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Thermal Degradation of Polychlorotrifluoroethylene, Poly-α,β,β-Trifluorostyrene, and Poly-*p*-Xylylene in a Vacuum[1]

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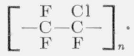
Polychlorotrifluoroethylene (Kel-F) (I), poly-*α*,*β*,*β*-trifluorostyrene (II), and poly-*p*-xylylene (III) were pyrolyzed under conditions of molecular distillation, and some of the light volatile fractions analyzed in the mass spectrometer. The volatiles from (I) consisted of 27.9 weight percent monomeric fragments, mostly monomer, and 72.1 percent large fragments of average molecular weight 904. In the case of (II), the volatiles consisted of 73.6 percent monomeric fragments, almost all monomer, and 26.4 percent large fragments of average molecular weight 458. The volatiles from (III) consisted of 3.6 percent monomeric fragments, not containing any monomer, and 96.4 percent large fragments of average molecular weight 661. Rates of thermal degradation, in terms of rates of volatilization, were also investigated. The activation energies calculated from these rates are 66, 67, and 76 kilocalories per mole for (I), (II), and (III), respectively. The following order of thermal stability was found: (III)>(I)>(II).

1. Introduction

It was shown in a previous publication [1][2] in the case of a number of simple polymers, that their thermal behavior in a vacuum, in the temperature range 250° to 550° C., is primarily a function of their molecular structure. In this paper a comparison is made between polymers that are similar to some of those previously studied, and yet differ from them in certain structural features. With this in view, the following polymers were selected for the present study:

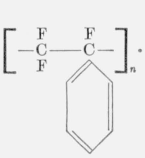
1. Polychlorotrifluoroethylene (Kel–F)



$$\left[-\overset{\mathrm{F}}{\underset{\mathrm{F}}{\mathrm{C}}}-\overset{\mathrm{Cl}}{\underset{\mathrm{F}}{\mathrm{C}}}-\right]_n.$$

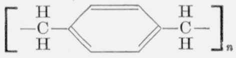
This polymer differs in structure from tetrafluoroethylene in that one fluorine atom is replaced with a chlorine atom.

2. Poly-*α*,*β*,*β*-trifluorostyrene



This polymer differs from polystyrene in that the hydrogen atoms in *α*,*β*,*β*-positions are replaced with fluorine atoms.

3. Poly-*p*-xylylene



This polymer differs from polybenzyl in that it contains two, instead of one, CH_2 groups between the phenyl groups in the chain. It is also isomeric with polystyrene; however, here the phenyl group is a part of the chain, while in polystyrene it is pending from every second carbon atom in the chain.

2. Apparatus and Experimental Procedure

The experimental work consisted of (1) a study of pyrolysis in a molecular still and a subsequent investigation of the decomposition products, and (2) measurements of rates of thermal degradation in a vacuum, as indicated by the loss in weight of a sample suspended from a spring balance.

In the pyrolysis study, samples weighing 15 to 30 mg were heated at various temperatures. In each case it took about 45 min to heat the sample to the required temperature, and this temperature was then maintained for 30 min. Four fractions were collected:

(I) Residue. This fraction was weighed on a semimicro balance, but was not investigated further.

(II) Heavy fraction, volatile at the temperature of pyrolysis, but not at room temperature. The weight of this fraction was calculated as the difference between the sum of the weights of the other three fractions and the original weight of the sample. The average molecular weight was determined by a microfreezing-point-lowering method.

(III) Light fraction volatile at room temperature, and containing monomer or monomer-size fragments. This fraction was weighed and then analyzed in the mass spectrometer.

(IV) Gaseous fraction, volatile at the temperature of liquid nitrogen. This fraction was also analyzed in the mass spectrometer and was found to consist of hydrogen. Its weight was calculated from its volume, pressure, and composition, and amounted to about 0.02 percent of the weight of the original

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[1] This work was supported in part by the Ordnance Corps, Department of the Army, and in part by the Federal Facilities Corporation, Office of Synthetic Rubber. This paper was presented at the National Meeting of the American Chemical Society in Cincinnati, Ohio, March 29–April 7, 1955.

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

sample. Details of apparatus and experimental procedure have been described previously [2, 3].

Rates of thermal degradation were determined for each polymer at several temperatures. A 5–7-mg sample of the polymer was placed in a platinum crucible suspended from a very sensitive tungsten helical spring balance, enclosed in a Pyrex glass housing, which could be evacuated to 10^{-5} to 10^{-6} mm Hg. An electric furnace was preheated to the temperature required for a particular run. The furnace was then placed in position to enclose that part of the glass apparatus that contained the crucible. It ordinarily required about 15 min from the time the furnace was placed in position, to the time at which the thermocouple under the crucible indicated the temperature required for the given experiment. There was some loss of weight of the sample by evaporation during this heating-up period. This loss was designated as the preliminary loss, and the zero time for any rate experiment was considered as the time when the thermocouple indicated that the operating temperature had been reached. The apparatus and experimental procedure have been described in detail in previous publications [1, 4, 5].

