Thermal Degradation of Poly(phenylene Oxides)

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Synopsis

The thermal degradation in vacuum of a number of halogenated poly(phenylene oxide) polymers has been studied by a weight loss method. In general the thermal stability decreased as the degree of substitution in the phenylene nuclei increased. The chloro derivatives were relatively more stable than the corresponding bromo derivatives. The majority of the polymers showed an initial rapid loss in weight followed by the formation of a highly stable residue. The good thermal stability of the simpler poly(phenylene oxides), coupled with their fusibility and solubility, indicate that they may be useful starting products for the preparation of practical materials.

INTRODUCTION

It has been shown in recent years that polymers composed solely of aromatic rings have high thermal stability. This is probably associated with the complete conjugation of the chain and the considerable delocalization of the π-electrons. Polyphenylenes tend to be brittle and intractable, however, and there has been considerable effort to introduce flexible links (e.g., —CH$_2$—, —O—, —S—) into the chain without loss of thermal stability. The present paper is concerned with the stability in vacuum of a number of poly(phenylene oxides). Preliminary results on some of these polymers have previously been reported.[1]

EXPERIMENTAL

Materials

The polymers examined were prepared by Dr. J. H. Golden of the Explosives Research and Development Establishment, Waltham Abbey, and by Drs. A. N. James, A. Kutner, and P. A. Marr of Queen Mary's College, London University. The preparations involved the decomposition of metal halogenophenoxides[2] and the oxidation of halogenophenols or Ullman condensation.[3-5] Elemental analyses of the polymers are given in Table I and molecular weights, solubilities, and softening temperatures in Table II.

Apparatus and Experimental Procedure

The apparatus and experimental procedure adopted for weight loss measurements in vacuum have been fully described previously.[1] In a

TABLE I
Elemental Analyses of Polymers

Polymer unit	Elements content calculated on	C content, % Found	C content, % Calc.	H content, % Found	H content, % Calc.	F content, % Found	F content, % Calc.	Cl content, % Found	Cl content, % Calc.	Br content, % Found	Br content, % Calc.	I content, % Found	I content, % Calc.	N content, % Found	N content, % Calc.
p-Phenylene oxide (1)	Br[C6H4O]38H	77.3	77.4	4.4	4.3	—	—	—	—	1.0	1.0	—	—	—	—
" (2)	[C6H4O]	79.9	78.3	4.0	4.3	—	—	—	—	—	—	—	—	—	—
m-Phenylene oxide	Br[C6H4O]10H	74.9	74.8	3.9	4.2	—	—	—	—	4.4	4.4	—	—	—	—
p,p'-Diphenylene oxide	[C12H8O]	80.4	85.7	4.2	4.8	—	—	—	—	8.8	—	—	—	—	—
p-2-Chlorophenylene oxide	[C6H3ClO]	58.8	57.0	2.1	2.4	—	—	27.1	28.0	—	—	—	—	—	—
p-2-Bromophenylene oxide	[C6H3BrO]	44.9	42.1	2.1	1.8	—	—	—	—	43.8	46.7	—	—	—	—
p-2,5-Dichlorophenylene oxide	[C6H4Cl2O]	47.5	44.9	1.1	1.7	—	—	43.4	43.7	—	—	—	—	—	—
p-2,6-Dichlorophenylene oxide	[C6H3Cl2O]	45.0	44.7	1.4	1.2	—	—	45.3	44.1	—	—	—	—	—	—
p-2,6-Dibromophenylene oxide	[C6H2Br2O]	30.2	28.8	1.2	0.8	—	—	—	—	65.1	64.0	—	—	—	—
p-2,3,6-Trichlorophenylene oxide	[C6HCl3O]	37.1	36.3	0.4	0.8	—	—	54.7	54.6	—	—	—	—	—	—
p-2,3,5,6-Tetrachlorophenylene oxide	[C6Cl4O]	29.5	31.3	0.03	—	—	—	60.8	61.7	—	—	—	—	—	—
p-2,3,5,6-Tetrabromophenylene oxide	[C6Br4O]	20.1	17.7	0.7	—	—	—	—	—	76.1	78.4	—	—	—	—
[(p-Phenylene oxide) (o-4-bromo-phenylene oxide)]	[(C6H4O)(C6H3BrO)4]	44.4	46.4	2.2	2.2	—	—	—	—	40.2	41.2	—	—	—	—
[(p-2,6-Dibromophenylene oxide) (o-4,6-dibromophenylene oxide)]	[C6H2Br2O]	30.4	28.8	1.1	0.8	—	—	—	—	66.0	64.0	—	—	—	—
o-6-Bromo-4-phenyl phenylene oxide	[C12H7BrO]	58.4	58.3	2.7	2.8	—	—	—	—	32.0	32.4	—	—	—	—
o-6-Bromo-4-p-chlorophenyl phenylene oxide	[C12H6ClBrO]	51.1	51.2	2.7	2.1	—	—	12.1	12.6	28.1	28.4	—	—	—	—
[(o-6-Fluorophenylene oxide) (p-phenylene oxide)]	86% C6H3FO, 14% C6H4O	66.1	67.0	3.2	2.9	15.2	15.2	—	—	—	—	—	—	—	—
[(o-4-Fluorophenylene oxide) (p-phenylene oxide)]	58% C6H3FO, 42% C6H4O	67.1	70.3	2.8	3.3	10.8	10.8	—	—	—	—	—	—	—	—
[(o-6-Bromophenylene oxide) (p-phenylene oxide)]	82% C6H3BrO, 18% C6H4O	44.8	45.6	2.2	2.0	—	—	—	—	42.0	41.7	—	—	—	—
[(o-4-Bromophenylene oxide) (p-phenylene oxide)]	65% C6H3BrO, 35% C6H4O	49.0	50.1	2.5	2.4	—	—	—	—	37.0	36.5	—	—	—	—

