Thermal Degradation of Poly(2,6-dimethyl-1,4-phenylene Oxide). I. The Mechanism of Degradation

J. JACHOWICZ, M. KRYSZEWSKI, and P. KOWALSKI,* *Polymer Institute, Technical University, Łódź 90542, Poland*

Synopsis

An analysis of products obtained from thermal degradation of poly(2,6-dimethyl-1,4-phenylene oxide) is presented. The techniques used for identification of monomeric and dimeric degradation products were gas chromatography and mass spectrometry. On the basis of this analysis a mechanism of thermal breakdown is established. It consists of the Fries-type rearrangement of the polymer chain in the first degradation step and statistical scission of benzyl bonds. The proposed degradation scheme accounts for the retention of ether linkage in the afterdegradation residue.

INTRODUCTION

The mechanism of thermal degradation of poly(2,6-dimethyl-1,4-phenylene oxide) has not, so far, been elucidated. Several publications have been written on the subject, but the attention of the authors was focused on the changes in chemical and physical structure occurring in the temperature range of 100°–250°C in which the polymer, usually in the form of blend with polystyrene, is technologically processed.[1-9] The precise degradation temperature range depends on many parameters of the degradation process, the most important one being the heating rate.

Thermal degradation of poly(2,6-dimethyl-1,4-phenylene oxide) (PDMPO) was studied under vacuum or in inert atmosphere using many techniques. Activation energies of the weight loss process were calculated from isothermal and nonisothermal thermogravimetric analysis (TGA) curves by Kopylow and Prawiednikow.[5] The activation energy of nonisothermal breakdown is 40.4 kcal/mole, calculated by the method elaborated by Reich.[10] The activation energy of isothermal process performed in the temperature range of 330°–400°C equals 13.5 kcal/mole. A considerably different value, 27 ± 2 kcal/mole, was obtained by Kim et al.[3] for measurements in the temperature range of 20°–600°C at heating rates of 1.2°, 3.0°, 5.0°, and 9.0°C/min.

Analyzed DSC and DTA curves show that the thermal decomposition of poly(2,6-dimethyl-1,4-phenylene oxide) is a rapid exothermic process occurring between 400° and 500°C.[8] The evaluated heat of breakdown equals 86.8 cal/g (10.4 kcal/mole). Examination of the decomposition products showed them to consist of the gases H_2, CH_4, C_2H_6, and CO; the benzene derivatives toluene, xylenes, and benzene; water; nonvolatile subliming phenols and oligomers 68%; and black, strongly crosslinked, amorphous residue, 26%.[1,8] It was concluded that the degradation of PDMPO is a statistical process,[9] although the degradation mechanism could not be established. The purpose of this study was to analyze

[1] Present address: Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Łódź, Poland.

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nonvolatile subliming products evolving during stepwise decomposition of poly(2,6-dimethyl-1,4-phenylene oxide) which could throw some light on the mechanism of thermal breakdown and formation of crosslinked residue.

EXPERIMENTAL

Polymer Sample

The sample of poly(2,6-dimethyl-1,4-phenylene oxide) was obtained from the Institute of Industrial Chemistry in Warsaw and had been produced by the Hay polimerization. The polymer had a number-average molecular weight of 20,500 g/mole determined by osmometry and weight-average molecular weight of 41,500 g/mole determined by light scattering. Prior to use the polymer was purified by three reprecipitations from benzene solution by methanol and dried overnight at 60°C under vacuum.

Polymer Degradation

The decomposition of the polymer was performed employing the "sealed tube" technique. Samples of PDMPO, 100 mg, were placed in a Pyrex apparatus and degassed under vacuum at 10^{-3} mm Hg. The samples were then pyrolized in an oven. Programmed heating conditions were used for all experiments, the heating rate being 200°C/min. Volatile degradation products were trapped out at liquid nitrogen temperature, and nonvolatile degradation products condensed on the walls of the tube near the pyrolized sample were washed out with a solvent (methylene chloride or benzene). The solution of the degradation products was subsequently subjected to mass-spectroscopic analysis or gas-chromatographic separations.

A solution of similar degradation products but obtained from the degradation of a 1.5-g sample was subjected to preparative gas-chromatographic separations.

