EVALUATION OF COMPOSITIONAL DISTRIBUTIONS OF STYRENE-MALEIC ANHYDRIDE COPOLYMERS BY THIN-LAYER CHROMATOGRAPHY / PYROLYSIS - GAS CHROMATOGRAPHY

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ABSTRACT

A method for the evaluation of the compositional distributions in styrene (St)-maleic anhydride (MAN) copolymers by thin-layer chromatography/pyrolysis-gas chromatography is described. A St-MAN copolymer sample (average St content = 75 mole %) was used after methyl esterification by diazomethane. The fractionated samples of the original copolymer were pyrolyzed at 590ºC using a Curie-point pyrolyzer and the resulting products were separated by gas chromatography. The resulting pyrograms were interpreted in terms of the compositional distributions of the copolymer. The St content in the samples could be determined using the linear relationship between the St content in the samples and [St]/({St] +[MA]) ratio (where MA - methyl acrylate) in the pyrolytic products. The fractionated samples having higher RF values proved to have a higher St content.

Gas chromatography; maleic anhydride; polymers; pyrolysis; styrene; thin-layer chromatography.

INTRODU CTION

Pyrolysis-gas chromatography (Py-GC) has been widely used for the structural characterization [1,2] and the compositional analysis [3,4] of various polymeric materials.

For the characterization of polymers it is important to evaluate not only the molecular weight but also the compositional distribution. Compositional distribution has been evaluated by thin-layer chromatography (TLC) [5] or gel-permeation chromatography (GPC) [6,7]. However, there is a need to establish a direct and simple method to analyze the composition of fractionated samples by other chromatographic methods. In these cases, however, the sample size of each fraction is quite limited - often being less

than sub-milligram quantities. In this paper, Py-GC is applied to the compositional analysis of samples fractionated by TLC.

Styrene (St)-maleic anhydride (MAN) copolymer is important in the field of polymer conjugation drugs. The antitumor activity of neocarziostatin conjugated with St-MAN copolymer has been noted recently [8], and the establishment of a method of characterization was required. In the polymerization process, St and MAN monomer units are known to form charge transfer complexes [9], and an alternating copolymer is synthesized from an equimolar mixture of the monomers. When the number of St units is larger than that of MAN monomer units, excess St units combine with each other to form blocks of St units in the polymer chain [10]. In this case, the compositional distribution needs to be determined for a given batch of the copolymer.

It is not easy to apply Py-GC to the analysis of polymers which have carboxylic groups owing to the low pyrolytic recovery of the associated monomer units [11]. Therefore the St-MAN samples were esterified (to form methyl esters) prior to Py-GC analysis.

The MAN unit in the sample is easily converted to maleic acid if it is not esterified. In this study the St-MAN copolymers were esterified prior to TLC. Furthermore, the samples fractionated by preparative TLC were analyzed by Py-GC in order to elucidate the compositional distribution of the original polymers.

EX PERI MENTAL

Sample

St-MAN copolymers (St content = 50, 67, and 75 mole %) obtained from Arco Co. were used without further purification. The methyl esterification of the sample was carried out according to a conventional procedure [12]. The original sample was refluxed in methanol and esterified with diazomethane. The esterified samples were prepared for subsequent Py-GC analysis.

Pyrolysis-gas chromatographic conditions

An inductive heating Curie-point pyrolyzer (Japan Analytical Industry, Model JHP-2) was attached to a gas chromatograph (Hitachi 163). Less than 0.1 mg of a sample was wrapped with a piece of foil, the Curie temperature of which was 590°C, and subjected to pyrolysis. A glass capillary column (50 m ×0.25 mm I.D., Sperco Co., SOFA HL, FFAP) was used for the gas chromatographic separation. Nitrogen was used as the carrier gas at a flow-rate of 1 ml/min in the capillary column with a 92 : 1 split. Scavenger gas at 60 ml/min was added at the column outlet just before the flame ionization detector. The column temperature was maintained at 100°C.

Identification of the peaks was carried out by a Py-GC/mass spectrometric (MS) system (JEOL, JMS-DX3O3), in the electron impact mode (70 eV).

