/QMS). In addition, special measurements were carried out by a pyrolysis-gas chromatography–mass spectrometer (Py-GC–MS) and a differential scanning calorimeter (DSC). The glass transition of the copolymers in influenced by the degree of imidization. The decomposition behaviour of pure styrene–maleic anhydride copolymer differs from that of styrene–methyl maleimide copolymer. The favoured process of degradation of maleic anhydride-rich structures is reaction in the chains, and that of methyl maleimide-rich structures is the random chain break.

Keywords: Styrene-maleic anhydride; Styrene-maleimide copolymers

1. Introduction

Imide polymers are known to be resistant to high temperatures [1–3]. Olefinic maleimide copolymers have an exceptional position because they contain polar heterocyclic structural units and flexible chain segments. Such copolymers have a particularly high chemical stability [4]. They can be used as compatibilizing

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materials and as blend components [5,6]. It is possible to prepare products with defined glass transition temperatures by polymer-analogous reaction of alternating olefine–maleic anhydride copolymers with primary amines of different chain length and/or different functionalities of hydrocarbon residue [7]. Both the glass transition temperature and the stability are important parameters in determining the processing temperature. The application of the polymers is also influenced by these parameters. The aim of the present work was to study the thermal behaviour of partially imidized styrene–maleic anhydride copolymers.

2. Experimental

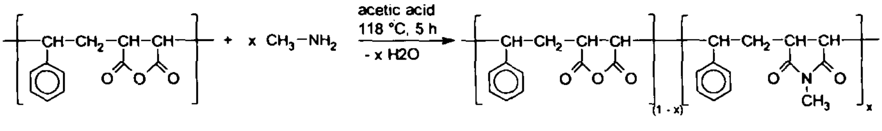
2.1. Materials

The alternating St/MAn copolymer ($\bar{M}_w = 300,000$ g mol^{-1}) produced by Buna AG Schkopau was used as the initial copolymer for the preparation of samples with different methyl maleimide contents. The polymer-analogous reaction was carried out by refluxing for 5 h at 118°C in acetic acid using 1.3 mol triethylamine per mol anhydride as catalyst, precipitating in water, filtering off and drying for 10 h at 100°C in a vacuum oven. The reaction is demonstrated in Scheme 1.

The degree of transformation of anhydride units into maleimide ones was determined by elemental analysis and IR spectrometry [7]. The transformation was found to be nearly quantitative. The given MMI content is to be seen in relation to the degree of imidization of the anhydride units.

2.2. Measurements

The thermoanalytical measurements were performed by a simultaneous thermal analyser and a quadrupole mass spectrometer system STA/QMS 409/429–403 (Netzsch) (ionization energy, 70 eV; detector, secondary electron multiplier) in the temperature range 10–500°C in a helium atmosphere at a heating rate of 10 K min^{-1}. The gas flow rate on inlet was 150 cm^{3} min^{-1}. The DSC/TG sample holder and aluminium sample pans were used. The investigated mass number range was 10–135. The measured intensities of the interesting mass numbers were normalized in relation to sample weight and molecular weight of the repeating unit. The areas under the curves of selected mass numbers were calculated for a quantitative comparison. The



Scheme 1

glass transition behaviour was studied by means of a DSC-7 (Perkin-Elmer) in the temperature range 50–280°C in a nitrogen atmosphere at a heating rate of 20 K min^{-1}. A stepwise heating (130, 150, 170, 190, 210, 250 and 280°C) and cooling programme was used for all samples to separate processes overlapping the glass transition, such as recyclization, especially for St/MAn. The sample weight for both methods was about 5 mg.

In addition, investigations were carried out by a pyrolysis-gas chromatography–mass spectrometer. The pyrolysis was done in a Pyroprobe 2000 (CDS Instruments) at different temperatures (250, 300, 350, 400, 450, 500 and 700°C) and a pyrolysis time of 10s. The gas chromatograph HP 5890 II (Hewlett Packard) containing a 25-m capillary column with liquid phase RB-5 (non-polar) was coupled with a quadrupole mass spectrometer HP 5971 (Hewlett Packard) ionization energy, 70 eV; detector, dynode electron multiplier). The following programme was used for the GC measurements: from $T_1 = 50°C$ ($t_1 = 2$ min) heated at a rate of 12 K min^{-1} to $T_2 = 250°C$ ($t_2 = 10$ min); injector temperature, 250°C; detector temperature, 280°C. The carrier gas was helium with a flow rate of 1 ml min^{-1}.