Instrumentation

Gas–liquid chromatography (GLC) analysis was carried out using a Varian Aerograph Series 2700 chromatograph equipped with a hydrogen flame ionization detector. For all separations, 2-m columns packed with 10% OV-101 glass were used. Programmed heating was used from 100° to 250°C at a heating rate of 10°C/min.

Preparative gas–liquid chromatography was carried out using a Varian Aerograph Model 711 chromatograph equipped with a hydrogen flame ionization detector. For initial separations of monomeric phenols from dimeric phenols, 12.5-ft columns packed with SE-30 were used, while for separations of monomeric phenols 25-ft SE-30 columns were employed. Gas chromatography–mass spectrometry (GC-MS) analysis was carried out using a 2091 LKB gas chromatograph–mass spectrometer connected to a PDP 11 digital computer.
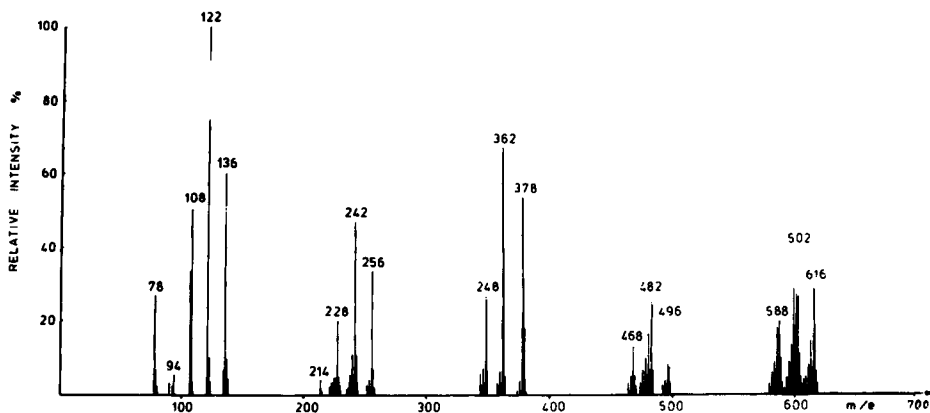
Fig. 1. Averaged mass spectrum of PDMPO degradation products.

RESULTS AND DISCUSSION

The solution of the products from poly(2,6-dimethyl-1,4-phenylene oxide) degradation was introduced into the ionization cell of the mass spectrometer after evaporation of the solvent. The mass spectra were recorded every several seconds as the cell temperature was gradually increased, and the mixture of degradation products was separated into several fractions. The higher the temperature in the ionization cell, the higher the oligomers that appeared in the spectra, Figure 1 shows an averaged spectrum of several fractions where one can see the characteristic triads or even pentads (not given in Fig. 1) of monomeric, dimeric, trimeric, etc., compounds. The difference between the corresponding peaks in a triad equals 14 mass units, and this suggests that the oligomers corresponding to them differ by a methyl group. This mass spectrum is very similar to that obtained for unsubstituted and methyl-substituted polybenzyls which were investigated by direct pyrolysis in a mass spectrometer.[12]

The monomeric and dimeric products were separated using gas chromatography (Fig. 2). They were also silylated with hexamethyldisilazane and separated by gas chromatography. The mass spectra of all individual compounds
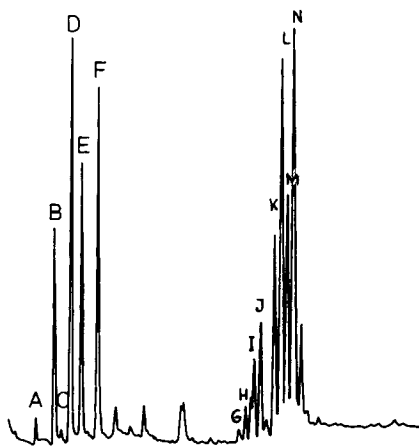

Fig. 2. Gas chromatogram of PDMPO degradation products.

were registered employing GC-MS. Products A, B, C, and D were identified using appropriate model compounds such as phenol (MW 94), o-cresol (MW 108), p-cresol (MW 108), and 2,6-dimethylphenol (MW 122). Products E and F were separated using preparative gas chromatography and identified by their mass and NMR spectra as 2,4-dimethylphenol (MW 122) and 2,4,6-trimethylphenol (MW 136).

