Pyrolysis of Some Polyvinyl Polymers at Temperatures Up to 1,200 °C

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A study was made of the thermal behavior in a vacuum of polystyrene, polytetrafluoroethylene, poly(α-methylstyrene), polypropylene, polyisobutylene, and poly(methyl methacrylate), when pyrolized at 500, 800, and 1,200 °C. The volatile products of degradation were collected and fractionated, and the fractions analyzed by mass-spectrometric and microcryoscopic methods. Generally, the results from 500 °C pyrolysis resemble those obtained previously from the same polymer at lower temperatures. The results at 800° and 1,200° indicate a much greater fragmentation of the pyrolysis products than at lower temperatures. Thus, for example, at 1,200° polystyrene yields less monomer but considerable greater amounts of C_2H_2, C_2H_4, C_3H_6, and C_4H_8 than at lower temperatures. Similarly, poly(α-methylstyrene) yields 100 percent monomer below 500 °C, but at 800 and 1,200 °C the yields are 88 percent and 34 percent, respectively. Also at the higher temperatures, pronounced amounts of H_2, CH_4, C_2H_2, C_2H_4, C_3H_6, C_3H_8, C_4H_8, C_6H_6, C_4H_8, and C_6H_8 are formed.

1. Introduction

While the literature contains a great deal of information on the behavior of polymers at temperatures up to about 500 °C, little is known about their behavior above this temperature. Natural crepe rubber was pyrolyzed up to 700 °C [1],[1] smoked crepe up to 650 °C [2], and polyisoprene up to 900 °C [3]. In all these experiments it was found that a higher temperature of pyrolysis produces a greater yield of isoprene in the degradation products [3, 4].

In the past few years a number of applications have been made of organic polymers as protective coatings for bodies subjected to very high temperatures. They have been used, for example, as the covering of the nose cones of missiles and satellites which develop considerable amounts of heat through friction with air at high velocities, and as the lining for the inner surface of nozzles that come in contact with the hot exhaust gases in jet propulsion. These applications have stimulated research on the thermal stability of polymers at high temperatures. In these investigations the heating of the materials has often been accomplished by means of an electric arc or by a stream of hot gas. However, in most of these experiments the polymeric materials were not in the pure state but contained extraneous materials such as carbon, glass, asbestos, etc. The products of degradation, therefore, consisted of a complex mixture of molecular fragments coming not only from the polymer but from the extraneous material as well. The gases from the arc or from the hot gas stream were an additional source of contamination of the products. This made it very difficult either to anlyze the products of degradation or to interpret the chemical reactions involved.

Studies were recently made by the present authors on the pyrolysis of polymers in a vacuum and, in some cases, in a helium atmosphere in the temperature range of 500 to 1,200 °C. The polymers thus investigated were: polystyrene up to 850 °C, and polyacrylonitrile, poly(vinylidene fluoride), and polytrivinylbenzene up to 800 °C [5]; polymethylene, poly(vinylidene fluoride), and polytrivinylbenzene up to 1,200 °C [6]; and silicone, phenolic, epoxy, and ester resins up to 1,200 °C [7]. The present investigation extends the program to cover a few simple vinyl polymers at temperatures ranging from 400 to 1,200 °C. These polymers include polystyrene, polytetrafluoroethylene, poly(α-methylstyrene), polypropylene, polyisobutylene, and poly (methyl methacrylate).

2. Materials Used

The materials used had the following characteristics:

(a) *Polystyrene.* Thermally prepared. Molecular weight 230,000, as determined by the osmotic pressure method.

(b) *Polytetrafluoroethylene.* Teflon tape 0.07 mm thick. Molecular weight not known, but estimated to be very high.

(c) *Poly(α-methylstyrene).* Flaky material obtained from the Dow Chemical Company. Prepared by low-temperature polymerization. Molecular weight 350,000, as determined by light scattering.

(d) *Polypropylene.* Fine white powder obtained from B. F. Goodrich Company. Prepared by the Ziegler method. Molecular weight between 50,000 and 100,000.

(e) *Polyisobutylene.* Pure grade white gum. Currently used as a National Bureau of Standards standard material for viscosity measurements. Molecular weight 1,560,000, as determined by the light-scattering method.

(f) *Poly(methyl methacrylate).* Prepared from the monomer at room temperature without the use of catalysts. Molecular weight 5,100,000, as determined by light scattering.

