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THERMAL DEGRADATION OF POLY(OXY-2,6-DIMETHOXY-1,4-PHENYLENE)

Tuure-Pekka Jauhiainen
Department of Chemistry and Biosciences, University of Joensuu, PL 111,
80101 Joensuu 10, Finland

ABSTRACT

The thermal degradation of poly(oxy-2,6-dimethoxy-1,4-phenylene), PPOO, has been studied by using thermogravimetry, infrared spectrometry and pyrolysis-gas chromatography-mass spectrometry. The thermal degradation of PPOO starts from the chain ends by the cleavage of 2,6-dimethoxy-2,5-cyclohexadiene-1,4-dione, 2,6-dimethoxyphenol, 3,5-dimethoxyphenol and oligomers. The actual decomposition of the main polymer chain takes place through the statistical C-O-bond breaking with the simultaneous hydrogen atom transfer. The methyl group migration from the aliphatic side chain to the phenylene ring has been confirmed. Besides the methoxy groups seem to split off mainly by eliminating methanol and methanal. The reliability of the information given by different methods used has been discussed.

INTRODUCTION

Poly(oxy-2,6-disubstituted-1,4-phenylenes) are linear polymers with an aromatic skeleton, a good thermal stability and good mechanical properties (ref. 1,2). As a continuation to our previous studies on the syntheses and solid state properties of these polymers the thermal degradation of PPOO has been studied (ref. 2-5).

The purpose of this work has been to clarify the initial decomposition mechanism of PPOO and to compare the reliability of the results given by different methods used to study the thermal degradation of polymers.

EXPERIMENTAL

Materials

The syntheses and analyses of the polymers used have been reported in detail elsewhere (ref. 2). The polymer chains have a free phenolic end group at one end and a 1,2,6-substituted phenylene ring at the other (ref. 2).

Measuring techniques

The thermogravimetric measurements were carried out with a Perkin-Elmer TGS-2 thermogravimetric analyser interfaced to a Hewlett-Packard 9825A desk top computer for the data collection and processing.

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The infrared spectra of the solid residues were measured with a Perkin-Elmer 297 spectrometer by using the KBr method.

The mass spectra were obtained with a JEOL JMS-D300 mass spectrometer combined with a JMA-3100/3500 mass analysis data processing system.

The pyrolyses were made by using a CDS Pyroprobe 100 filament pyrolyser connected to the mass spectrometer through a Carlo Erba Fractovap 4160 gas chromatograph. The column used was a 25 m silica capillary column containing a SE-52 stationary phase.

RESULTS AND DISCUSSION

Thermogravimetric measurements

The thermogravimetric curves for PPOO's with different molar masses are presented in Fig. 1.

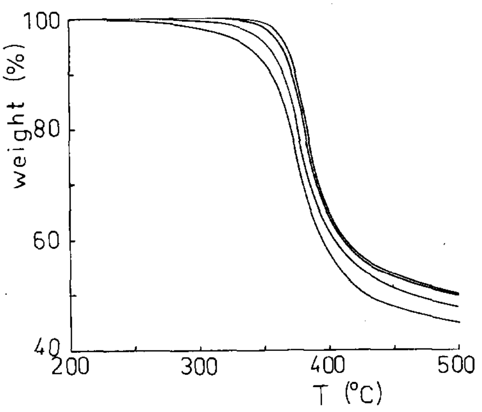


Fig. 1. The thermogravimetric curves for PPOO's with different molar masses, the heating rate 5 K/min, the nitrogen flow rate 50 ml/min, the sample weight 1 mg.

1	M_v = 83 100	g/mol
2	M_v = 19 600	"
3	M_v = 5 500	"
4	M_v = 1 900	"

According to Fig. 1 the thermal degradation of PPOO starts from the chain ends and is followed by a process which does not depend on the molar mass indicated by the same steepness of the thermogravimetric curves during the actual weight loss.

The amount of the solid residue at 500°C with the high molar mass PPOO (1) is 50 %, which is a remarkably higher value than measured in connexion with poly(oxy-2,6-dimethyl-1,4-phenylene), PPO, or with poly(oxy-2,6-bis(1-methylethyl-1,4-phenylene), PPrO, 37 % versus 2 % (ref. 5). The degradation products of PPOO have a higher tendency to crosslink. The solubility of PPOO in chloroform disappears after a weight loss of 5 to 10 % increasing inversely to the molar mass.