The dimeric products G, H, I, J, K, L, M, and N were analyzed by a gas chromatograph connected to a mass spectrometer. The peaks G, H, I, J, K, L, M, and N correspond to compounds of MW 228, 242, 242, 256, 228, 242, 242, and 256, respectively. Silylation of these dimers showed that dimers G, H, I, and J add one silyl group, while compounds K, L, M, and N add two silyl groups. It follows immediately that dimers G, H, I, and J possess one hydroxyl group while dimers K, L, M, and N possess two hydroxyl groups.

The similarity of the mass spectrum of poly(2,6-dimethyl-1,4-phenylene oxide) degradation products and the mass spectra of polybenzyls degradation products[10,11] leads to the conclusion that the first degradation step is the Fries-type rearrangement reaction during which the ether bond in the backbone is replaced by a C–C bond, which is further supported by the fact that there is a chromatogram symmetry (Fig. 2) indicating that monomeric products B, D, E, and F correspond to dimeric products K, L, M, and N, respectively.

The Fries-type rearrangement reaction occurs according to the following scheme:
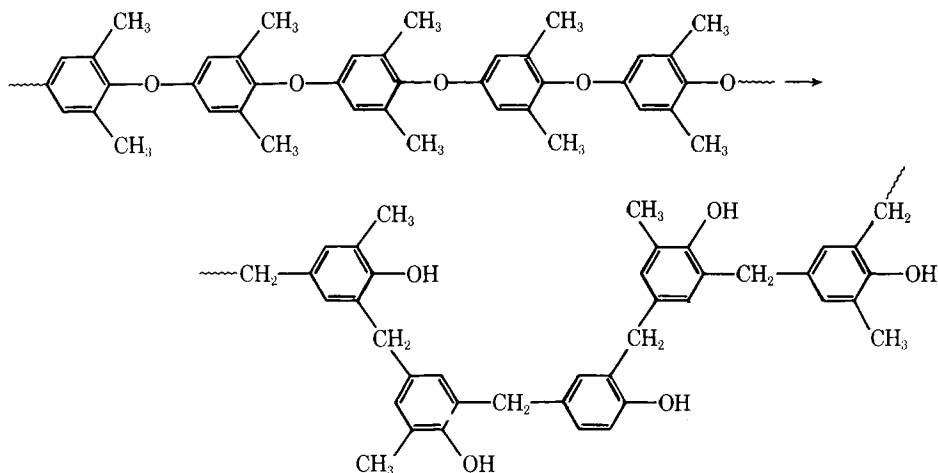
The thus rearranged polymer backbone decomposes by statistical scission of the C–C bonds, forming as the main degradation products the monomeric phenols B, D, E, and F and the dimeric phenols K, L, M, and N (Scheme 1). The structure of these dimers was confirmed by the analysis of their mass spectra and by the analysis of the mass spectra of their silyl and deuterium analogues.