Compound														
Monofluoro-difluorophenylene oxide, 80% C_6H_3FO (o- and p-), 20% $C_6H_2F_2O$ (2,6)	59.8	63.5	2.1	2.5	19.8	20.0	—	—	—	—	—	—	—	—
Monofluoro-monobromo(2,4 and 2,6)phenylene oxide, 92% C_6H_2FBrO (2,4 and 2,6), 8% $C_6H_2Br_2O$ (4,6)	35.7	37.1	1.5	1.1	8.9	8.9	—	—	44.6	44.5	—	—	—	—
Monofluoro-monobromo(4,6)/dibromo (2,6) phenylene oxide, 92% C_6H_2FBrO (4,6), 8% $C_6H_2Br_2O$ (2,6)	36.3	37.1	1.3	1.1	8.8	8.9	—	—	44.5	44.5	—	—	—	—
Monofluoro-monoiodo(2,4 and 2,6)/diiodo (4,6) phenylene oxide, 86% C_6H_2FIO (2,4 and 2,6), 14% $C_6H_2I_2O$ (4,6)	33.8	34.3	0.8	0.9	—	—	—	—	—	—	46.8	46.9	—	—
Monofluoro-monoiodo(4,6)/diiodo (2,6) phenylene oxide, 88% C_6H_2FIO (4,6), 12% $C_6H_2I_2O$ (2,6)	32.6	33.0	0.8	0.9	9.8	10.0	—	—	—	—	49.1	49.1	—	—
2,5-Pyrazylene oxide/p-phenylene oxide, $Cl(C_{10}H_6O_2N_2)_{14}H$	62.9	63.7	3.4	3.2	—	—	1.4	1.3	—	—	—	—	14.5	14.8
4,6-Pyrimidylene oxide/p-phenylene oxide, $Cl(C_{10}H_6O_2N_2)_{23}H$	64.1	64.5	3.7	3.2	—	—	0.76	0.76	—	—	—	—	13.1	14.2
4,6-Pyrimidylene oxide/p-2,3,5,6-tetrachlorophenylene oxide, $(C_{10}H_4O_2N_2Cl_4)$	36.7	37.0	0.8	0.6	—	—	44.3	43.8	—	—	—	—	8.1	8.4
2,4-Quinazolylene oxide/p-phenylene oxide, $H(C_{14}H_8O_2N_2)_3C_6H_3O_2$	70.1	70.5	3.5	3.7	—	—	—	—	—	—	—	—	10.6	10.3