TLC conditions

An Iatroscan (Iatron, TH-10) system with a flame ionization detector was used to obtain a thin-layer chromatogram of the fractionation of the samples. The TLC separation of the samples was carried ou with rods coated with silica gel (Chromarod S) using chloroform-ethyl acetate (8 : 2, v/v) solvent.

A preparative TLC plate (Merck, silica gel 60 F-254) was used for the preparation of the sample fractions under the same separation conditions as mentioned above. The main components of the original sample were developed between the RF values of 0.5-0.75 on the TLC plate. Then three fractions were prepared at RF=0-0.05, 0.5-0.7 and 0.7-0.75. The fractionated samples were extracted with acetone, and the extract was then subjected to Py-GC analysis.

RESULTS AND DISCUSSION

Compositional analysis by Py-GC

The pyrogram of the St-MAN copolymer after methyl esterification is shown in Fig. 1. In the conventional splitting mode operation, the sample composition actually entering the capillary column sometimes differs from the original one depending on the volatility of each component [13]. Therefore, in this work only the low boiling point pyrolytic products were

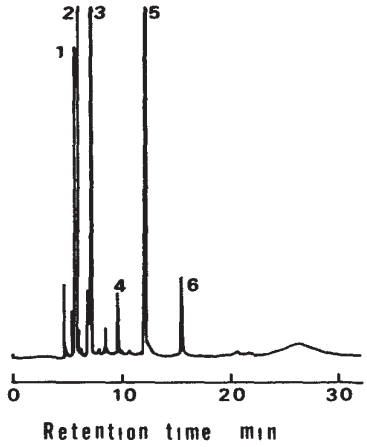

Fig 1 Typical pyrogram of samples Peaks 1 = methanol 2 = methyl acrylate 3 = toluene 4 = 2 phenylpropane 5 = styrene 6 = 3 phenyl 1 propene

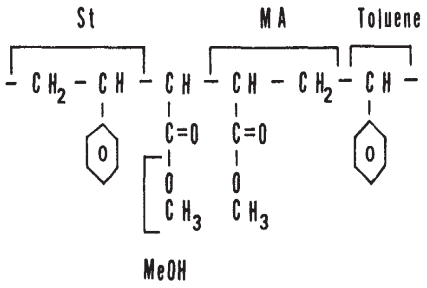

Fig 2 Degradation of the methyl esterified St–MAN copolymer

subjected to analysis. The main pyrolytic products of the sample are methanol, methyl acrylate (MA), toluene and styrene.

These products are associated with the corresponding chemical structures shown in Fig. 2. MA and methanol, and St and toluene are formed from MAN and St units in the sample, respectively. In Table 1, the proportions of these four main pyrolytic products are shown for three copolymer samples (St content = 50, 67 and 75 mole %). As the number of St units increases in the St-MAN copolymer, the content of St in the pyrolytic products increases, while that of methanol, MA and toluene decreases. The reason why

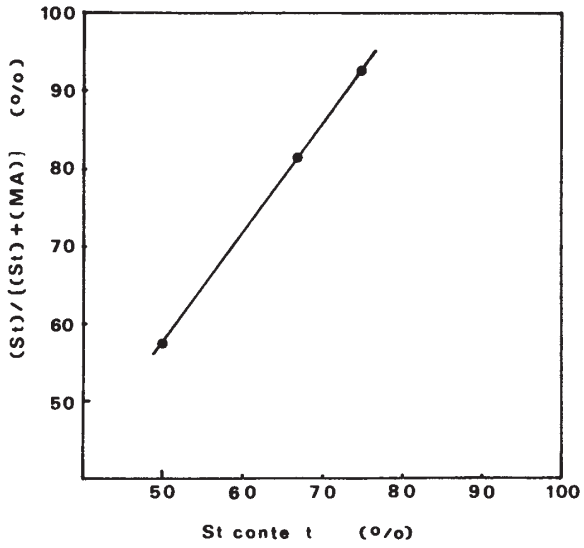

Fig 3 Relationship between the St content in the St–MAN copolymer and the [St]/([St]+[MAN]) ratio in the pyrolytic products

TABLE 1

Proportion of pyrolytic products

St content (mole %)	Proportion of pyrolytic products (mole %)			
	Methanol	MA	Toluene	Styrene
50	48 2	16 9	10 7	24 2
67	28 1	12 0	8 1	51 8
75	13 8	7 2	1 9	77 1

toluene decreases as the number of St units increases is believed to be that the pyrolytic yield of toluene from St-MAN dyad in the polymers is higher than that from the St-St dyad.