We have also tried to isolate the intermediate product of the degradation reaction. In order to obtain it, the PDMPO sample was placed in a Pyrex tube, degassed at 10^{-3} mm Hg, and then heated under isothermal conditions at 380°C for 2 hr. The IR spectrum of the polymer degraded in this way shows the appearance of a band at 3500 cm^{-1}, which corresponds to O–H bond oscillations and bands at 1150 and 990 cm in the region of strong phenol absorption (Fig. 3).
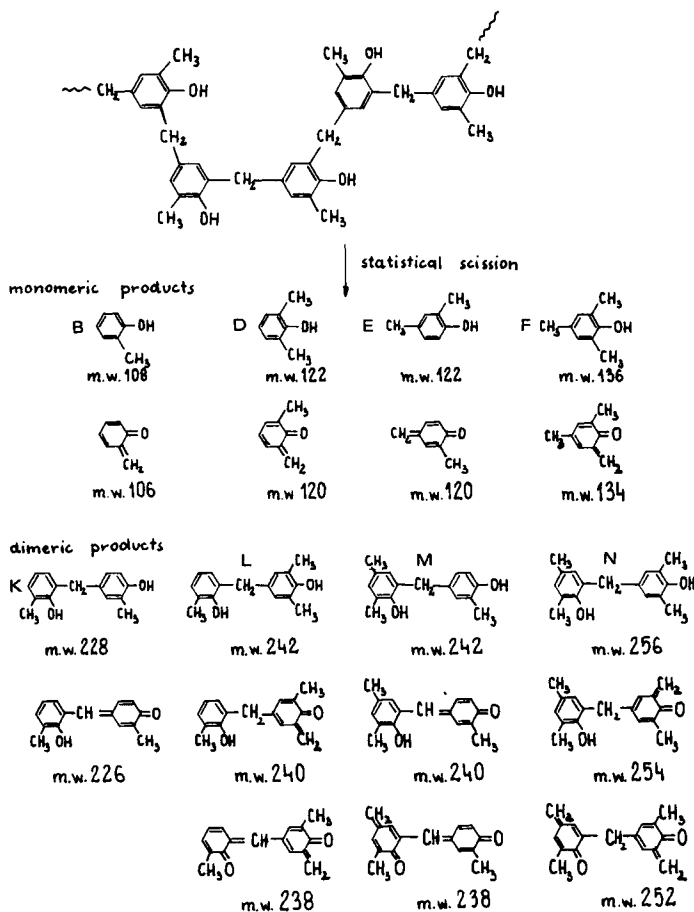
Scheme 1. The monomeric and dimeric scission products from the completely rearranged polymer chain.

This result, it seems, can be treated as proof of rearrangement in the first degradation step during which the formation of hydroxyl groups takes place. On the other hand, it is impossible to obtain in this way the intermediate product completely rearranged since at this temperature, 380°C, polybenzyls are unstable. What we detect, then, are the hydroxyl groups in the partially rearranged chain.

Przybylski et al.[12] stated that disproportionation and proton transfer reactions are the main elementary degradation reactions of polybenzyls. In order to discuss the processes taking place during the degradation of PDMPO, two cases should be taken under consideration.

In the case of the chain which is completely rearranged, there are four possible elementary reactions, k_1, k_2, k_3, and k_4 (Scheme 2). Each of them requires the hydroxyl or benzyl proton transfer which was found to be the case in the degradation of methyl-substituted and unsubstituted polybenzyls.[12] All these reactions lead to the formation of two polymer ends—one of which after further scission reactions will mainly yield monomeric, dimeric, and higher oligomeric

phenols, and the second of which is the source of monomeric, dimeric, etc., compounds with *para-* or *ortho*-quinomethid bonds. These products possess a molecular mass smaller by 2 and 4 mass units than the molecular masses of the principal phenolic oligomers, and their molecular ions appear in the mass spectrum of the degradation products either for dimeric degradation products or for higher oligomers. We have also separated the quinomethid products of degradation from the phenolic fraction using column chromatography (benzene solution of the degradation products with a 1-m column, 1 cm in diam., packed with Kieselgel, 0.2–0.5 mm, Merck). However, detailed analysis of its composition needs further investigation.

It can also be seen in the mass spectrum of the degradation products (Fig. 1) that compounds of molecular mass smaller by 6 and 8 mass units for tetramer, for example, are present as well. This cannot be explained in terms of chain scission reactions which lead to the formation of quinomethid structures at the end of the produced oligomers. Based on this it may be argued that the other possible degradation mechanism is chain scission reactions leading to free radicals which can be quenched by hydrogen transfer to or from the substrate.

All monomeric and dimeric products of the completely rearranged chain are shown in Scheme 1. The methanedylidene structures of dimeric products resulting from the proposed mechanism are of such instability that they are not mentioned in Scheme 1. The identified monomeric and dimeric products formed from the completely rearranged backbone are designated B, D, E, F and K, L, M, N, while other suggested possible structures are given below.

