

Pyrolysis of Polyisobutene (Vistanex), Polyisoprene, Polybutadiene, GR-S, and Polyethylene in a High Vacuum¹

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Samples of polyisobutene, polyisoprene, polybutadiene, GR-S, and polyethylene, weighing about 25 to 50 milligrams, were pyrolyzed in a vacuum of about 10^{-6} millimeter of mercury in a specially designed apparatus at temperatures ranging between 300° to 475° C. The volatile products of pyrolysis were separated into four fractions: (IV) gaseous, volatile at -196° C; (IIIA) liquid, at -75° C; (IIIB) liquid, at 25° C and (II) wax-like fraction, volatile at the temperature of pyrolysis. The gaseous fraction was analyzed in the mass spectrometer and was found to consist in all cases of CH_4 . The liquid fraction, IIIA, was analyzed similarly and was found to give a mass spectrum characteristic for any given polymer. A molecular weight determination of the wax-like fraction by the microfreezing-point-lowering method, showed it to vary from 543 to 739, depending on the polymer from which the fraction was obtained. It is shown that the method of pyrolytic fractionation of high molecular weight polymers, in conjunction with mass spectrometer analysis of the more volatile fractions, can serve as a means of identifying the polymers.

I. Introduction

The method of pyrolytic fractionation of polymers, in conjunction with mass-spectrometer analysis of the more volatile fractions, has been described previously in the case of polystyrene [1].² Briefly, this method consists in heating a 25- to 50-mg sample of a polymer, spread as a thin film on a platinum tray, in a high vacuum at 300° to 500° C. The products of pyrolysis are (I) a solid residue; (II) a wax-like fraction, volatile at the temperature of pyrolysis, but not volatile at room temperature; (III) a liquid fraction, volatile at room temperature; and (IV) a gaseous fraction, volatile at the temperature of liquid air or liquid nitrogen. The liquid and gaseous fractions are analyzed in the mass spectrometer, whereas the wax-like fraction is tested for its average molecular weight by a microfreezing-point-lowering method. Pyrolytic fractionation has now been extended to the study of other hydrocarbon polymers covering

polyisobutene (Vistanex), polyisoprene, polybutadiene, polyethylene, and a copolymer, GR-S, consisting of 75 percent of butadiene and 25 percent of styrene.

The mass spectrometer is a relatively new analytical tool and requires a preliminary investigation of mass-spectra of all individual pure compounds in a mixture before it can be used with due calibration to analyze such a mixture. This imposes certain limitations on the study of polymers by way of mass spectrometric analysis of decomposition products of pyrolysis. The above polymers and copolymer were selected for this investigation with these limitations in view. However, mass spectral data are being accumulated at the present time in various laboratories and are being compiled by the National Bureau of Standards [2]. These data are gradually broadening the scope of analysis in two directions, to include a greater number and variety of compounds, and to extend the mass range so that compounds of higher molecular weight could be analyzed. It will, therefore, be possible in the future to apply the method of pyrolytic fractiona-

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² Figures in brackets indicate the literature references at the end of this paper.

tion to polymers and copolymers of a more complicated structure and containing, in addition to carbon and hydrogen, also oxygen, nitrogen, sulfur, chlorine, and other elements.

One object of this investigation was to find a relationship between the structural formulae of polymers and their refractoriness under the influence of heat. This in turn could serve as a clue to the chemical and physical properties of the polymers. To take a specific example, the effect of double bonds and their frequency in the macromolecular chain, also the size, frequency, and distribution of side chains, on the number and size of fragments obtained in the pyrolysis, is one of the problems investigated here. Another object was to broaden the application of mass spectrometry to the identification and analysis of polymers in general. At the present stage of development, the mass spectrometer can be used to analyze masses up to a little over 100. It so happens that the most significant part in the mass spectrum of the volatile products of pyrolysis lies in this mass range, also that this part of the spectrum is characteristic of any given polymer so far studied. This leads to the possibility of using mass spectrometric analysis in conjunction with pyrolytic fractionation as a general method to identify polymers and to determine the extent of their purity.

With the extension of the range of mass spectrometric analysis to larger masses than 100, it will be possible to study the larger fragments obtained in the pyrolysis of polymers. This additional information will lead to a better understanding of the structure and to a greater refinement of the analysis of high-polymer substances.

II. Review of the Literature

Most of the work on pyrolysis of high polymers was done in the past on natural rubbers. Bolland and Orr [3] carried out pyrolysis of rubber in a vacuum at 220° to 270° C. Standinger and co-workers [4, 5] employed temperatures of 300° to 400° C and a pressure of 0.1 to 0.3 in one case, and 1 atm in another. Midgley and Henne [6] and Bassett and Williams [7] used temperatures of 600° to 700° C and atmospheric pressure. In all this work the products of pyrolysis contained considerable amounts of isoprene and dipentene. As to pyrolysis of synthetic polymers, Seymour

[8], employing temperatures of 150° to 500° C and pressures of 0.5 mm and 1 atm, found that the order of thermal stability in the case of three polymers was: polyethylene > polystyrene > polyisobutene. Recently, Wall [9] pyrolyzed at 400° C in a vacuum 1-mg samples of rubber, polyethylene, polyisobutene, polystyrene, polyisoprene, and other polymers and analyzed the products of pyrolysis in a mass spectrometer.

III. Apparatus and Experimental Procedure

The same apparatus and experimental procedure as were used in the work on polystyrene, were used also in this work, but with some slight modifications. The modified apparatus is shown in figure 1. It differs from the previous apparatus in that

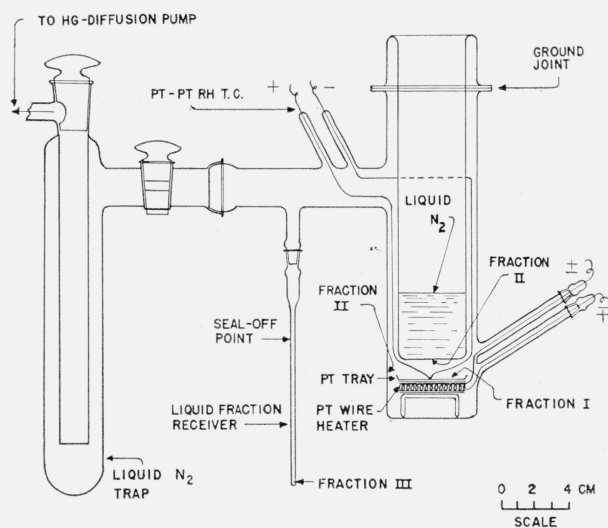


FIGURE 1. Modified pyrolysis apparatus.

the large tapered ground joint between the pyrolysis still and the condenser has been replaced by a horizontal flanged joint. The upper flange of this joint is connected to an outer jacket around the condenser instead of directly to the condenser. This was done to avoid excessive cooling of the joint by the liquid nitrogen in the condenser. The thermocouple wires, instead of passing through the joint, pass this time through tubes attached to the side arm leading to the evacuating system. In this way ordinary vacuum grease could be used in the ground joint instead of hard wax, which had to be melted with a flame.