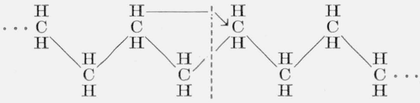
In all the rate experiments the percentage of the sample volatilized at any given temperature was plotted against time. These plots can be used as a basis for constructing graphs of logarithm of residue at time t versus time. For some polymers these graphs are straight lines, indicating a first-order reaction [6], and the slopes of these lines are the rate constants for the respective temperatures. For other polymers the reaction is not of first order, and the plots of logarithm of residue versus time are curved lines. The three polymers of this investigation belong to the second class. In this case, other methods of plotting the results were adopted: (1) K_1–rates, which are expressed in percent volatilized based on original sample per minute, at any given time t, were plotted against cumulative percentage volatilization at t. (2) K_2–rates, which are expressed in percent volatilized based on the residue at any time t, per minute, were plotted against cumulative percentage volatilization at t. Usually, one or the other, or both, sets of plots are straight lines in the range of about 10- to 80-percent volatilization.

It was not possible to make an accurate and detailed study of initial rates with the present experimental setup. It is planned to make such a study by degrading polymer samples by pyrolysis slowly at low temperatures, using automatic recording of the rates of volatilization. In the present work, the apparent initial rates were obtained by extrapolating the main parts of the rate plots to zero evaporation.

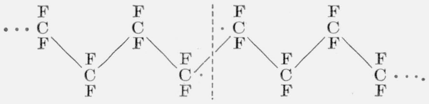
While the apparent initial rates can serve as a measure of thermal stability, it is perhaps more accurate, for the purpose of comparing thermal stability of various polymers, to use a value designated as T_h and defined as the temperature, in degrees centigrade, at which a sample of a given polymer loses half its weight by evaporation during 45 min of heating in a vacuum up to this temperature, followed by 30 min of heating at this temperature. Most of the weight loss takes place during the last 30 min.

3. Mechanism of Thermal Degradation of Polymers

A possible mechanism of thermal degradation through scissions has been described in a previous paper [1]. According to this mechanism, degradation by heat takes place through scissions of the polymer chain. In some cases the scissions are accompanied by transposition, as in polymethylene,



resulting in one olefin and one paraffin end. In other cases the scissions result in two free radical ends, as in polytetrafluoroethylene,

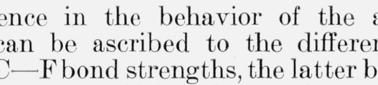


The free radicals then proceed to depolymerize into monomer by a chain reaction,

The difference in the behavior of the above two polymers can be ascribed to the difference in the C—H and C—F bond strengths, the latter being greater that the former. Although there is a great deal of disagreement among investigators in regard to numerical values of bond strengths, there seems to be a general agreement as to their relative strengths. Thus, in the case of bonds with which this investigation is concerned, the bonds can be arranged in the following order:

C—F>C—H>C—Cl>C—C.

In the case of polychlorotrifluoroethylene, as will be shown below, the volatiles consist partly of monomer and partly of large fragments. This is due to the weakness of the C—Cl bond, so that transposition of chlorine during scissions takes place. However, since there is only one chlorine atom on every second carbon, this transposition is limited. As a result, some scissions are accompanied by transposition,



without monomer formation, while other scissions result in formation of free radical ends, followed by monomer formation.

As to what happens to the residue during thermal degradation, some information is found in the literature on polystyrene [4, 7, 8], poly-α- and poly-β-deuterostyrene [7], polymethyl methacrylate [9], polyethylene [10], polymethylene [11], and polyisobutylene [12]. It was found, with all these polymers, that there is an initial rapid drop in molecular weight during the first few percent volatilization, or even before volatilization begins, followed by a much slower drop in molecular weight as volatilization proceeds. This rapid initial drop in molecular weight may be due to weak links [13] or to other causes. However, it is quite possible that the deviation of the initial rates from the linearity of the subsequent K_1- or K_2-rates is due, to a large extent, to this rapid initial drop in molecular weight. It was also found that additives, such as benzoyl peroxide, affect initial rates of thermal degradation, as was shown in the case of polymethyl methacrylate [14].

One should be able to find a difference in the shape of the curves for molecular weight of residue versus volatilization, beyond the first few percent volatilization, depending on whether the mechanism of degradation is of the polymethylene type or the polytetrafluoroethylene type. However, the literature data are inconclusive with regard to this point. While in the case of polymethyl methacrylate, which degrades by the same mechanism as polytetrafluoroethylene, degradation was carried out to about 90 percent loss of weight [9], polymethylene was degraded to only about 14 percent volatilization [11]. As for polyethylene, the investigation was made at a temperature below volatilization [10].

