

Thermal Degradation in Oxygen of Polymers with Aromatic Rings in the Chain

JOYCE M. LANCASTER and W. W. WRIGHT,
Royal Aircraft Establishment, Farnborough, Hampshire, England

Synopsis

The thermal degradation in oxygen of fifteen polymers containing aromatic rings in the chain has been studied by a weight loss method. The relative thermal stabilities of the different polymers have been determined and, where possible, the overall activation energy for breakdown. The results have been compared with those for samples of the same polymers degraded in vacuum. The most thermally stable of the polymers examined under oxidizing conditions was poly(2,6-dichlorophenylene oxide), with a stability comparable with that of a copolymer of tetrafluoroethylene and hexafluoropropylene.

INTRODUCTION

We have previously reported^{1,2} the results of the thermal degradation in vacuum of a series of polymers containing aromatic rings in the chain. In practice, polymers are much more likely to be used under oxidizing conditions, and the present paper cites data for the thermooxidative breakdown of a representative selection of the polymers previously examined, including those which showed most promise in inert conditions. Results in vacuum and in oxygen are compared.

EXPERIMENTAL

Materials

The fifteen polymers studied were prepared by Golden of the Explosives Research and Development Establishment, Waltham Abbey, and by Kutner of Queen Mary's College, London University. The polymers are listed in Table I. Full details of their elemental analyses, molecular weights, solubilities, and softening temperatures have been given previously.^{1,2}

Apparatus and Experimental Procedure

Weight loss measurements in 300 mm. Hg pressure of oxygen were made on 8-10 mg. samples using a sensitive quartz spring balance and a circulating oxygen system, which have been fully described elsewhere.³ All experiments were carried out isothermally.

TABLE I
List of Polymers Studied

Poly(<i>m</i> -phenylene)
Poly(phenylene carbonyl)
Poly(<i>p</i> -phenylene oxide)
Poly(<i>p</i> -2,6-dichlorophenylene oxide)
Poly(<i>p</i> -2,3,5,6-tetrachlorophenylene oxide)
Poly(<i>p,p'</i> -diphenylene methylene)
Poly(<i>p</i> -phenylene ethylene) (two samples, different methods of preparation)
Poly(<i>p</i> -2,5-dimethylphenylene methylene)
Poly(<i>p</i> -2,3,5,6-tetramethylphenylene ethylene)
Poly(2,6-naphthylene ethylene)
Poly(9,10-anthrylene ethylene)
Condensation product of terephthalyl chloride and fluorene
Condensation product of terephthalyl chloride and naphthalene
Condensation product of 2,7-fluorenedisulphonyl chloride and diphenyl ether

RESULTS AND DISCUSSION

Relative Thermal Stabilities

The relative thermal stabilities of the different polymers have been compared by plotting the percentage loss in weight after an arbitrary time (2 hr.) at constant temperature against temperature. The results are

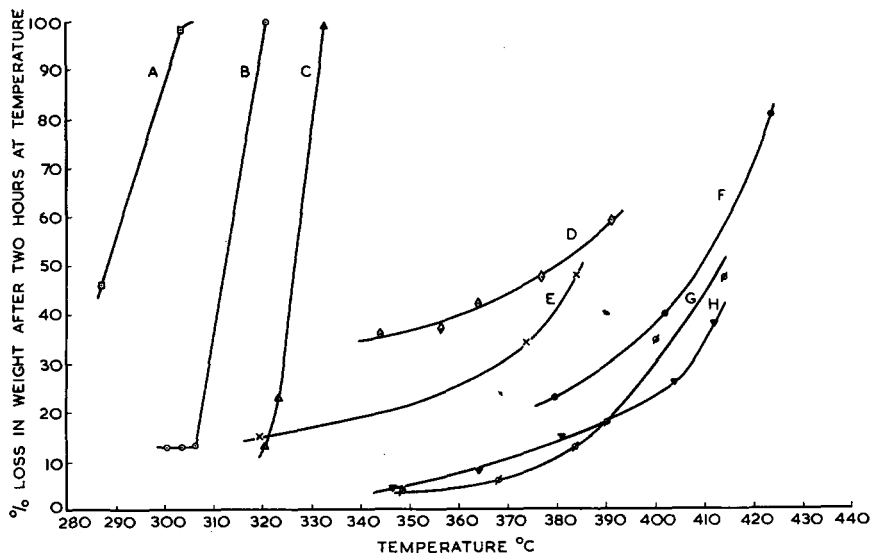


Fig. 1. Comparison of thermal stabilities in oxygen of various $-\text{CH}_2-$ and $-\text{CH}_2-\text{CH}_2-$ linked polymers: (A) poly(*p*-2,3,5,6-tetramethylphenylene ethylene); (B) poly(*p,p'*-diphenylene methylene); (C) poly(*m*-phenylene); (D) poly(*p*-phenylene ethylene)-pyrolytic route; (E) poly(9,10-anthrylene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