Another modification consisted in changing the distance between the pyrolysis tray and the condenser from 1.7 to 1.2 cm. In this way it was possible to collect more of the condensate on the liquid nitrogen condenser and less on the inner wall of the pyrolysis still.

Modification of the experimental procedure involved some changes in the fractionation and designation of the fractions. The nonvolatilized residue was collected and designated as fraction I as in the case of polystyrene pyrolysis. The wax-like fraction, volatile at the temperature of pyrolysis but not volatile at room temperature, was deposited as previously in two parts, a larger part on the liquid nitrogen-cooled condenser and a smaller part on the inner wall of the apparatus. The larger part was collected from the condenser and its weight determined directly, whereas the weight of the smaller part was calculated by subtracting the sum of the other volatile fraction from the weight of the total pyrolyzed part. On the average, in all the experiments reported in this paper, that part of the wax-like fraction that collected on the condenser represented about 95 percent of the total wax-like fraction when the pyrolyzed part was only a few percent of the original sample; this dropped to about 74 percent when the pyrolyzed part reached 10 percent of the sample and stayed at this level all the way down to complete pyrolysis. The sum of the two parts of the wax-like fraction was designated as fraction II, without stating the amount of each part, as this was not deemed important. In case of the polystyrene work, the larger part of the wax-like fraction amounted, on the average, to 64 percent of the total and was designated as fraction II, whereas the smaller part, which deposited on the wall of the apparatus, amounted to 36 percent and was designated as fraction IV.

In collecting the liquid fraction III, the same procedure was followed as previously, except that in the case of polyisobutene, polybutadiene, GR-S, and polyethylene this fraction was divided into a more volatile fraction IIIA and a less volatile one IIIB, in order to facilitate mass spectrometer analysis. However, in the case of polyisoprene, mass spectrometer analysis could be carried out on fraction III in its entirety.

The gaseous fraction was collected in the same manner as in the previous work but was designated as fraction IV instead of V. This fraction

consisted mainly of CH_4 mixed with some CO , CO_2 , and air.

Only fractions IIIA (or III in the case of polyisoprene) and IV were analyzed in the mass spectrometer. Small amounts of air found in the gaseous fraction were most likely due to adsorption on the wall of the apparatus, the heater, and the sample, or to its solution in the sample. Although most of this air was eliminated in the preliminary heating stage, as described in the previous paper, some of it was freed at the higher temperature. Small amounts of CO_2 and CO found in fraction IV could have come from the reaction of the polymer with adsorbed or dissolved oxygen or with oxygen present as a part of the polymer. The smaller the extent of pyrolysis in any given experiment, the greater the proportion of the impurities in fraction IV and, in cases where the pyrolyzed part was only a few percent of the original sample, the gaseous fraction consisted almost entirely of CO_2 , CO , and air.

Some CO_2 was found in fractions III or IIIA in most of the experiments. Small amounts of solvents, such as benzene, ethanol, etc., also found their way into fraction III or IIIA of some of the experiments. These were undoubtedly due to adsorption. Here again the smaller the pyrolyzed part, the more conspicuous were the impurities. The results of mass spectrometer analysis shown in this paper are based on calculations from which the impurities found in fractions III, IIIA, or IV were excluded. In case of fractions III or IIIA, the percentages of impurities are shown below the tables of analysis. In case of fraction IV, these impurities are not shown.

Fraction IIIB was not analyzed in the mass spectrometer because of the complexity of the spectrum and lack of spectra of the individual compounds it contained. No attempt was made to determine its average molecular weight by the microfreezing-point-lowering method, because this fraction was too small in the case of all polymers to make such a determination. Fraction II was analyzed for its average molecular weight by the microfreezing-point-lowering method in cyclohexane, benzene, or camphor. Some attempts were made to apply this method to the determination of the average molecular weight of the residue (fraction I), but the temperature drop was only a few tenths of a degree, and the results were considered unreliable.

The microfreezing-point-lowering method consisted in determining the average temperature between beginning of melting and collapse of the column of solidified solution contained in a sealed capillary tube. This method was tested on pure substances with the following results (the 3 figures following each compound in the order given stand for the molecular weight, as given by the empirical formulas, as determined by the micro-method in benzene and as determined by the same method in cyclohexane): Decane, 142, 141, 125; 1-methylnaphthalene, 142, — 125; dodecane, 170, 174, 143; 2,2,4-trimethyl-3-isopropyl-3-pentanol, 172, — 153; glycerol tripropionate, 260, —, 264; dibutyl phthalate, 278, 268, 276; glycerol tributyrate, 302, —, 305; butyl phthalyl butyl glycolate, 336, —, 337. In the case of benzene as solvent, the results seem to be fairly close to the actual values. In the case of cyclohexane, the results are too low for some compounds for reasons that are not wholly apparent. Molecular weight of fraction II from polyethylene was determined for camphor by Rast's micromethod [10]. All molecular weights of fraction II reported in this paper represent averages of three to four determinations.

IV. Pyrolysis of Polyisobutene (Vistanex)

The material used in these experiments was prepared by dissolving commercial Vistanex in benzene and precipitating with methanol. This was repeated twice and the methanol removed by evacuation. A 2-percent solution of the purified polyisobutene in benzene was used in the pyrolysis experiments. Experimental conditions and results of pyrolysis and fractionation are shown in table 1. Fifteen experiments were carried out at temperatures varying between 313° and 460° C. Weight of the sample varied from about 21 to 60 mg, and in one case it was 82.9 mg. The solution of the polymer was spread on a platinum tray with an evaporating surface of about 12 cm². The benzene was evaporated in a vacuum to a constant weight, and a layer of the polymer 17 to 50 μ thick was thus obtained. After evacuation of the apparatus and a preliminary heating, as described in the previous paper, the temperature was raised from about 135° C to the temperature of pyrolysis during 40 to 50 min, depending on the final temperature, a higher temperature requiring a longer time. The same

procedure was followed in the case of the other polymers. The Vistanex, as well as the other polymers, formed in the tray a uniform layer with a glossy surface, and it was difficult to observe at what temperature the polymer melted. Duration of pyrolysis at the maximum temperature was 30 min in all experiments with Vistanex.

TABLE 1. *Pyrolytic fractionation of polyisobutene (Vistanex)*

Ex-periment number	Weight of sample	Tem-perature	Dura-tion	Fractions in weight percent of original sample				Fraction III in percentage of total pyrolyzed part
				I Resi-duce	II Non-volatile at room tem-perature	III Volatile at room tem-perature	IV Gas-eous fraction	
1---	24.9	313	30	97.2	2.4	0.4	0	14.2
2---	22.5	344	30	83.0	11.3	5.7	Trace	33.5
3---	56.7	361	30	64.3	25.3	10.3	0.07	28.9
4---	58.0	362	30	65.2	24.3	10.4	.08	29.9
5---	45.4	378	30	20.7	52.4	26.8	.12	33.8
6---	52.7	401	30	0.2	68.5	31.1	.20	31.2
7---	82.9	401	30	.3	79.3	20.2	.22	20.3
8---	49.2	401	30	.1	69.4	30.3	.19	30.3
9---	49.6	402	30	.4	68.4	31.0	.22	31.1
10--	48.9	402	30	.5	70.8	28.5	.23	28.6
11--	23.2	407	30	.4	66.6	32.8	.22	32.9
12--	55.2	415	30	.3	68.9	30.5	.25	30.6
13--	60.0	418	30	.1	69.0	30.7	.22	30.7
14--	20.9	450	30	.2	64.7	34.9	.22	34.9
15--	45.4	460	30	.0	67.0	32.8	.22	32.8
Average fraction III in percentage of total pyrolyzed part for all experiments, except 1 and 7.....								31.5±0.8

It can be seen from table 1 that thermal decomposition, under the experimental conditions employed, begins at 300° and is almost complete at 400° C. At higher temperatures, decomposition was undoubtedly complete before the 30 min were over. The purpose of employing temperatures above 400° C was to see what effect a faster rate of decomposition will have on the nature and relative amounts of the fractions.