4. Results

4. 1. Polychlorotrifluoroethylene

This polymer[3] was in the form of a transparent sheet 0.2 mm thick. It contained no additives and had an average molecular weight of 100,000. Experimental conditions and results of pyrolysis are shown in table 1. The light fraction III is, on the average from three experiments, 27.9 percent of the total volatilized part, as compared with almost 100 percent in the case of polytetrafluoreothylene [5]. Mass spectrometer analysis of this fraction showed it to consist of about 90 to 95 mole percent monomer, the rest being a mixture of C_3F_5Cl and $C_3F_4Cl_2$. Thus, the yield of monomer was actually 26 to 27 percent of the total volatilized part, as compared with almost 100 percent for polytetrafluoroethylene. When pyrolyzed in bulk [15] in nitrogen at atmospheric pressure, polychlorotrifluoroethylene yields 67 percent monomer. Bulk pyrolysis gives similar results in the case of other polymers [16, 17].

In figure 1 the percent of polymer volatilized is plotted against temperature for the experiments shown in table 1. The value of T_h for polychloro-

TABLE 1. *Pyrolytic fractionation of polymers*

Experiment	Temperature	Fractions of original sample I Residue	 II Nonvolatile at room temperature	 III Volatile at room temperature	Fraction III in percent of total volatilized part
Polychlorotrifluoroethylene (Kel–F)					
	°C	*wt* %	*wt* %	*wt* %	*wt* %
1	347	98.9	--------	--------	--------
2	380	47.5	37.5	15.0	28.6
3	401	1.2	71.5	27.3	27.6
4	418	0.6	70.0	27.4	27.6
Average					27.9±0.4
Poly-α, β, β-trifluorostyrene					
1	333	70.0	7.5	22.5	75.1
2	348	34.5	16.6	48.9	74.6
3	365	4.8	22.0	73.2	77.0
4	382	0.9	32.2	66.9	67.5
Average					73.6±1.5
Poly-*p*-xylylene					
1	419	85.7	--------	--------	--------
2	431	56.6	41.7	1.7	3.8
3	439	33.5	63.2	3.3	4.9
4	449	8.5	89.5	2.0	2.2
5	464	2.5	93.9	3.6	3.6
Average					3.6±0.7

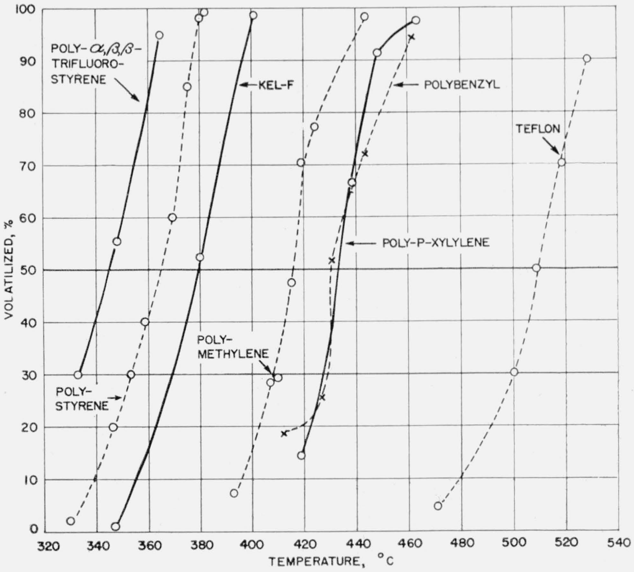


FIGURE 1. *Relative thermal stability of polychlorotrifluoroethylene (Kel-F), poly-α,β,β-trifluorostyrene and poly-p-xylylene.*

The other polymers are shown for comparison. In each experiment the sample was heated up to the required temperature in 45 min and then kept at this temperature for 30 min.

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[3] The authors are indebted to H. S. Kaufman of the W. M. Kellogg Co. for supplying this polymer.

trifluoroethylene is about 380° C, as compared with 416° for polymethylene, and 509° for polytetrafluoroethylene.

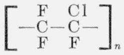
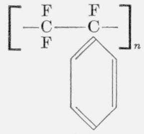
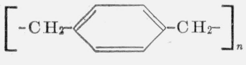
The residue, fraction I, was a transparent glass. The heavy volatile fraction II had an average molecular weight of 904, as determined by the freezing-point lowering in camphor. This value is higher than those observed for other vinyl polymers, but fluorocarbon compounds are known to have higher vapor pressures than hydrocarbons.

The rates of thermal degradation of polychlorotrifluoroethylene were investigated at five temperatures. The experimental conditions and results are shown in table 2. In figure 2, percentage volatilization is plotted against time. It can be seen from this figure that the preliminary losses by volatilization are from 0 to 3 percent. The K_2-rates, in percent volatilized based on the residue per minute, are shown plotted in figure 3. These plots are straight lines above 10 to 20 percent volatilization, and the apparent initial rates are obtained by extrapolation to zero volatilization. The values of these initial rates are shown in table 2. The activation energy, as calculated from these initial rates, using Arrhenius' equation, is 66 kcal/mole. The apparent initial rate of thermal degradation of polymers at 350° C, $K_{350°}$ was selected for the purpose of comparing thermal stability of polymers [1]. If this rate is not conveniently determined experimentally, it can be calculated from a given rate at a given temperature by means of a modified Arrhenius' equation:

$$\log_{10} K_{350°C} = \frac{E\left(1.605\times10^{-3}-\frac{1}{T_1}\right)}{2.303\,R} + \log_{10} K_1,$$

where K_1 is the rate corresponding to the absolute temperature, T_1, and R is the gas constant. For polychlorotrifluoroethylene, this rate is 0.044 percent per min, as compared with 0.000002 percent for polytetrafluoroethylene.