The infrared spectra of the residues show that the aliphatic side chains have split off below 500°C. Due to the band at 3450 cm^{-1} the residue contains free phenolic groups. Otherwise it has a highly aromatic structure indicated by the broad shallow v(C=C) band at 1600 cm^{-1}, whereas C-O-C-bonds between aromatic rings do not exist at noticeable amounts.

Owing to the smaller-sized residue with the low molar mass sample in Fig. 1 the degradation from the chain ends does not lead to the crosslinking as much as that from the middle of the polymer skeleton.

CI mass spectra

The thermogravimetric measurements were simulated by heating the polymer sample in a quarz capillary in the direct inlet of the mass spectrometer. To simplify the spectra the chemical ionization with isobutan as a reagent gas was used (ref. 6). Referring to the mass spectra of the pure compounds run through a gas chromatograph the only strong peak in the CI spectra with isobutan is $(M+1)^+$. However it has been found out before that with some o-quinones the $(M+2)^+$ peak may have a noticeable intensity, when the direct

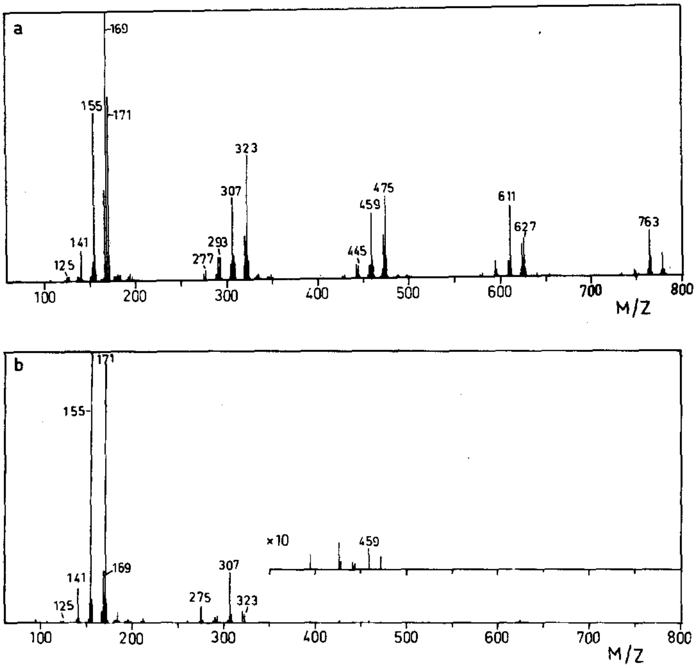


Fig. 2. The CI mass spectra of the degradation products for a low (a) and a high (b) molar mass PPOO at 370°C, the heating rate 5 K/min, the sample weight 50 μg, isobutan as a reagent gas.

inlet is used (ref. 7).

The spectra were recorded every 5 seconds. Thus it was possible to follow the changes in the degradation products as a function of temperature. Two typical mass spectra are presented in Fig. 2.

The peak groups of the different oligomeric degradation products are visible in Fig. 2. The percentage of the higher oligomers is greater with the low molar mass polymer. Obviously they split off directly from the chain ends and are the reason for the smaller amount of the solid residue with the low molar mass polymer.

The most apparent difference between the spectra in Fig. 2 is the mass peak at 169. This points to the oxidation of the phenolic chain end to 2,6-dimethoxy-2,5-cyclohexadiene-1,4-dione in the early stage of the thermal degradation, see Table 2. This kind of degradation product cannot exist among higher oligomers.

Besides, the proportion of the free monomers (155), dimers (307), trimers (459), etc. is noticeably higher at the beginning of the thermal degradation than at higher temperatures, especially with the low molar mass polymer.

The degradation of the polymer skeleton is characterized mainly by the $(M+1)^+$ peaks at 141, 155 and 171. The probable compounds are 3-methoxy-1,2-benzenediol, 2,6-dimethoxyphenol, 3,5-dimethoxyphenol and 2,6-dimethoxy-1,4-benzenediol. Their existence presupposes a hydrogen atom transfer to the oxygen atom in the main chain. However, it must be noticed that, for example, in the connexion of 3-methoxy-1,2-benzenediol the primary degradation product in the direct inlet of the mass spectrometer can be 3-methoxy-3,5-cyclohexadiene-1,2-dione (ref. 7).

