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THERMAL STABILITY OF SUBSTITUTED POLY-XYLYLENES

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

Functionalization of the polymer with chlorine and sulphonic 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 depropagation reaction yields low-molecular weight polymers, while a simultaneous zip reaction forms 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*-xylylene containing 10% of *o*-xylylene units is less stable than the homopolymer.

In this work we studied how the insertion of *m*-xylylene units in poly-*p*-xylylene 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.

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Experimental

The polymers were prepared by Wurtz synthesis. The chlorides of the monomers were dissolved in dioxane. Na_2K 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*-xylelene (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

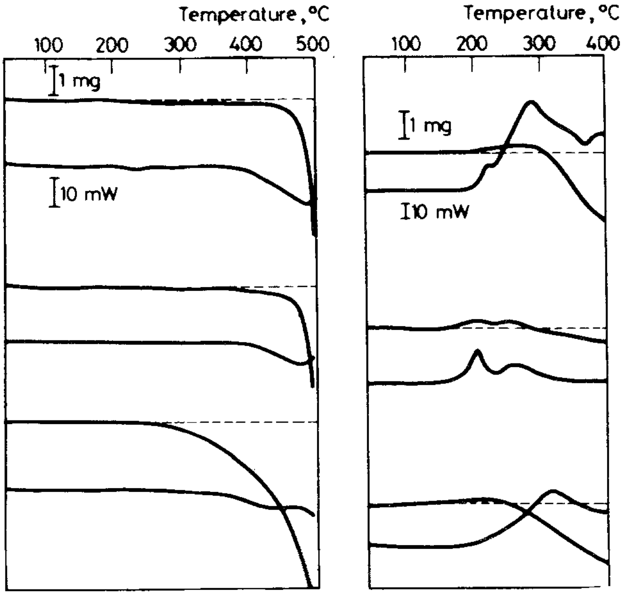

Fig. 1 TG–DTA traces in flowing N_2 (left) and air (right) of (from top to bottom) poly-*p*-xylylene, poly-*m*, *p*-xylylene, poly-*p*-xylylene-thienylene

chain, and that only the loss of fragments of the polymer may produce terminal carboxylic groups in detectable amounts.

The decomposition under nitrogen flow is almost unmodified by the replacement of a fourth of the *p*-xylylene units by *m*-xylylene. Conversely, oxidative degradation begins at lower temperature and its further development is slower. A possible explanation of the former behaviour is that the larger amount of abnormal structures in the chain of the heteropolymer would allow an easier formation of oxidized intermediates, while the presence of non-linear segments in the chain would account for more frequent rearrangements of radicals and for the observed slower degradation.

The insertion of thienylenic units destabilizes the polymer both under air and nitrogen flow. It is likely that the sulphide group may play a role of free-radical source [6], so as to speed up the degradation.

The thermal decomposition of chlorinated polymers is reported in Fig. 2. Most chlorine is lost before the degradation of the polymer chain. This result can be compared with the data of Joesten [5], who remarked the good stability of the chlorine atoms bonded to the aromatic ring, and suggested that the loss of weight of our samples before the polymer decomposition could correspond to chlorine atoms bonded to the ethylene bridges.

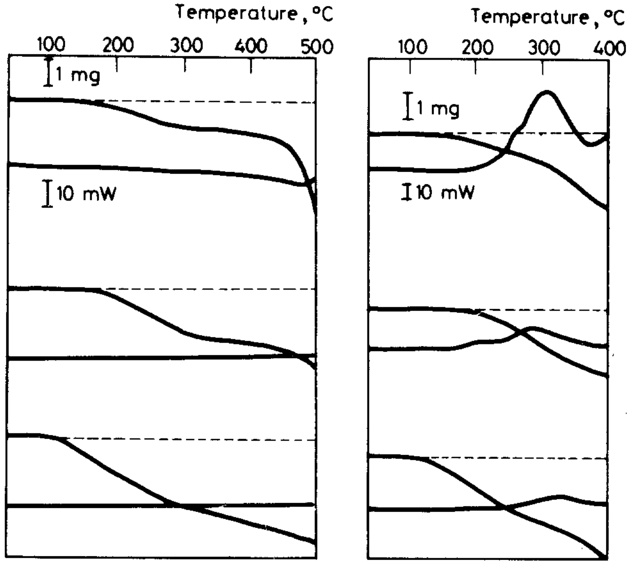

Fig. 2 TG–DTA traces in flowing N_2 (left) and air (right) of chlorinated polymers: from top to bottom poly-*p*-xylylene, poly-*m*, *p*-xylylene, poly-*p*-xylylene-thienylene

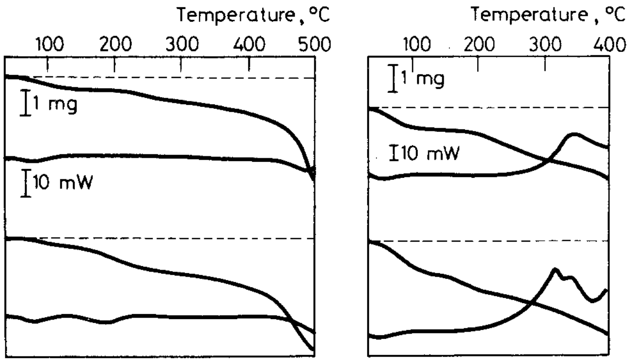

Fig. 3 TG–DTA traces in flowing N_2 (left) and air (right) of sulphonated polymers: from top to bottom poly-*m*, *p*-xylylene, poly-*p*-xylylene-thienylene

The decomposition of sulphonated polymers is shown in Fig. 3. The main features of the curves are the slow dehydration and the decomposition of the sulphonic group, which begins at low temperature.

The most interesting feature in the behaviour of the substituted samples, either chlorinated or sulphonated ones, is that the degradation of the polymer chain is slower than in the case of the unsubstituted polymers. This effect is very clear for samples heated under nitrogen, where the weight loss at 500° is greater in the unsubstituted polymers than in the substituted ones. This occurs in spite of the fact that the major contribution to the loss of weight is due, at least in the latter case, to the loss of substituent groups.

It is possible to account for this effect by assuming that the residual functional groups may inhibit the formation or the propagation of the radicals required for the degradation.

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Zusammenfassung — Die Einführung von Metaeinheiten in die Kette von Poly-p-xylen setzt sowohl die Einsetztemperatur des oxydativen Abbaues als auch die Zersetzungsgeschwindigkeit herab. Die Einführung von Chlor und Sulfogruppen erhöht trotz der geringen Stabilität der Substituenten die Temperaturbeständigkeit der Kette.

Резюме — Введение мета-заместителей в поли-п-ксилен приводит к уменьшению температуры окислительного распада и скорости разложения. Наличие в полимере сульфогруппы и хлора делает цепь более стойкой к высокотемпературной обработке, несмотря на низкую устойчивость таких заместителей.