

Thermal Degradation of Polymers with Aromatic Rings in the Chain

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Synopsis

The thermal degradation in vacuum of polymers containing aromatic or heterocyclic rings linked by various groups has been studied by a weight loss method. The most stable of the polymers examined were those with $-\text{CO}-$, mixed $-\text{SO}_2-$ and $-\text{O}-$, or $-\text{SO}_2-$ linkages. The stability of these were superior to or comparable with poly-*p*-phenylene and poly-*m*-phenylene. The particular combinations of aromatic nuclei and linking groups used did not result in tractability as most of the polymers were insoluble and infusible, even though of low molecular weight. Substitution in the aromatic nuclei could improve tractability, though at the expense of thermal stability.

INTRODUCTION

One of the promising methods of obtaining heat-resistant polymers appears to be by the synthesis of materials containing carbon and heterocyclic rings in the chain, and several review articles¹⁻³ have appeared on the topic, notably by Russian authors. Polymers composed solely of aromatic rings tend to be brittle and rather intractable, and hence attention has been directed to the introduction of flexible linkages into the chain together with the aromatic groups. We have reported earlier on aromatic polyamides⁴ and poly(phenylene oxides),⁵ containing $-\text{NHCO}-$ and $-\text{O}-$ linkages, respectively. In the present paper thermal stability results are cited for polymers containing linkages such as $-\text{CH}_2-$, $-\text{CH}_2-\text{CH}_2-$, $-\text{NH}-$, $-\text{CO}-$, $-\text{SO}_2-$, $-\text{NHCOCONH}-$, $-\text{NHCSNH}-$, $-\text{NHSO}_2-$, and $-\text{SO}_2\text{O}-$, either alone or in combination. Preliminary results on some of the $-\text{CH}_2-$ and $-\text{CH}_2\text{CH}_2-$ linked polymers were given at the Society of Chemical Industry symposium on thermal degradation of polymers.⁶

EXPERIMENTAL

Materials

The polymers examined were prepared by Dr. J. H. Golden of the Explosives Research and Development Establishment, Waltham Abbey, and by Dr. A. Kutner of Queen Mary's College, London University. The majority of the materials containing $-\text{CH}_2-$ and $-\text{CH}_2\text{CH}_2-$ links were

TABLE

		Elemental analyses	
No.	Polymer unit	Linkages between aromatic nuclei	Elements content calculated on
1	<i>p</i> -Phenylene	Single bond	$[C_6H_4]_nCl_2$
2	<i>m</i> -Phenylene	"	$[C_6H_4]_{10}Cl_2$
3	<i>p,p'</i> -Diphenylene methylene	Single bond and —CH ₂ —	$[(C_6H_4)_2CH_2]_{10}Br_2$
4	<i>p</i> -2,5-Dimethyl phenylene methylene	—CH ₂ —	$[C_8H_2(CH_3)_2CH_2]_{12}Cl$
5	<i>p</i> -2,3,5,6-Tetramethyl phenylene methylene	"	$[C_8(CH_3)_4CH_2]_2Cl$
6	<i>p</i> -Phenylene ethylene (lithium route)	—CH ₂ CH ₂ —	$[C_8H_4CH_2CH_2]_{77}Br_2$
7	<i>p</i> -Phenylene ethylene (pyrolysis route) ^a	"	$-(C_8H_4CH_2CH_2)-$
8	<i>p</i> -2,5-Dimethoxyphenylene ethylene	"	$-(C_8H_4[CH_3O]_2CH_2CH_2)-$
9	<i>p</i> -2,3,5,6-Tetramethyl phenylene ethylene	"	$[C_8(CH_3)_4CH_2CH_2]_{100}Cl_2$
10	2,6-Naphthylene ethylene	"	$[C_{10}H_6CH_2CH_2]_{21}Br_2$
11	9,10-Anthrylene ethylene	"	$-(C_{14}H_8CH_2CH_2)-$
12	<i>p</i> -Phenylene imine	—NH—	$HO[C_6H_4NH]_6C_6H_4OH$
13	From <i>p</i> -phenylenediamine and 2,4-dichloroquinazoline ^a	"	$H[NHC_6H_4NH(C_6H_4N_2)]_3Cl$
14	<i>p,p'</i> -Diphenylene- <i>N,N'</i> -oxamide	Single bond and —NHCOCONH—	$-(C_6H_4C_6H_4NHCOCONH)-$
15	<i>p,p'</i> -Diphenylene- <i>N,N'</i> -thiourea	Single bond and —NHCSNH—	$NH_2[C_6H_4C_6H_4NHCSNH]_4C_6H_4C_6H_4NH_2$
16	Phenylene carbonyl	—CO—	$H[C_6H_4CO]_{15}OH$
17	Naphthylene carbonyl	"	$H[C_{10}H_6CO]_7OH$
18	From terephthalyl chloride and naphthalene	—CO—	$H[C_{10}H_6COC_6H_4CO]_6C_{10}H_7$
19	From terephthalyl chloride and fluorene	"	$H[C_{13}H_9COC_6H_4CO]_6OH$
20	From terephthalyl chloride and dibenzofuran	"	$H[(C_{12}H_8O)COC_6H_4CO]_{12}H_7O$
21	From terephthalyl chloride and dibenzthiophene	"	$H[(C_{12}H_8S)COC_6H_4CO]_2C_{12}H_7S$
22	From terephthalyl chloride and phenoxathiin	"	$H[(C_{13}H_8OS)COC_6H_4CO]_2C_{12}H_7OS$
23	From 2,7-fluorene disulfonyl chloride and naphthalene ^a	—SO ₂ —	$-(C_{10}H_6SO_2C_{10}H_6SO_2)-$
24	From 2,7-fluorene disulfonyl chloride and dibenzofuran	"	$H[(C_{12}H_8O)SO_2C_{12}H_8SO_2]_2C_{12}H_7O$
25	From 2,7-fluorene disulfonyl chloride and dibenzthiophene	"	$H[(C_{12}H_8S)SO_2C_{12}H_8SO_2]_2C_{12}H_7S$
26	From 2,7-fluorene disulfonyl chloride and phenoxathiin	"	$-(C_{13}H_8OS)SO_2C_{12}H_8SO_2-$

