

Pyrolytic Fractionation of Polystyrene in a High Vacuum and Mass Spectrometer Analysis of Some of the Fractions^{1,2}

By Samuel L. Madorsky and Sidney Straus

Samples of polystyrene of an average molecular weight of about 230,000 and weighing 25 to 50 mg, were pyrolyzed in a vacuum of 10^{-6} mm of mercury at 350° to 420° C. Time of pyrolysis varied from 0.5 to 4 hours. The following fractions were obtained: (1) A solid residue having an average molecular weight of 2,182, (2) a wax-like fraction consisting of a mixture of a dimer, trimer, and tetramer of styrene, with an average molecular weight of 264, (3) a liquid fraction consisting of 94.3 mole percent of styrene, 5.6 mole percent of toluene, and traces of ethyl benzene and methyl styrene, (4) a gaseous fraction consisting mainly of carbon monoxide. Composition of all fractions and relative amounts of the wax-like and liquid fractions were found to be independent of time and temperature of pyrolysis, or of the amount of the original sample of polystyrene. A maximum yield of styrene, amounting to 42 weight percent of the original sample of polystyrene, was obtained at 420° C. The fact that only small fragments, not larger than the tetramer, were volatilized, leads to the conclusion that the larger fragments remain entangled in the mass of macromolecules and break up into smaller fragments, which then volatilize.

I. Introduction

Pyrolytic fragmentation and fractionation of polymers and identification of the fragments can serve as an effective means of studying structure and properties of the polymers under investigation. Pyrolysis of polymers results in fragments whose molecular weights and vapor pressures vary through a wide range. In order to facilitate the identification of these fragments, it is imperative to separate the mixture into fractions and apply suitable analytical methods to identify the various fractions. This paper describes a method and an apparatus for carrying out pyrolysis of polymers and fractionation of the products of pyrolysis under conditions of molecular distillation. Polystyrene was selected as the subject of this investigation because of the simplicity of its structure and the ease with which some of its fractions can be analyzed by means of the mass spectrometer.

Staudinger and Steinhof³ pyrolyzed 208 g samples of polystyrene in glass retorts by external heating and obtained a complex mixture of hydrocarbons. They used atmospheric pressure in one instance and a pressure of 0.1 mm of Hg in another. Fractional distillation of the products yielded a monomer, dimer, trimer, and some tetramer of styrene, and other compounds. They report that at atmospheric pressure and at a temperature of 400° to 500° C, rapid decomposition of polystyrene takes place resulting in the formation mostly of the monomer and some dimer. At 310° to 350° C and atmospheric pressure, slow decomposition takes place with the formation mostly of the monomer, a good deal of the dimer, and some trimer. At a pressure of 0.1 mm, where the fragments are more easily removed from the hot zone by distillation, the products of pyrolysis at 290° to 320° C are the monomer, dimer, trimer, and some tetramer.

However, thermal decomposition, when carried

¹ This paper was presented at the High Polymer Forum during the New York meeting of the American Chemical Society, Sept. 15 to 19, 1947.

² This paper is also appearing in the May issue of Industrial and Engineering Chemistry.

³ H. Staudinger and A. Steinhof, *Ann.* **517**, 35 (1935).

out in a high vacuum, could be interpreted more easily for the following reasons: The products of pyrolysis remain free from admixtures from the atmosphere; fractions of higher molecular weight could be distilled off without secondary pyrolysis; and separation of the products of pyrolysis into fractions could be carried out most effectively under conditions of molecular distillation.

The method was investigated in a series of experiments using temperature, time, and size of sample as variables. In each case, a weighed amount, 25 to 50 mg, of pure polystyrene, of an average molecular weight of about 230,000,⁴ was spread as a thin layer in a platinum tray having an evaporating surface of about 12 cm². The tray was then heated in a vacuum of about 10⁻⁶ mm of Hg for periods of time ranging from 0.5 to 4 hr and at temperatures varying between 350° and 420° C. The distillate was first collected on a

⁴ Molecular weight determination was made by Samuel G. Weissberg of the National Bureau of Standards, by the osmotic pressure method.

liquid-air cooled condenser placed at a distance of 1.7 cm from the evaporating surface, then separated into fractions by redistillation and the fractions weighed. All the weighings were made on a microbalance to an accuracy of about 0.05 mg.