3. Results and dsicussion

3.1. Glass transition behaviour

The determination of the glass transition temperatures was problematic. All samples were preheated to 100°C to eliminate adsorbed water. Fig. 1a shows, as an example, the DSC curves of the St/MAn copolymer. The comparison of DSC heating curve I and the temperature dependence of mass number 18 for H_2O measured by mass spectrometry (Fig. 1b) suggests that the endothermic peak correlates with the H_2O production during the recyclization reaction and anhydride formation. This means that the sample contained a small amount of acid with a tendency to hydrolyse. For this reason, the stepwise temperature program was used to separate the glass transition from overlapping processes, as demonstrated in Fig. 1a, curves II.

In this way, the T_g of St/MAn copolymer was found at 213°C. Jarm and Bogdanic [8] reported that the presence of partially hydrolysed anhydride groups in the St/MAn copolymer lowers the T_g, but the experiments of the present work show that the T_g is overlapped by the described endothermic process of recyclization to anhydride, which suggests a lower T_g ($\bar{M}_w = 480{,}510$ and $T_g = 177°C$ [8]; $\bar{M}_w = 300{,}000$ and $T_g = 213°C$, present work). If the described problems are not taken into account and the flank of the DSC curve I in Fig. 1a is interpreted as the glass transition, then an apparent T_g can be observed similar to the value of Jarm and Bogdanic [8]. Another reason to use stepwise heating was to prevent as far as possible the decarboxylation process which begins above 210°C (Fig. 1b) and may change the glass transition temperature.

Fig. 2 shows the dependence of T_g on MMI content. A strong increase in T_g was found up to 10% MMI; then T_g decreased with further increase in MMI content. The same tendency could be confirmed by viscosity measurements in solution [7]. Moore and Pickelman [3] reported that significantly higher solution viscosities were found for

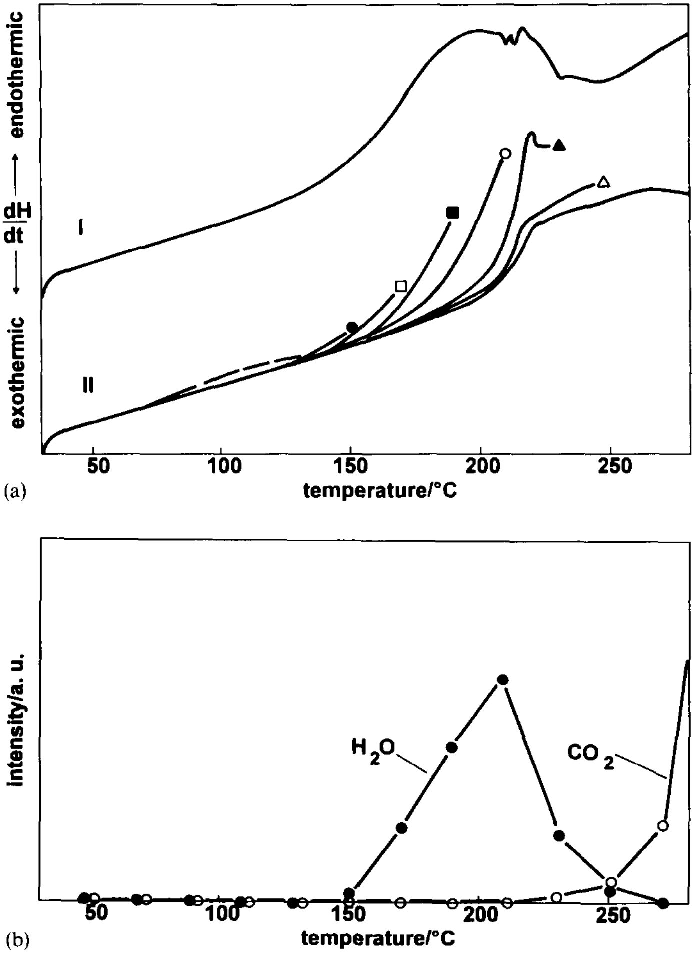


Fig. 1. a. DSC curves of St/MAn copolymer: I, continuous scan; II, scans of stepwise heating to 130°C (---), 150°C (-●-), 170°C (-◇-), 190°C (- ~ -), 210°C (-○-), 230°C (-x-), 250°C (-Δ-), 280°C (—).
b. Temperature dependence of selected mass numbers of St/MAn copolymer: H_2O (18) (-●-), CO_2 (44) (-○-).