I

of polymers

	C content, %		H content, %		Br content, %		Cl content %		N content, %		S content, %		O content, %	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
1	80.6	79.8	5.2	4.4					15.7					
2	89.0	89.2	5.5	5.0					5.9					
3	88.5	88.6	5.9	5.7	5.7	5.7								
4	89.3	89.3	8.3	8.3					2.4					
5	89.7	88.0	9.7	9.3			2.6	2.6						
6	90.7	90.4	7.5	7.6	2.0	2.0								
7	88.3	92.3	7.3	7.7										
8	73.0	73.2	7.6	7.3										
9	87.9	89.6	9.1	10.0			0.34	0.34						
10	92.5	92.3	6.3	6.4	1.6	1.3								
11	94.4	94.1	6.0	5.9										
12	75.5	76.5	5.3	5.5					12.5	12.4				
13	64.0	65.0	3.9	4.2			8.9	9.1	18.3	21.7				
14	69.9	70.6	5.6	4.2					10.9	11.8				
15	70.4	70.6	4.9	4.8					12.6	12.9	11.2	11.8		
16	79.8	79.8	3.9	3.9									15.9	16.2
17	84.0	84.3	3.9	4.0									11.7	11.6
18	84.5	84.8	5.0	4.1									10.5	11.0
19	82.9	83.9	4.8	4.2									11.3	12.0
20	82.5	82.4	4.7	3.9									12.5	13.7
21	77.0	76.8	4.1	3.4							11.5	11.8	7.7	7.9
22	72.5	72.6	3.6	3.2							10.7	10.8	13.2	13.4
23	65.5	66.0	3.3	3.3							12.4	15.3	15.6	15.3
24	68.9	68.6	3.7	3.3							11.7	11.8	17.6	16.2
25	64.6	65.0	3.2	3.1							18.9	19.9	11.9	12.0
26	61.1	61.2	3.4	2.9							19.0	19.6	16.6	16.3

(continued)

TABLE

Elemental analyses

No.	Polymer unit	Linkages between aromatic nuclei	Elements content calculated on
27	From 1,5-naphthalene disulfonyl chloride and dibenzofuran	"	$H[(C_{12}H_8O)SO_2C_{10}H_6SO_2]_n C_{12}H_7O$
28	From 1,5-naphthalene disulfonyl chloride and dibenzthiophene	"	$\{-(C_{12}H_6S)SO_2C_{10}H_6SO_2-\}$
29	From 2,7-dibenzofuran disulfonyl chloride and hydroquinone	$-SO_2O-$	$H[OC_6H_4OSO_2(C_{12}H_8O)SO_2]_n OC_6H_4OH$
30	From 2,7-dibenzofuran disulfonyl chloride and <i>p</i> -phenylenediamine ^a	$-SO_2NH-$	$H[HNC_6H_4NHSO_2(C_{12}H_8O)SO_2]_n NHC_6H_4NH_2$
31	<i>p</i> -Phenylene ethylene <i>p</i> -phenylene oxide	$-CH_2CH_2-$ and $-O-$	$[C_8H_4CH_2CH_2C_6H_4O]_n Br_2$
32	<i>p</i> -Phenylene ethylene <i>p</i> -phenylene sulfone	$-CH_2CH_2-$ and $-SO_2-$	$\{-(C_8H_4CH_2CH_2C_6H_4SO_2)-\}$
33	From terephthalyl chloride and diphenyl ether	$-CO-$ and $-O-$	$H[C_6H_4OC_6H_4COC_6H_4CO]_{10}OH$
34	From 4,4'-diphenyl ether disulfonyl chloride and diphenyl ether	$-SO_2-$ and $-O-$	$H[C_6H_4OC_6H_4SO_2]_n C_6H_4OC_6H_5$
35	From 4,4'-diphenyl ether disulfonyl chloride and naphthalene ^a	"	$C_{12}H_7SO_2C_6H_4OC_6H_4SO_2C_{10}H_7$
36	From 4,4'-diphenyl ether disulfonyl chloride and fluorene	"	$H[C_{12}H_8SO_2C_6H_4OC_6H_4SO_2]_n C_{12}H_9$
37	From 4,4'-diphenyl ether disulfonyl chloride and dibenzofuran	$-SO_2-$ and $-O-$	$(C_{12}H_7O)SO_2C_6H_4OC_6H_4SO_2(C_{12}H_7O)$
38	From 4,4'-diphenyl ether disulfonyl chloride and dibenzthiophene	"	$H[(C_{12}H_6S)SO_2C_6H_4OC_6H_4SO_2]_n (C_{12}H_7S)$
39	From 2,7-fluorene disulfonyl chloride and diphenyl ether	"	$H[C_6H_4OC_6H_4SO_2C_{10}H_6SO_2]_{10} C_6H_4OC_6H_5$
40	From 1,5-naphthalene disulfonyl chloride and diphenyl ether	"	$H[C_6H_4OC_6H_4SO_2C_{10}H_6SO_2]_n C_6H_4OC_6H_5$
41	From 4,4'-diphenyl ether disulfonyl chloride and <i>p</i> -phenylenediamine	$-NHSO_2-$ and $-O-$	$H[HNC_6H_4NHO_2SC_6H_4OC_6H_4SO_2]_n HNC_6H_4NH_2$
42	From 4,4'-diphenyl ether disulfonyl chloride and <i>m</i> -aminophenol	$-NHSO_2-$ and $-SO_2O-$ and $-O-$	$H[HNC_6H_4OSO_2C_6H_4OC_6H_4SO_2]_n NHC_6H_4OH$