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[1] Figures in brackets indicate the literature references at the end of this paper.

3. Apparatus and Experimental Procedure

The apparatus used in the pyrolysis studies was the same as that used in the pyrolysis of polytrivinylbenzene and other polymers [6, 7], except that the fused quartz tube holding the sample tube was replaced with a platinum tube. Samples weighing 15 to 30 mg were heated in a vacuum by quickly moving a preheated furnace into position surrounding the sample for pyrolysis. For temperatures of 500 °C or lower a 5-min period was used to heat up the sample from room temperature to the temperature of pyrolysis, followed by a 30-min period at the pyrolysis temperature. Fluctuation of the final temperature was ±2 °C. For higher temperatures a 2-min preheating period was followed by a 5-min heating period at the required temperature, and fluctuation of the operating temperature was ±5 °C. The residues were weighed, and the volatile products were collected and fractionated. The following volatilized fractions were obtained: (a) A waxlike fraction, designated as V_{pyr}, volatile at the temperature of pyrolysis, but not at room temperature, and consisting of large molecular fragments deposited in the apparatus just beyond the hot zone; (b) a light fraction, V_{25}, volatile at room temperature, collected in a liquid-nitrogen-cooled trap; and (c) a gaseous fraction, V_{-190}, not condensable at the temperature of liquid nitrogen. In some cases a fraction, V_{-80}, volatile at the temperature of dry ice, was also collected. Analyses of fractions V_{25}, V_{-80}, and V_{-190} were made by means of a mass spectrometer.

4. Experimental Detail

4.1. Polystyrene

It was shown in an earlier study [5] on pyrolysis of polystyrene at 362 and 850 °C in a vacuum, and in helium at atmospheric pressure, that a higher temperature, a higher pressure, or both, cause a greater fragmentation of the volatile products. This study has now been extended to temperatures up to 1,200 °C. The volatile products were collected and fractionated in the usual manner, and the more volatile fractions were analyzed in the mass spectrometer.

Distribution of fractions from pyrolysis in a vacuum at 400, 500, 800, and 1,200 °C is shown in table 1, and from pyrolysis at similar temperatures in helium, in table 2. Results of analysis of the volatile products from pyrolysis in a vacuum are shown in table 3 and those from pyrolysis in helium are shown in table 4. As seen from tables 3 and 4, the yield of monomer C_8H_8 from vacuum pyrolysis decreases with increase of temperature, while in pyrolysis in helium the decrease is so drastic that at 1,200 °C only 0.6 percent of monomer is produced.

There is some discrepancy between the results shown in tables 1, 2, 3, and 4 of this paper and those obtained previously at 362 and 850 °C [5, 8]. However, this may be due to the fact that in this work the time of collecting fraction V_{25} by means of liquid nitrogen was 3 hr instead of the 1 hr in the previous work. The longer period of collection of V_{25} was used in all the experiments described in this paper.

TABLE 1. *Pyrolysis of polystyrene in a vacuum*

Experiment	Weight of sample	Temperature	Volatilization	Fractions based on total volatilized		
				V_{pyr}	V_{25}	V_{-190}
	mg	°C	%	%	%	%
1	14.85	400	98.8	46.9	53.1	....
2	14.25	400	92.0	43.3	56.7	....
3	20.4	500	100.0	36.5	63.5	....
4	19.9	500	100.0	38.6	61.4	....
5	17.9	800	99.7	28.2	71.8	....
6	16.7	800	100.0	22.8	77.2	....
7	19.5	1200	98.0	34.4	65.0	0.6
8	13.4	1200	96.1	33.6	66.0	.4

TABLE 2. *Pyrolysis of polystyrene in helium*

Experiment	Weight of sample	Temperature	Volatilization	Products based on total volatilized	
				V_{pyr} *	V_{25}
	mg	°C	%	%	%
9	19.6	500	100.0	35.2	64.8
10	15.7	500	100.0	28.4	71.6
11	18.7	800	98.5	40.0	60.0
12	16.6	800	99.1	39.8	60.2
13	16.1	1200	95.3	74.6	25.4

* Fraction V_{-190} could not be separated from the helium. In vacuum pyrolysis V_{-190} appeared in small amounts only at 1,200 °C (table 1). Here fraction V_{-190} is included in V_{pyr}.