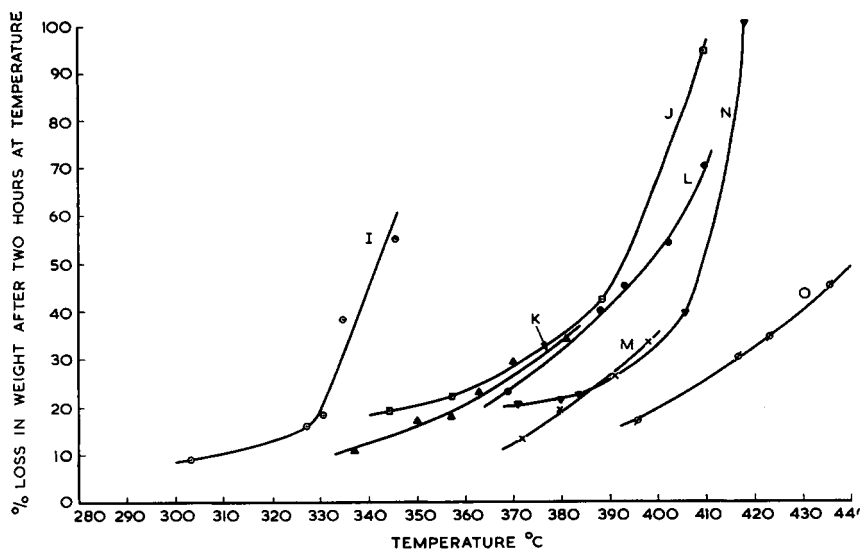


Fig. 2. Comparison of thermal stabilities in oxygen of aryl polymers linked by various groups: (*I*) poly(*p*-2,3,5,6-tetrachlorophenylene oxide); (*J*) condensation product of 2,7-fluorenedisulfonyl chloride and diphenyl ether; (*K*) poly(*p*-phenylene oxide); (*L*) condensation product of terephthalyl chloride and naphthalene; (*M*) poly(phenylene carbonyl); (*N*) condensation product of terephthalyl chloride and fluorene, and (*O*) poly(*p*-2,6-dichlorophenylene oxide).

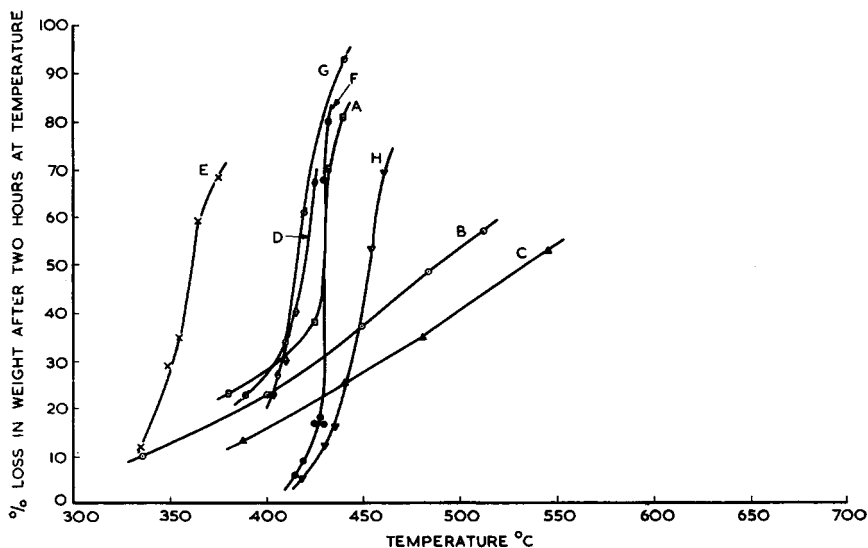


Fig. 3. Comparison of thermal stabilities in vacuum of various $-\text{CH}_2-$ and $-\text{CH}_2-\text{CH}_2-$ linked polymers: (*A-H*), as in Fig. 1.