II. Apparatus and Experimental Procedure

The apparatus is shown diagrammatically in figure 1. It is made of glass and resembles a Dewar flask except for a ground joint at the upper end for the purpose of introducing or removing the platinum tray from the apparatus. The tray is heated by means of a platinum-wire heating element incased in the form of a fine helix in short lengths of glass tubing and held together between two stainless steel disks. An oil pump and a Hg diffusion pump, not shown in the figure, serve to evacuate the system to a sticking vacuum, preliminary to pyrolysis. Another Hg diffusion pump,

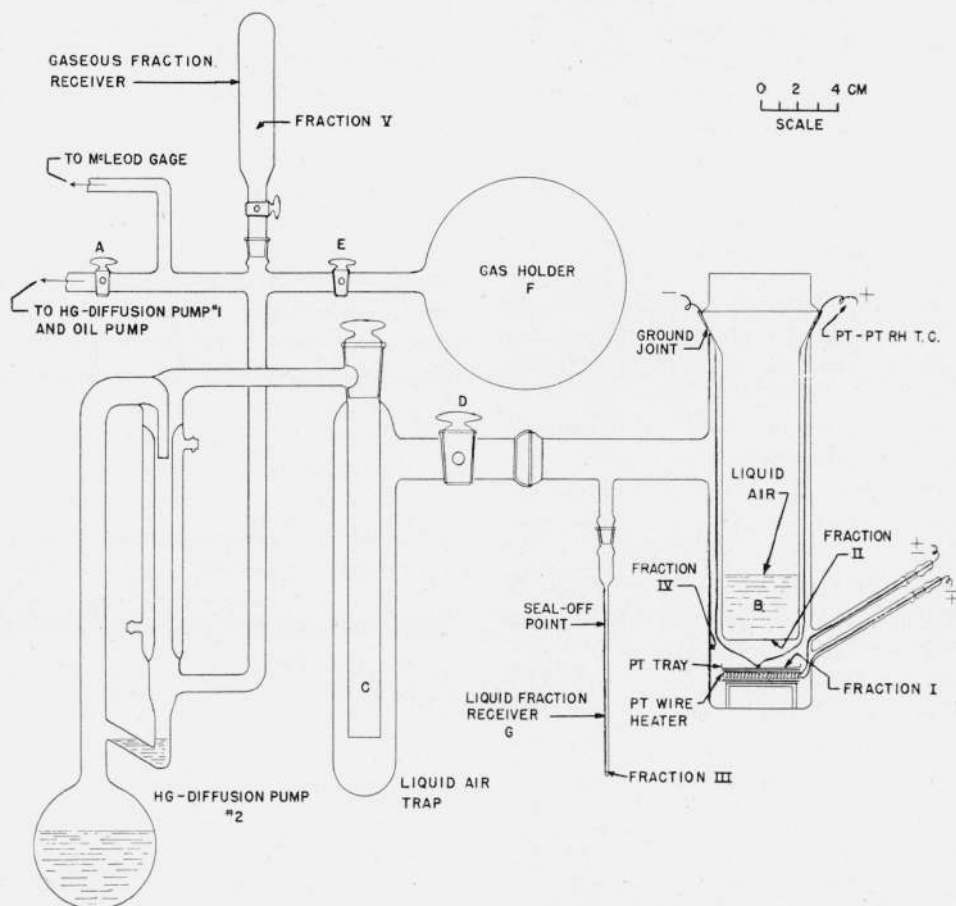


FIGURE 1. Molecular still for pyrolysis of high polymers.

capable of operating against a pressure of several centimeters of Hg, serves to collect the gaseous fraction during pyrolysis. Difficulties due to desorption of gases from the heater and the inner surface of the outer jacket in the hot zone were overcome by a preliminary heat treatment of the apparatus. This treatment consisted in maintaining the heater and tray at about 200° C for 1½ hr, and at the same time flaming gently the outer jacket. After this preliminary heating, the outer jacket was kept cool during pyrolysis of the sample by means of a water-cooled coiled tube surrounding the jacket. A blank experiment, without polystyrene in the tray, showed that by following such a procedure the total amount of air desorbed in 1 hr of heating from 200° to 400° C, followed by ½ hr of heating at 400° C, was 0.007 ml at normal temperature and pressure. Temperature of pyrolysis was measured by means of a Pt-PtRh thermocouple spotwelded to the tray at its center.

