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# Synthesis and Thermal Characterization of Poly [Oxy-2,6-bis (1-Methylethyl)-1.4-Phenylene]

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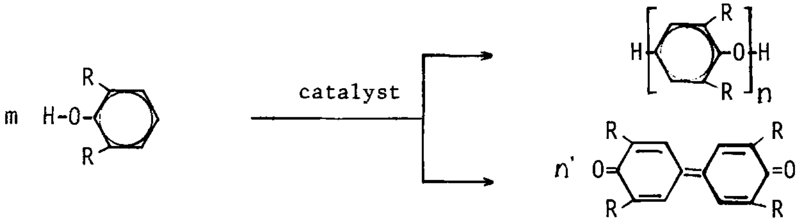
## SUMMARY

2,6-bis(1-methylethyl)phenol has been polymerized using $Ag_2O$-triethylamine complex as catalyst. The yield of the polymer was 20 % and the number-average molar mass was 5630 g/mol. The heat capacities of the polymer were measured from 270 to 480 K with a computerized DSC. The glass transition temperature $T_g$ was 425.5 K and $\Delta C_p$ at $T_g$ was 0.10 J $K^{-1} g^{-1}$. The thermal stability of the polymer was characterized by means of thermogravimetry and compared with other poly(oxy-2,6-disubstituted-1,4-phenylenes).

## INTRODUCTION

In recent years efforts have been made to polymerize 2,6-bis(1-methylethyl)phenol by using the oxidative coupling mechanism (1-5). The oxidative coupling of 2,6-disubstituted phenols can take place in two ways:



Owing to the steric hindrance of the bulky side groups of 2,6-bis(1-methylethyl)phenol the products have mostly been different kinds of quinones (3) or other insoluble material difficult to characterize (4). However the primary monomeric and the secondary polyphenoxy radicals essential for the polymerization have been found by ESR-spectrometry (1-2).

As a continuation to our previous studies on the syntheses and thermal properties of poly(oxy-2,6-disubstituted-1,4-phenylenes) (6-8) poly[oxy-2,6-bis(1-methylethyl)-1,4-phenylene] has been synthesized, spectroscopic and thermal characterized.

## EXPERIMENTAL

### Syntheses

Dried, finely powdered silver oxide, 0.030 mol, was dispersed at 25°C temperature in a vigorously stirred solution of chloroform containing 6 % triethylamine. Oxygen was removed by leading dry nitrogen into the solution. To this mixture 0.015 mol of 2,6-bis(1-methylethyl)phenol was added. After 4 h the silver waste was removed by centrifugation. The waste was washed twice with chloroform. The polymer was then precipitated by pouring the reaction solution into a douple volume of methanol containing a small amount of conc. HCl.

The raw product was purified by dissolving it three times in chloroform, by centrifugating and precipitating in methanol. Poly[oxy-2,6-bis(1-methylethyl)-1,4-phenylene] (PPrO) was dried 8 h at 100°C in a vacuum of a water aspirator.

### Measuring techniques

The IR spectra were measured with a Perkin-Elmer 297 spectrometer as a film on a KBr disc. The $^1H$ NMR spectra were recorded on a JEOL PMX-60 spectrometer with chloroform as solvent.

The number-average molar mass was determined by the vapour pressure osmometry using a Knauer n:o 11.00 osmometer. The molar mass distribution was checked with a Perkin-Elmer Series 2/1 liquid chromatograph. The column used was Shodex GPC A-803/S and the eluent chloroform.

The heat capacities were obtained with a Perkin-Elmer DSC-2 differential scanning calorimeter using a sapphire disc as a standard. The accuracy of the measurements was better than ± 1 % (8). Thermogravimetric measurements were made with a Perkin-Elmer TGS-2 thermogravimetric analyser.

## RESULTS AND DISCUSSION

### Syntheses

The yield of the polymer was 20 %. Because of the heterogenous nature of the catalysis it was impossible to determine the amount and composition of the quinones.

The number-average molar mass of the polymer was 5630 ± 60 g/mol. The molar mass distribution was wide, which is typical of the oxidative coupling reaction of 2,6-disubstituted phenols (6). There exists a small but not in significant tail in the molar mass distribution reaching over 80 000 g/mol, which was the exclusion limit of the column used for the measurments. One possible reason for the high molar mass fraction might be the coupling of whole polymer chains.

Triethylammine was necessary to the polymerization of 2,6-bis(1-methylethyl)phenol, which is in accord with the behaviour of 2,6-dimethoxyphenol (7). This might support the mechanism for C-C- and C-O-couplings given by Roubaty and Revillon (9). According to them the high pH of the solution prevents the primary monomeric radicals to loose a second electron and to produce a phenoxy cation, which is necessary for the C-C-coupling (9).

## Spectrometric analyses

The $^1$H NMR spectrum of the polymer showed three kinds of signals, at 6.61 ppm due to phenyl protons, at 3.10 ppm (broad septet) assignable to -CH protons and at 1.03 ppm (douplet) ascribable to $-CH_3$ protons. The ratio of the peak areas corresponded to the structure proposed.

