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Original Scientific Paper

Determination of the Percentage of Divinylbenzene in Copolymer Styrene-Divinylbenzene by Means of Pyrolysis and Mass Spectrometry

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Pyrolytic degradation of linear and crosslinked polystyrene has been studied by analysis of the volatile degradation products by mass spectrometry. The gas fraction $V_{300\,C}$ was analyzed immediatly after pyrolysis or 24 hours later. Resulting degradation products are formed in primary pyrolytic process and secondary reactions. The content of divinylbenzene in the copolymer was related to the quotient k which represents the ratio of light to heavy components in the fraction $V_{30^0\,C}$.

INTRODUCTION

The copolymer styrene-divinylbenzene (crosslinked polystyrene) has a threedimensional crosslinked structure resulting from the polyfunctionality of divinylbenzene. The degree of crosslinking is determined by the fraction of divinylbenzene in the copolymer. The resulting properties of the copolymer are therefore a function of its divinylbenzene content.

The purpose of this work is to determine the degree of crosslinking **i. e.** the fraction of incorporated divinylbenzene by means of pyrolytic degradation of the copolymer styrene-divinylbenzene.

Thermal degradation of this copolymer was first studied by Winslow and Matreyek[1]. Their work was primarily concerned with the thermal behaviour rather than the structural analysis of degradation products and the degradation process was studied by the rate of volatilization measured with a quartz spring balance. Strauss and Madorsky[2,3] carried out a systematical investigation of the thermal stability and determined the rate of degradation and activation energies in vacuum up to 1,200° C. They identified also the volatile degradation products by means of mass spectrometry. However, they were using a device for pyrolytic fractionation and their results differ from the results reported in this paper. Araki and Takayama[4] in their work on the pyrolytic degradation of the copolymer methyl-metacrylate-styrene used the method of few characteristic peaks of mass spectrogram and Philips[5] used it in a study of the pyrolytic degradation of rubber polymers. It is this method we have applied in this work.

EXPERIMENTAL

Samples

Linear polystyrene (prepared without divinylbenzene) was Dylene type 8 of the Koppers Comp. Inc. with a viscosity average molecular weight 302,000 and a weight average molecular weight determined by light scattering 416,000. Styrene-

-divinylbenzene copolymers were prepared at the Research Institute OKI, Zagreb. It was not possible to determine the total amount of residual monomer because the copolymer is not soluble and only the residues in the surface *i. e.* in its close vicinity are measured. The determination was done by iodometric titration[6]. The values thus obtained did not exceed 0.3%.*

Method of Work

Pyrolysis was carried out in sealed pyrex tubes of 60—65 mm length, 4 mm i. d. and 6 mm o. d. Differences in volume between tubes were very small. After the tubes were filled with the samples a set of 16 tubes + 1 blank (for the vacuum test) were sealed on the manifold, which was connected on one side to the vacuum system and on the other side to a Mc Leod manometer.

The tubes were evacuated for three hours, then sealed off at total air pressure of 5 μ and placed in the oven in vertical position. One can assume that all the samples were exposed to equal heating conditions. Temperature was measured by a mercury thermometer on the tube holder. The variation of temperature was $\pm 2^0$ C. Duration of the pyrolysis was measured with a stop-watch. After the pyrolysis was finished the sealed tubes were cooled for one hour and the samples were subjected to analysis. The sample was introduced into the inlet system of the mass spectrometer by means of a simple device which was constructed for this purpose. Essentialy, the device consisted of the bottom sealed glass tube connected by a 60 mm long PVC tube to a ground joint fitting to the inlet system of the mass spectrometer. The PVC tube was washed and evacuated for 3—4 hours at room temperature before starting the analysis, so that no traces of volatile products could be detected. After the evacuation to the steady vacuum of 10^{-3} torr the sample tubes were broken by applying force through the plastic tube. Exactly 15 seconds after breaking the sample tube the valve separating the sampling device from the sampling system of the mass spectrometer was closed. The temperature variation in laboratory was rather high, averaging $(30 \pm 2.5)\ ^0$C. The analysed gaseous fractions are refered as $V_{30^0\,C}$

Upon introduction into the sampling system the sample expanded and the total pressure was indicated by the micromanometer. The analysis was carried out by a mass spectrometer of the Consolidated Electrodynamics Corp., Pasadena, U.S.A., Model 21—103 C.