Tsuge et al. have observed that, in the case of St-MA copolymers, there is little boundary effect in the dimer products, therefore the dyad concentration in the polymer can be evaluated directly using the associated dimer concentration in the pyrolytic products [14]. In this study, as shown in Fig. 3, we found that there is a linear relationship between the [St]/([St] + [MA]) ratio in the pyrolytic products and the St monomer unit concentration in the samples. The composition of St-MAN copolymers can be determined by using the linear relationship presented in Fig. 3. The standard deviation and the coefficients of variation of [St]/[MA] ratio for five runs are 1.8 and 5.7%, respectively.

Py-GC evaluation on TLC separation

The sample (St content = 75 mole %) was developed by preparative TLC and the three fractionated samples (Nos. 1-3), which developed at different R_F values on TLC plate (No. 1 = 0-0.05, No. 2 = 0.5-0.7, No. 3 = 0.7-0.75) were prepared for Py-GC analysis. The chromatograms of the preparatively fractionated samples measured by the Iatroscan are shown in Fig. 4. The R_F

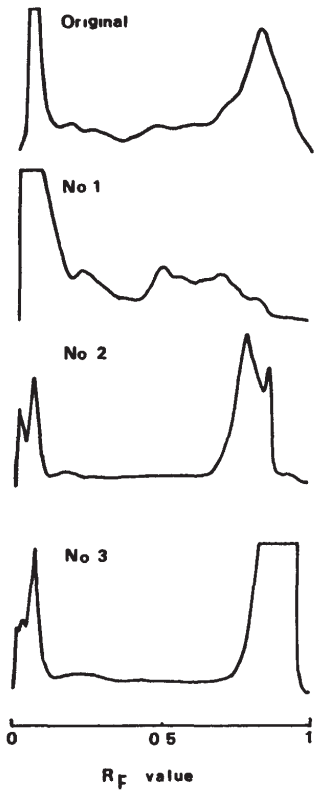

Fig 4 Thin layer chromatogram of preparatively fractionated samples

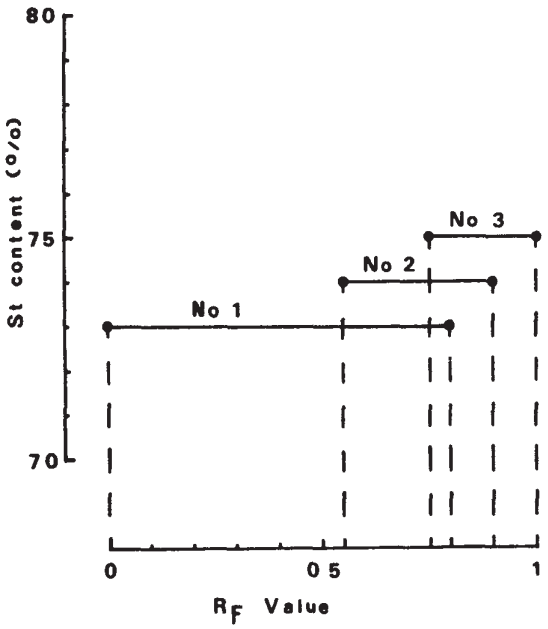

Fig 5 Relationships between the St content in the samples and associated R_F values

values of sample No. 1 range very widely between 0 and 0.8, and those of samples No. 2 and 3 are about 0.55-0.90 and 0.75-1, respectively. In Fig. 5, the relationships between the St content in the samples and the associated R_F values are shown. The St content is determined by Py-GC using the relationships shown in Fig. 3. The result indicates that the samples having higher St contents have higher PF values. The compositional distributions of St-MAN copolymer can therefore be evaluated using the chromatogram shown in Fig. 4. Thus, the compositional distributions of polymers can easily be evaluated by TLC/ Py-GC.

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