The following procedure was employed. A sample of polystyrene,⁵ in the form of a 0.5 percent solution in benzene, was placed in the platinum tray, and the benzene evaporated at 100° to 110° C, followed by evacuation for about 1 hr to a constant weight. The tray was then placed on the heater in the apparatus and the pressure reduced to a sticking vacuum. After a preliminary heating at 200° C, as described above, the system was shut off from the oil pump and Hg diffusion pump 1 by means of stopcock *A*. Liquid air was then placed in the inner cup *B* of the Dewar-like apparatus, also around the liquid-air trap *C*, and Hg diffusion pump 2 was turned on. Temperature of the tray was then raised to the required point and then kept constant for the required time. All the products of pyrolysis, except those not condensable at the temperature of liquid air, collected on the liquid-air condenser *B*. A gaseous fraction *V*, not condensable at the temperature of liquid air, was collected in the space between the Hg diffusion pump 2 and stopcocks *A* and *E*. At the end of pyrolytic operation, stopcock *D* was closed, diffusion pump 2 turned off and the gas allowed to expand to stopcock *D*. The volume between stopcocks *A*, *E*, and *D*, as calibrated by means of the gas holder *F*, was about 2 liters. Pressure was measured by means of a McLeod gage not shown

⁵ We are indebted to Arthur Roche, Dow Chemical Co., for this polystyrene. It was prepared by polymerizing pure styrene, without a catalyst, in an atmosphere of nitrogen, for 48 hours at 120° C.

in the figure. A sample of gas in the receiver was used for analysis in the mass spectrometer. The weight of the gaseous fraction could then be determined from a knowledge of its volume, pressure, and composition.

To separate the other fractions, the liquid air was removed from condenser *B*, and a liquid air container placed under liquid fraction receiver *G*. Fraction III, volatile at room temperature, was thus collected in the small receiving tube *G*. This tube was then sealed without melting it off and later weighed. Instead of collecting only one fraction III, it would be possible to collect fractions III_a, III_b, etc., by maintaining the condenser *B* at various temperatures between that of liquid air and room temperature.

Part of the condensate on *B*, volatile at the temperature of pyrolysis but nonvolatile at room temperature, was collected as fraction II by dissolving it in benzene in a platinum crucible, vaporizing the benzene, and weighing the residue. The residue in the tray itself was weighed as fraction I.

Evaporation from a liquid or solid surface into a vacuum follows Lambert's cosine law, and, therefore, a part of the products of pyrolysis failed to condense on *B* and deposited on the inner wall of the outer jacket in the neighborhood of the platinum tray. As the jacket was maintained at the temperature of tap water during pyrolysis, that part of the deposit on its wall that was volatile at room temperature, reevaporated and condensed on the liquid-air condenser *B*. The nonvolatile residue on the jacket, designated as fraction IV, was not collected, and its weight is assumed to be equal to the difference obtained by subtracting the sum of the weights of fractions I, II, III, and V from the weight of polystyrene used. It is safe to assume that fraction IV has approximately the same composition as fraction II.

III. Pyrolytic Fractionation of Polystyrene

Results of 20 fractionation experiments are shown in table 1. In experiments 1 to 14, inclusive, temperature of pyrolysis was varied from 350° to 420° C, and the duration of each experiment was 0.5 hr. Pyrolysis of polystyrene, according to these data, begins at about 350° C and is practically complete at 400° C. In experiments 3, 5, 6, 12, and 13, the amount of sample used was about twice as much as in the other

TABLE 1. *Pyrolytic fractionation of polystyrene*

Experiment number	Weight of sample	Temperature	Duration	In weight percent of original sample				
				I Residue	II Nonvolatile at room temperature	III Volatile at room temperature	IV On wall of apparatus	V Gaseous fraction
	<i>mg</i>	<i>°C</i>	<i>hr</i>					
1.....	25.50	350	0.5	95.76	3.41	0.20	0.53	0.10
2.....	23.91	350	.5	96.36	1.76	1.04	0.77	.07
3.....	48.33	361	.5	86.44	3.50	4.68	5.31	.07
4.....	24.66	379	.5	52.80	14.36	23.56	9.17	.11
5.....	40.56	387	.5	50.86	17.08	22.85	9.04	.17
6.....	47.85	390	.5	41.19	20.83	27.06	10.81	.11
7.....	23.98	397.5	.5	8.92	30.90	41.82	18.20	.16
8.....	24.16	400	.5	2.56	32.78	43.58	20.72	.16
9.....	23.32	400	.5	11.53	31.64	38.84	17.86	.13
10.....	25.52	400	.5	5.25	37.34	40.32	16.96	.13
11.....	24.86	401	.5	5.27	31.94	42.72	19.84	.13
12.....	56.88	401	.5	0.04	34.48	36.41	29.00	.07
13.....	55.15	405	.5	1.67	35.71	36.80	25.77	.05
14.....	21.73	420	.5	0.83	34.01	44.59	20.45	.12
15.....	47.69	361	1.0	77.88	8.62	9.29	4.11	.10
16.....	48.54	361	2.0	59.35	16.30	16.75	7.45	.15
17.....	63.22	364	3.0	21.53	35.25	30.61	12.53	.08
18.....	48.55	364	4.0	8.36	29.22	33.63	18.71	.08
19.....	54.79	376	1.0	19.64	32.62	26.19	21.51	.04
20.....	56.85	378	1.0	14.08	34.53	37.70	13.65	.04