In the last column of table 1 the yield of the liquid fraction III is shown in percentage of total pyrolyzed part. In experiment 1 the liquid fraction weighed about 0.1 mg. Since the accuracy of weighing on the semimicrobalance was about 0.05 mg, the accuracy of weighing 0.1 mg was very low. In experiment 7 the original sample was too large, weighing 82.9 mg, and

spattering from the tray during pyrolysis was observed. This spattering resulted in an increase in fraction II and decrease in fraction III. The yield of fraction III in all the other experiments was practically constant, the average being 31.5 ± 0.8 percent.

Mass-spectrometer analysis of the gaseous fraction IV was made for experiments 4, 6, 8, 10, and 12. The analysis showed the presence, in addition to CH_4 , of small amounts of CO , H_2 , O_2 , and traces of CO_2 . The yield of fraction IV in percentage of the original sample was calculated for experiments 4, 6, 8, 10, and 12 on the basis of volume, pressure, and mass-spectrometer analysis, after excluding all the gaseous constituents, except CH_4 . Yields of CH_4 for the other experiments were interpolated from those determined experimentally. In percentage of total pyrolyzed part, the yield of CH_4 for experiments 4, 6, 8, 10, and 12 is practically constant, the average being 0.22. As the yields of the liquid and gaseous fractions are both constant, the yield of the wax-like fraction, which is obtained by subtracting the sum of the other two fractions from 100, is also constant and is equal on the average to 68.3 percent of the total pyrolyzed part.

In attempting to analyze fraction III in the mass spectrometer, it was found that the heavier constituents, consisting of eight or more carbons, interfered with the analysis of the lighter constituents. According to a table compiled by Stull [11], the temperatures at which paraffins, monoolefins, and diolefins have a vapor pressure of 1 mm are as follows: 1,3-pentadiene -71.8° ; *n*-pentane -76.6° ; 1-hexane -57.5° ; *n*-hexane -53.9° ; 2-heptene -35.8° ; *n*-heptane -34.0° ; 2-methyl-2-heptene -16.1° ; and *n*-octane -14°C .

In view of this it would be possible to separate compounds consisting of eight or more carbons at a temperature near that of dry ice. This was accomplished in the following manner. Fraction III was first collected in a long sealed tube, 1.7-mm inside diameter and 25 to 30 cm long. By immersing one end of the tube in liquid nitrogen, the fraction was concentrated at that end, and the tube was bent in the center, by means of a flame, in the form of a U. The cold end was then removed from the liquid nitrogen and placed in a dry-ice-acetone mixture at -75°C , and the other end was immersed in liquid nitrogen. Distillation was continued for 3 min. In this way the less volatile compounds remained in the end of the tube at -75°C , whereas the more volatile ones collected at the other end. The tube was then melted at the center and the two fractions separated, the heavier one as fraction IIIB and the lighter one as fraction IIIA. In all cases the distribution between IIIA and IIIB was about 70 and 30 percent of the total fraction III. Since the total yield of fraction III was 31.5 percent, the yields of IIIA and IIIB were, on the average, 22.0 and 9.5 percent, respectively.

Mass spectrometer analysis of fraction IIIA are shown in table 2 for seven experiments. Most of fraction IIIA consists of isobutene, the average being 92.8 mole percent. The next significant constituent, neopentane, amounts to 6 percent, on the average. In addition to these there is 1.6 percent of isobutane and 0.2 percent of pentenes. The last column of table 2 shows the average yield of components in percentage of total pyrolyzed part. The yield of the monomer, isobutene, according to this table is 20.18 percent.

TABLE 2. Mass-spectrometer analysis of fraction IIIA obtained in the pyrolysis of polyisobutene

Experiment Number.....	3	4	7	9	10	12	13	Average for all experiments	Average component in percentage of total pyrolyzed part, weight percent	
Temperature of pyrolysis, ° C.....	361	362	401	402	402	415	420			
Part pyrolyzed, percent.....	35.7	34.8	99.7	99.6	99.5	99.6	99.9			
Component	Molecular weight	Mole percent								
Isobutene.....	56.1	90.3	89.6	93.9	92.7	93.0	93.0	92.8	92.8	20.180
Isobutane.....	58.1	1.4	1.3	1.9	1.5	1.6	1.6	1.7	1.6	0.320
Pentenes.....	70.1	0.5	0.7	-----	0.4	-----	-----	0.2	0.2	.048
Neopentane.....	72.1	7.8	8.4	4.2	5.4	5.4	5.4	5.3	6.0	1.502
Total.....	-----	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	22.050
CO ₂	44	Trace	Trace	Trace	Trace	Trace	Trace	Trace	-----	-----

No mass-spectrometer analyses were made of fractions IIIB, for the reasons explained above. Judging from the fact that fraction IIIA consisted mainly of the monomer and that fraction IIIB was not volatile at -75°C , but was volatile at room temperature, it can be assumed that the latter fraction consisted of the dimer and trimer.

Fraction II was soluble in cold benzene or cyclohexane. The results of five molecular weight determinations are shown in table 3, the average being 543. In making these determinations, an ordinary thermometer, having 3 deg centigrade per 1-cm length and carrying 0.2-deg divisions, was used. On the same consideration as in the case of fraction IIIB, fraction II most likely contained polymeric fragments consisting on the average of 9 to 10 monomers. The residue (fraction I) was soluble in cold benzene or cyclohexane. No molecular weight determinations were made of this fraction.

TABLE 3. Average molecular weight of wax-like fraction (II) obtained in the pyrolysis of polyisobutene

Experiment number	Temperature of pyrolysis	Part pyrolyzed	Freezing point lowering of C_6H_{12}	Molecular weight
	$^{\circ}\text{C}$	Percent	$^{\circ}\text{C}$	
3.....	361	35.7	1.25	507
4.....	362	34.8	1.90	518
6.....	401	99.8	2.43	506
8.....	401	99.9	2.50	612
9.....	402	99.6	1.60	570
Average.....	-----	-----	-----	543

V. Pyrolysis of Polyisoprene

A 27-g sample of commercial polyisoprene was extracted three times with 300-ml portions of ethanol-toluene azeotrope. The sample was stored, wet with the azeotrope, under benzene. A dilute solution of the purified material in benzene was used in the pyrolysis experiments. Results of 13 experiments are shown in table 4. It appears from this table that pyrolysis begins at 300° and is almost complete at 400°C . On the whole, polyisoprene decomposes more readily than polyisobutene. Except for experiments 1, 2, and 3 at low temperatures, the yield of fraction III is fairly constant and is equal on the average to 11.3 ± 0.4 percent of the total pyrolyzed part. The yield of fraction IV was obtained from mass-spectrometer analysis for experiments 1, 2, 4, 5, 7, 11, and 13.