^a Incomplete elemental analysis.

I (continued)

of polymers

	C content, %		H content, %		Br content, %		Cl content, %		N content, %		S content, %		O content, %	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
27	64.0	64.1	3.6	3.0							15.9	14.4	18.0	18.5
28	60.9	60.6	3.1	2.8							17.1	22.0	11.2	14.7
29	54.7	54.7	3.3	2.7							14.2	14.6	28.1	28.0
30	55.3	55.4	4.4	3.6					9.1	9.2	9.1	14.1	17.8	17.6
31	82.9	83.0	6.1	6.0	3.2	3.2								
32	68.2	68.8	4.9	5.0							13.2	13.1		
33	79.2	79.5	4.6	4.0									16.5	16.4
34	68.9	68.1	3.9	4.1							12.0	10.1	16.9	17.7
35	68.9	69.7	3.9	4.0							12.3	11.6	11.9	14.5
36	69.2	69.6	4.1	3.9							12.4	11.8	13.8	14.7
37	71.2	68.7	4.2	3.3							8.4	10.2	16.2	17.8
38	60.2	61.5	3.6	3.0							18.7	19.9	15.6	15.5
39	65.0	65.9	4.4	3.6							13.0	13.4	17.0	17.1
40	63.7	64.2	3.8	3.5							14.0	14.0	18.1	18.2
41	54.5	54.5	4.4	3.7					7.4	8.2	14.6	14.9	18.5	18.6
42	54.3	54.2	3.6	3.4					3.5	4.0	15.3	15.1	22.9	23.4

prepared by reaction of phenyllithium with the requisite halogenomethyl or di(halogenomethyl) aromatic compounds.^{7,8} Most of the other polymers were formed by condensation reactions in anhydrous hydrofluoric acid.⁹ Elemental analyses of the polymers are given in Table I and molecular weights, which are calculated from these, solubilities, and softening temperatures in Table II.

Apparatus and Experimental Procedure

Weight loss measurements in vacuum were made on 8–10 mg. samples by use of a sensitive quartz spring balance, which has been fully described previously.⁶ Experiments were either done isothermally or at a rate of temperature rise of 3°C./min.

RESULTS AND DISCUSSION

Form of Weight Loss Curves

The curves of weight loss versus time at temperature for the polymers examined isothermally fall into two groups. In the first group there was an initial very rapid loss in weight, largely occurring during the heating-up period, followed by stabilization of the residues, or a very slow rate of breakdown. This behavior has been observed previously for polyacrylonitrile,¹⁰ copolymers of perfluorocyclohexa-1,3-diene and butadiene,⁵ and poly(phenylene oxides).⁵ It is possible with the polymers under consideration that breakdown resulted in the formation of fused ring structures. The second group of polymers was characterized by a much more gradual loss in weight, although even with these, stabilization sometimes occurred at high weight loss values. Division of the polymers into the two groups is shown in Table III. There is no clear-cut explanation for the difference in behavior of the individual polymers, although with the exception of the tetramethylphenylene ethylene polymer, all those materials containing the ethylene moiety are in group 2.

A slight difference was observed with the two poly(*p*-phenylene ethylene) samples. That prepared by pyrolysis of *p*-xylene showed a high rate of weight loss from the start of the experiment, whereas in the case of that prepared by reaction of phenyllithium and *p*-bisbromomethylbenzene the rate increased gradually to a maximum value. Madorsky had earlier reported¹¹ a similar result for the pyrolytic product.