TABLE 2. *Rates of thermal degradation of polymers*

Polymer	Temperature	Duration of experiment	Total volatilized	Initial rate of volatilization	Activation energy
	° *C*	*min*	%	*%/min*	*kcal*
Polychlorotrifluoroethylene				K_2	
 $\left[-\mathrm{CF_2}-\mathrm{CFCl}-\right]_n$	365	400	78.1	0.20	
	370	300	82.9	.28	
	375	200	75.0	.42	
	380	160	82.3	.58	
	385	130	83.2	.84	66
Poly-α, β, β-trifluorostyrene				K_1	
	325	360	59.7	0.27	
	330	410	72.1	.43	
	335	200	64.3	.60	
	340	200	79.9	1.02	67
Poly-p-xylylene				K_2	
	415	230	80.4	0.06	
	420	170	88.9	.10	
	425	110	91.6	.16	
	430	80	93.3	.23	76

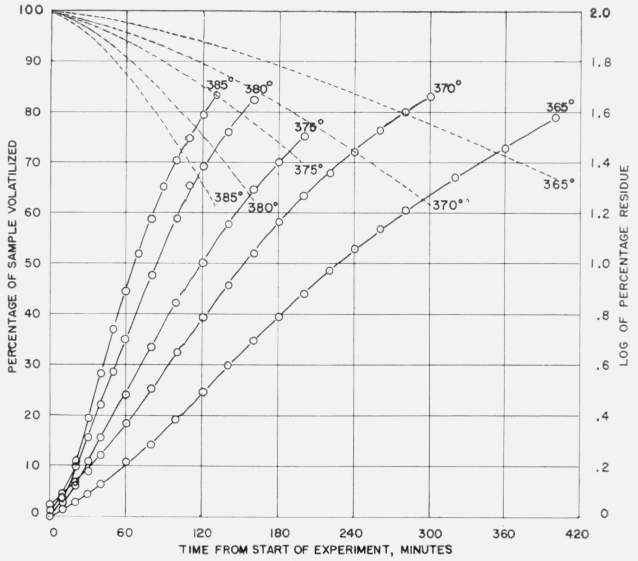


FIGURE 2. *Thermal degradation of polychlorotrifluoroethylene.*

______, Percentage of sample volatilized versus time; --------, $\log_{10}$ of percentage residue versus time.

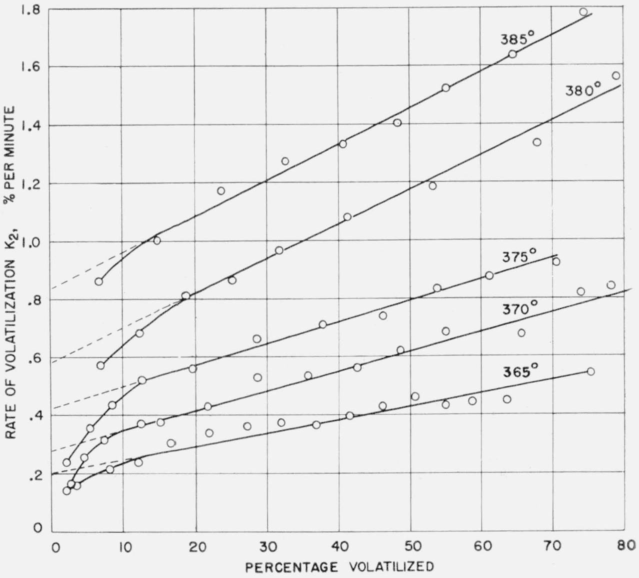


FIGURE 3. *Rates of volatilization of polychlorotrifluoroethylene in percent of residue per minute, as a function of percentage volatilization.*

4.2. Poly-α, β, β-trifluorostyrene

This polymer,[4] in the form of white light flakes, was prepared by R. S. Corley, of Polaroid Corp., from the monomer at 50° C, using a small amount of dodecylamine as emulsifier. The emulsion was coagulated by the addition of 1-percent sodium sulfate. The product was purified by washing thoroughly with ethanol to remove the emulsifier, dimer, and alcohol-

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[4] The authors are indebted to the Signal Corps Engineering Laboratory, Fort Monmouth, N. J., for supplying this polymer.