experiments of this series. In experiments 3, 15, and 16 the temperature was the same 361° C, and the time was varied from 0.5 to 2 hr. In experiments 17 and 18 the temperature was the same, 364° C, and the time was 3 and 4 hr, respectively. Fractions I to V are listed in table 1. In general, gradual decrease of fraction I and a gradual increase of fraction III, II, and IV with temperature and time, are indicated in this table. As to the gaseous fraction V, it is about the same in all experiments, the average being 0.10 percent by weight of the sample of polystyrene used.

In table 2, fractions II and IV for each experiment are shown combined as one fraction, nonvolatile at room temperature. Ratios of volatile fraction (III) to the nonvolatile fraction (II+IV) are shown in the last column of this table. With a few exceptions, this ratio is about the same for all experiments, the average for experiments 3 to 20, inclusive, being 0.74. Staudinger and Steinhöfer obtained in one experiment, carried out at a pressure of 0.1 mm and a temperature of 290° to 320° C, a ratio of 0.83.

In figure 2, fractions I (residues), fractions II+IV (nonvolatile at room temperature), and

TABLE 2. *Ratio of volatile (III) to nonvolatile (II+IV) fraction in the pyrolysis of polystyrene*

Experiment number	Temperature	Time	III volatile	II+IV nonvolatile	Ratio III/II+IV
			at room temperature	at room temperature	
	<i>°C</i>	<i>hr</i>	<i>Percent</i>	<i>Percent</i>	
1.....	350	0.5	0.20	3.94	0.05
2.....	350	.5	1.04	2.53	.41
3.....	361	.5	4.68	8.81	.53
4.....	379	.5	23.56	23.53	1.00
5.....	387	.5	22.85	26.12	.87
6.....	390	.5	27.06	31.64	.85
7.....	397.5	.5	41.82	49.10	.85
8.....	400	.5	43.58	53.50	.82
9.....	400	.5	38.84	49.50	.78
10.....	400	.5	40.32	54.30	.74
11.....	401	.5	42.72	51.78	.82
12.....	401	.5	36.41	63.48	.57
13.....	405	.5	36.80	61.48	.60
14.....	420	.5	44.59	54.46	.82
15.....	361	1	9.29	12.73	.73
16.....	361	2	16.75	23.75	.71
17.....	364	3	30.61	47.78	.64
18.....	364	4	33.63	47.93	.70
19.....	376	1	26.19	54.13	.48
20.....	378	1	37.70	48.18	.78
Average ratio for experiments 3 to 20 incl.....					0.74
Staudinger and Steinhöfer.....					.83

fractions III (volatile at room temperature), are plotted in weight percent of original samples of polystyrene against temperature of pyrolysis. Only experiments 1 to 14, inclusive, where the time of pyrolysis was the same, 0.5 hr., are shown in this figure.

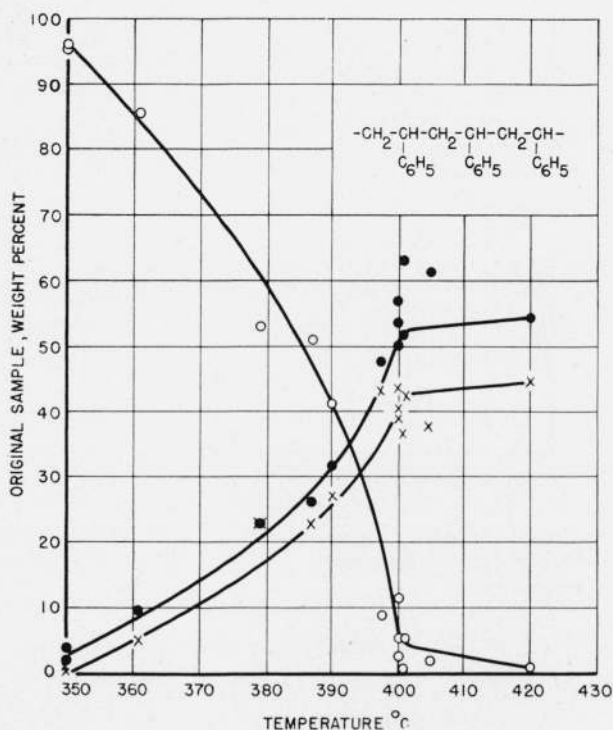


FIGURE 2. Fractions obtained in the pyrolysis of polystyrene.