TABLE II

Molecular Weights, Solubilities, and Softening Temperatures of Polymers

Polymer unit	Molecular weight[a]	Solubility[b]	Softening temperature, °C.
p-Phenylene oxide (1)	7700 (E)	Insoluble	315
" " (2)	2800 (C)	Soluble	285–290
m-Phenylene oxide	1800 (E)	Insoluble	465 (sinters)
p,p'-Diphenylene oxide	2000 (C)	Soluble	155
p-2-Chlorophenylene oxide	—	Soluble	270–273
p-2-Bromophenylene oxide	—	Soluble	240–245
p-2,5-Dichlorophenylene oxide	—	Soluble	215–220
p-2,6-Dichlorophenylene oxide	9600 (C)	Soluble	190–195
p-2,6-Dibromophenylene oxide	3150 (C)	Soluble	240–245
p-2,3,6-Trichlorophenylene oxide	—	Soluble	230–235
p-2,3,5,6-Tetrachlorophenylene oxide	1450 (C)	Soluble	195–200
p-2,3,5,6-Tetrabromophenylene oxide	—	Soluble	300–310
[(p-Phenylene oxide)(o-4-bromophenylene oxide)]	≫4000	Insoluble	No change up to 500
[(p-2,6-Dibromophenylene oxide)(o-4,6-dibromophenylene oxide)]	2800 (C)	Soluble	210
o-6-Bromo-4-phenylphenylene oxide	1400 (C)	Soluble	265–270
o-6-Bromo-4-p-chlorophenyl phenylene oxide	—	Soluble	310
[(o-6-Fluorophenylene oxide)(p-phenylene oxide)]	3300	Soluble	200–210
[(o-4-Fluorophenylene oxide) (p-phenylene oxide)]	4200	Soluble	210–220
[(o-6-Bromophenylene oxide) (p-phenylene oxide)]	3100 (C)	Soluble	190–200
[(o-4-Bromophenylene oxide) (p-phenylene oxide)]	4200	Soluble	200–210
Monofluoro-difluorophenylene oxide	4900	Soluble	220–230
Monofluoro-monobromo(2,4 and 2,6)/dibromo(4,6)phenylene oxide	—	Soluble	190–200
Monofluoro-monobromo (4,6)/dibromo(2,6) phenylene oxide	2900	Soluble	190–210
Monofluoro-monoiodo(2,4 and 2,6)/diiodo(4,6)phenylene oxide	1200	Soluble	160–170
Monofluoro-monoiodo (4,6)/diiodo(2,6)phenylene oxide	1300	Soluble	170–180
2,5-Pyrazylene oxide/p-phenylene oxide	2600 (E)	Soluble conc. H₂SO₄	>300
4,6-Pyrimidylene oxide/p-phenylene oxide	4700 (E)	Soluble conc. H₂SO₄	>300
4,6-Pyrimidylene oxide/p-2,3,5,6-tetrachlorophenylene oxide	—	Insoluble	>300
2,4-Quinazolylene oxide/p-phenylene oxide	800	—	>400

[a] (E) denotes endgroup analysis; (C) denotes cryoscopic measurements.

[b] Insoluble denotes insolubility in a range of organic solvents, either hot or cold.

number of cases, larger samples of polymer, 30–50 mg., were degraded at
constant temperature for 1 hr. under high vacuum and the gaseous degradation products fractionated into those volatile at room temperature
and those volatile at the temperature of liquid nitrogen. The fractions
were analyzed in a mass spectrometer. X-ray examinations were made of
some of the involatile residues.