TABLE 3. *Analysis of volatile products from pyrolysis of polystyrene in a vacuum*

Component*	At 400 °C		At 500 °C		At 800 °C		At 1,200 °C	
	No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8
	%	%	%	%	%	%	%	%
H_2							0.1	0.1
C_2H_4							.1	
C_2H_2							5.0	4.2
C_3H_6						1.6	3.6	5.0
C_3H_4						0.4	1.5	2.0
C_6H_6	2.0	2.3	1.5	0.5	0.8	1.6	5.2	7.1
C_7H_8	4.0	3.6	1.1	3.4	1.8	3.9	0.6	1.8
C_8H_8	46.5	50.0	56.4	51.4	47.4	47.6	41.6	41.1
C_8H_{10}	0.2	0.3						
C_9H_{10}	.4	.5	4.5	6.1	21.8	22.2	6.3	4.4
V_{pyr}	46.9	43.3	36.5	38.6	28.2	22.8	34.4	33.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

* Components are in weight percent of total volatiles.

TABLE 4. *Analysis of volatile products from pyrolysis of polystyrene in helium*

Component*	At 500 °C		At 800 °C		At 1,200 °C
	No.9	No.10	No.11	No.12	No.13
	%	%	%	%	%
C_2H_4	0.1				0.6
C_2H_2			8.5	5.8	2.6
C_3H_6			0.4		0.2
C_3H_4			0.2		
C_4H_8		2.5			
C_4H_6					
C_6H_6	.7	1.4	16.2	13.5	12.6
C_7H_8	6.5	12.5	7.7	7.2	1.3
C_8H_8	0.9		0.6		
C_8H_{10}	53.7	49.1	9.8	12.5	0.6
C_9H_{10}				0.8	
C_9 and up	4.5	5.1	18.0	18.0	7.6
V_{pyr}	35.2	28.4	40.0	39.8	74.6
Total	100.0	100.0	100.0	100.0	100.0

* Components are in weight percent of total volatiles.

4.2. Polytetrafluoroethylene

It was shown in our previous work [9] that polytetrafluoroethylene (Teflon), when pyrolyzed in a vacuum at temperatures up to 538 °C, yields about 95 percent monomer. In the present work the effect of higher temperatures of pyrolysis on the nature and relative amounts of the volatiles is revealed. Distribution of fractions and analysis of volatile products are shown in tables 5 and 6. The HF in the products at 1,200 °C was calculated from the mass spectrometer analysis of SiF_4, which forms in the reaction of HF with glass in the presence of even a trace of H_2O. In contrast with low-temperature pyrolysis, the products from pyrolysis at higher temperatures contain, in addition to monomer, considerable amounts of larger fragments collected as fraction V_{pyr}.

TABLE 5. *Pyrolysis of polytetrafluoroethylene in a vacuum*

Experiment	Weight of sample	Temperature	Volatilization	Fractions based on total volatilized [a]	
				V_{pyr}	V_{35}
	mg	°C	%	%	%
1	24.7	800	17.2	0	100
2	20.2	800	16.1	0	100
3	14.1	800	29.7	0	100
4	8.5	800	100	1.8	98.2
5	10.9	1200	100	11.8	88.2
6	10.7	1200	100	16.9	84.1

[a] Fraction V_{-130} appeared in trace amounts.

TABLE 6. *Analysis of volatile products from pyrolysis of polytetrafluoroethylene in a vacuum*

Component [a]	At 500 °C		At 800 °C		At 1,200 °C	
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
	%	%	%	%	%	%
HF	0	0	0	0	0.2	0.5
CF_4	1.5	1.2	1.0	1.8	1.7	2.6
C_2F_4	94.8	95.1	92.5	89.9	81.0	75.2
C_3F_6	3.7	3.7	5.9	6.5	5.3	5.8
V_{pyr}	0	0	0	1.8	11.8	15.9
Total	100.0	100.0	100.0	100.0	100.0	100.0

[a] Components are in weight percent of total volatiles.

4.3. Poly(α-methylstyrene)

When heated in a vacuum at temperatures below 400 °C, poly(α-methylstyrene) decomposes almost completely into monomer [10]. The effect of a higher temperature on the distribution of fractions in the pyrolysis of this polymer is shown in table 7. Considerable amounts of fractions V_{pyr} and V_{-130} are produced at the expense of fraction V_{35}. This effect is even more clearly indicated in table 8, where analysis of the volatile fractions from pyrolysis of the polymer is shown.