In the preliminary experiments pyrolysis was carried out at various temperatures within the range of 380—550^0 C in order to find the temperature at which the differences between copolymers with varying amounts of divinylbenzene are most pronounced. Mass spectra of the products obtained by pyrolysis at 382^0 C for 20 to 30 minutes show a very low content of volatile material and the analysis cannot be performed with sufficient accuracy. Pyrolysis at 550^0 C during 5 minutes yields a great amount of gaseous fractions consisting mostly of light hydrocarbons and the resulting mass spectra are almost identical regardless of the composition of the copolymer. Due to the high temperature a total decomposition of the polymer structure takes place. It was found that the most suitable working temperature was 419^0 C. According to Strauss and Madorsky[2] the degradation products obtained under a certain pressure of inert gas are different from those obtained in air atmosphere. The presence of oxygen in the air leads to secondary oxydation reactions. The presence of an inert gas causes secondary reactions as well but only indirectly. Inert gas molecules prevent diffusion of volatile components from inside the bulk polymer melt to the gaseous phase, thus prolonging their stay in the heating zone. In this work, the experiments were carried out in helium atmosphere and in air, yet the mass spectra were almost identical in both cases.

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* The authors are indebted to Mrs. Lj. Lovrić, Mrs. B. Mimica and Mrs Lj. Anušić for the characterization of polymer samples.

RESULTS

Table I shows the dependence of volatile components on the content of divinylbenzene in the copolymer. The method of weighing the residue after analysis of the fraction $V_{30^0 C}$ has been used and the weight of volatile components was determined from the difference:

weight of $V_{30^0 C}$ = weight of the pyrolytic tube — weight of the residue

Average values are given.

TABLE I

Pyrolysis of Styrene-divinylbenzene Copolymer at 419^0 C

% DVB in copolymer	0	3	5	8	12	16	20	25	35
Loss in weight measured immediately after pyrolysis (%)	13.2	10.6	8.9	7.1	6.0	5.2	3.3	2.6	1.6
Loss in weight measured 24 hrs after pyrolysis (%)	11.2	7.9	6.9	5.9	4.5	3.2	1.6	1.0	0.9

It is obvious that the amount of the gas fraction developed by pyrolysis decreases very fast as the degree of crosslinking increases. At the higher degrees of crosslinking this dependence is a little less pronounced.

It is of interest to point out that the mass spectra taken one day after the pyrolysis are different from the ones scanned the same day. Qualitative and quantitative analysis of fraction $V_{30^0 C}$ are given in Tables II and III. The total amount of gaseous degradation products decreases with increasing divinylbenzene content.

TABLE II

Analysis of the Fraction $V_{30^0 C}$ at 419^0 C (weight percent) (pyrolysis time 20 minutes, analysis immediately after pyrolysis)

% DVB Component	0	3	5	8	12	16	20	25	35
Methane	1.3	2.2	2.1	4.5	3.1	4.5	9.9	12.0	17.2
Ethene	—	2.6	1.7	2.4	1.7	8.3	20.8	34.6	41.5
Propane and propene	15.2	8.8	6.8	11.1	12.1	14.2	18.8	23.8	29.0
Benzene	4.2	4.4	3.2	4.2	3.6	3.4	3.7	1.8	1.2
Toluene	45.6	51.5	53.2	48.2	45.9	41.6	30.3	15.7	7.1
Ethylbenzene	21.0	24.1	25.5	24.3	23.7	21.1	12.3	8.2	3.2
Styrene	9.7	3.0	3.9	3.0	6.0	3.3	2.4	1.7	0.3
Cumene	2.7	3.0	3.3	2.0	3.6	3.2	1.4	1.9	0.3
Others*	0.3	0.4	0.3	0.4	0.3	0.4	0.4	0.3	0.2

* CO, CO_2, C_2H_2, C_2H_6

TABLE III

Analysis of the Fraction $V_{30^0\,C}$ *at 419⁰ C (weight percent) (pyrolysis time 20 minutes, analysis performed 24 hours after pyrolysis)*

% DVB Component	0	3	8	12	20	35
Methane	1.9	2.9	3.0	7.1	12.8	17.0
Ethene	—	4.0	3.3	9.7	31.5	43.9
Propane and propene	11.2	11.4	12.4	21.9	30.1	27.6
Benzene	1.2	2.5	3.6	2.8	1.6	0.8
Toluene	55.9	49.5	45.6	31.9	13.7	5.8
Ethylbenzene	23.5	22.8	22.4	15.6	6.8	3.1
Styrene	3.5	3.8	6.2	7.8	2.3	0.6
Cumene	2.5	2.7	3.1	2.8	0.8	0.8
Others*	0.3	0.4	0.4	0.4	0.4	0.4