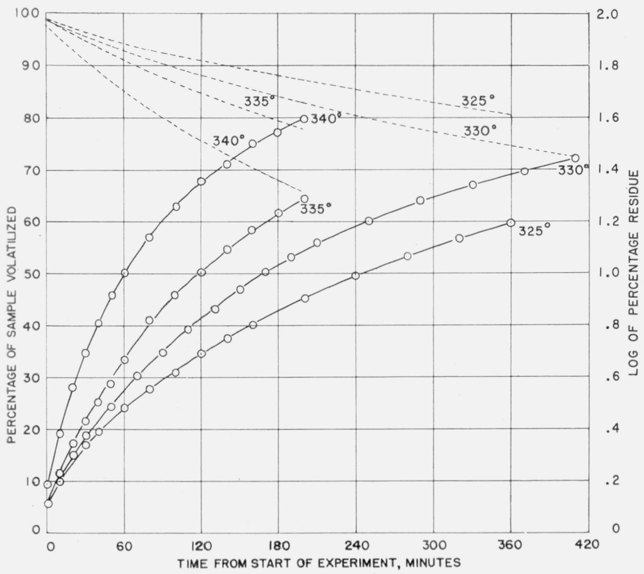


FIGURE 4. *Thermal degradation of poly-α,β,β-trifluorostyrene.*
______, Percentage of sample volatilized versus time; --------, logarithm $_{10}$ of percentage residue versus time.

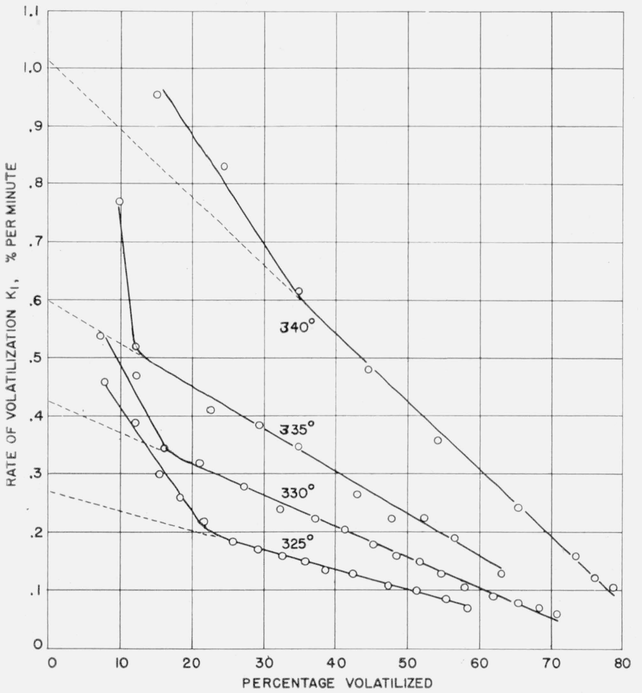
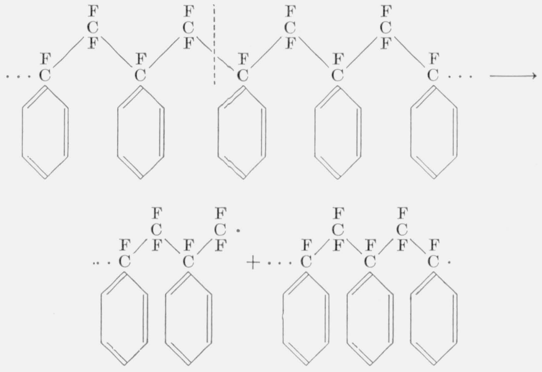


FIGURE 5. *Rates of volatilization of poly-α,β,β-trifluorostyrene in percent of original sample per minute, as a function of percentage volatilization.*

soluble low polymers, and was then vacuum dried. Preliminary experiments on pyrolysis and rate of degradation showed that the polymer contained a considerable amount of short-chain molecules. A 2-g sample was fractionated by dissolving at room temperature in 100 ml benzene and precipitating with 35 ml methanol. About 1 g of heavy fraction was thus obtained. This operation was repeated on the heavy fraction, resulting in 0.5 g of a still heavier fraction. This last fraction was freeze-dried and used in the experiments described here. On the basis of information with regard to the molecular weight by osmotic determination of the original material, the weight average molecular weight of the twice-fractionated 0.5 g heavy fraction was estimated to be at least 300,000.

Experimental conditions and results of pyrolysis of poly-α, β, β-trifluorostyrene at four temperatures are shown in table 1. The amount of fraction III in percent of total volatilized part is about 74 percent, as compared with 42 percent for ordinary polystyrene [1]. Temperature of 50 percent volatilization, T_h, as seen from figure 1, is 342° C, as compared with 364° for ordinary polystyrene [18]. There does not seem to be any satisfactory explanation at present for the greater stability of polystyrene as compared with poly-α, β, β-trifluorostyrene.

Mass spectrometer analysis showed fraction III to consist almost entirely of the monomer. Judging from the large monomer yield in the pyrolysis of poly-α, β, β-trifluorostyrene, the mechanism of degradation consists mainly of scissions without transposition, resulting in two free radicals:



These free radicals then break up into monomers by a chain reaction (unzipping). The lack of transposition of fluorine here could be ascribed to the high C—F bond strength.