partially converted St/MAn (reaction with ammonia to St/MI) copolymers than for the starting material or the completely imidized sample. The T_g values of the pure St/MAn and pure St/MMI copolymers are very close to each other, since only the anhydride units of the initial copolymer were changed into maleimide units. An increase in molecular weight in this way cannot be expected. One reason might be an intermolecular link by intermolecular imide formation [3] which leads to an apparent increase in molecular weight.

For this reason, the polymer-analogous reactions were carried out in polymer solutions of different concentrations (1–15%) [7]. The viscosity and T_g results of these

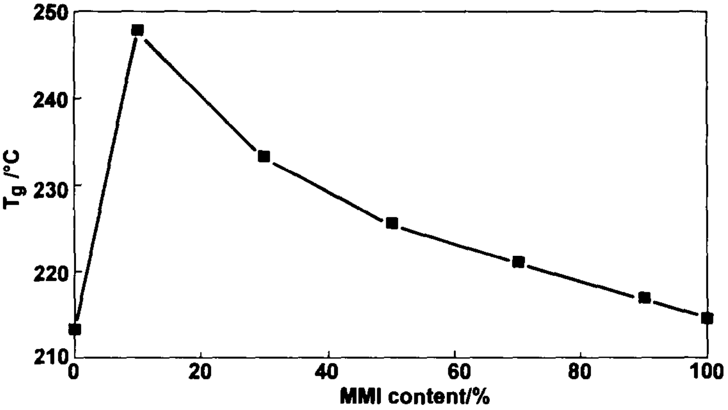


Fig. 2. The dependence of the glass transition temperature on MMI content.

samples did not show significant differences on changing the concentration of the polymer solution, which means that the intermolecular imidization reaction could not be detected even in a concentrated solution.

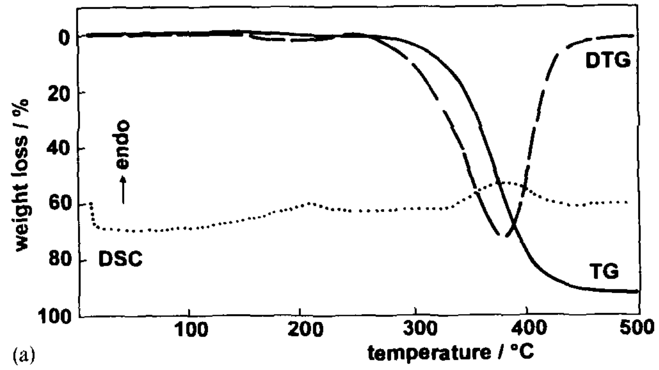
Although this anomalous behaviour cannot be explained at present, it is assumed that the random distribution of a small amount of maleimide units in the chains leads to chemical heterogeneities and hinders the chain folding. With increasing MMI content, the copolymer becomes more and more homogeneous and the glass transition decreases.

3.2. Decomposition behaviour

Fig. 3a and b show the DSC, TG, and DTG curves of the simultaneous experiments of St/MAn copolymer and the corresponding St/MMI copolymer. The recyclization process of the partially hydrolysed St/MAn up to 250°C has already been discussed in connection with the glass transition behaviour.

Maleimide copolymers are generally much more resistant to weight loss than maleic anhydride copolymers [3], because they contain energetically and sterically more favourable imide groups. Comparison of the curves in Fig. 3a and b shows that St/MMI is more stable.

The shapes of the DTG curves of the two copolymers differ and indicate that the decomposition of St/MAn is not a single-step process. The determined TA–MS data and the results of Py-GC–MS allow separation of the processes. At the beginning of degradation above 210°C, carbon dioxide was found, confirmed by Py-GC–MS investigations. Investigations by van Duin and Klumperman [9] on low molecular weight model compounds showed that carbon dioxide is generated by formation of a spirodilactone structure. ^{13}C NMR on an externally annealed St/MAn sample demonstrated that decarboxylation in the copolymer occurs between two neighbouring anhydride groups, see Scheme 2, below. The maximum of the decarboxylation process could be determined to be at about 330–340°C.