Yields for the other experiments were obtained by interpolation. The average yield in percentage of total pyrolyzed part is 0.016. The average yield of fraction II is therefore $100 - (11.3 + 0.016) = 88.7$ percent.

TABLE 4. Pyrolytic fractionation of polyisoprene

Experiment number	Weight of sample	Temperature	Duration	Fractions in weight percent of original sample				Fraction III in percentage of total pyrolyzed part
				I Residue	II Non-volatile at room temperature	III Volatile at room temperature	IV Gaseous fraction CH_4	
	mg	$^{\circ}\text{C}$	min					
1	56.8	302	30	97.6	2.0	0.4	0	16.7
2	49.8	302	30	97.0	2.5	.5	Trace	16.7
3	51.3	325	30	89.9	7.9	2.2	Trace	21.8
4	50.6	352	30	51.5	43.0	5.5	0.005	11.3
5	53.0	354	30	45.8	49.7	4.5	.006	8.3
6	52.5	354	60	21.1	70.0	8.9	.012	11.3
7	57.0	354	90	20.0	70.0	10.0	.014	12.5
8	51.8	380	30	16.6	73.9	9.5	.014	11.4
9	44.1	380	30	8.9	81.5	9.6	.014	11.5
10	52.6	380	30	8.7	80.7	10.6	.014	11.6
11	49.5	400	30	5.4	83.3	11.3	.020	11.9
12	56.5	403	30	3.7	84.6	11.7	.021	12.2
13	58.6	405	30	3.8	84.6	11.6	.025	12.1
Average fraction III in percentage of total pyrolyzed part for experiments 4 to 13, inclusive.....								11.3 \pm 0.4

In analyzing fraction III in the mass spectrometer, it was found that the heavier components, consisting of eight or more carbons, did not interfere with the analysis of the lighter components. In view of this, fraction III was not divided into fractions IIIA and IIIB, but was analyzed directly. Results of mass-spectrometer analyses of fraction III for nine experiments are shown in table 5. These analyses show the presence in this fraction of small amounts of ethanol, acetone, methyl-ethyl ketone, benzene, toluene, and CO_2 . In experiments 1 and 2, where the total pyrolyzed part was only 2.4 and 3.0 percent, respectively, the relative amounts of impurities due to absorbed and dissolved gases and liquids appear exaggerated. Considering experiments 4 to 13, we can see from table 5 that the most abundant constituent of fraction III is isoprene, amounting on the average to 90.8 mole percent. Next in abundance are the pentenes, 4.6 percent; cyclopentadienes, 1.5 percent; butenes, 1.2 percent, and hexadienes, 1 percent.

TABLE 5. Mass-spectrometer analysis of liquid fraction (III) obtained in the pyrolysis of polyisoprene

Experiment number.....		1	2	4	5	6	7	10	12	13	Average of 4 to 13, incl.	Average component in percentage of total pyrolyzed part, weight percent
Temperature of pyrolysis, °C.....		302	302	352	354	354	354	380	403	405		
Part pyrolyzed, percent.....		2.4	3.0	48.5	54.2	78.9	80.0	91.3	96.3	96.2		
Component	Molecular weight	Mole percent										
Butenes.....	56.1	4.5	2.4	0.9	0.9	1.1	1.2	0.8	1.2	1.2	1.1	0.051
Cyclopentadienes.....	66.0	1.9	2.4	2.1	1.8	-----	1.4	1.2	1.5	2.4	1.5	.081
Isoprene.....	68.1	60.0	72.2	91.6	91.2	92.0	89.4	91.2	90.6	89.8	90.8	5.150
Pentenes.....	70.1	4.3	2.6	3.5	3.6	4.6	5.5	5.2	5.0	4.9	4.6	0.277
Cyclohexadienes.....	80.1	0.6	0.8	0.3	0.1	0.3	0.5	0.3	0.3	0.3	0.3	.020
Hexadienes.....	82.1	3.5	3.0	1.0	1.4	1.2	1.2	.8	.8	.7	1.0	.068
Hexenes.....	84.1	0.6	0.8	0.1	0.1	0.2	0.2	.1	.2	.2	0.1	.007
Cycloheptadienes.....	94.1	1.4	1.7	.2	.3	.2	.3	.2	.1	.1	.2	.015
Heptadienes.....	96.1	1.2	1.3	.3	.4	.3	.3	.2	.2	.2	.3	.023
Heptenes.....	98.1	12.9	1.8	-----	.1	-----	.1	-----	.1	.2	.1	.008
Dipentene.....	136.1	9.1	11.0	-----	.1	.1	-----	-----	-----	-----	-----	-----
Total.....	-----	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	5.700
Mole percentage of impurities in original analysis												
Ethanol.....	46.0	6.9	8.5	0.2	0.5	0.5	0.5	0.2	0.2	-----	-----	-----
Acetone.....	58.0	2.5	3.2	.5	.7	.5	.5	.3	.3	0.3	-----	-----
Me-eth ketone.....	72.1	1.4	2.1	.1	.1	.1	.1	.1	.1	.1	-----	-----
Benzene.....	78.0	1.1	4.7	.2	.1	.1	.2	-----	-----	-----	-----	-----
Toluene.....	92.1	0.3	0.3	-----	-----	-----	-----	-----	-----	-----	-----	-----
CO ₂	46.0	38.6	27.6	7.2	19.0	4.8	4.4	3.4	5.6	3.9	-----	-----

Dipentene, which is the dimer of isoprene, showed up in the mass spectra of fraction III of experiments 1 and 2, but not in those of the other experiments. Dipentene has a vapor pressure of 1 mm at 14° and 5 mm at 40.4° C [11]. Since fraction III was collected at room temperature, it contained all the dipentene formed in the pyrolysis. On the other hand, the trimer, consisting of 15 carbons would have too low a vapor pressure to distill into fraction III at room temperature. In view of this, it can be assumed that fraction III contained, in addition to the compounds shown in table 5, also a considerable amount of dipentene. In experiments 1 and 2, where the total weight of fraction III was small, the partial vapor pressure of dipentene was sufficiently large to show its presence in appreciable amounts. In the other experiments the large amount of a volatile compound, such as isoprene, suppressed the vapor pressure of dipentene, so that the latter did not show up in the spectrum. Fraction III from experiment 8 was expanded into a large volume in a specially designed apparatus described previously [1] and an expanded sample analyzed in the mass spectrometer. Peaks indicating the presence of a large amount of dipentene appeared in the spectrogram, but no quantitative

data could be obtained as to its relative amount.