4.4. Polypropylene and Polyisobutylene

Pyrolysis of these two polymers in a vacuum has been studied previously at temperatures up to about 400 °C. For polypropylene the yield of monomer-size molecules, fraction V_{35}, is about 14 percent [11] and for polyisobutylene about 32 percent [4]. At higher temperatures fractions V_{35} are produced in larger amounts, as shown in tables 9 and 10.

TABLE 7. *Pyrolysis of poly(α-methylstyrene) in a vacuum*

Experiment	Weight of sample	Temperature	Amount of volatilization	Fractions based on total volatilized		
				V_{pyr}	V_{35}	V_{-130}
	mg	°C	%	%	%	%
1	10.2	500	99.0	0	100	0
2	11.3	500	99.4	0	100	0
3	8.0	800	100.0	11.2	88.7	0.1
4	10.1	800	100.0	5.4	94.3	.3
5	7.9	1200	98.7	34.3	54.2	11.5
6	9.2	1200	98.4	32.6	61.1	6.3

TABLE 8. *Analysis of volatile products from pyrolysis of poly(α-methylstyrene) in a vacuum*

Component [a]	At 500 °C		At 800 °C		At 1,200 °C	
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
	%	%	%	%	%	%
H_2			0.1	0.1	1.7	1.3
CH_4			.3	.3	6.8	3.1
C_2H_6					0.6	0.7
C_3H_8			.5	.1	3.6	3.2
C_3H_6			.6	.3	1.0	1.8
C_2H_2			.6	.2	0.7	0.4
C_4H_8					.5	1.9
C_6H_6			2.0	1.1	9.3	13.3
C_7H_8			0.4	0.3	0.1	3.6
C_8H_8					2.8	4.2
C_9H_{10}	100.0	100.0	83.9	92.2	33.0	33.9
V_{pyr}	0	0	11.2	5.4	34.3	32.6
Total	100.0	100.0	100.0	100.0	100.0	100.0

[a] Components are in weight percent of total volatiles.

TABLE 9. *Pyrolysis of polypropylene in a vacuum*

Experiment	Weight of sample	Temperature	Volatilization	Fractions based on total volatilized		
				V_{pyr}	V_{35} [a]	V_{-130}
	mg	°C	%	%	%	%
1	10.0	400	76.5	76.7	23.3	Trace
2	10.5	400	82.4	79.2	20.5	Trace
3	11.0	500	99.6	82.4	17.6	Trace
4	9.6	800	100.0	20.6	79.3	0.1
5	9.4	1200	98.9	22.4	75.8	1.8
6	40.8	1200	98.9	31.7	53.7	14.6

[a] Includes V_{-35} fraction.

TABLE 10. *Pyrolysis of polyisobutylene in a vacuum*

Experiment	Weight of sample	Temperature	Volatilization	Fractions based on total volatilized		
				V_{pyr}	V_{35} [a]	V_{-130}
	mg	°C	%	%	%	%
1	15.9	400	99.2	53.3	42.7	0
2	14.1	400	98.6	57.6	42.5	0
3	17.0	600	98.4	51.1	47.8	1.1
4	15.8	600	99.4	52.1	46.9	1.0
5	13.8	800	99.6	3.6	94.8	1.6
6	12.9	800	99.2	3.1	94.5	2.4
7	14.1	1200	98.6	14.7	66.8	18.5
8	14.0	1200	97.5	7.8	73.3	19.1

[a] Includes V_{-35} fraction.

Analyses of the volatile fraction from pyrolysis of these two polymers are shown in tables 11 and 12. As compared with pyrolysis at temperatures below 500 °C, [4, 8, 11] the yields of monomers, C_3H_4 and C_4H_8, are much higher at the higher temperatures. However, in the case of polyisobutylene at 1,200 °C the yield of C_4H_8 is very low and the yields of fragments of lower molecular weight, particularly of H_2, CH_4, and C_2H_4, are very high.