* CO, CO_2, C_2H_2, C_2H_6

DISCUSSION

One can assume that the crosslinking of polystyrene decreases the possibility of liberation of aromatic structures by pyrolysis. Instead, fragmentation of these structures is most probable. Accordingly, in the styrene-divinylbenzene copolymer, the fraction of small molecules in the volatile part of the pyrolysate will increase with increasing degree of crosslinking. In Fig. 1. the ratio of the light components to the total volatile pyrolysates is plotted *vs.* percent of divinylbenzene. Light components include C_1 to C_3 hydrocarbons with *m/e* ranging from mass 14 to 45. The total content of volatile components is designated as Σ_{14} and represents the sum of the peaks from *m/e* 14 to the end of spectrum.

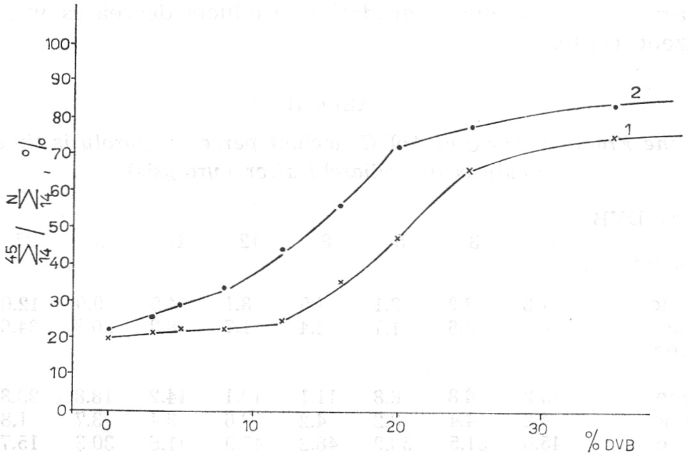


Fig. 1. Ratio $\sum_{m/e14}^{m/e45} \Big/ \sum_{m/e14}^{m/e\,N}$ **N = 120**

(1) immediatly after pyrolysis
(2) 24 hours after pyrolysis

On the basis of the indicated dependence of the composition of the degradation products on the degree of crosslinking we have tried to define an empiric factor k which would be directly related to the content of divinylbenzene. It was found that this factor can be defined as follows:

$$k = \frac{\text{peak height at } (m/e\ 15 + m/e\ 16 + m/e\ 27 + m/e\ 28 + m/e\ 44)}{\text{peak height at } (m/e\ 51 + m/e\ 78 + m/e\ 91 + m/e\ 106)}$$

The absolute peak heights of the mass spectrum are used in the quotient. To each of the peaks involved correspond the following structures:

m/e 15 — methyl-radical
m/e 16 — base peak of methane
m/e 27 — radical $—CH{=}CH_2$
m/e 28 — base peak of ethene
m/e 44 — »parent« peak of propane and CO_2
m/e 51 — mass characteristic for the cleavage products of the aromatic ring
m/e 78 — base peak of benzene
m/e 91 — benzyl or tropylium ion, base peak in many alkylbenzenes
m/e 106 — »parent« peak of ethylbenzene.

Carbon dioxide appears in traces. It originates from the oxygen present in the pyrolytic tube and possibly from the occluded catalyst. The average values of the coefficient k plotted against percent of divinylbenzene give the curves which are presented in Fig. 2. The reproducibility of k values in dependence of divinylbenzene content is shown in Table IV. The curve 1 in Fig 2 relates to the analysis carried out few hours after pyrolysis and the curve 2 to the analysis carried out 24 hours later.

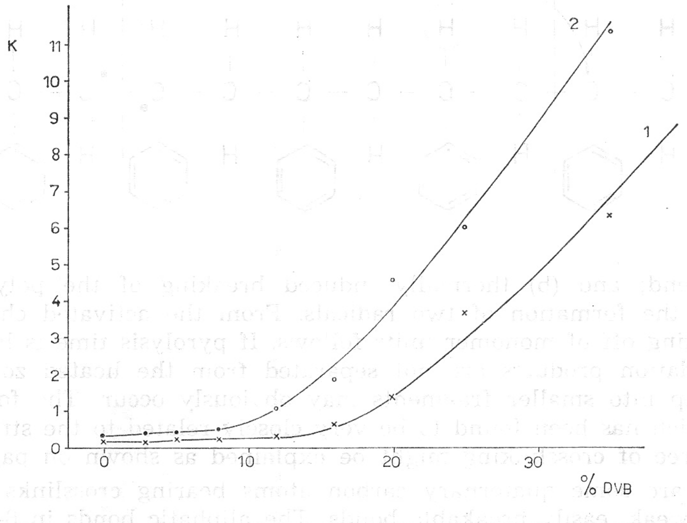


Fig. 2. Average value of k for copolymer styrene-divinylbenzene
(1) immediatly after pyrolysis
(2) 24 hours after pyrolysis