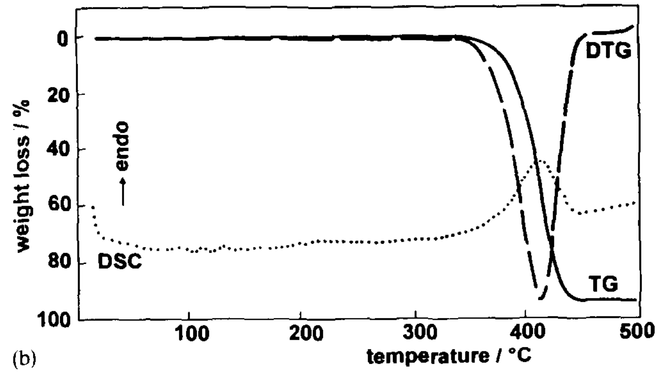
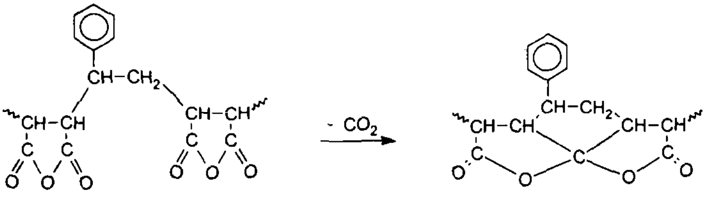


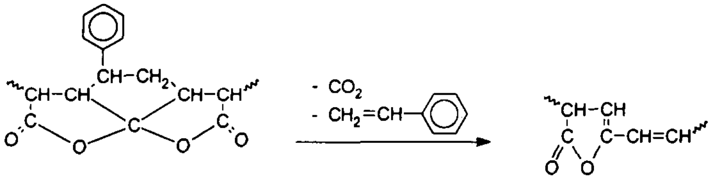
Fig. 3. a. DSC, TG and DTG curves of St/MAn copolymer. b. DSC, TG and DTG curves of St/MMI copolymer.



Scheme 2

In a second step, besides CO_2, the comonomer styrene was also obtained by TA-MS above 330°C and by Py-GC-MS at 400°C. It can be assumed that a lacton structure, see Scheme 3 (below), formed.

With further increase in temperature, complete degradation with chain destruction takes place and products listed in Table 1 were detected. The maximum was found at about 380°C corresponding to the DTG peak temperature. A DTG peak temperature at 380°C for St/MAn copolymers was also found by Jarm and Bogdanic [8].



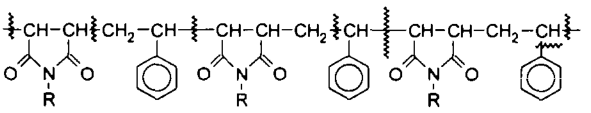
Scheme 3

Table 1
Identified products of the copolymers in dependence of MMI content at a pyrolysis temperature of 500°C

Retention time/min	Mass number	Identified product	MMI content %						
			0	10	30	50	70	90	100
1.3	44	Carbon dioxide	■	■	■	■	■	■	■
1.6	57	Methane, isocyanato-				■	■	■	■
2.5	78	Benzene	■	■	■	■	■	■	■
3.8	92	Toluene	■	■	■	■	■	■	■
5.5	106	Benzene, ethyl-	■	■	■	■	■	■	■
5.8	104	Benzene, ethenyl-(styrene)	■	■	■	■	■	■	■
6.4	120	Benzene, 1-ethyl-3-methyl-	■	■	■	■	■	■	■
6.7	111	Methyl maleimide (MMI)		■	■	■	■	■	■
6.8	118	Benzene, 1-ethenyl-3-methyl-	■	■	■	■	■	■	■
6.9	120	Benzene, propyl-	■	■	■	■	■	■	■
7.4	118	Benzene, 1-ethenyl-1-methyl-	■	■	■	■	■	■	■
8.1	130	Benzene, 1,3-butadienyl-	■	■	■	■			
8.2	125	MMI + CH_2				■	■	■	■
9.2	113	2,5-pyrrolidinedione, 1-methyl-		■	■	■	■	■	■
9.4	127	2,5-pyrrolidinedione, 1-methyl- + CH_2(?)				■	■	■	■
9.7	139	MMI + $(CH_2)_2$					■	■	■
11.9	142	Naphthalene, 1-methyl	■	■					
13.3	168	Cyclic substituted benzene	■	■					
16.1	196	Cyclic substituted benzene	■	■					
17.2	215	Styrene + MMI (?)				■	■	■	■