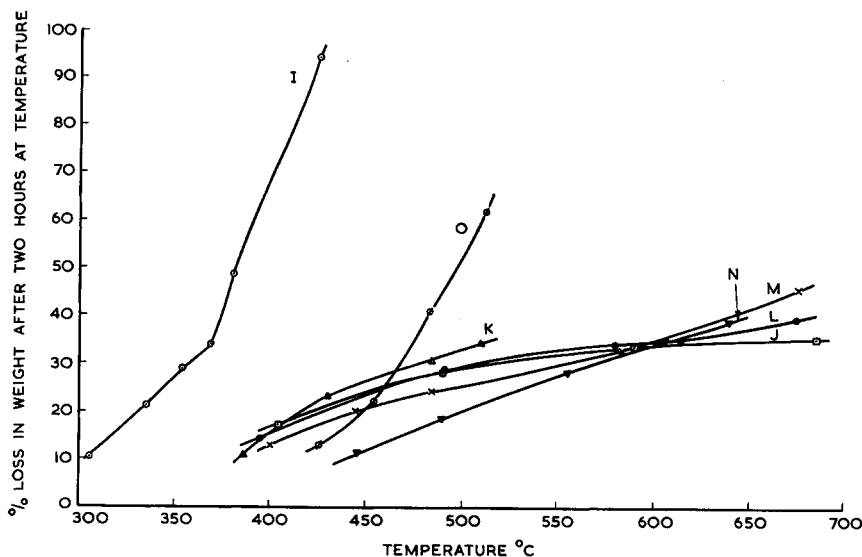


Fig. 4. Comparison of thermal stabilities in vacuum of aryl polymers linked by various groups: (I-O), as in Fig. 2.

shown in Figures 1 and 2, and the corresponding data for experiments in vacuum in Figures 3 and 4, for comparison purposes. The effect of the change in conditions is perhaps more clearly illustrated in Table II, which

TABLE II
Relative Thermal Stabilities of Polymers in Oxygen and Vacuum

Polymer	Temperature for 25% weight loss in 2 hr., °C.		Temperature difference, °C.
	In vacuum	In oxygen	
Terephthalyl chloride/fluorene	532	389	-143
Poly(phenylene carbonyl)	505	389	-116
Terephthalyl chloride/naphthalene	462	372	-90
Poly(2,6-dichlorophenylene oxide)	459	409	-50
2,7-Fluorenedisulphonyl chloride/diphenyl ether	455	365	-90
Poly(<i>p</i> -phenylene oxide)	443	368	-75
Poly(<i>m</i> -phenylene)	440	324	-116
Poly(2,6-naphthylene ethylene)	440	402	-38
Poly(<i>p</i> -phenylene ethylene)-lithium route	429	383	-56
Poly(<i>p,p'</i> -diphenylene methylene)	408	396	-12
Poly(<i>p</i> -phenylene ethylene)-pyrolysis route	404	<344	>-60
Poly(<i>p</i> -2,5-dimethylphenylene methylene)	396	309	-87
Poly(<i>p</i> -2,3,5,6-tetramethylphenylene ethylene)	390	<287	>-103
Poly(9,10-anthrylene ethylene)	347	359	+12
Poly(<i>p</i> -2,3,5,6-tetrachlorophenylene oxide)	343	333	-10

TABLE III
Overall Activation Energies of Degradation of Polymers

Polymer	Activation energy E kcal./mole	Derivation of E	Activation energy from specific rate plot at various per cent volatilization, kcal./mole				Activation energy for degradation in vacuum, kcal./mole
			10%	20%	30%	40%	
Terephthalyl chloride/fluorene	52	Zero-order plot	—	—	—	—	—
Poly(phenylene carbonyl)	29	Maximum rates	—	26	26	24	—
Terephthalyl chloride/naphthalene	38	First-order plot	—	—	—	—	—
Poly(2,6-dichlorophenylene oxide)	50	Second-order plot	—	44	42	41	—
2,7-Fluorenedisulfonyl chloride/diphenyl ether	—	—	30	28	31	31	—
Poly(<i>p</i> -phenylene oxide)	—	—	43	37	30	—	—
Poly(2,6-naphthylene ethylene)	38	First-order plot	29	29	35	35	48
	33	Maximum rates	—	—	—	—	—
Poly(<i>p</i> -phenylene ethylene)-lithium route	53	First-order plot	—	—	—	—	93
Poly(<i>p</i> -2,5-dimethylphenylene methylene)	51	First-order plot	51	42	41	46	55

quotes the temperatures at which 25% loss in weight would occur in 2 hr., either in vacuum, or under 300 mm. oxygen pressure.