RESULTS AND DISCUSSION

Form of Weight Loss Curves

The behavior of most of the polymers examined isothermally was characterized by an initial rapid weight loss followed by stabilization, the percentage volatilization at which this occurred being dependent upon the
temperature of pyrolysis. This stabilization effect may be due to the splitting off of substituents from the aromatic nuclei followed by the formation
of fused ring systems. The residues from the pyrolyses of poly(p-phenylene oxide) at various temperatures were examined by x-ray methods and
the carbon and hydrogen contents also determined. The x-ray measurements indicated that after pyrolysis at 400°C. some features of the original
polymer structure persisted. For a 600°C. pyrolyzate, the arrangement
was completely random, while for a 1000°C. pyrolyzate there was evidence
of the presence of structures containing three to four fused rings and some
slight alignment of these. The elemental analysis of the residue obtained
at 400°C. was very close to that of the original polymer, whereas at temperatures above this there was an increase in the carbon and a decrease in
the hydrogen content. The results were not unequivocal, however, as up
to 6% of the residue remained uncombusted in oxygen.

At the lower temperatures used, poly(p-2,3,6-trichlorophenylene oxide)
and poly(p-2,3,5,6-tetrabromophenylene oxide) showed a much more
gradual loss in weight before stabilization than did the other polyphenylene
oxides.

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 (Figs. 1 and 2). For
the majority of the polymers, stabilization had occurred within 2 hr. from
the start of the experiment, and in these cases no correction was made for
the heating-up period. If, however, stabilization had not occurred within
2 hr., the loss in weight was expressed as a function of the amount of polymer remaining when constant temperature was attained. The polymers
are listed in Table III in order of their thermal stabilities based on the figures, together with the temperature at which 50% weight loss occurred in 2
hr. From Table III it can be seen that the thermal stability tends to decrease as the degree of substitution in the aromatic nuclei increases, i.e.,

the order of stability is poly(phenylene oxide) > monosubstituted poly-(phenylene oxides) > disubstituted poly(phenylene oxides) > trisubstituted poly(phenylene oxides) > tetrasubstituted poly(phenylene oxides). The anomalous behavior of poly(p-2,5-dichlorophenylene oxide) may be due to the presence of the alternative reaction product, 2,3,7,8-tetrachlorodibenz-p-dioxin. This particular polymer sample had a large weight loss (about 60%) at the low temperature of 150°C., followed by little further loss until temperatures greater than 350°C. The latter may therefore mark the true onset of breakdown of the polymer.

TABLE III
Order of Thermal Stability of Poly(phenylene Oxides) Examined Quantitatively

Polymer	Temperature at which 50% weight loss occurs in 2 hr., °C.
Poly(m-phenylene oxide)	40% loss at 610°C.
Poly(p-2-chlorophenylene oxide)	590
Poly(p-phenylene oxide) (1)	33% loss at 515°C.
Poly[(o-4-bromophenylene oxide)(p-phenylene oxide)]	550
Poly(p-2,6-dichlorophenylene oxide)	480
Poly(p-phenylene oxide) (2)	480
Poly(p-2-bromophenylene oxide)	510
Poly(o-6-bromo-4-p-chlorophenylphenylene oxide)	470
Poly(p-2,6-dibromophenylene oxide)	445
Poly(p,p'-diphenylene oxide)	43% loss at 470°C.
Poly[(o-4-fluorophenylene oxide)(p-phenylene oxide)]	455
Poly(p-2,3,6-trichlorophenylene oxide)	425
Poly(o-6-bromo-4-phenylphenylene oxide)	445
Poly[(p-2,6-dibromophenylene oxide)(o-4,6-dibromophenylene oxide)]	425
Poly(p-2,3,5,6-tetrabromophenylene oxide)	380
Poly(p-2,3,5,6-tetrachlorophenylene oxide)	370
Poly(p-2,5-dichlorophenylene oxide)	135

With the exception of the tetrasubstituted polymer, the chloro deriva-tives were more stable than the corresponding bromo derivatives; this probably reflects the greater strength of the C—Cl as compared with the C—Br bond.