Relative Thermal Stabilities

Quantitative Results. The relative thermal stabilities of the different polymers have been compared by plotting the loss in weight after an arbitrary time (2 hr.) at temperature against temperature. For polymers in group 1, stabilization had normally occurred within 2 hr. of the start of the experiment, and this figure was therefore taken as the weight loss after 2 hr. at constant temperature. For polymers in group 2, the loss in weight

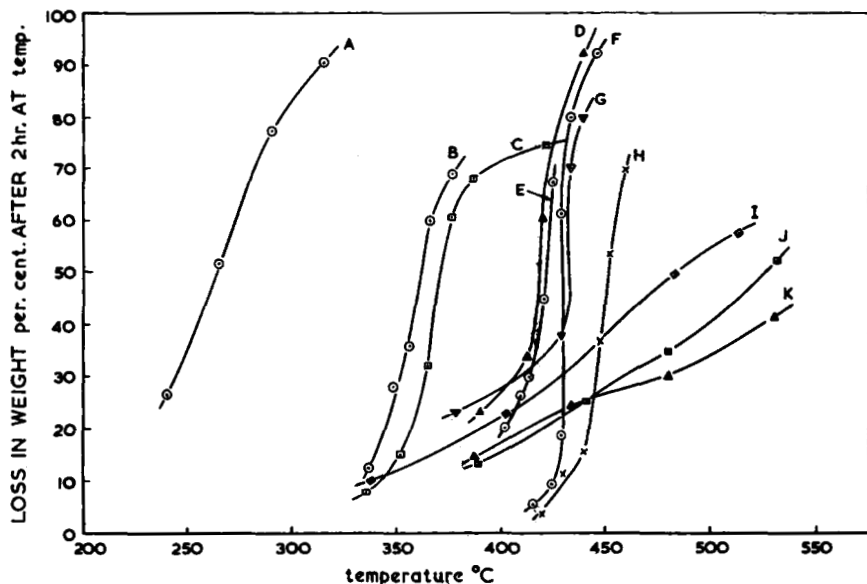


Fig. 1. Comparison of thermal stabilities of various $-\text{CH}_2-$ and $-\text{CH}_2\text{CH}_2-$ linked polymers: (A) poly(*p*-2,3,5,6-tetramethylphenylene methylene); (B) poly(9,10-anthrylene ethylene); (C) poly(*p*-2,5-dimethoxyphenylene ethylene); (D) poly(*p*-2,5-dimethylphenylene methylene); (E) poly(*p*-phenylene ethylene), pyrolysis route; (F) poly(*p*-phenylene ethylene), lithium route; (G) poly(*p*-2,3,5,6-tetramethylphenylene ethylene); (H) poly(2,6-naphthylene ethylene); (I) poly(*p,p'*-diphenylene methylene); (J) poly-*m*-phenylene; (K) poly-*p*-phenylene.

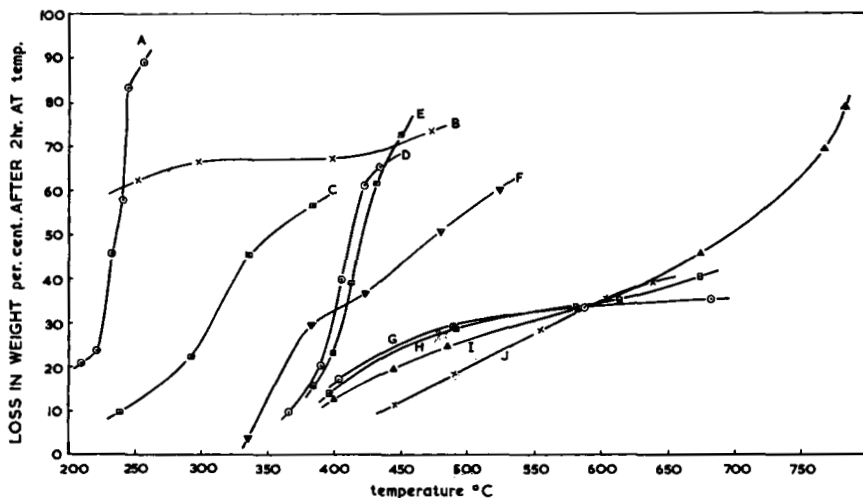


Fig. 2. Comparison of thermal stabilities of aryl polymers linked by various groups: (A) poly(*p,p'*-diphenylene-*N,N'*-thiourea); (B) poly(naphthylene carbonyl); (C) poly(*p,p'*-diphenylene-*N,N'*-oxamide); (D) poly(*p*-phenylene ethylene *p*-phenylene sulfone); (E) poly(*p*-phenylene ethylene *p*-phenylene oxide); (F) poly-*p*-phenylene-imine; (G) polymer from 2,7-fluorenedisulfonyl chloride and diphenyl ether; (H) polymer from terephthalyl chloride and naphthalene; (I) poly(phenylene carbonyl); (J) polymer from terephthalyl chloride and fluorene.