The decomposition behaviour of St/MMI copolymer is different from that of St/MAn, as can be seen in Fig. 3b. The TA–MS measurements suggest that the copolymer is not completely imidized. A small amount of carbon dioxide was detected in the range up to 350°C. The degree of imidization could be estimated to about 99%. Independent of this, only one decomposition step with a DTG peak maximum at about 410–415°C could be observed, which is comparable to the maximum of detected mass numbers, e.g. 104 = styrene and 111 = methyl maleimide. Py-GC–MS measurements also revealed the presence of these two main products, as well as the other products listed in Table 1.

For the St/MMI copolymer, a random chain break can be assumed while the maleimide unit is preserved (see Scheme 4, below).



Scheme 4

The behaviour of partially imidized copolymers is shown in Fig. 4 including the DTG peak temperature and the estimated temperature ranges of the maximum intensity of the mass numbers for carbon dioxide, styrene and methyl maleimide. These mass numbers were selected in consideration of the decomposition behaviour of the pure copolymers St/MAn and St/MMI. The corresponding temperature dependence of these mass numbers is demonstrated in Fig. 5a–c.

A degree of imidization of 10% results in a certain increase in stability. Independent of the degree of imidization for all copolymers, the first decomposition product was carbon dioxide, also confirmed by Py-GC–MS. The imidized products show only a small amount of CO_2 (see Fig. 5a) in the temperature range of the pure St/MAn copolymer. The maximum of the detected CO_2 increased from 330–340°C to 380°C and above (see also Fig. 4). The randomly distributed imide groups seem to decrease the probability of decarboxylation between two neighbouring anhydride units. This reaction becomes more and more unlikely and the mechanism of decarboxylation is changed. It can be assumed that this process runs within one anhydride group. Investigations of an St/MAn copolymer containing 15 mol% randomly distributed anhydride also showed that the decarboxylation temperature shifts to significantly higher values in comparison to the alternating copolymer, because a reaction of two neighbouring anhydride groups is very improbable.

The main degradation of imidized copolymers begins above 330°C as demonstrated in Fig. 5b and c. The maximum of the detected mass numbers for styrene, methyl

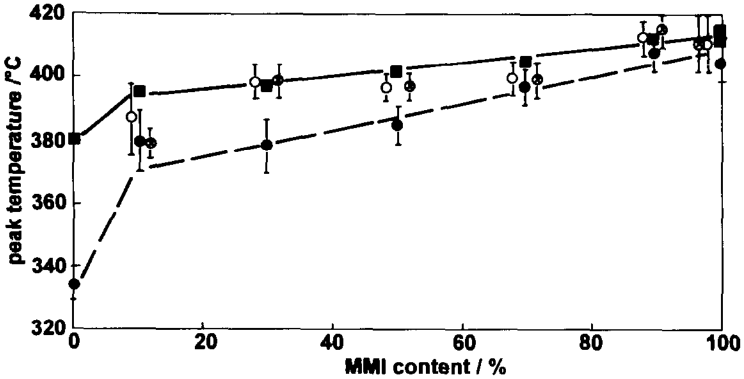


Fig. 4. Peak temperature as a function of MMI content DTG data (straight line) ■, estimated range for detected carbon dioxide (dashed line) –●–, styrene –○–, and methyl maleimide –x–.