Molecular models indicate that the least stable of the polymers are rigid molecules incapable of free rotation about the oxygen atoms.

The two different methods of preparation of poly(p-phenylene oxide) results in samples of differing stability.

Qualitative Results. In some cases isothermal experiments were not carried out, but the weight loss was recorded as a 5–10 mg. sample of poly-mer was heated from ambient temperature to 800°C. at a rate of approxi-mately 3°C./min. The results are summarized in Table IV. Several of the polymers examined isothermally were also treated in a similar manner, for comparison purposes. It can be seen that the weight losses recorded

TABLE IV. Thermogravimetric Analysis Results on Poly(phenylene Oxides)

Polymer	Temperature at which weight loss commences, °C	Total loss in weight, at various temperatures, %						
		200°C.	300°C.	400°C.	500°C.	600°C.	700°C.	800°C.
Poly(m-phenylene oxide)	300	—	—	4	10	23	33	38
Poly(p-phenylene oxide) (1)	290	—	3	8	18	24	31	31
Poly[(o-4-bromophenylene oxide)(p-phenylene oxide)]	260	—	4	14	22	50	61	68
Poly(p-2,6-dichlorophenylene oxide)	430	—	—	—	18	69	76	77
Poly(p-phenylene oxide) (2)	260	—	2	7	18	46	57	61
Poly(o-6-bromo-4-p-chlorophenylphenylene oxide)	360	—	—	4	29	77	89	93
Poly(p,p'-diphenylene oxide)	160	3	13	26	41	52	55	55
Poly[o-6-bromo-4-phenylphenylene oxide]	280	—	3	28	53	64	70	76
Poly[(p-2,6-dibromophenylene oxide)(o-4,6-dibromophenylene oxide)]	200	—	5	24	51	66	78	81
Poly(p-2,3,5,6-tetrachlorophenylene oxide)	280	—	2	22	88	92	98	98
Poly[(o-4-bromophenylene oxide)(p-phenylene oxide)]	150	3	9	20	33	42	49	55
Poly[(o-6-bromophenylene oxide)(p-phenylene oxide)]	170	2	4	14	25	46	60	70
Poly[(o-4-fluorophenylene oxide)(p-phenylene oxide)]a	160	3	6	20	40	43	50	59
Poly[(o-6-fluorophenylene oxide)(p-phenylene oxide)]	180	2	12	25	37	55	63	67
Poly(monofluorodifluorophenylene oxide)	150	3	13	30	38	45	54	76
Poly[monofluoro-monobromo (2,4 and 2,6)/dibromo(4,6)phenylene oxide]a	170	1	6	14	41	61	73	77
Poly[monofluoro-monoiodo (2,4 and 2,6)/diiodo(4,6)phenylene oxide]	150	2	4	32	51	58	62	65
Poly[monofluoro-monobromo (4,6)/dibromo (2,6) phenylene oxide]a	180	1	11	29	49	59	66	70
Poly[monofluoro-monoiodo (4,6)/diiodo (2,6) phenylene oxide]a	150	6	16	34	48	57	63	66
Poly[(4,6-pyrimidylene oxide)(p-2,3,5,6-tetrachlorophenylene oxide)]	270	—	5	14	30	43	49	—
Poly[(2,4-quinazolylene oxide)(p-phenylene oxide)]	240	—	22	36	42	52	58	—
Poly[(4,6-pyrimidylene oxide)(p-phenylene oxide)]	270	—	6	23	61	77	83	—
Poly[(2,5-pyrazylene oxide)(p-phenylene oxide)]	210	—	34	60	74	80	85	—

a Average for several samples.