○, Residue; ●, nonvolatile at room temperature; X, volatile at room temperature.

IV. Analysis of Fractions

Only the gaseous fraction (V) and the fraction volatile at room temperature (III), could be analyzed in the Consolidated mass spectrometer used in this work. Fraction V was found to consist chiefly of CO. The CO was probably due to the reaction of polystyrene with oxygen held in the original polystyrene in dissolved or combined form. Weight of the gaseous fraction was determined in each case from its volume, pressure, and mass spectrometer analysis. It amounted, on the average, to 0.1 percent of the original weight of polystyrene.

Fraction III was collected as a clear colorless liquid in a small tube, about 1.7-mm inside diameter and 7 cm long. Its weight was determined by weighing the tube before and after the experi-

ment, allowing for the air removed in the evacuation. This fraction weighed anywhere between a fraction of a milligram and 20 mg. As the expansion chamber of the mass spectrometer could hold only a few milligrams of this fraction in gaseous form at the vapor pressure of the components of this fraction, it was found necessary to use a special expansion apparatus in preparing a sample for analysis. This expansion apparatus is shown in figure 3. It consists of a chamber that can be

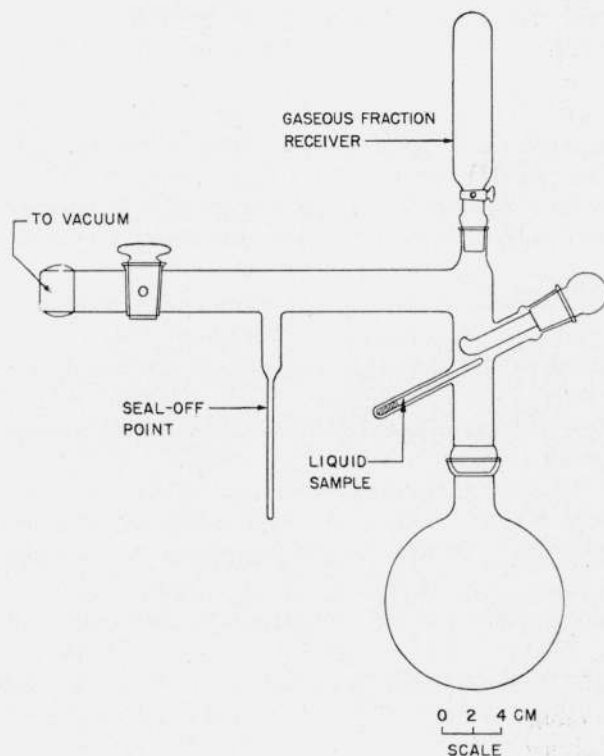


FIGURE 3. Apparatus for expanding liquid samples in a vacuum.

evacuated to a sticking vacuum. The volume of this chamber could be varied to suit the size of fraction III, by means of a removable bulb varying in size from 25 to 500 ml. The apparatus is provided with a break-off valve and a sample tube in which a gaseous sample was collected for analysis in the mass spectrometer. After collecting the sample, the rest of the expanded material was collected in a small tube by means of liquid air and the tube sealed off. Fragments of the broken tube that held fraction III were collected and weighed before and after washing thoroughly with benzene to see whether it contained a nonexpanded residue. The residue varied from zero to a few percent of the total weight of fraction III.

The Consolidated mass spectrometer has a range of analysis of molecular weight up to about 130 to 150. This range includes the monomer, styrene, and other fragments having one benzene ring. If fraction III contained any fragments with more than one benzene ring, say, a dimer, these fragments would not show up in the mass spectrometer analysis. In order to check on this, two sample tubes containing fraction III from experiments 5 and 6, were broken in the open air and the contents allowed to expand at room temperature. Figure 4 shows loss of weight in percent of original weight of fraction III plotted against time in days. In both cases expansion leveled off at 95.5 percent loss, indicating that fraction III contained 4.5 percent in polymerized form. Sample 6 expanded more slowly because the tube in which it was contained was bent sharply in the form of a U. The fact that styrene polymerizes slowly even at room temperature was confirmed by a molecular weight determination of fraction III by the method of freezing point lowering in cyclohexane. The molecular weight varied from about 100 to 114, depending on age of fraction.