In the case of the partially rearranged chain there are eight elementary reac-
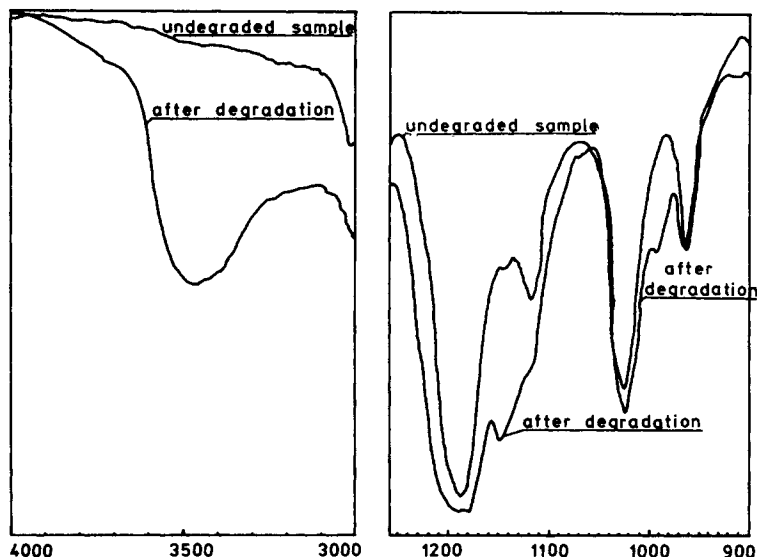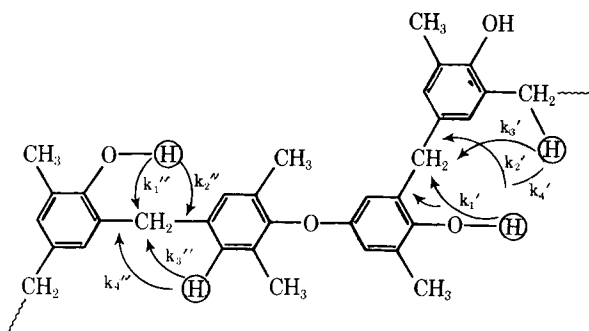

Fig. 3. Changes in the infrared absorption spectrum of PDMPO degraded under vacuum at 380°C for 2 hr.

tions to be considered:

Reactions k_3'' and k_4'' give rise to unstable and reactive structures. It is probable, then, that recombination reactions are due to the radicals formed in these reactions. According to this model, the partially rearranged chains, i.e., those containing ether bonds, can take part in recombination reactions. As a result, black, strongly crosslinked residue is formed. Its IR spectrum shows that the ether linkage is retained.[8] As a result of k_1', k_2', k_3', k_4', k_1'', and k_2'' reactions, the following unrearranged dimers (with one hydroxyl group) are formed:

MW 228

G

MW 242

H

MW 242

I

MW 256

J
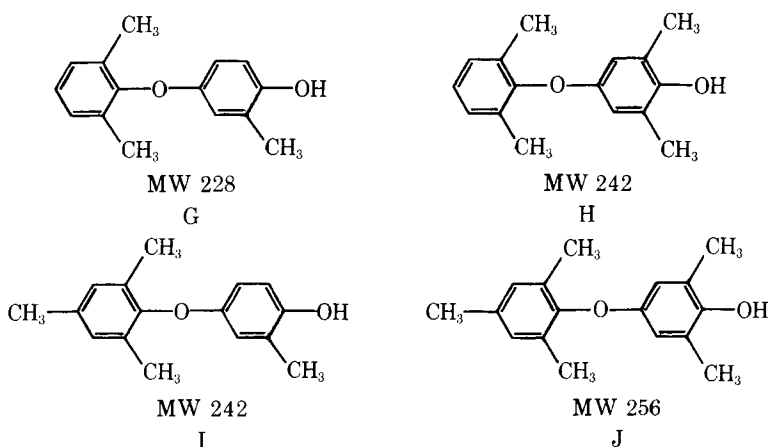
These dimers appear on the chromatogram of the degradation products under peaks G (MW 228), H (MW 242), I (MW 242), and J (MW 256).