TABLE II.—Molecular Weight, Solubility, and Softening Point of Polymers

Polymer unit	Molecular weight	Solubility	Softening temperature, °C.
<i>p</i> -Phenylene	450?	Sparingly soluble in high boiling solvents (diphenyl, diphenyl ether)	>400
<i>m</i> -Phenylene	1,200?	Solubility less than that of <i>p</i> -derivative	>400
<i>p,p'</i> -Diphenylene methylene	2,800	Appreciably soluble in high boiling solvents	>400
<i>p</i> -2,5-Dimethylphenylene methylene	1,450?	Partially soluble in aromatic solvents	225–230
<i>p</i> -2,3,5,6-Tetramethylphenylene methylene	1,350	Soluble in nitrobenzene, diphenyl	255
<i>p</i> -Phenylene ethylene (lithium route)	8,150	Practically insoluble	Softens at 250°C.; no flow
<i>p</i> -Phenylene ethylene (pyrolysis route)	—	Insoluble in organic solvents	>400
<i>p</i> -2,5-Dimethoxyphenylene ethylene	—	Soluble in bromoform, bromobenzene, nitrobenzene	215
<i>p</i> -2,3,5,6-Tetramethylphenylene ethylene	20,850	Practically insoluble	Shrinks and becomes yellow at 300°C.; softens at 480°C.; no flow
2,6-Naphthylene ethylene	12,650	Insoluble in organic solvents	>400
9,10-Anthrylene ethylene	—	Insoluble in organic solvents	>400
<i>p</i> -Phenyleneimine	550	Very slightly soluble in organic solvents; soluble in conc. H ₂ SO ₄ , formic acid, phenols	>400
From <i>p</i> -phenylenediamine and 2,4-dichloroquinazoline	750	Insoluble in organic solvents	>400
<i>p,p'</i> -Diphenylene- <i>N,N'</i> -oxamide	—	Slightly soluble in benzyl benzoate; soluble in conc. H ₂ SO ₄	>400
<i>p,p'</i> -Diphenylene- <i>N,N'</i> -thiourea	1,100	Soluble in conc. H ₂ SO ₄	No softening, but all volatilized by 350°C.
Phenylene carbonyl	1,600	Insoluble in organic solvents; soluble conc. H ₂ SO ₄	>400
Naphthylene carbonyl	1,100	Insoluble in organic solvents	>400
From terephthalyl chloride and naphthalene	1,150	Insoluble in organic solvents; partially soluble in conc. H ₂ SO ₄	>400
From terephthalyl chloride and fluorene	1,200	Soluble in dichloroacetic acid, conc. H ₂ SO ₄	>400

From terephthalyl chloride and dibenzofuran	450	Soluble in dichloroacetic acid, conc. H_2SO_4	>400
From terephthalyl chloride and dibenzthiophene	800	Insoluble in organic solvents; partially soluble in conc. H_2SO_4	>400
From terephthalyl chloride and phenoxathiin	1, 200	Insoluble in organic solvents; partially soluble in conc. H_2SO_4	>400
From 2,7-fluorene disulfonyl chloride and naphthalene	—	Soluble in dichloroacetic acid, conc. H_2SO_4	>400
From 2,7-fluorene disulfonyl chloride and dibenzofuran	1, 100	Soluble in dichloroacetic acid, conc. H_2SO_4	280-310
From 2,7-fluorene disulfonyl chloride and dibenzthiophene	1, 600	Partially soluble in dichloroacetic acid; soluble in conc. H_2SO_4	290-310
From 2,7-fluorene disulfonyl chloride and phenoxathiin	—	Partially soluble in dichloroacetic acid; soluble in conc. H_2SO_4	>400
From 1,5-naphthalene disulfonyl chloride and dibenzofuran	3, 100	Insoluble in organic solvents	>400
From 1,5-naphthalene disulfonyl chloride and dibenzthiophene	—	Insoluble in organic solvents	>400
From 2,7-dibenzofuran disulfonyl chloride and hydroquinone	1, 300	Insoluble in organic solvents	>400
From 2,7-dibenzofuran disulfonyl chloride and <i>p</i> -phenylenediamine	900	Insoluble in organic solvents	>400
<i>p</i> -Phenylene ethylene <i>p</i> -phenylene oxide	5, 050	Soluble in chloroform, bromoform	150
<i>p</i> -Phenylene ethylene <i>p</i> -phenylene sulfone	—	Insoluble in organic solvents	Softens at 225-230°C.; no flow; becomes "rubbery" at higher temperatures
From terephthalyl chloride and diphenyl ether	3, 000	Soluble in dichloroacetic acid, conc. H_2SO_4	>400
From 4,4'-diphenyl ether disulfonyl chloride and diphenyl ether	650	Partially soluble in dichloroacetic acid; soluble in conc. H_2SO_4	>400

(continued)

TABLE II (continued)