Component [a]	At 400 °C		At 500 °C	At 800 °C	At 1,200 °C	
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
	%	%	%	%	%	%
H_2				0.1	0.1	0.4
CH_4	0.1	0.1		.4	2.6	9.6
C_2H_2	.1	.1		.3	6.8	4.3
C_2H_4	.4	.3	0.4	6.0	13.1	19.0
C_2H_6	.3	.3	.3	0.7	1.0	0.9
C_3H_6	.6	.4	.8	8.4	8.5	6.5
C_3H_6	.6	.6	.4	17.9	18.4	12.6
C_3H_8	.5		.6	2.3	1.9	0.6
C_4H_4				0.7	2.8	2.4
C_4H_6				3.0	5.1	4.1
C_4H_8	2.5	1.7	.6	12.4	8.1	2.9
C_4H_{10}	1.8	1.3	.7	1.3	0.5	
C_5H_6				0.5	.8	1.6
C_5H_8	0.8	0.6	.6	3.0	2.1	0.8
C_5H_{10}	3.3	3.8	2.0	10.2	4.1	.3
C_5H_{12}	2.1	2.3	3.0	1.9		
C_6H_6					1.6	2.9
C_6H_{12}	0.7	0.6	0.7	1.7	0.7	
C_6H_{12}	4.0	3.7	3.0	4.0	.4	
C_7H_{14}	0.2	1.4	1.9			
C_7H_{14}	2.2	1.8	1.0			
C_8H_{16}	2.1	1.6	1.4			
C_9H_{18}			0.7			
V_{pr}	76.7	79.2	82.4	29.6	22.4	31.7
Total	100.0	100.0	100.0	100.0	100.0	100.0

[a] Components are in weight percent of total volatiles.

Component [a]	At 400 °C		At 500 °C		At 800 °C		At 1,200 °C	
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7	No. 8
	%	%	%	%	%	%	%	%
H_2							2.7	1.6
CH_4					1.2		17.6	10.1
C_2H_2					0.8	1.1	6.8	7.3
C_2H_4			0.9	0.6	2.7	5.0	9.6	13.6
C_2H_6							1.6	1.2
C_3H_4	0.5		1.1	1.6	3.0	5.4	14.9	18.5
C_3H_6							0.9	1.0
C_3H_8			0.7	1.3			4.8	4.4
C_4H_4					2.1	1.3	4.5	4.2
C_4H_6						0.7	4.5	5.9
C_4H_8	35.6	31.5	38.0	34.9	72.7	65.3	10.6	16.3
C_4H_{10}	0.7	0.7						
C_5H_6							0.6	1.9
C_5H_8			0.7				0.7	2.4
C_6H_6					5.7	1.7		1.1
C_9 and up	9.9	10.3	7.4	8.5	9.2	16.9	5.1	5.9
V_{pr}	53.3	57.5	51.2	52.1	3.6	3.1	14.7	7.6
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] Components are in weight percent of total volatiles.

4.5. Poly(methyl methacrylate)

Poly(methyl methacrylate) decomposes primarily into monomer on heating in a vacuum at temperatures up to about 350 °C [10]. However, when the temperature is raised to 1,200 °C considerable amounts of other fragments, both larger and smaller than the

monomer, appear among the volatiles. Table 13 shows the distribution of volatile fractions for 500, 800, and 1,200° C pyrolysis. The appearance of preponderant amounts of V_{-190} at 1,200 °C is particularly notable and is mainly due to the formation of CO, CO_2, H_2, CH_4, C_2H_2, and C_2H_4, as indicated in table 14. It was found that fractions V_{25} and V_{-190} from pyrolysis at 800 and 1,200 °C, if allowed to stand for more than a day, tended to repolymerize and thus give misleading results. All the analyses of these two fractions were therefore made on the same day that they were produced and collected.

Experiment	Weight of sample	Temperature	Volatilization	Fractions based on total volatilized		
				V_{pr}	V_{25}	V_{-190}
	mg	°C	%	%	%	%
1	10.3	500	100	3.6	96.4	0
2	9.9	500	100	2.3	97.7	0
3	8.5	800	100	11.2	88.7	0.1
4	11.3	800	100	8.8	91.1	.1
5	9.8	1200	100	5.0	29.4	65.6
6	9.8	1200	100	5.2	28.2	65.6