CONCLUSIONS

The proposed mechanism of thermal breakdown of poly(2,6-dimethyl-1,4-phenylene oxide) accounts for the composition of the main degradation products. It also seems to account for the retention of ether linkage in the afterdegradation residue and thus explains the mechanism of crosslinking. Both these processes—the polymer cleavage into small oligomeric fragments and the formation of crosslinking bonds—require in the first degradation step main-chain rearrangement with the formation of C–C bonds and liberation of hydroxyl groups. This exothermic process was already investigated for low molecular weight ar-
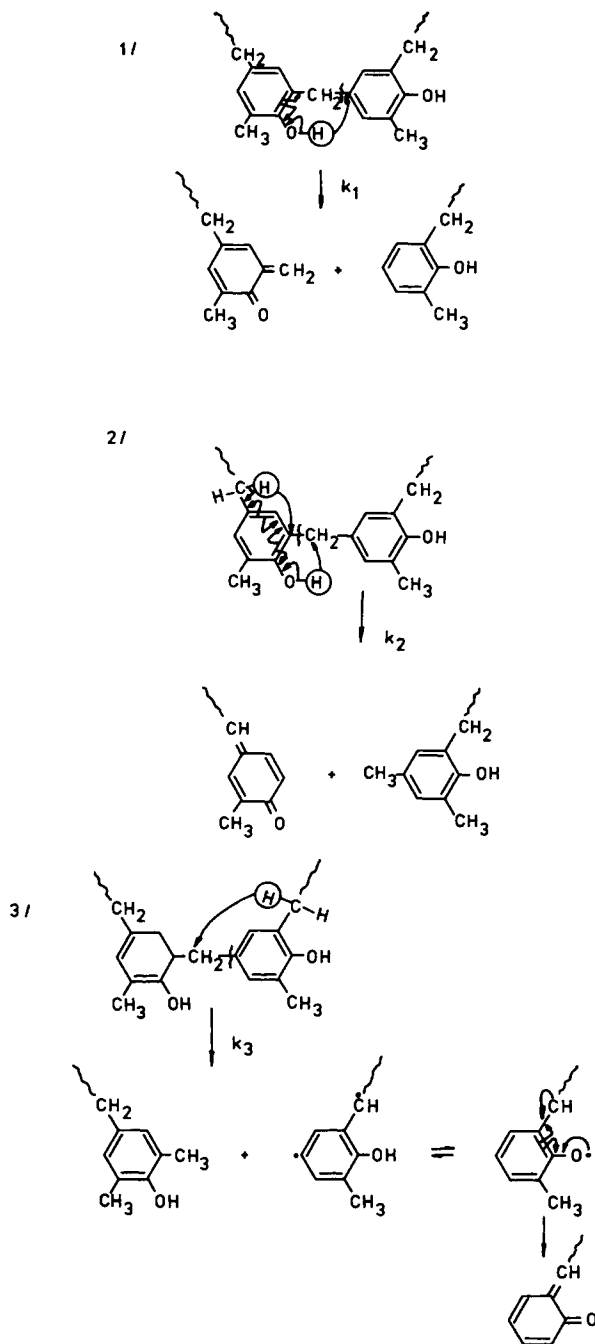
Scheme 2. The mechanism of scission of the completely rearranged polymer chain.

omatic ethers.[13] It was observed that this reaction can be induced either thermally or by UV radiation. This is why we suppose that crosslinking bonds in this polymer produced during its thermal or photochemical degradation in the lower-temperature range may be due to reactions similar to those leading to its complete breakdown. On the other hand, under oxidative conditions the
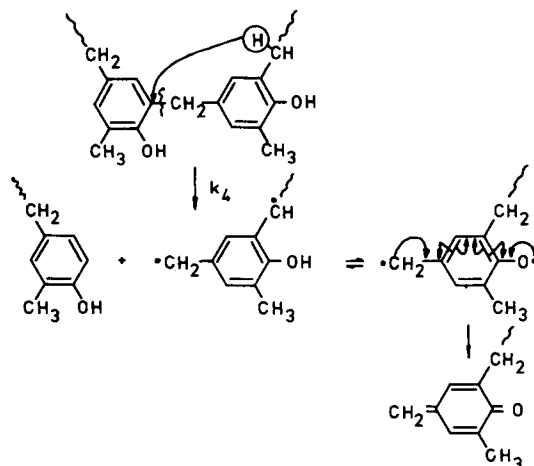
Scheme 2. *(Continued from previous page.)*

dominant role may be played by the chain reactions of formation and decomposition of hydroperoxides in the pendent methyl group.

A similar degradation scheme was observed in the case of poly(2-methyl-1,4-phenylene oxide) and copolymers obtained from oxidative polycondensation of phenol, o-cresol, and 2,6-dimethylphenol. These investigations will be the subject of subsequent publications.

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