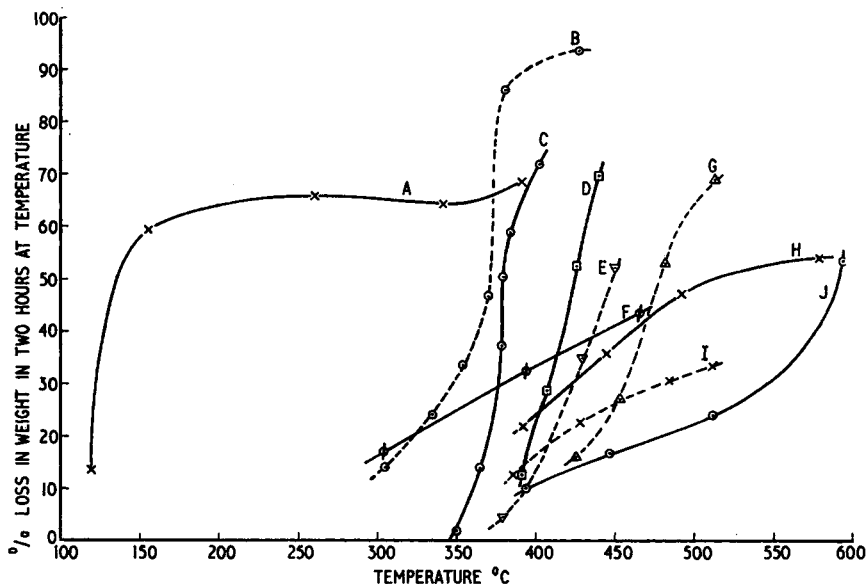Fig. 1. Relative thermal stabilities of poly(phenylene oxides) prepared by decomposition of metal halogenophenoxides: (A) poly(p-2,5-dichlorophenylene oxide); (B) poly-(p-2,3,5,6-tetrachlorophenylene oxide); (C) poly(p-2,3,5,6-tetrabromophenylene oxide); (D) poly(p-2,3,6-trichlorophenylene oxide); (E) poly(p-2,6-dibromophenylene oxide); (F) poly(p,p-diphenylene oxide); (G) poly(p-2,6-dichlorophenylene oxide); (H) poly-(p-2-bromophenylene oxide); (I) poly(p-phenylene oxide); (J) poly(p-2-chlorophenylene oxide).

with rising temperature serve, on the whole, to place the polymers in the same order of relative thermal stability as the isothermal experiments. Single tests carried out in this way may therefore be used with a reasonable amount of confidence as sorting tests for polymers of high thermal stability.

There was little difference in the stability of the polymers prepared by the oxidation of fluorophenols, in fact an "average curve" may be drawn from which the results for all the samples differ very little.

Anomalous behavior compared with the pure poly(phenylene oxide) chains is observed when heterocyclic rings are also incorporated in the chain, since the stability of a pyrimidylene oxide–tetrachlorophenylene oxide polymer appears to be greater than that of an analogous polymer with unsubstituted phenylene units.