Polymer unit	Molecular weight	Solubility	Softening temperature, °C.
From 4,4'-diphenyl ether disulfonyl chloride and naphthalene	550	Soluble in dichloroacetic acid, conc. H ₂ SO ₄	>400
From 4,4'-diphenyl ether disulfonyl chloride and fluorene	1,100	Partially soluble in dichloroacetic acid; soluble in conc. H ₂ SO ₄	>400
From 4,4'-diphenyl ether disulfonyl chloride and dibenzofuran	650	Partially soluble in dichloroacetic acid, conc. H ₂ SO ₄	280
From 4,4'-diphenyl ether disulfonyl chloride and dibenzothiophene	2,550	Soluble in dichloroacetic acid, conc. H ₂ SO ₄	170-220
From 2,7-fluorene disulfonyl chloride and diphenyl ether	4,750	Partially soluble in dichloroacetic acid; soluble in conc. H ₂ SO ₄	>400
From 4,5-naphthalene disulfonyl chloride and diphenyl ether	2,300	Insoluble	300
From 4,4'-diphenyl ether disulfonyl chloride and <i>p</i> -phenylenediamine	1,700	Insoluble in organic solvents	260-280
From 4,4'-diphenyl ether disulfonyl chloride and <i>m</i> -aminophenol	2,100	Insoluble in organic solvents	150-155

TABLE III
Type of Isothermal Weight Loss Curve Shown by Polymers

Group 1 ^a	Group 2 ^b
<i>p</i> -Phenylene	<i>p</i> -Dimethylphenylene methylene
<i>m</i> -Phenylene	<i>p</i> -Phenylene ethylene (lithium route)
<i>p,p'</i> -Diphenylene methylene	<i>p</i> -Phenylene ethylene (pyrolysis route)
<i>p</i> -2,3,5,6-Tetramethyl phenylene methylene	<i>p</i> -2,5-Dimethoxyphenylene ethylene
<i>p</i> -2,3,5,6-Tetramethyl phenylene ethylene	2,6-Naphthylene ethylene
<i>p</i> -Phenyleneimine	9,10-Anthrylene ethylene
<i>p,p'</i> -Diphenylene- <i>N,N'</i> -oxamide	<i>p,p'</i> -Diphenylene- <i>N,N'</i> -thiourea
Phenylene carbonyl	<i>p</i> -Phenylene ethylene <i>p</i> -phenylene oxide
Naphthylene carbonyl	<i>p</i> -Phenylene ethylene <i>p</i> -phenylene sulfone
From terephthalyl chloride and naphthalene	
From terephthalyl chloride and fluorene	
From 2,7-fluorene disulfonyl chloride and diphenyl ether	

^a Characterized by a very rapid initial loss in weight, followed by stabilization, or a very slow rate of breakdown.

^b Characterized by a much more gradual loss in weight with time at temperature; stabilization may occur at high weight loss values.

was expressed as a percentage of the amount of polymer remaining when constant temperature was attained, thus allowing for any variations which may have occurred during the heating-up period. The results are given in Figures 1 and 2, and in Table IV the polymers are listed in order of thermal stability based on the temperature at which 50% weight loss would occur in 2 hr. It is evident that the most stable of the polymers on a weight-loss basis were those linked by carbonyl groups, though the poly(naphthylene carbonyl) was very much an exception. This material volatilized to a considerable extent at temperatures as low as 250°C. but showed little further degradation if the temperature was raised to values approaching 500°C. On the basis of these results, it is suspected that this particular polymer must have contained a large proportion of low molecular weight material. The next most stable polymers were the simple unsubstituted *meta* and *para* polyphenylenes. The stability of these is, if anything, less than that of the *meta* and *para* poly(phenylene oxides) previously examined.⁵ This is in contrast to the aliphatic series, polyethylene, polypropylene, poly(ethylene oxide), and poly(propylene oxide), where incorporation of oxygen into the backbone of the chain results in a considerable lowering of thermal stability.¹² The least stable of the polymers examined, besides the poly(naphthylene carbonyl) already mentioned, were poly(*p,p'*-diphenylene-*N,N'*-thiourea), poly(*p,p'*-diphenylene-*N,N'*-oxamide), and poly(*p*-2,3,5,6-tetramethylphenylene methylene). Degradation of these commenced in the range 200–250°C. The tetramethylphenylene methylene polymer would not have been expected to degrade at so much lower a temperature than the other polymers

