THERMAL STABILITY OF SUBSTITUTED POLY-XYLYLENES

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The insertion of meta units in the chain of poly-p-xyylene decreases both the onset temperature of oxidative degradation and the rate of decomposition.

Functionalization of the polymer with chlorine and sulphonate groups makes the chain more resistant to high temperature treatments, notwithstanding the low stability of the substituent groups.

The thermal decomposition of poly-p-xylylenes proceeds through random chain scissions of the ethylene bridges [1, 2]. A subsequent depagation reaction yields low-molecular weight polymers, while a simultaneous zipper reaction yields hydrogen and leaves unsaturated bridges. Scission reactions can be terminated by H· radicals or by rearrangement of chain radicals.

The oxidative degradation scantily differs from the previous path, but the initial chain scission proceeds through oxygen-containing intermediates [3].

Previous papers on the subject payed little attention to the influence of the monomer isomerism on the thermal stability of the polymer. A significant exception was the work of Krovtsov [4], who observed that poly-p-xyylene containing 10% of o-xyylene units is less stable than the homopolymer.

In this work we studied how the insertion of m-xyylene units in poly-p-xyylene can affect the thermal stability. Moreover we also studied the effects of a group (thienylene) which is able to modify the radical balance of the degradation, when inserted in the chain.

The study of the influence of the insertion of halogen atoms on the thermal stability of poly-p-xylylenes was begun by Joesten [5], who examined samples obtained by polymerization of the products of the pyrolysis of halogenated dimers. The importance of the poly-xylylenes as solid electrolytes and eligible materials for membrane cells led us to study the stability of poly-xylylenes functionalized by chlorination or sulphonation.
Experimental

The polymers were prepared by Wurtz synthesis. The chlorides of the monomers were dissolved in dioxane. Na$_2$K alloy, prepared from the metals molten in xylene and washed in dioxane, was drop by drop added into the boiling solvent. After 48 hrs of reaction the excess alloy was destroyed by adding methanol. The polymers obtained were filtered, washed with water, acetone and ether and vacuum dried. The amount of chlorine present in the monomers was quantitatively recovered from the washing water.

The samples prepared were
- poly-$p$-xylylene,
- poly-$m,p$-xylylene (para/meta molar ratio 3),
- poly-$p$-xylylene-thienylene (xylylene/thienylene molar ratio 3).

Chlorination of the polymers was carried out in a saturated NaCl solution at 353 K by bubbling chlorine in the presence of FeCl$_3$. The amount of chlorine in the substituted polymers was 33.3% and 48.3% for poly-$m,p$-xylylene (1.5 chlorine atoms per monomer unit) and poly-$p$-xylylene-thienylene (two chlorine atoms per monomer unit), respectively.

The sulphonation reaction was carried out by adding liquid SO$_3$ to the polymer suspended in 1,1-dichloroethane at 273 K. According to the titration, the amount of substituted polymer per acid equivalent was 473 and 438 g for sulphated poly-$m,p$-xylylene and sulphonated poly-$m$-xylylene-thienylene, respectively (in both cases about four monomer units per sulphonic group).

Powdered polymers were heated under flowing nitrogen or air in a Mettler TA2000C thermoanalyzer for simultaneous TG–DTA. 10 mg samples and a 10 deg/min heating rate were used.

Results and discussion

The thermal behaviour of the unmodified polymers is represented in Fig. 1. The temperature of degradation onset is clearly lower under air flow than under inert gas. The weight increase at the beginning of the oxidative degradation is also clearly detected. IR spectra of samples heated at 493 and 543 K support the attribution of the two subsequent weight uptakes by the unsubstituted poly-xylylenes. Both exhibit well-defined bands at 1270, 1590 and 3560 cm$^{-1}$, which may correspond to dimeric carboxylic groups, but samples heated at 543 K show also a strong band at 1720 cm$^{-1}$, which corresponds to free carboxylic groups. These data can be interpreted by assuming that oxidation may begin at internal sites of the