Component [a]	At 500 °C		At 800 °C		At 1,200 °C	
	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
	%	%	%	%	%	%
H_2					0.9	1.1
CH_4					5.9	6.2
C_2H_2					2.6	3.5
C_2H_4			0.7	0.7	5.3	4.7
C_2H_6					1.4	1.1
C_3H_4	0.7	1.0	.3	1.4	6.7	5.6
C_2H_4O			.3	0.8		
C_3H_6			.1	.7	5.2	5.6
C_3H_6O			.3			
C_4H_4			.4		1.2	0.5
C_4H_6			.3		1.4	3.0
C_4H_8			2.0	1.0	1.3	2.0
$C_5H_8O_2$	93.0	93.4	80.5	83.1	16.5	9.3
C_5H_8			0.3			
C_6H_{10}			1.0	1.0	0.7	2.0
C_6H_{12}			0.7			
C_7H_8	0.1		.2		1.3	1.9
CO	2.3	0.8	.6	1.8	31.3	31.4
CO_2	0.3	.5	1.1	0.7	9.8	12.6
V_{pr}	3.6	2.3	11.2	8.8	5.0	5.2
Total	100.0	100.0	100.0	100.0	100.0	100.0

[a] Components are in weight percent of total volatiles.

5. Discussion

As indicated in this paper, the method of heating a polymer sample consisted in moving quickly a furnace preheated to the required temperature into position to surround the sample. It is safe to assume that in the earlier work below 500 °C and also in most cases in the present work at 500 °C most of the pyrolysis took place at or near the specified temperature since the reactions proceed at a moderate rate. However, at the temperatures of 800 and 1,200 °C, where the rates of degradation are extremely high, it is quite certain that most of the volatilizable part of a given sample would degrade

and evaporate while its temperature was rising from room temperature to 800 or 1,200 °C. An idea of the speeds of reactions at these temperatures can be gained from the fact that below 500 °C the rates were found generally to double for every rise of 10°. The only limitation on this rate is the limited rate of heat transfer to the sample to furnish the heat required in the endothermic reactions. Under these circumstances the data obtained at the higher temperatures indicate only a general trend in the results of pyrolysis as a function of temperature, on the assumption that a higher initial temperature results in a higher pyrolysis temperature.

Fraction V_{pyr} from pyrolysis of the various polymers discussed in this paper consisted of molecular fragments too large to be analyzed by the mass spectrometer at our disposal, and the amounts collected were too small to be analyzed even by microchemical methods. Instead, the fractions were checked for their average molecular weight by a microcryoscopic method. The results are shown in table 15. Results for polymethylene are shown for comparison. Here again, as in the case of the lower molecular weight fractions, the higher the temperature of pyrolysis the greater is the fragmentation of the products, except in the case of polystyrene. It can be safely assumed that the V_{pyr} fragments consist of parts of the main chain, partially degraded.

TABLE 15. *Average molecular weight of fraction V_{pyr} from pyrolysis of polymers at various temperatures*

Polymer	Temperature of pyrolysis		
	500 °C	800 °C	1,200 °C
Polystyrene	264	372	476
Poly(α-methylstyrene)			309
Polypropylene	854		525
Polyisobutylene	643		338
Poly(methyl methacrylate)			245
Polymethylene, in vacuum	690	562	473
Polymethylene, in helium	324	377	250

Another point to be considered in connection with this work is the mechanism of degradation. The results of measurements of relative amounts of the gaseous fractions and their chemical composition reflect two principal mechanisms: (a) a primary thermal degradation, and (b) a subsequent degradation involving thermal and catalytic cracking reactions in the hot chamber, similar to those that take place in petroleum cracking.

Results of pyrolysis at 500 °C do not differ essentially from those obtained previously at lower temperatures. However, results of pyrolysis at 800 and 1,200 °C show a conspicuous departure from those obtained below about 500 °C. This departure consists mainly in an increased fragmentation of the degradation products and in the appearance of V_{pyr} fraction in some cases where such a fraction is absent at lower temperatures. Pyrolysis in a neutral atmosphere such as helium also results in greater fragmentation of the volatile products due to their slower escape from the hot zone. Thus, in the case

of polystyrene, monomer is the main constituent in the V_{25} fraction when pyrolysis in a vacuum takes place at temperatures up to 500 °C. At 800 and 1,200 °C the yield of monomer is diminished, and C_2H_2, C_2H_4, and C_6H_4 appear in increasing amounts. Similarly, pyrolysis at 800 and 1,200 °C in helium at atmospheric pressure yields small amounts of monomer, only 0.8 wt-% at 1,200 °C, and appreciable amounts of C_2H_2 and C_4H_6. Formation of C_6H_6 can be assumed to take place as follows:

$$\cdots \longrightarrow \cdots + C_6H_6$$
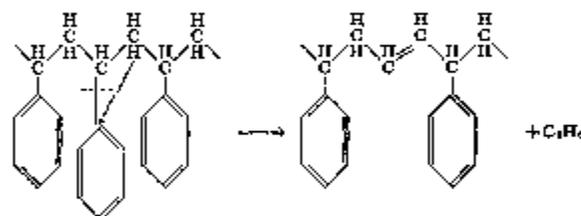
or a phenyl group may split off as a free radical causing a scission in the backbone of the chain

$$\cdots \longrightarrow \cdots + \cdots + C_6H_5$$
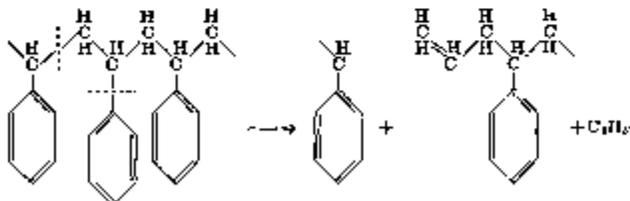
The free radicals could then absorb H from the surrounding medium causing further scissions. Compounds C_2H_2 and C_2H_4 could form through scissions in the backbone of the polymer chain, or they could form from the monomer. In either case, these reactions result in a decrease of the yield of monomers.

With polytetrafluoroethylene, the main product of pyrolysis at the lower temperatures is C_2F_4, with small amounts of C_3F_6 and CF_4. At the higher temperatures C_2F_4 is still the dominant product, but in addition there also appears small amounts of HF. There is no fraction V_{pyr} formed at temperatures up to 500 °C and only a small amount at 800, but at 1,200 °C the yield of this fraction is considerable. It was postulated in our earlier work [9] that this polymer breaks up at free radical ends of chains by an unzipping process to yield mostly monomers. The overall reaction is of first order [9, 12, 13]. This can be explained on the ground that the unzipping process is preceded by a process of scission of C—C chain bonds into free radicals. This reaction is slower and random and is therefore rate determining and of first order. The absence of any V_{pyr} at low temperatures is probably due to the fact that at these temperatures unzipping, once started, proceeds until the whole chain is consumed, so that large fragments (V_{pyr}) do not appear among the volatile products. At the higher temperatures some of the shorter free radical chains evaporate before they have a chance to decompose into monomer, thus yielding volatile fractions of V_{pyr} size.

With poly(α-methylstyrene) the distinction between low and high temperature pyrolysis is clear-cut. At lower temperatures the product consists

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of 100 percent monomer. At 800 and 1,200 °C various smaller fragments, from H_2, CH_4, C_2H_2, and other small hydrocarbons up to C_7H_8 make their appearance. In addition to these there are among the degradation products at the higher temperature a considerable amount of V_{pyr} size fragments, whereas at the lower temperature the yield of V_{pyr} is zero. The mechanism of degradation of this polymer is similar to that of polytetrafluoroethylene, and the reaction is of first order [14]. The appearance of larger molecules found in fraction V_{pyr} could be caused by the vaporization at higher temperatures of some of these molecules before they have time to break up into the monomer by the unzipping process. The formation of small molecules found in fraction V_{-100} is most likely caused by cracking of the larger molecules in the hot zone of the apparatus.

In the pyrolysis of polypropylene, the monomer, C_3H_6, appears in small amounts below about 500 °C. At 800 and 1,200 °C its yield is considerable. The reverse is true of V_{pyr}, due to the cracking of the V_{pyr} fragments into smaller molecules in the hot zone. There is some H_2 and larger amounts of CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6, C_4H_8, and C_5H_{10} at the higher temperatures than at the lower. In this respect the mechanism of degradation of polypropylene is similar to that of polymethylene [6].

Pyrolysis of polyisobutylene generally follows the same pattern as that of polypropylene, except for the fact that at 800 °C the yield of monomer is higher than at 500 or at 1,200 °C. On comparing the yield of V_{pyr} for the three temperatures, it appears that there is an inverse relationship between these products so that one may assume that at 500 and 800 °C the increase of monomer yield is at the expense of V_{pyr}.

Degradation of poly(methylmethacrylate), like that of polytetrafluoroethylene and poly(α-methylstyrene), yields at the higher temperatures less amounts of monomer than at the lower temperatures. Judging from table 14, the monomer decomposes at the higher temperatures, particularly at 1,200 °C, to yield considerable amounts of CO, CO_2, CH_4, C_2H_2, C_2H_4 and similar compounds.

6. References

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