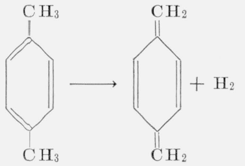
The heavy fraction II had an average molecular weight of 458, as determined by the freezing-point-lowering method in benzene. This molecular weight corresponds to a trimer, and could consist of a mixture of dimer, trimer, and tetramer, as in the case of polystyrene, poly-α and poly-β-deuterostyrenes, and poly-*m*-methylstyrene [14]. While the weight ratio of fractions II and III in poly-α, β, β-trifluorostyrene is 74:26, the mole ratio is 89:11, so that only a few large molecules have evaporated. The residue, fraction I, was glassy and light brown in color.

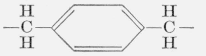
Measurements of rates of degradation were carried out at four temperatures. Experimental conditions and results are shown in table 2. Cumulative percentage volatilization is plotted against time in figure 4. A preliminary loss of weight of 6 to 10 percent is shown. Rates K_1, in percent volatilized based on original sample per min, are shown in figure 5. The initial rates were obtained by extrapolation to zero time, and are shown numerically in table 2. The activation energy based on these rates is 67 kcal/mole, as compared with 58–59 determined previously for polystyrenes [14]. Rate, $K_{350°}$, of thermal degradation at 350°, calculated as in the case of polychlorotrifluoroethylene, is 2.4, as compared with 0.14, 0.24, 0.27, and 0.90 determined previously [4, 14] for poly-β-deuterostyrene, polystyrene, poly-α-deuterostyrene, and poly-*m*-methylstyrene, respectively.

4.3. Poly-*p*-xylylene

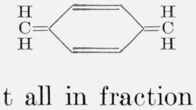
This polymer[5] was prepared by the Szwarc pyrolysis method, and is the same as the one used by the Polaroid investigators in their work [19] on poly-*p*-xylylene. It is a light-yellow powder and is described by Livingston [20] as "apparently all crosslinked." Its molecular weight was unknown, but must be quite high, judging from the fact that on pyrolysis the initial rate was not excessive, as is the case with low molecular weight polymers.

Szwarc's method [21, 22] for the preparation of poly-*p*-xylylene consists of heating gaseous *p*-xylene at about 800° C. At this temperature, *p*-xylene loses hydrogen to form 3,6-dimethylene-1,4-cyclohexadiene,



which is stable in the gaseous phase, but is labile in the condensed phase, and polymerizes at about 0°C. to form poly-*p*-xylylene. On the basis of X-ray analysis and energy of formation of this polymer, Szwarc assumes that it has a linear structure with  as the repeating unit. However, other investigators [19, 23, 24], on the basis of high crystallinity, infusibility, insolubility in most of the ordinary solvents, and of other chemical, as well as physical, properties of poly-*p*-xylylene, came to the conclusion that this polymer is highly crosslinked.

Results of pyrolysis experiments are shown in table 1 and figure 1. Fraction III, in percent of the total volatilized part, is 3.6. Mass spectrometer analysis of this fraction is shown in table 3. As seen from this table, the monomer,



does not appear at all in fraction III. Fraction II was found by the freezing-point-lowering method in camphor to have an average molecular weight of 661. The residue was light brown. The T_h value, as seen from figure 1, is 432, as compared with 430 for polybenzyl and 364 for polystyrene. Thus, polybenzyl and poly-*p*-xylylene approach polytetrafluoroethylene, with a T_h of 509 [5] in thermal stability. This is most likely due to the fact that the highly resonating benzene ring forms a part of the polymer backbone in these two polymers. On the other hand, styrene, which is isomeric with poly-*p*-xylylene, but has the benzene ring pending from every second carbon in the polymer backbone, is less thermally stable than polybenzyl or poly-*p*-xylylene.

TABLE 3. *Mass-spectrometer analysis of fraction III collected at room temperature in the pyrolysis of poly-p-xylylene*

Component	Temperature of pyrolysis, ° C			Average
	419	431	464	
	Mole %	*Mole %*	*Mole %*	*Mole %*
Methyl-ethyl-benzene (C_9H_{12})	7.5	7.0	6.0	6.8
Methyl-styrene	5.7	2.9	3.2	3.9
Xylene	68.0	83.1	84.5	78.6
Toluene	12.2	5.6	6.3	8.0
Benzene	6.6	1.4	-----	2.7
Total	100.0	100.0	100.0	100.0

Results of rate measurements are shown in table 2. Percentage volatilization versus time is shown in figure 6. As seen from this figure, the preliminary losses vary from about 3 to 5 percent volatilization. The K_2 rate curves are plotted as solid lines in figure 7. These curves, when extrapolated to zero volatilization, run close together, and the rates are subject to considerable error. The initial K_2-rates are shown in table 2. The activation energy calculated on the basis of these rates is 76 kcal, as compared with 53 for polybenzyl [1]. As a check on the accuracy of the activation energy for poly-*p*-xylylene, the K_1-rates are shown plotted as interrupted lines in figure 7. The K_1-rates at the position of maxima are shown in table 4, and the activation energy calculated on the basis of these maximum K_1-rates is about the same as that calculated from the initial K_2-rates. A surprising similarity to polystyrene [4], with regard to the mechanism of thermal degradation, is the shape of the K_1 and K_2-rate curves for poly-*p*-xylylene, which point to a reaction intermediate between a first and a zero order, the same as in polystyrene.