In order to estimate the yield of dipentene in fraction III, this fraction in the case of experiments 8, 9, and 11 was divided into IIIA and IIIB, by a procedure described above, and the two parts weighed on the semimicro balance. The distribution between the two parts was 5.7 and 5.6 percent in IIIA and IIIB, respectively. On this basis the yield of isoprene is 5.15 percent of the total pyrolyzed part, as shown in the last column of table 5. It is not likely that fraction IIIB contained much of the trimer of isoprene. The trimer contains 15 carbons and a compound of similar molecular weight, for example, pentadecane, C₁₅H₃₂, has a vapor pressure of 1 mm at 91.6° C. On this consideration, the yield of dipentene was about 5.6 percent of the total pyrolyzed part. Whether the ratio of yields of isoprene to dipentene varies with temperature of pyrolysis and if so, in what direction, is not clear from this investigation.

The wax-like fraction (II) was soluble in cold benzene or cold cyclohexane. The results of molecular weight determinations in cyclohexane are shown in table 6. The average of five determinations is 577, which means that on the average the fragments in this fraction consisted of about 8 to 9

monomer units. The residue, fraction I, was also soluble in cold benzene or cold cyclohexane, but no molecular weight determinations were made of this fraction.

TABLE 6. Average molecular weight of wax-like fraction (II) obtained in the pyrolysis of polyisoprene

Experiment No.	Temperature of pyrolysis	Part pyrolyzed	Freezing point lowering of C ₆ H ₁₂	Molecular weight
	° C	%	° C	
4.....	352	48.5	2.70	610
6.....	354	78.9	3.45	542
7.....	354	80.0	3.10	572
12.....	403	96.3	2.90	578
13.....	405	96.2	2.25	581
Average.....	-----	-----	-----	577

VI. Pyrolysis of Polybutadiene

A sample of polybutadiene was purified by dissolving it in benzene and precipitating with methanol. This operation was repeated several times and finally the sample, freed from methanol, was dissolved in benzene to make a dilute solution. Results of 12 pyrolysis experiments are shown in table 7. As seen from this table, polybutadiene is more refractory than polyisobutene, polyisoprene, or polystyrene, when heated under similar conditions. This polymer begins to break up at about 350° C, and decomposition is almost complete at 477° C. The yield of fraction III in percentage of total pyrolyzed part, stays fairly constant, on the average at 14.0±1.0 percent, up to a temperature of pyrolysis of 400° to 425° C. Above this temperature the yield drops to a small fraction of the above value, as indicated in the last column of table 7. The yield of the gaseous fraction (IV), on the contrary, stays constant at about 0.30 percent of the total pyrolyzed part throughout the entire temperature range.

Fraction III was divided into fractions IIIA and IIIB volatile at -75° C and room temperature and amounting to 4.2 and 9.8 percent of the total pyrolyzed part, respectively. Mass spectrometer analyses of fraction IIIA are shown for nine experiments in table 8. These experiments cover the entire range of pyrolysis from 6.1- to almost 100-percent decomposition. A gradual decrease in the content of 1,3-butadiene, the principal constituent of fraction IIIA, and a corresponding increase in the content of most of the

TABLE 7. Pyrolytic fractionation of polybutadiene

Experiment number	Weight of sample	Temperature	Duration	Fractions in weight percent of original sample				Fraction III in percentage of total pyrolyzed part
				I Residue	II Non-volatile at room temperature	III Volatile at room temperature	IV Gaseous fraction	
1	49.9	350	30	93.9	5.3	0.8	Trace	13.1
2	63.6	351	30	93.2	6.0	.8	Trace	11.8
3	54.4	400	30	81.5	15.5	3.0	Trace	16.2
4	50.3	400	30	80.2	17.2	2.5	0.06	12.6
5	51.3	401	60	76.9	19.0	4.0	.08	17.3
6	50.1	401	120	67.4	27.5	5.0	.11	15.3
7	50.7	425	30	53.7	40.7	5.5	.12	11.8
8	31.2	450	30	19.4	72.1	8.3	.23	10.3
9	52.7	450	30	14.4	78.7	6.6	.25	7.7
10	50.3	450	30	13.7	81.1	5.0	.23	5.8
11	40.4	477	30	.9	92.5	6.3	.28	6.4
12	51.1	500	30	.3	97.2	2.2	.30	2.2
Average fraction III in percentage of total pyrolyzed part for experiments 1 to 7, inclusive.....								14.0±1.0

other constituents of this fraction, with rise in temperature of pyrolysis or extent of pyrolysis, is noted. On the other hand, butene, the second largest constituent, passes through a maximum at 20- to 30-percent decomposition. Yields of the various components in percentage of total pyrolyzed part are shown in the last column of table 8 for experiment 5, which seems to have approximately the average composition of fraction IIIA. Yield of the monomer, 1,3-butadiene, in experiment 5 is 1.515 percent; however, considering other experiments, this yield varies from 2.27 for experiment 1 to 0.67 percent for experiment 9.

Fraction IIIB could not be analyzed in the mass spectrometer, and no determination was made of its average molecular weight. On the basis of the same arguments given in the case of polyisoprene, this fraction most likely consists of the dimer of butadiene and in the form of vinyl cyclohexene, which is the analogue of dipentene:

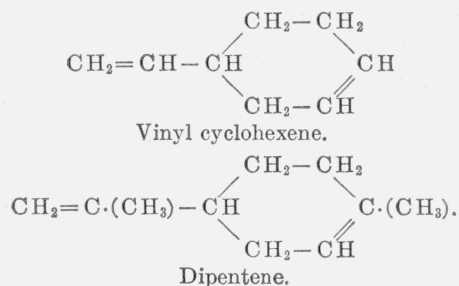


TABLE 8. Mass-spectrometer analysis of fraction IIIA obtained in the pyrolysis of polybutadiene

Experiment number.....		1	3	4	5	6	7	9	10	12 ^a	5 Compo- nents in percentage of total pyrolyzed part, weight percent
Temperature of pyrolysis, ° C.....		350	400	400	401	401	425	450	450	500	
Part pyrolyzed, percent.....		6.1	18.5	19.8	23.1	32.6	46.3	85.6	86.3	99.7	
Component	Molecu- lar weight	Mole percent									
Ethylene.....	28.0	----	4.9	6.0	7.3	7.5	11.6	8.4	11.7	13.0	0.166
Ethane.....	30.0	0.8	5.0	5.1	8.5	11.1	14.6	18.5	16.5	17.2	.208
Propadiene.....	40.0	----	----	----	1.0	0.9	----	0.8	----	1.2	.032
Propylene.....	42.0	3.8	9.2	9.3	5.8	8.1	16.8	14.6	14.9	9.4	.198
Propane.....	44.0	0.9	1.3	1.5	4.2	5.8	5.4	9.8	8.0	7.7	.151
1,3-Butadiene.....	54.1	58.9	40.9	42.2	34.4	26.7	28.2	13.2	20.7	22.1	1.515
Butenes.....	56.1	11.7	21.3	19.3	26.1	26.1	14.5	23.6	16.5	12.4	1.190
Butanes.....	58.1	1.0	2.2	2.0	2.9	3.9	4.0	6.1	5.1	5.1	0.138
Cyclopentadienes.....	66.1	2.5	1.6	1.3	0.7	0.4	0.4	0.1	0.3	0.4	.037
Pentadienes.....	68.1	8.5	6.2	6.1	4.2	3.3	1.2	1.0	1.6	3.1	.233
Pentenenes.....	70.1	1.0	3.5	3.1	3.4	3.3	2.1	2.4	3.0	3.2	.194
Pentanes.....	72.1	----	1.0	1.1	1.5	1.6	1.2	1.5	1.7	1.7	.088
Cyclohexadienes.....	80.1	3.6	0.4	0.5	----	----	----	----	----	----	----
Hexadienes.....	82.1	7.2	2.2	2.3	----	1.1	----	----	----	0.3	----
Hexenes.....	84.1	0.1	0.2	0.2	----	0.1	----	----	----	.4	----
Total.....	----	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	97.2	4.15
CO.....	28	----	----	----	----	----	----	----	6.3	----	----
CO ₂	44	21.2	8.8	8.5	0.5	----	0.3	0.2	----	0.7	----