TABLE IV
Order of Thermal Stability of Polymers Examined Quantitatively

Polymer unit	Temperature at which 50% weight loss occurs in 2 hr., °C.
Phenylene carbonyl	700
From terephthalyl chloride and fluorene	>640
From 2,7-fluorene disulfonyl chloride and diphenyl ether	>690
From terephthalyl chloride and naphthalene	>680
<i>p</i> -Phenylene	>540
<i>m</i> -Phenylene	525
<i>p,p'</i> -Diphenylene methylene	485
<i>p</i> -Phenyleneimine	480
2,6-Naphthylene ethylene	450
<i>p</i> -Phenylene ethylene (lithium route)	430
<i>p</i> -2,3,5,6-Tetramethylphenylene ethylene	430
<i>p</i> -Phenylene ethylene <i>p</i> -phenylene oxide	425
<i>p</i> -Phenylene ethylene (pyrolysis route)	420
<i>p</i> -2,5-Dimethylphenylene methylene	420
<i>p</i> -Phenylene ethylene <i>p</i> -phenylene sulfone	415
<i>p</i> -2,5-Dimethoxyphenylene ethylene	375
9,10-Anthrylene ethylene	360
<i>p,p'</i> -Diphenylene- <i>N,N'</i> -oxamide	350
<i>p</i> -2,3,5,6-Tetramethylphenylene methylene	265
<i>p,p'</i> -Diphenylene- <i>N,N'</i> -thiourea	230
Naphthylene carbonyl	<250

of similar structure examined, but molecular models show that this structure is very sterically hindered, there being very little freedom of movement of the benzene nuclei.

The order of stability of the polymers containing ethylene linkages was poly(2,6-naphthylene ethylene) > poly(*p*-phenylene ethylene) > poly(9,10-anthrylene ethylene). The insolubility of these polymers precluded molecular weight determinations (other than from elemental analysis) and characterization, and hence it is difficult to advance reasons for the observed order. The stability of the two poly(*p*-phenylene ethylene) samples were roughly comparable, the polymer produced by pyrolysis of *p*-xylene being less stable at the lower temperatures used.

Qualitative Results. Thermogravimetric analysis figures for polymer samples heated from ambient temperature to 700–800°C. at a rate of approximately 3°C./min. are given in Table V. This table includes an order of relative thermal stability based on a comparison of the weight loss values over the temperature range 300–700°C. Examination of this order shows that it is very little different from that already given for the isothermal experiments. The most stable group of polymers is that linked by carbonyl groups, this being followed by the mixed —SO₂— and —O— linked materials and then by those linked by —SO₂— alone. The unsub-

stituted poly(phenylene oxides)⁵ are intermediate between the —CO— and mixed —SO₂— and —O— linked polymers.

Overall Activation Energies

The overall activation energies for the degradation process have been calculated by a variety of methods from the isothermal results for the polymers in group 2, i.e., those whose weight loss curves showed a gradual increase with time at temperature. It was impracticable with the type of rate curves obtained for polymers in group 1 to form any reliable estimate of the overall activation energy. The results are given in Table VI together with the method of calculation used. Zero order indicates that average rates were used as the rate constants for calculation of the activation energy; first order that values were derived from a plot of log residue versus time; second order that values were derived from a plot of reciprocal of the residue versus time. Initial rate indicates that a plot of rate of volatilization, expressed as a function of the original weight of material, except in the case of poly-*p,p'*-diphenylene-*N,N'*-thiourea where the rate was expressed as a percentage of the residue, versus the percentage volatilized was extrapolated to zero weight loss and the apparent initial rates used; maximum rate is self-explanatory; specific rate indicates that the rate of volatilization at a specific per cent volatilization (10, 20, or 30%) was taken for each temperature. The different methods of calculation give values with a maximum scatter of 7 kcal./mole.

The result for poly(*p*-phenylene ethylene) prepared by pyrolysis of *p*-xylene is close to that (73 kcal./mole) quoted by Madorsky¹³ for a similar polymer. The higher value of the activation energy obtained for the sample prepared by the lithium route may be because the material is less highly branched. For the thermal degradation of a soluble poly(*p*-phenylene ethylene) in solution, Schaeffgen¹⁴ showed that decomposition was by a first-order random cleavage mechanism with an activation energy of 58 kcal./mole. All these values are much higher than the value of 48 kcal./mole determined for the gaseous decomposition of dibenzyl.¹⁵

The overall activation energies for degradation of the poly(2,6-naphthylene ethylene) and poly(9,10-anthrylene ethylene) are considerably lower than those for poly(*p*-phenylene ethylene) and for polymethylene (73 kcal./mole).¹³ They are more akin to that of a branched polyethylene (64 kcal./mole).¹³

CONCLUSIONS

Although the molecular weight of most of the materials examined was low, some of them possessed very good thermal stability in vacuum. The results indicate that aryl polymers linked by groups such as —CO—, —O—, and —SO₂— have stabilities superior to that of poly-*p*-phenylene and poly-*m*-phenylene. Unfortunately, with the particular aromatic nuclei concerned, the presence of these linkages did not confer the desired degree