Results of mass spectrometer analysis of fraction III are shown in the case of nine experiments in table 3. Relative composition of this fraction seems to be independent of the original amount of polystyrene used or of duration or temperature of pyrolysis. The results are given in mole percent and indicate that this fraction consists on the average of 94.3 percent of styrene, 5.6 percent of toluene, and traces of ethyl benzene and methyl styrene. Styrene yield in weight percent of the

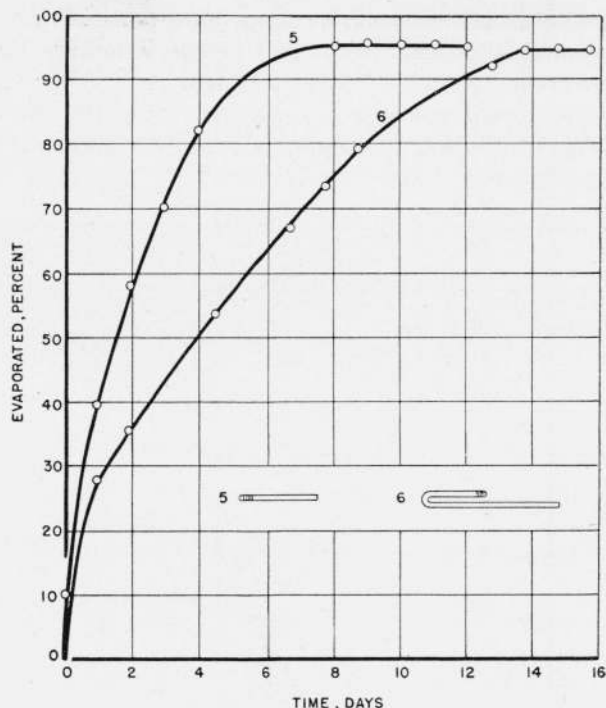


FIGURE 4. Evaporation at atmospheric pressure and room temperature of the liquid fraction from pyrolysis of polystyrene.

original weight of polystyrene used is also shown in this table. At 400° C, the average yield of styrene (in experiments 7, 9, and 10) is 36.86 percent.

Fraction I is a light-brown horny solid and fraction II a tan-colored wax-like material. These fractions, being nonvolatile at room temperature, could not be analyzed in the mass spectrometer. The average molecular weight of these fractions

TABLE 3. Mass spectrometer analysis of fraction III, volatile at room temperature

Experiment number	Weight of sample	Time	Temperature	Styrene (yield in percent of sample)	Fraction III			
					Styrene	Toluene	Ethyl benzene	Methyl styrene
	mg	hr	° C		Mole %	Mole %	Mole %	Mole %
2	23.91	0.5	350	0.96	91.8	8.0	0.1	0.1
15	47.69	1.0	361	8.56	92.2	7.8	0	0
16	48.54	2.0	361	15.88	94.1	5.9	0	0
17	63.22	3.0	364	29.63	96.1	3.9	0	0.04
18	48.55	4.0	364	31.85	94.0	6.0	0	.02
4	24.66	0.5	379	22.67	95.5	4.4	0.06	.03
7	23.98	.5	397.5	40.32	95.7	4.2	.06	0
9	23.32	.5	400	37.00	94.7	5.2	.1	0
10	25.52	.5	400	38.58	95.0	5.0	0	0
Average values					94.3	5.6		

was determined with a Beckman thermometer by the method of freezing point lowering in a solution of cyclohexane. In case of fraction II, the freezing point lowering was about 2° to 2.5° C. and in the case of fraction I, the lowering was about 0.2° C. The molecular weight was calculated by means of formula

$$M = \frac{F \times 1,000 \times w}{\Delta F \times W},$$

where

F = molar freezing point lowering; 20° C. for cyclohexane

w = weight of solute in g

W = weight of solvent in g

ΔF = actual freezing point lowering.

The results are shown in table 4.