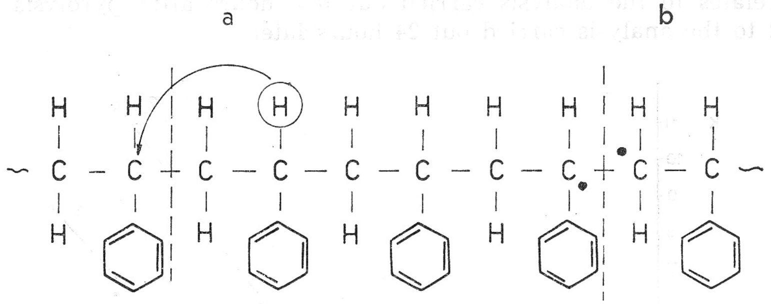
TABLE IV

Relative Standard Errors of k Values

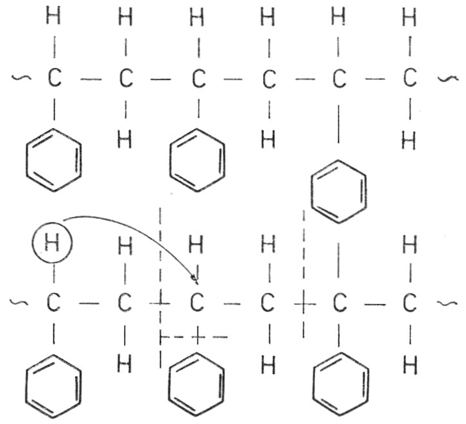
% DVB	Mean	Relative standard error
0%	0.332	± 1.4%
3%	0.386	± 1.9%
5%	0.448	± 2.1%
8%	0.512	± 2.5%
12%	1.052	± 1,8%
16%	1.907	± 0.9%
20%	4.61	± 0.4%
25%	6.02	± 0.4%
35%	11.39	± 0.3%

Curve 1 can be applied with sufficient accuracy to the analysis of copolymer containing more than 12% of divinylbenzene, while curve 2 seems preferable for copolymers with lower divinylbenzene content.

The time dependable results indicate that the primary pyrolytic reactions are followed by secondary reactions. On account of these secondary reactions it is not possible to establish the mechanism of the proper degradation reactions and of the appearance of particular components. According to the general pattern the breaking of the polystyrene chain occurs regularly at the backbone C—C bond in β-position to the phenyl double bond, since these are the weakest bonds. Two types[2] of breaking may occur: (a) chain scissions accompanied by hydrogen transfer and formation of one saturated and one unsaturated end; and (b) thermally induced breaking of the polymer chain leading to the formation of two radicals. From the activated chain ends a rapid splitting off of monomer units follows. If pyrolysis time is long enough and degradation products are not separated from the heated zone, further breaking up into smaller fragments may obviously occur. The formation of ethene, which has been found to be very closely related to the structure, *i. e.* to the degree of crosslinking might be explained as shown on page 423.



There are some quaternary carbon atoms bearing crosslinks which are linked by weak, easily breakable bonds. The aliphatic bonds in β-position to the phenyl double bond break easily as well and this is often followed by hydrogen transfer. The rupture of bonds in such a structure lead to the



liberation of ethene. The mechanism of benzene formation has been determined elsewhere[7]. In a similar way propane and propene are obtained. A part of light components is probably formed by breaking of benzene rings.

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IZVOD

Određivanje postotka divinilbenzena u kopolimeru stiren-divinilbenzen pomoću pirolize i spektrometra masa

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Opisana je metoda za ispitivanje linearnog i umreženog polistirena (kopolimera stiren-divinilbenzen). Pirolizom uzoraka u staklenoj ampuli dobivaju se plinovita frakcija $V_{30^{0}\,C}$ i tekući ostatak. Frakcija $V_{30^{0}\,C}$ analizira se pomoću spektrometra masa. Pomoću kvocijenta *k,* koji predstavlja omjer lakih i težih komponenata u frakciji, može se odrediti postotak divinilbenzena u kopolimeru. Metoda je dovoljno osjetljiva za kopolimere sa stupnjem umreženosti, većim od 8%, dok u području ispod te vrijednosti nije dovoljno pouzdana.

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