The most thermally stable of the polymers examined in oxygen was poly(*p*-2,6-dichlorophenylene oxide). Most of the polymers showed appreciable decomposition in the temperature range 340–410°C., but poly(2,3,5,6-tetramethylphenylene ethylene), poly(*p,p'*-diphenylene methylene), poly(*m*-phenylene), and poly(2,3,5,6-tetrachlorophenylene oxide) decomposed below this between 280 and 340°C. The behavior of the poly(*p,p'*-diphenylene methylene) and the poly(*m*-phenylene) was surprising in that, in vacuum, they showed typical stabilization effects, i.e., no further loss in weight after a period of time at constant temperature, whereas in oxygen complete breakdown occurred over a very narrow temperature range. There is no obvious explanation for this. The poly(*p*-phenylene ethylene) prepared by reaction of phenyl lithium with *p*-bisbromomethyl benzene was appreciably more stable than the polymer prepared by pyrolysis of *p*-xylene, the difference being much more marked than in vacuum. It is likely that the latter polymer is much more highly branched. The order of the stability of the polymers containing dimethylene linkages was the same in both oxygen and vacuum, i.e., poly(2,6-naphthylene ethylene) > poly(*p*-phenylene ethylene) > poly(9,10-anthrylene ethylene). The last named polymer was the only one of those examined, whose stability was, if anything, superior in oxidizing to inert conditions.

Much greater differences in stability amongst the polymers were observed in vacuum than in oxygen. In comparison with fluorine-containing polymers,⁴ the effect of the presence of oxygen was much more deleterious, the average drop in temperature for a given weight loss being of the order of 70°C., compared with 20°C. for the fluorocarbons.

Overall Activation Energies

The overall activation energy for degradation was calculated by whatever method was most applicable to the results. In other words, standard zero-, first-, or second-order plots were tried, or the use of maximum rates, or rates taken for a definite fixed conversion. The results are summarized in Table III, together with such data as are available for experiments in vacuum. For six of the polymers, none of the methods of analysis gave satisfactory Arrhenius plots.

CONCLUSIONS

The majority of the polymers examined had a much lower stability under oxidizing than under inert conditions. The exceptions to this were poly(9,10-anthrylene ethylene), poly(*p*-2,3,5,6-tetrachlorophenylene oxide), and poly(*p,p'*-diphenylene methylene). The first two, however, were the polymers with the lowest inherent stability.

The most stable polymer was poly(2,6-dichlorophenylene oxide), whose stability in oxygen was comparable to that of a copolymer of tetrafluoroethylene and hexafluoropropylene.

References

1. J. M. Cox, B. A. Wright, and W. W. Wright, *J. Appl. Polymer Sci.*, **9**, 513 (1965).
2. J. M. Lancaster, B. A. Wright, and W. W. Wright, *J. Appl. Polymer Sci.*, **9**, 1955 (1965).
3. W. W. Wright, *Soc. Chem. Ind. (London)*, Monograph No. 13, 1961, p. 248.
4. J. M. Cox, B. A. Wright, and W. W. Wright, *J. Appl. Polymer Sci.*, **8**, 2951 (1964).

Résumé

La dégradation thermique à l'oxygène de quinze polymères contenant des cycles aromatiques dans la chaîne a été étudiée par la méthode de perte en poids. Les stabilités thermiques relatives des différents polymères ont été déterminées et lorsque c'était possible, les énergies d'activation globale de destruction, déterminées. Les résultats ont été comparés avec ceux des échantillons des mêmes polymères dégradés sous vide. Le polymère thermiquement le plus stable examiné dans des conditions d'oxydation, était le poly(2,6-dichlorophénylène oxyde), avec une stabilité comparable à celle d'un copolymère de tétrafluoroéthylène et d'hexafluoropropylène.

Zusammenfassung

Der thermische Abbau von fünfzehn Polymeren mit aromatischen Ringen in der Kette unter Sauerstoff wurde nach einer Gewichtsverlustmethode untersucht. Die relative thermische Stabilität der verschiedenen Polymeren und, wenn möglich, die Bruttoaktivierungsenergie für die Zersetzung wurden bestimmt. Die Ergebnisse wurden denjenigen an im Vakuum abgebauten Proben der gleichen Polymeren verglichen. Das thermisch stabilste der unter oxydierenden Bedingungen untersuchten Polymeren war Poly-2,6-dichlorphenylenoxyd, dessen Stabilität derjenigen eines Copolymeren aus Tetrafluoräthylen und Hexafluorpropylen vergleichbar ist.

Received January 20, 1967

Prod. No. 1569