^a In addition to the components indicated here, there were also 1.4% heptadienes and 1.4% vinyl cyclohexene.

The gaseous fraction (IV) was also analyzed in the mass spectrometer. As in the case of the other polymers, this fraction consisted chiefly of CH₄ mixed with some CO, N₂, O₂, and CO₂. Actual analyses of this fraction were made for experiments 1, 4, 5, 6, 9, and 10. Values for the other experiments were interpolated from the experimental values. Yield of CH₄ in percentage of total pyrolyzed part is fairly constant and is equal on the average to 0.29 percent of the total pyrolyzed part (table 7).

The wax-like fraction (II) was soluble in benzene, but not in cyclohexane. Molecular weight determination of this fraction by the micro-freezing-point-lowering method was, therefore, carried out in benzene. The results are given in table 9. The average of six determinations is 739, signifying that the average fragment in fraction II consisted of about 13 to 14 monomers. The residue was not soluble either in benzene or cyclohexane.

The peculiar behavior of polybutadiene in giving on pyrolysis lower yields of fraction III at temperatures above 425° C, is undoubtedly due to spattering, which was observed to take place when the tray was heated too fast. In this

case incompletely pyrolyzed material reached the condenser. As a result, the yield of fraction III was reduced, and fraction II acquired a higher average molecular weight. Turning back to table 9, we see that the molecular weight of fraction II is greater for temperatures of 450° or above than for temperature below 450° C. In the case of polysiobutene, in experiments 14 and 15, table 1, the temperature of pyrolysis was 450° and 460° C, respectively, but no spattering

TABLE 9. Average molecular weight of wax-like fraction (II) obtained in the pyrolysis of polybutadiene

Experiment number	Temper- ature of pyrolysis	Part pyrolyzed	Freezing point lowering of C ₆ H ₆	Molecular weight
	° C	%	° C	
5 ^a	401	23.1	} 0.55	700
6.....	401	32.6		
7.....	425	46.3	.60	666
8.....	450	80.6	.48	788
9.....	450	85.6	.30	772
10.....	450	86.3	.67	726
11.....	477	99.1	.60	784
Average.....	----	----	----	739

^a Molecular weight determination was made on the combined fractions II from experiments 5 and 6.

occurred, because most of the material was pyrolyzed before these temperatures were reached.

VII. Pyrolysis of GR-S

GR-S, consisting of 75 percent of butadiene and 25 percent of styrene, was dissolved in benzene and precipitated with methanol. This was repeated several times and the precipitate freed from methanol and dissolved in benzene. Results of pyrolysis and fractionation of nine samples are shown in table 10. Here, as was the case with polybutadiene, the yield of fraction III stays constant at lower temperatures, then drops at 426° C or above. The average of the constant for the first five experiments is 11.8 ± 0.4 percent of the total pyrolyzed part. Fraction III was separated into fractions IIIA, yield 3.93 percent, and IIIB, yield 7.9 percent. Mass-spectrometer analyses of fraction IIIA for all nine experiments are shown in table 11. These analyses resemble very closely those obtained for fractions IIIA from polybutadiene. Apparently, styrene and toluene, which are decomposition products in the pyrolysis of polystyrene [1], were retained in fraction IIIB, due to their low vapor pressure at -75°C . According

TABLE 10. *Pyrolytic fractionation of GR-S*

Ex-periment number	Weight of sam-ple	Tem-perature	Dura-tion	Fractions in weight percent of original sample				Fraction III in per-cent- age of total pyrolyzed part
				I Resi- due	II Non- volatile at room tem- perature	III Volatile at room tem- perature	IV Gas- eous frac- tion	
1	52.7	352	30	93.1	6.1	0.8	trace	11.6
2	45.5	375	30	80.1	17.8	2.0	0.05	10.0
3	46.3	375	30	62.2	32.9	4.8	.10	12.7
4	41.0	400	30	44.5	48.3	7.1	.13	12.8
5	44.7	400	30	43.5	49.6	6.8	.12	12.0
6	59.3	426	30	28.3	65.3	6.2	.15	8.7
7	51.6	450	30	5.4	87.4	7.0	.16	7.4
8	46.5	450	30	0.3	93.6	5.9	.17	5.9
9	47.8	455	30	.4	92.7	6.7	.17	6.7
Average of fraction III in percentage of total pyrolyzed part for experiments 1 to 5, inclusive.....								11.8±0.4

to Stull's table [11], the temperatures at which styrene and toluene have a vapor pressure of 1 mm are -7° and -26.7°C , respectively. In GR-S pyrolysis, as in the case of polybutadiene, the content of 1,3-butadiene drops, and that of most of the other significant constituents of fraction IIIA rises with rise in temperature. Composition of

TABLE 11. *Mass-spectrometer analysis of fraction IIIA obtained in the pyrolysis of GR-S*

Experiment number.....	1	2	3	4	5	6	7	8	9	5 Components in percentage of total pyrolyzed part, weight percent	
Temperature of pyrolysis, ° C.....	352	375	375	400	400	426	450	450	455		
Part pyrolyzed, percent.....	6.9	19.9	37.8	55.5	56.6	71.7	94.6	99.7	99.6		
Component	Molec- ular weight	Mole percent									
Ethylene.....	28.0	3.5	4.8	8.1	11.1	11.5	11.4	12.6	12.6	10.9	0.266
Ethane.....	30.0	1.4	1.8	6.0	9.8	10.6	10.0	11.3	12.7	12.0	.263
Propadiene.....	40.0	0.4	0.2	0.2	0.5	0.4	0.7	0.8	-----	0.8	.013
Propylene.....	42.0	.4	1.8	8.3	7.9	9.9	4.7	4.9	10.4	9.1	.344
Propane.....	44.0	1.7	2.2	2.7	4.4	4.9	4.2	5.8	4.5	5.7	.177
1,3-Butadiene.....	54.1	63.3	63.9	57.7	43.8	42.6	43.9	36.6	38.5	38.6	1.906
Butenes.....	56.1	8.8	11.1	13.5	13.6	13.8	16.1	15.6	13.0	12.7	0.634
Butanes.....	58.1	3.3	1.3	1.5	3.2	2.8	2.6	3.1	3.5	3.7	.134
Cyclopentadienes.....	66.1	1.7	1.5	0.1	0.3	0.2	0.5	0.7	0.2	0.3	.011
Pentadienes.....	68.1	6.7	7.0	.9	2.6	1.2	2.3	3.5	1.7	2.4	.058
Pentenes.....	70.1	1.0	1.2	.7	1.8	1.2	2.4	3.1	1.6	2.2	.069
Pentanes.....	72.1	-----	-----	.3	1.0	0.9	0.9	1.1	1.3	1.4	.054
1,3-Cyclohexadienes.....	80.1	4.5	1.4	-----	-----	-----	-----	0.2	-----	-----	-----
Hexadienes.....	82.1	3.0	1.6	-----	-----	-----	0.2	.5	-----	0.1	-----
Hexenes.....	84.1	0.3	0.2	-----	-----	-----	.1	.2	-----	.1	-----
Total.....	-----	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	3.930
CO ₂	44	29.0	9.1	9.9	12.8	7.9	0.2	-----	6.0	7.8	-----
Benzene.....	-----	0.4	0.2	-----	-----	-----	-----	-----	-----	-----	-----