Among the oligomeric peaks in the CI spectrum following series can be separated; $(nM+16+3)^+$, $(nM+3)^+$, $(nM-14+3)^+$ and $(nM-28+3)^+$, where M is 152. In addition, a series $(nM-30+3)^+$ indicating the splitting of a methoxy group can be identified, but its intensity is very low. The identification of the compounds in the main series is obvious.

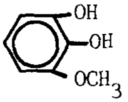
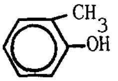
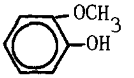
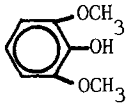
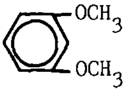
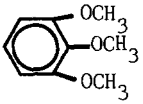
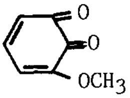
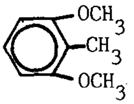
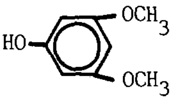
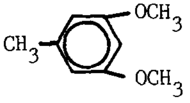
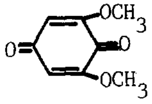
Pyrolysis-gas chromatography-mass spectrometry

To identify the degradation products a series of pyrolysis-gas chromatography-mass spectrometry measurements were carried out. The pyrolysis temperature varied from 325 to 700°C, the sample amount being 50 µg. Both EI and CI mass spectra were recorded to get the correct mass peak. After initial interpretation of the spectra the structures were confirmed with the spectra of pure compounds. The identified compounds are listed in Table 1.

The relative amounts of the degradation products depend critically on the pyrolysis temperature and time. Therefore no quantitative data is given.

TABLE 1

The structures of the pyrolysis products for poly(oxy-2,6-dimethoxy-1,4-phenylene).

number	M	compound	number	M	compound
1	16	CH_4			
2	30	CH_2O	11	140	
3	32	CH_3OH			
4	44	CO_2	12	152	
5	108		13	138	
6	124		14	154	
7	138		15	168	
8	138*		16	168	
9	152		17	154	
10	152		18	168	

* no reference spectrum

The proportion of the compounds 8, 11, 14, 17 and 18 increases, when the pyrolysis temperature is lowered.

CONCLUSIONS

The thermal degradation of PPOO starts from the chain ends by the oxidation of the phenolic end group to 2,6-dimethoxy-2,5-cyclohexadiene-1,4-dione, by the cleavage of 2,6-dimethoxyphenol, 3,5-dimethoxyphenol and oligomers.

No such Fries-type rearrangement as proposed by Jachowicz et al. (ref. 8) for PPO exists with PPOO. The decomposition of the polymer chain takes place through statistical C-O-bond breakings. Referring to the CI mass spectra, the hydrogen atom transfer is associated with this process.

The aliphatic side chains disappear below 500°C. The rupture of the CH_3-O-bonds predominates at lower temperatures (Compounds 8,11).

The transfer of the methyl group to the phenylene ring is confirmed (Compounds 9,10). On the other hand no verification for the migration of the whole methoxy group was found in this work. It seems obvious that the cleavage of the C-O-bond close to the phenylene ring is followed by the elimination of methanol or methanal.

The pyrolysis by heating in the direct inlet of the mass spectrometer is a very efficient method for studying the stages of the thermal decomposition of polymers as a function of temperature. By using the chemical ionization with a "soft" reagent gas, such as isobutan, the molecular peaks can be separated without losing the sensitivity of mass spectrometry. However, this method does not give enough information about the structures of the degradation products, and in the behaviour of the compounds during the chemical ionization there may be differencies such as the high $(M+2)^+$ peak with the o-quinones. Therefore the co-use of this method with the pyrolysis-gas chromatography-mass spectrometry gives more detailed information about the processes.

REFERENCES

1 A.S. Hay, Polym. Eng. Sci., 16 (1976) 1.
2 T.P. Jauhiainen, Makromol. Chem., 183 (1982) 915.
3 T.P. Jauhiainen, Makromol. Chem., 183 (1982) 925.
4 T.P. Jauhiainen, Angew. Makromol. Chem., 104 (1982) 107.
5 T.P. Jauhiainen, Polymer Bulletin, in press.
6 Y. Shimizu and B. Munso, J. Polym. Sci. Polym. Chem. Ed., 17 (1979) 1991.
7 S. Ukai, K. Hirose, A. Tatematsu and T. Goto, Tetrahedron Lett., (1967) 4999.
8 J. Jachowicz, M. Kryszewski and P. Kowalski, J. Appl. Polym. Sci., 22 (1978) 2892.