TABLE 4. Average molecular weight of fractions I and II by the method of freezing point lowering in cyclohexane

Experiment number	Temperature ° C.	Time hr.	Average molecular weight	
			Fraction I	Fraction II
15	361	1	-----	266
16	361	2	-----	263
17	364	3	2,078	265
19	376	1	2,214	261
20	378	1	2,255	259
12	401	0.5	-----	266
13	405	.5	-----	266
	-----	-----	2,182±70	264±2
Staudinger and Steinhofer	-----	-----	-----	263

The average molecular weight of fraction I, based on three determinations, is 2,182±70. For fraction II, the average of seven determinations is 264±2. If fraction II were to consist of equal amounts of the dimer, molecular weight 208, and trimer, molecular weight 312, the average molecular weight would be 250. A slight preponderance of the trimer, or the presence of a small amount of the tetramer, molecular weight 416, or both, could account for the actual average molecular weight of 264. Staudinger and Steinhofer pyrolyzed a 208-g sample of polystyrene at a pressure of 0.1 mm and temperature of 290° to 320° C and obtained, in addition to styrene, 19.32 percent of dimer, 23.08 percent of trimer, and 3.85 percent of tetramer. The average molecular weight

of a mixture of dimer, trimer, and tetramer in the above proportions is 263.

V. Discussion of Results

Pyrolysis of polystyrene was carried out in this work under most favorable conditions of molecular distillation, where fragments of high molecular weight, if formed, would have a chance to escape into the gaseous phase and collect on the condenser. The fact that the condensate consisted of small fragments, i. e., the monomer, dimer, trimer, and perhaps some tetramer, indicates that we are not dealing here with a simple case of molecular distillation, but that distillation here is subservient to conditions of pyrolytic decomposition.

Let us first consider rate of pyrolysis as compared with rate of vaporization of the fragments. It took about 30 minutes to pyrolyze 25 to 50 mg of polystyrene at 400° C. Rate of vaporization of a similar amount of material, under conditions of molecular distillation can be calculated by means of Langmuir's equation⁶ for evaporation from a liquid or solid surface:

$$m = P \sqrt{\frac{M}{2\pi RT}}, \text{ where}$$

m = grams of material evaporated per square centimeter of surface per second.

P = vapor pressure in dynes per square centimeter.

M = molecular weight of the material.

R = gas constant in ergs per degree C.

T = absolute temperature.

The vapor pressure of a mixture of the monomer, dimer, trimer, and tetramer in contact with polystyrene, is not known, but it can safely be assumed to be at least 50 mm at, say, 350° to 400° C. Molecular weight of the mixture will be assumed as 200. Then, since total evaporating surface is 12 cm², we have

$$m = 50 \times 1333.22 \times 12 \times \sqrt{\frac{200}{2\pi \times 8.3 \times 10^7 \times 623}} = 20 \text{ g.}$$

per second. Thus it would take a small fraction of a second to vaporize 25 to 50 mg of material involved in the pyrolysis.

In the work of Staudinger and Steinhofer, external pressure of 1 atmosphere was used in one

⁶ I. Langmuir, Phys. Rev. **2**, 329 (1913).

case and of 0.1 mm Hg in another. In either case, the pressures were too high for molecular distillation and it might be expected that large fragments would be returned to the hot zone by kinetic agitation and be pyrolyzed further into smaller fragments. However, in our case, where the external pressure was 10^{-6} mm of Hg fragments greater than the trimer or tetramer, once formed, would have a vapor pressure sufficient to remove it from the hot zone and bring it to the condenser. It is, therefore, surprising that the fragments collected in our work were no greater than those obtained by Staudinger and Steinhofer in their pyrolysis at a pressure of 0.1 mm Hg. In fact, there is a close agreement between our results and those of Staudinger and Steinhofer carried out at 0.1 mm pressure, as shown in table 5. In this table two experiments of Staudinger and Steinhofer, (1), at atmospheric pressure and (2) at 0.1 mm, are compared with our experiments 7, 9,

and 10. In experiments (1) the amounts of monomer, dimer, and trimer collected were 62.5, 19.32, and 3.85 percent, respectively, of the original weight of polystyrene used. In experiment (2), the fractions collected were a monomer, dimer, trimer, and tetramer in amounts of 38.46, 19.32, 23.08, and 3.85 percent, respectively. Total of the dimer, trimer, and tetramer in the latter case was 46.15 percent. In the case of the present work, the averages for experiments 7, 9, and 10, were 40.33 percent for the monomer and 50.97 percent for the sum of the dimer, trimer, and tetramer. In addition to this, the average molecular weight of fraction II of our work is 264 as compared with the mean molecular weight of 263 for the dimer, trimer, and tetramer in experiment (2) of Staudinger and Steinhofer.