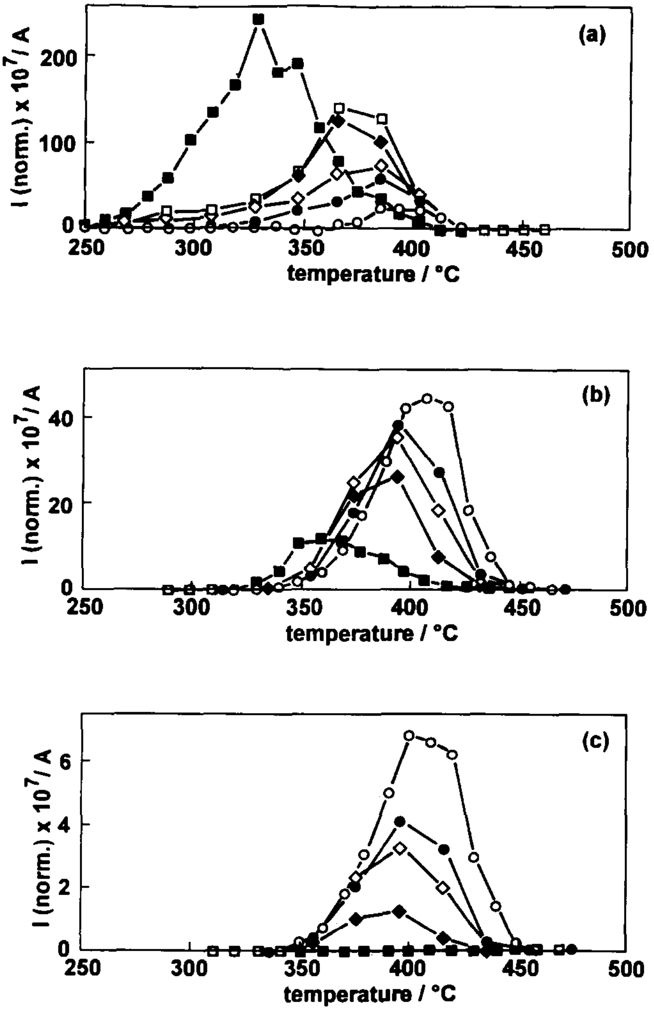


Fig. 5. Change in normalized intensity of detected mass numbers as a function of the temperature and MMI content: (a) carbon dioxide (44), (b) styrene (104), (c) methyl maleimide (111). MMI content in %: ■, 0; □, 10; ◆, 30; ◇, 50; ●, 70; ○, 100.

maleimide and the others listed in Table 1 was found in the range of the DTG peak temperature.

Fig. 6 shows the comparison of calculated areas under the curves of selected mass numbers as a function of MMI content. The observed dependence illustrates a drastic reduction of CO_2 at an MMI content of 10% due to the randomly distributed imide groups and the hindered decarboxylation as shown in Scheme 2, below. The linear increase of the area of methyl maleimide confirms the assumption that this unit is preserved.

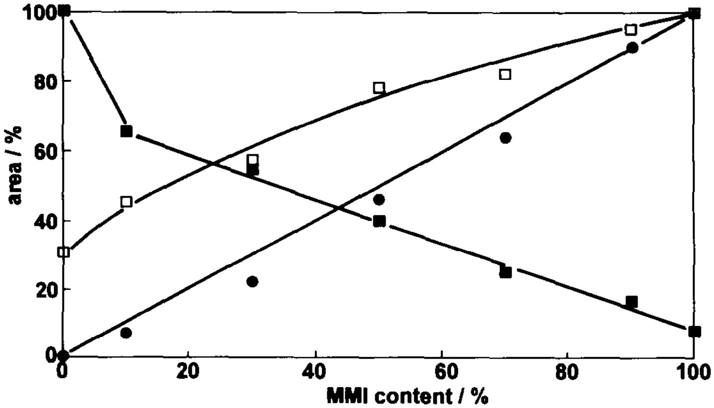


Fig. 6. Comparison of calculated areas of selected mass numbers as a function of MMI content: ■, carbon dioxide ■; □, styrene; ●, methyl maleimide.

The results for partially imidized copolymers suggest the conclusion that the favoured degradation process of maleic anhydride-rich structures is the reaction in the polymer chain followed by complete decomposition. Methyl maleimide-rich structures decompose by random chain break.

4. Hypothesis of the main steps of degradation

St/MAn copolymers decompose in the following way:

1. Decarboxylation of two neighbouring anhydride groups by formation of a spirodilactone structure.
2. Further decarboxylation and separation of the comonomer styrene by formation of the following lactone structure.
3. Complete chain destruction.

St/MMI copolymers decompose by random chain break.

The favoured degradation process is dependent on the type of copolymer: reaction in the polymer chain for maleic anhydride-rich structures; and random chain break for methyl maleimide-rich structures.

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