From 2,7-fluorene disulfonyl chloride and dibenzofuran	300	—	1	17	25	38	39	—	16
From 2,7-fluorene disulfonyl chloride and dibenzthiophene	260	—	3	19	33	37	37	40	18
From 2,7-fluorene disulfonyl chloride and phenoxathiin	240	—	6	17	26	31	35	37	15
From 1,5-naphthalene disulfonyl chloride and dibenzofuran	220	—	5	19	26	30	33	—	13 =
From 1,5-naphthalene disulfonyl chloride and dibenzthiophene	200	—	8	35	43	48	49	—	25
From 2,7-dibenzofuran disulfonyl chloride and hydroquinone	260	—	3	8	14	25	31	33	6
From 2,7-dibenzofuran disulfonyl chloride and <i>p</i> -phenylenediamine	230	—	6	29	41	46	50	57	24
<i>p</i> -Phenylene ethylene <i>p</i> -phenylene oxide	250	—	2	4	68	76	83	—	30
<i>p</i> -Phenylene ethylene <i>p</i> -phenylene sulfone	270	—	3	6	57	72	74	—	27
From terephthalyl chloride and diphenyl ether	250	—	6	18	27	44	48	52	21
From 4,4'-diphenyl ether disulfonyl chloride and diphenyl ether	290	—	2	9	21	35	38	—	11
From 4,4'-diphenyl ether disulfonyl chloride and naphthalene	260	—	3	13	21	35	39	41	12
From 4,4'-diphenyl ether disulfonyl chloride and fluorene	240	—	5	12	21	37	38	—	13 =
From 4,4'-diphenyl ether disulfonyl chloride and dibenzofuran	240	—	2	8	18	31	33	38	10
From 4,4'-diphenyl ether disulfonyl chloride and dibenzthiophene	200	—	21	50	53	72	76	77	33
From 2,7-fluorene disulfonyl chloride and diphenyl ether	260	—	2	7	14	21	25	26	3
From 1,5-naphthalene disulfonyl chloride and diphenyl ether	240	—	6	22	27	40	43	—	20
From 4,4'-diphenyl ether disulfonyl chloride and <i>p</i> -phenylenediamine	230	—	11	55	67	73	77	80	34
From 4,4'-diphenyl ether disulfonyl chloride and <i>m</i> -aminophenol	200	—	4	28	34	39	43	47	22

TABLE VI
Overall Activation Energies for Degradation of Polymers

Polymer unit	Activation energy, kcal./mole	Method of calculation*
<i>p</i> -2,5-Dimethylphenylene methylene	52	Zero order
	59	First order
	55	Initial rates
<i>p</i> -Phenylene ethylene (lithium route)	E_{10}	} Specific rates
	E_{20}	
	E_{30}	
<i>p</i> -Phenylene ethylene (pyrolysis route)	81	Zero order
	76	Maximum rates
<i>p</i> -2,5-Dimethoxyphenylene ethylene	55	Zero order
	54	Initial rates
2,6-Naphthylene ethylene	48	Maximum rates
9,10-Anthrylene ethylene	59	Second order
	60	Initial rates
<i>p-p'</i> -Diphenylene- <i>N,N'</i> -thiourea	52	Initial rates
<i>p</i> -Phenylene ethylene <i>p</i> -phenylene oxide	(43)	Zero order
	47	First order
	40	Initial rates
<i>p</i> -Phenylene ethylene <i>p</i> -phenylene sulfone	(48)	Zero order
	46	First order
	51	Initial rates

* See text.

of tractability, as most of the polymers showed no signs of softening below 400°C. and were soluble only in liquids such as concentrated sulphuric acid. Substitution in the aromatic nuclei would probably lead to more amenable properties, but only at the expense of thermal stability. For reasonable mechanical strength these low molecular weight polymers would need to be linked together by use of a technique such as the Friedel-Crafts reaction.¹⁶

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Résumé

On a étudié, par une méthode de perte de poids, la dégradation thermique sous vide de polymères contenant des noyaux aromatiques ou hétérocycliques liés par des groupes différents. Les plus stables des polymères examinés sont ceux contenant les liens $-\text{CO}-$, $-\text{SO}_2-$ et $-\text{O}-$ mélangés, ou $-\text{SO}_2-$. La stabilité de ces derniers est supérieure ou comparable au poly(*p*-phénylène) et au poly(*m*-phénylène). Les combinaisons particulières de noyaux aromatiques et de groupes liés employés, ne provoquent pas une amélioration à la traction quoique plusieurs des polymères, de bas poids moléculaires, soient insolubles et infusibles. La substitution dans les noyaux aromatiques peut améliorer le pouvoir à la traction bien que ce soit au dépens de la stabilité thermique.

Zusammenfassung

Der thermische Abbau von Polymeren mit aromatischen oder heterozyklischen, durch verschiedene Gruppen verknüpften Ringen im Vakuum wurde nach einer Gewichtsverlustmethode untersucht. Die untersuchten stabilisierten Polymeren waren diejenigen mit $-\text{CO}-$, gemischten $-\text{SO}_2-$ und $-\text{O}-$ oder $-\text{SO}_2-$ Brücken. Ihre Stabilität war derjenigen von Poly(*p*-phenylen) und Poly(*m*-phenylen) überlegen oder vergleichbar. Die verwendeten speziellen Kombinationen von aromatischen Kernen und Brückengruppen führten nicht zu verarbeitbaren Stoffen, da die meisten der Polymeren, obgleich niedermolekular, unlöslich und unschmelzbar waren. Durch Substitution im aromatischen Ring könnte die Bearbeitbarkeit, allerdings auf Kosten der thermischen Stabilität, verbessert werden.

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