fraction IIIA in percentage of total pyrolyzed part is shown in the last column for experiment 5, which seems to have about the average percentage of components for all the experiments. The yield of butadiene, according to this table, is 1.906 percent for experiment 5. Considering the other experiments, this yield varies from 2.14 percent for experiment 1 to 1.71 percent for experiment 9. Although in the case of pyrolysis of polystyrene, fraction III, which consists mostly of styrene, could be analyzed in the mass spectrometer, fraction IIIB from pyrolysis of GR-S could not be similarly analyzed, because of the complexity of the spectrum arising from the presence in this fraction of the dimer of butadiene, presumably vinyl cyclohexene.

The gaseous fraction was analyzed in the mass spectrometer only for experiments 2, 4, 5, and 9. The other values were interpolated from those determined experimentally. The results are shown in table 10. The average yield of CH₄ is 0.19 percent. Fraction II was only slightly soluble in cyclohexane, but soluble in benzene. Results of molecular weight determinations for four experiments are shown in table 12. The average molecular weight is 712, corresponding approximately to a composition of eight to nine units of butadiene and three units of styrene per fragment. Fraction I was soluble in cold or hot benzene, but not in cyclohexane, cold or hot.

TABLE 12. Average molecular weight of the wax-like fraction (II) obtained in the pyrolysis of GR-S

Experiment No.	Temperature of pyrolysis	Part pyrolyzed	Freezing point lowering of C ₆ H ₆	Molecular weight
	° C.	%	° C.	
3.....	375	37.8	.60	707
5.....	400	56.6	.60	726
6.....	426	71.7	.57	687
7.....	450	94.6	.50	728
Average.....	-----	-----	-----	712

VIII. Pyrolysis of Polyethylene

The polyethylene used in this investigation was a pure-grade polymer having an average molecular weight of about 20,000. It could not be dissolved in the ordinary solvents and was used in the form of a suspension in benzene. Polyethylene proved very resistant to thermal decomposition.

Pyrolysis started at 360° and was almost complete at 475° C. The results of 13 experiments are shown in table 13. Here the yield of fraction III was very small, the average being 3.4±0.5 percent of the total pyrolyzed part. There is a considerable variation from this average in the individual experiments, but this is to be expected in view of the fact that the weight of the liquid fraction was only 0.25 to 1.5 mg, and the accuracy of weighing was not better than 0.05 mg. Duration of experiments at maximum temperatures varied from 30 to 90 min.

TABLE 13. Pyrolytic fractionation of polyethylene

Experiment Number	Weight of sample	Temperature	Duration	Fractions in weight percent of original sample				Fraction III in percentage of total pyrolyzed part
				I Residue	II Non-volatile at room temperature	III Volatile at room temperature	IV Gaseous fraction	
1	mg	° C.	min.					
1	54.3	360	30	98.6	1.3	0.1	Trace	7.1
2	71.9	400	60	87.8	11.6	.6	...do...	4.9
3	54.5	401	30	85.2	13.9	.9	...do...	6.1
4	56.6	405	30	76.5	23.1	.4	...do...	1.7
5	67.2	405	60	83.0	16.3	.7	...do...	4.1
6	57.6	405	30	82.4	16.8	.8	...do...	4.2
7	57.6	405	90	78.9	20.6	.5	...do...	2.4
8	65.5	429	30	29.7	67.9	2.4	...do...	3.4
9	59.1	429	30	37.3	61.6	1.1	...do...	1.8
10	56.0	430	60	29.4	68.4	2.2	...do...	3.1
11	59.9	431	60	11.4	86.1	2.5	...do...	2.8
12	64.6	431	90	6.1	91.3	2.6	...do...	2.8
13	36.4	475	30	1.4	95.5	3.1	...do...	3.1
Average fraction III in percentage of total pyrolyzed part for all experiments except 1.....								3.4±0.5

Fraction III was divided into fractions IIIA and IIIB in the manner described above. Mass-spectrometer analyses of fraction IIIA for four experiments are shown in table 14. Polyethylene is unique in the sense that the macromolecular chain is devoid of any marks indicating the monomeric units from which it is built. Thermal decomposition, according to table 4, seems to follow a random pattern giving rise mostly to straight chain paraffins and monoolefins. It is likely that fractions IIIB and II consist of the same types of molecules, except that they are longer. The four analyses shown in table 14 resemble each other very closely, in spite of the fact that the temperature of pyrolysis varied

TABLE 14. Mass-spectrometer analysis of fraction IIIA obtained in the pyrolysis of polyethylene

Experiment number.....	4	9	10	13	Average of experiments 4 to 13, inclusive	Average component in percentage of total pyrolyzed part, weight percent	
Temperature of pyrolysis, ° C.....	405	429	430	475			
Part pyrolyzed, percent.....	23.5	62.7	70.6	98.6			
Component	Molecular weight	Mole percent					
Ethylene.....	28	4.8	4.0	4.1	4.2	4.3	0.025
Ethane.....	30	14.3	13.4	10.9	11.2	12.4	.076
Propadiene.....	40	1.2	-----	-----	-----	0.3	.002
Propylene.....	42	-----	3.7	10.8	6.1	5.2	.045
Propane.....	44	15.3	10.3	16.2	17.5	14.8	.136
Butenes.....	56.1	24.5	25.8	22.7	25.4	24.6	.282
<i>n</i> -Butane.....	58.1	16.8	22.1	18.6	18.7	19.1	.225
Pentadienes.....	68.1	-----	0.3	0.4	0.9	0.4	.005
Pentenes.....	70.1	8.3	8.4	6.7	6.7	7.5	.108
<i>n</i> -Pentane.....	72.1	6.8	7.7	6.2	3.9	6.2	.091
Hexadienes.....	82.1	0.8	0.3	-----	-----	0.3	.005
Hexenes.....	84.1	3.5	2.7	2.4	4.1	3.2	.056
<i>n</i> -Hexane.....	86.1	1.6	1.1	0.8	1.3	1.2	.022
1-Heptene.....	98.1	0.5	0.1	.2	-----	0.2	.004
<i>n</i> -Heptane.....	100.1	1.6	.1	-----	-----	.4	.008
Total.....	-----	100.0	100.0	100.0	100.0	100.0	1.1
CO ₂	44	0.3	3.6	-----	2.1	-----	-----

from 405° to 475° C., and the extent of decomposition varied from 23.5 to almost 100 percent. The average composition of fraction III in percentage of total pyrolyzed part is shown in the last column of table 14.