TABLE 4. *Maxima on K_1 rate-curves for poly-p-xylylene*

Temperature	Maxima
° C	*%/min*
415	0.50
420	.76
425	1.26
430	1.76

The $K_{350°}$ initial rate calculated from K_2-rates is 0.002, as compared with 0.006 percent for polybenzyl [1] and 0.24 percent per minute for polystyrene [4].

Even if we assume that poly-*p*-xylylene has a highly cross-linked structure, some parts of the

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[5] The authors are indebted to the Polaroid Corp. for supplying them with this polymer.

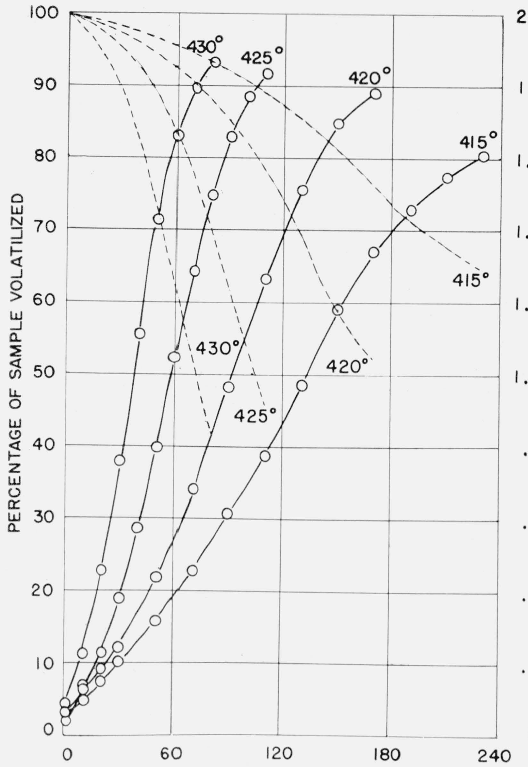


FIGURE 6. *Thermal degradation of poly-p-xylylene.*

______, Percentage of sample volatilized versus time; --------, logarithm$_{10}$ of percentage residue versus time.

polymer would be linear. It was shown by Szwarc that the monomer, 3,6-dimethylene-1,4-cyclohexadiene,

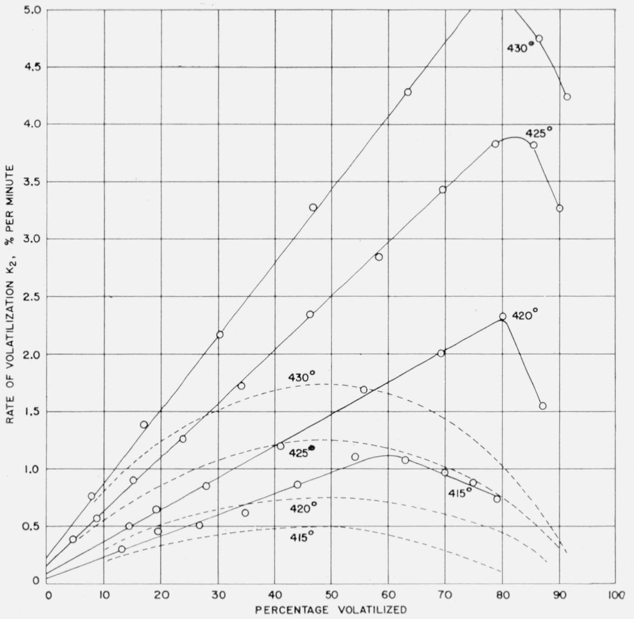
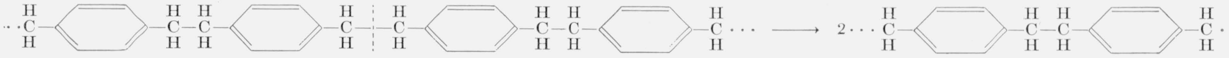


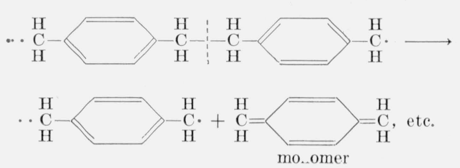
FIGURE 7. *Rates of volatilization of poly-p-xylylene, residue per minute as a function of percentage volatilization.*

The interrupted lines represent K_1-rates, in percent volatilized based on original sample per minute.

is stable in the gaseous phase. This monomer can be expected to form as part of the volatile product and remain stable while in the gaseous state. The mechanism of monomer formation could be as follows: A thermal scission occurs at the —CH_2—CH_2— bond, which is in β-position to double bonds in benzene rings on both sides. This scission takes place without hydrogen transposition and results in two free radicals:



These radicals could then unzip into monomers:



In order to check on the existence of the monomer in the pyrolysis of poly-p-xylylene, a sample of the polymer was pyrolyzed directly into the ionizing chamber of the mass spectrometer [6] by a method developed by Bradt, Dibeler, and Mohler [25]. The mass spectrogram consists of a series of peaks of formulae $nX+1$ and $nX-1$, where X is the monomer unit $CH_2:C_6H_4:CH_2$, molecular weight 104. With increase of n from 2 to 8, the intensity decreases from 1,000 to 10 (on an arbitrary scale), as shown in table 5. There are also smaller peaks with one or two CH_2 radicals taken from or added to $nX+1$. The amount of monomer, 3,6-dimethylene-1,4-cyclohexadiene, could not be determined quantitavely, in view of unknown contributions from the dimer, trimer, tetramer, etc., to the 104 peak. However, this amount is estimated as considerably less than 10 mole percent. Xylene, molecular weight 106, is present to the extent of about 1 mole percent. The highest peak is for $m/e=105$. This peak could be due chiefly to contributions from the larger ions which are multiples of X. Peaks at 207 and 209 are due to dimer, those at 311 and 313 to trimer, etc. These results are in general agreement with those obtained from pyrolysis, where the bulk of the vola-

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[6] The authors are indebted to Paul Bradt and F. L. Mohler, of the Mass Spectrometry Section, for carrying out this experiment and interpreting the results.

TABLE 5.[a] *Mass spectrograph of poly-p-xylylene pyrolyzed directly into the ionizing chamber of the mass spectrometer at 381° C.*

(Only the more conspicuous peaks are shown.)

m/e	Peaks on the basis of 105 m/e=1,000	Monomer multiple ±1
103	16	X−1 monomer
104	135	X
105	1, 000	X+1
106	95	------ xylene
207	334	2X−1 dimer
209	204	2X+1
311	84	3X−1 trimer
313	42	3X+1
415	22	4X−1 tetramer
416	23	4X
417	19	4X+1
519	19	5X−1 pentamer
521	19	5X+1
623	24	6X−1 hexamer
727	20	7X−1 heptamer
831	10	8X−1 octamer

[a] This table is from a paper now in preparation by Paul Bradt and F. L. Mohler.

tiles consisted of fraction II, having an average molecular weight of 661, while fraction III consists mainly of xylene.

Poly-*p*-xylylene and polybenzyl are two examples of polymers in which the phenyl group constitutes a part of the chain backbone. Both polymers are thermally stable, and do not yield the monomer unit as part of the volatile products. It was shown in the case of polybenzyl [1] that the configuration of the chain is such that monomer formation by unzipping is not to be expected. However, in the case of poly-*p*-xylylene, one could expect a considerable amount of monomer instead of the small amount actually found, which should be stable in the gaseous phase, according to the work of Szwarc. The absence of a large amount of monomer in the volatiles in the gaseous state could be explained on the basis of resonance in the poly-*p*-xylylene, which prevents the free radical end of the chain from unzipping in the same manner as in the case, for example, of polytetrafluoroethylene, polychlorotrifluoroethylene, and other polymers.

5. Comparative Thermal Stability of Polymers

It was pointed out above that a comparison of thermal stability of polymers can be made on the basis of their initial rates of volatilization. These initial rates were not determined experimentally, but were obtained by extrapolating to zero volatilization the main parts of the rate curve extending from about 10 to 80 percent volatilization. In making this comparison, the rates K_{350° of all the polymers are calculated to 350° C. Perhaps a more accurate comparison can be made on the basis of the T_h values of polymers. This value was defined as the temperature at which a polymer sample will lose half its weight when heated in a vacuum for 30 min at this temperature, preceded by a 45-min heating-up period to this temperature. Table 6 shows a comparison of thermal stability of 16 polymers on the basis of K_{350° and T_h. With a few slight deviations, the two comparisons run parallel.

TABLE 6. *Relative stability of polymers*

Polymer	K_{350°-rates		T_h	
	Percent per min	Reference	° *C*	Reference
Polytetrafluoroethylene	0. 000002	[5]	509	[5]
Poly-*p*-xylene	. 002	------	432	------
Polybenzyl	. 006	[1]	430	[1]
Polymethylene	. 004	[1]	407	[1]
Polyethylene	. 008	[4]	404	[11]
Polypropylene	. 069	------	387	------
Polychlorotrifluoroethylene	. 044	[1]	380	[1]
Poly-β-deuterostyrene	. 14	[1]	372	[1]
Polyvinylcyclohexane	. 45	[17]	369	[18]
Polystyrene	. 24	[4]	364	[18]
Poly-α-deuterostyrene	. 27	[17]	362	[18]
Poly-*m*-methylstyrene	. 90	[17]	358	[18]
Polyisobutylene	2. 4	[1]	348	[1]
Poly-α,β,β-trifluorostyrene	2. 4	------	342	------
Polymethylmethacrylate	5. 2	[17]	327	[18]
Poly-α-methylstyrene	230	[17]	278	[18]

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