Overall Activation Energies

For the majority of the polymers examined isothermally it was impracticable with the type of rate curves obtained to form any reliable estimate of the overall activation energy for the degradation process. The exceptions were poly(p-2,3,6-trichlorophenylene oxide) and poly(p-2,3,5,6-tetrabromophenylene oxide). For these two polymers, the rates of volatilization were taken for a definite fixed conversion (10, 20, or 30%) at a series of
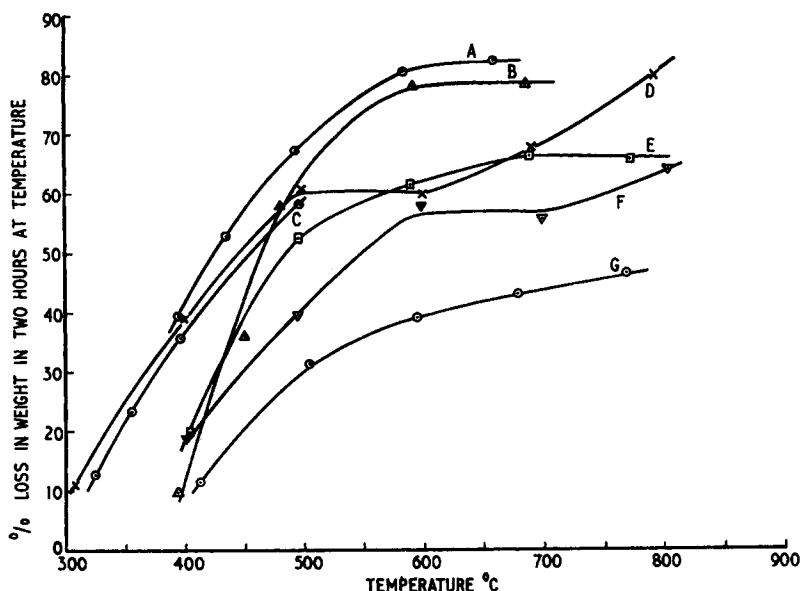
Fig. 2. Relative thermal stabilities of polyphenylene oxides prepared by oxidation of halogenophenols or Ullman condensations: (*A*) poly[(*p*-2,6-dibromophenylene oxide) (*o*-2,6-dibromophenylene oxide)]; (*B*) poly[*o*-6-bromo-4-*p*-chlorophenylphenylene oxide]; (*C*) poly[(*o*-4-fluorophenylene oxide)(*p*-phenylene oxide)]; (*D*) poly[*o*-6-bromo-4-phenylphenylene oxide]; (*E*) poly(*p*-phenylene oxide); (*F*) poly[(*o*-4-bromophenylene oxide)(*p*-phenylene oxide)]; (*G*) poly(*m*-phenylene oxide).

temperatures and used as reaction constants for calculation of an overall activation energy. The values obtained were 51, 51, and 55 kcal./mole and 45, 40, and 43 kcal./mole for the chlorine- and bromine-containing polymers, respectively. The rate equations for the early part of their breakdown may therefore be represented by $k = 10^{12} \exp \{-52,000/RT\}$ and $k = 10^{10} \exp \{-43,000/RT\}$, respectively.

Breakdown Products

The major part of the degradation products from the poly(phenylene oxides) consisted of material volatile at the temperature of pyrolysis but not at room temperature. Examination in a mass spectrometer of the products volatile at room temperature (not more than 4% of the total) showed them to consist of a complex mixture, hence giving little information as to the mechanism of breakdown.

CONCLUSIONS

The unsubstituted or lightly substituted poly(phenylene oxides) possess good thermal stability in vacuum. Their molecular weight is too low to permit reasonable mechanical properties to be expected, but since most of the polymers studied are soluble and possess softening points, the use of a suitable crosslinking agent could very well lead to useful materials.

References

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Résumé

On a étudié la dégradation thermique dans le vide d'un certain nombre d'oxydes de polyphénylène halogéné par une méthode de perte de poids. En général, la stabilité thermique diminue quand le degré de substitution dans les noyaux phénylènes augmente. Les dérivés chlorés sont relativement plus stables que les dérivés bromés correspondants. La majorité des polymères présente une perte de poids initiale rapide suivie par la formation d'un résidu très stable. La bonne stabilité thermique des oxydes de polyphénylènes plus simples ainsi que leur fusibilité et leur solubilité indiquent qu'ils peuvent être des produits de départ utiles à la préparation de matériel pratique.

Zusammenfassung

Der thermische Abbau einer Anzahl halogenierter Polyphenyloxydpolymerer im Vakuum wurde nach einer Gewichtsverlustmethode untersucht. Im allgemeinen nahm die thermische Stabilität mit zunehmendem Substitutionsgrad im Phenylenkern ab. Die Chlorderivate waren verhältnismässig stabiler als die entsprechenden Bromderivate. Die Mehrzahl der Polymeren zeigte einen raschen Anfangsgewichtsverlust, worauf die Bildung eines hochgradig stabilen Rückstands erfolgte. Die gute thermische Stabilität der einfacheren Polyphenylenoxyde zeigt zusammen mit ihrer Sdhmelzbarkeit und Löslichkeit, dass sie brauchbare Ausgangsprodukte für die Darstellung praktisch verwendbarer Stoffe sein können.