Fraction IIIB can be assumed to consist of paraffins and olefins containing 8 to 15 carbons in the chain. The gaseous fraction contained only a trace of CH₄. The wax-like fraction (II) was quite insoluble in cold benzene, although soluble in hot benzene. The average molecular weight of this fraction was determined by the microfreezing-point-lowering method in camphor. The re-

sults are shown in table 15. The amount of material in fraction II was too small in most experiments, and it was found necessary in some cases to combine the yields from two experiments for a molecular-weight determination. The average of four determinations was 692, corresponding to an average straight-chain hydrocarbon fragment of about 50 carbons. The residue was a horny substance insoluble in cyclohexane or benzene, hot or cold.

IX. Discussion of Results

It was shown in the course of this investigation that fractionation of the volatile products of pyrolysis facilitates the analysis of the products whether by means of the mass spectrometer or by other means. One striking result of this investigation is that in the case of polyisobutene and polyisoprene the yield of the monomer is practically constant within a wide range of temperature, duration of experiment, amount of sample used, or extent of pyrolysis. The same was found true in the pyrolysis of polystyrene [1]. In the case of polybutadiene the yield of the monomer decreases markedly with the rise in temperature of pyrolysis. As to polyethylene, one cannot speak of a monomer, because the macromolecular chain does

TABLE 15. Average molecular weight of wax-like fraction (II) obtained in the pyrolysis polyethylene

Experiment number	Temperature of pyrolysis	Part pyrolyzed	Freezing point lowering of camphor	Molecular weight
5.....	° C	%	° C	690
6.....	405	17.0	4.8	
8.....	405	17.6	5.4	691
10.....	429	70.3		
11.....	430	70.6	5.0	687
9.....	431	88.6		
12.....	429	62.7	5.6	699
-----	431	93.9		
-----	-----	-----	Average...	692

not have any distinctive marks to indicate the unit from which it was built. Nevertheless, the relative amounts of small fragments up to about eight carbons remains fairly constant through the range 405° to 475° C.

It was pointed out in the previous paper that pyrolysis of polymers, unlike molecular distillation, is a very slow process. Although in the latter case only distillation is involved, in the case of pyrolysis, distillation follows fragmentation, and the rate of the combined process is necessarily that of fragmentation. In view of this, the vapor phase will be very unsaturated, even with regard to the larger fragments at the high temperatures employed and will, therefore, not be very sensitive to the total pressure. On comparing [1] the work of Staudinger and Steinhöfer, who pyrolyzed polystyrene at a pressure of 0.1 mm Hg, with that of Madorsky and Straus, who used a pressure of about 10^{-5} , it was found that the results were about the same, the yield of the monomer being 43.5 and 40 percent of the total pyrolyzed part, respectively. A comparison of the yield of isoprene obtained in this investigation with those found in the literature, is given in table 16. The yields are shown in percentage of total pyrolyzed part. There seems to be a good agreement between the yield obtained in the present work with that obtained by Staudinger and Fritschi, at a pressure of 0.1 to 0.3 mm, or even with that of Staudinger and Geiger at a pressure of 1 atm, the values being 5.15, 4.9, and 4.2 percent, respectively. The yield obtained by Wall, who worked at a temperature and pressure comparable to those used here but used samples of only 1 mg, is in good agreement with the present work on syn-

thetic polyisoprene, 5 percent, but not for natural rubbers, where the yield was 2 percent. The yield obtained by Midgley and Henne, who worked at a temperature of 700° C and at atmospheric pressure, was twice that obtained by Staudinger and coworkers, or by us. Particularly interesting are the results of Bassett and Williams, who studied the effect of rate of heating on yield. The yield of isoprene was increased in their work from 8.3 percent, when the heating rate was slow, to 12.9 percent, when the heating was fast. On dropping 1-g pieces of rubber on a hot metal surface maintained at 600° C, the yield of isoprene was raised to 19.2 percent.

Yields of the various fractions obtained in pyrolysis are summarized in table 17, and the average molecular weights of these fractions are summarized in table 18. Polystyrene is included in these tables for the purpose of comparison. Even in the case of polybutadiene and GR-S, where composition of fraction IIIA varies with temperature, the average molecular weight of the fraction as a whole is practically constant throughout the temperature range. In table 18, the values for fractions II, IIIA, and IV were determined experimentally, whereas those for fraction IIIB were estimated on the assumption that it consisted of a mixture of hydrocarbons with 8 to 15 carbons.

Fraction III contains the monomer, as well as the other small fragments, of pyrolysis. The yield of this fraction can be used as an indication of relative fragmentation of polymers during pyrolysis. In this respect, the polymers, as seen from table 17, fall into three groups: (1) polystyrene and polyisobutene; (2) polyisoprene, polybuta-

TABLE 16. Yield of isoprene in the pyrolysis of natural and synthetic polyisoprene
Comparative results obtained by various investigators

Investigators	Reference	Polymer	Temperature	Rate of heating	Pressure	Weight of sample	Yield of isoprene
			° C		mm	g	%
Present work.....		Synthetic polyisoprene.....	300 to 400	Slow.....	10^{-6}	0.050	5.15
Staudinger and Fritschi.....	[4]	Natural rubber.....	275 to 320	do.....	0.1 to 0.3	170	4.9
Staudinger and Geiger.....	[5]	do.....	^a 300 to 400	do.....	760	100	4.2
Wall.....	[9]	Synthetic polyisoprene.....	400	do.....	10^{-3}	0.001	5
Do.....	[9]	Balata.....	400	do.....	10^{-3}	.001	2
Do.....	[9]	Natural crepe.....	400	do.....	10^{-3}	.001	2
Midgley and Henne.....	[6]	do.....	700	Fast.....	760	7,200	10
Bassett and Williams.....	[7]	Smoked crepe.....	580	Slow.....	760	250	8.3
Do.....	[7]	do.....	650	Fast.....	760	250	12.9
Do.....	[7]	do.....	600	Very fast.....	760	100	19.2

^aTemperature of pyrolysis is not given for this experiment. It was estimated to be in this range from the description.

butenes, followed by *n*-butane, *n*-propane, and *n*-ethane.

Pyrolytic fractionation of polymeric substances, in conjunction with mass spectrometer analysis of the light fractions, offers an easy, quick, and dependable method for the analysis of these substances. Each polymer gives a characteristic spectrum in the mass range up to about 105, as shown in figure 3. With the further development of the mass spectrometer and the extension of its range to higher masses, this new method should prove valuable not only in the identification and determination of purity of polymers and copolymers, but in the study of their structure and properties as well. By connecting the pyrolysis apparatus directly to the mass spectrometer, analysis of the more volatile fractions could be further facilitated and expedited.

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