The fact that only small fragments, no larger than the tetramer were obtained in the present work, in spite of the favorable conditions for

TABLE 5. *Pyrolytic fractionation of polystyrene*

Experimental conditions	Staudinger and Steinhofer		Present work for experiment—			Average for experiments 7, 9, 10
			7	9	10	
Weight of sample.....g.....	208	208	0.02398	0.02332	0.02552	
Pressure.....mm Hg.....	760	10^{-1}	10^{-6}	10^{-6}	10^{-6}	
Temperature.....°C.....	310 to 350	290 to 320	397.5	400	400	
Duration.....hr.....	6	12	0.5	0.5	0.5	
GASEOUS FRACTION (V)						
Component	In weight percent of original sample					
CO.....			0.16	0.13	0.13	0.14
FRACTION VOLATILE AT ROOM TEMPERATURE (III)						
Styrene.....	62.5	38.46	40.32	37.00	38.58	38.64
Ethyl benzene.....			0.02	0.04	0.00	0.02
Toluene.....			1.48	1.80	1.74	1.68
Total.....	62.5	38.46	41.82	38.84	40.32	40.33
FRACTION NONVOLATILE AT ROOM TEMPERATURE (II+IV)						
Dimer.....	19.32	19.32				
Trimer.....	3.85	23.08				
Tetramer.....	0	3.85				
Total.....	23.17	46.25	49.10	49.50	54.40	50.97
FRACTION (I)						
Residue.....	9.62	11.54	8.92	11.53	5.25	8.57

molecular distillation, is in qualitative agreement with the view expressed by Frenkel,⁷ who states that: Linear or chain-like macromolecules cannot exist in the gas phase, for, instead of evaporating, they must be disintegrated or depolymerized into smaller units, mainly monomeric or dimeric. Frenkel further points out that the vapor phase will consist of fragments in which the number of units is equal to W_1/U_1 , where W_1 is dissociation energy and U_1 is evaporation energy of the monomer. In the case of polystyrene, W_1 , the energy required to rupture a C to C bond, is approximately 80 kcal, and U_1 , latent heat of vaporization of styrene, is about 9 kcal. Therefore, $W_1/U_1=80/9=9$. Since the polystyrene chain has a uniform structure throughout its length (except for the ends), fragments from a monomer to a nonamer should be equally possible. The average molecular weight of the mixture of all the fragments, except the monomer, should, therefore, be much higher than 264. The fact that the average molecular weight of fraction II was only 264 could be explained by assuming that larger fragments split off along with the smaller fragments, but that the former remain entangled in the macromolecules and split further into smaller fragments. This assumption could explain the fact that pyrolysis of polystyrene is a slow process.

VI. Summary

Pyrolysis of small samples of polystyrene, of molecular weight of about 230,000, was carried out in a vacuum of 10^{-6} mm of Hg and at temperatures between 350° and 420° C. Time of pyrolysis was varied from 0.5 to 4 hr. Results indicate that pyrolysis begins at about 350° C and is almost

complete at 400° C. The volatile products of pyrolysis were separated into one gaseous fraction, one liquid fraction, volatile at room temperature, one wax-like fraction, nonvolatile at room temperature, and a horny-like residue. The gaseous fraction amounted on the average to 0.1 percent by weight of the original sample of polystyrene and consisted chiefly of CO. The liquid fraction consisted of 94.3 mole percent of styrene and 5.6 mole percent of toluene. The wax-like fraction consisted of a mixture of dimer, trimer, and some tetramer, with an average molecular weight of 264 ± 2 . A hard tan-colored residue, which was obtained in the experiments at lower temperatures, was found to have an average molecular weight of $2,182 \pm 70$. Weight ratio of the liquid fraction to the wax-like fraction in all the experiments above 350° C is close to a constant, independent of amount of original polystyrene used, of duration or temperature of pyrolysis. Composition of each fraction is also independent of these variables. Maximum yield of styrene was obtained at 420° C and amounted to 42 percent by weight of the original polystyrene. A comparison of this work, which was carried out under most favorable conditions of molecular distillation, with the work of Staudinger and Steinhöfer, who pyrolyzed a 208-g sample of polystyrene at a pressure of 0.1 mm Hg and at a temperature of 290° to 320° C, shows a remarkable similarity of results.

The authors wish to thank Robert M. Reese, who made the mass spectrometric analyses, and Dorothy Thompson and Laura Williamson, who made the computations of these analyses in connection with this work.

WASHINGTON, September 5, 1947.

⁷J. Frenkel, *Kinetic theory of liquids*, p. 451 (Oxford at the Clarendon Press, 1916).