In the IR spectrum the main absorption bands were 3070 (v C-H arom.), 2965 ($v_{as}$ $CH_3$), 2930 (v C-H), 2870 ($v_s$ $CH_3$), 1725 (summation band for 1,2,3,5-substitution), 1605, 1595 and 1465 (v C=C), 1445 ($d_{as}$ $CH_3$), 1385 and 1363 ($d_s$ $CH_3$), 1325 (?), 1180 (v C-O), 965 (?) and 862 ($\gamma$ C-H arom. 1,2,3,5-substitution) $cm^{-1}$.

According to the IR and NMR spectra the polymer is linear without any noticeable amount of brancing.

## Thermal analyses

Outside the glass transition region from 270 to 410 K the specific heats were smoothed by linear regression.

$$C_p = 0.258337 + 0.003835\ T \quad (J\ K^{-1}\ g^{-1})$$

Prior to the glass transition measurements the thermal histories of the samples were standardized by cooling twice 10 K/min from 480 to 380 K. The heating rate was 10 K/min and $T_g$ was obtained by the extrapolation to the baseline of the glassy state. The specific heat at the glass transition region has been presented in Figure 1.

The mean value for $T_g$ was 425.5 K and $\Delta C_p$ at $T_g$ was 0.10 J $K^{-1}g^{-1}$.

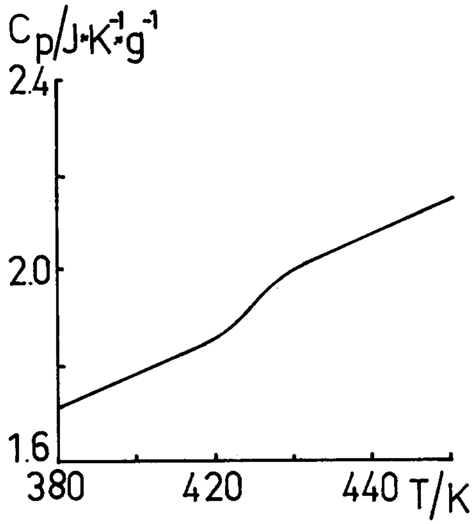


Fig 1. The specific heat of poly - [oxy-2,6-bis(1-methylethyl)-1,4-phenylene] in the glass transition region

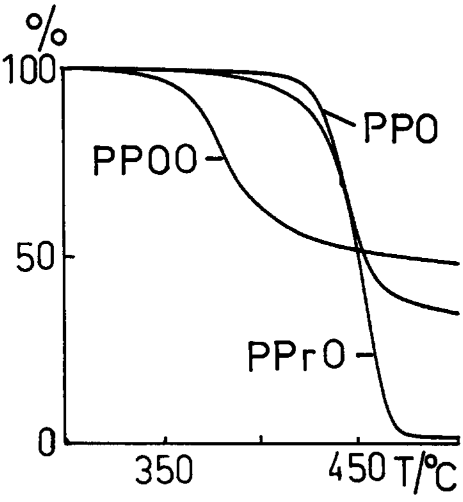


Fig. 2. Thermogravimetric curves for some poly(oxy-2,6-disubstituted-1,4-phenylenes), heating rate 5 K/min, the flow rate of $N_2$ 50 ml/min

The glass transition temperature of a polymer depends on the molar mass, the intermolecular forces and the intramolecular chain stiffness. $T_g$ of poly(oxy-2,6-dimethoxy-1,4-phenylene) (PPOO) with the same molar as PPrO is 441 K and that of poly(oxy-2,6-dimethyl-1,4-phenylene) (PPO) is 472 K (6). The intermolecular forces and the chain packing are decisive for the molecular motion of these polymers in the solid state (6). So it can be assumed that the higher size and stiffness of the 1-methylethyl side groups in PPrO loosen the polymer matrix and cause the lowering of $T_g$ compared with PPOO and PPO.

$\Delta C_p$ at $T_g$ for PPrO is small compared with other poly(oxy-2,6-disubstituted-1,4-phenylenes) (6). Referring to the "bead" model presented by Wunderlich the mean value for $\Delta C_p$/"bead" is 11 J $K^{-1}mol^{-1}$ (10). The value for $\Delta C_p$ of PPrO, 0.10 J $K^{-1}g^{-1}$ = 17.6 J $K^{-1}mol^{-1}$, is a little lower than that of two beads. The $\Delta C_p$/"bead" values for other poly(oxy-2,6-disubstituted-1-4-phenylenes) measured before are systematically higher than the mean value for all the polymers (6,10). The lower value of PPrO must reflect a stiffer molecular structure and a smaller change of the conformation of the polymer backbone at $T_g$.

The thermal degradation curves of PPO, PPOO and PPrO measured by TG are presented in Figure 2.

The solid residue at 500°C is very small with PPrO compared with PPO and especially with PPOO.

According to Jachowicz et. al. the thermal degradation of PPO starts through the Fries-type rearrangement of two monomeric units followed by statistical chain scission (11). Besides monomeric and dimeric degradation products there exists a highly cross-linked residue.

Thermal degradation mechanism of PPrO must deviate essentially from that of PPO and PPOO. It is not a simple, statistical C-O-bond breaking, because there is a great number of monomeric degradation products in the pyrolysis gas chromatogram of PPrO (12). The work on the mechanism of the thermal degradation of PPrO is continuing.

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