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Polymers with iodonium salt structure in the side chain

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Summary

We investigated the synthesis of polymer-bound iodonium salts with chloride as anion by polymer analogous reaction. The structure of polymers was determined with NMR-spectroscopy, MS-analysis as well as by model substances. The polymers give transparent films on glass, they decomposed during irradiation and eliminated HCl. The HCl-elimination in the films can be detected with indicators and also with potentiometric titration with $AgNO_3$.

Introduction

Iodonium salts are well known compounds in the field of cationic polymerization. Different working groups investigated the iodonium salts, their synthesis, characterization, and their reactivity (1, 2, 3). More interesting are polymeric iodonium salts prepared by two different groups (4, 5). Crivello and coworkers described the synthesis and characterization of diaryliodonium salts and polymer-bound diaryliodonium salts with complex anions (4, 6, 7, 8).

In connection with investigations about photochromic layers we are interested in the synthesis of polymeric iodonium salts with chloride as anion. We want to show that during the photolysis of these salts analytical amounts of HCl are released.The following equations (1-3) illustrate the reaction path of the photolysis.

$$P{-}Ar_2J^{\oplus}Cl^{\ominus} \xrightarrow{h\cdot v} \left[P{-}Ar_2J^{\oplus}Cl^{\ominus}\right]^{*} \qquad (1)$$

$$\left[P{-}Ar_2J^{\oplus}Cl^{\ominus}\right]^{*} \longrightarrow P{-}ArJ^{\oplus\cdot} + Ar\cdot + Cl^{\ominus} \qquad (2)$$

$$P{-}ArJ^{\oplus\cdot} + S{-}H \longrightarrow S\cdot + P{-}ArJ + H^{\oplus} \qquad (3)$$

S = solvent
P = polymer

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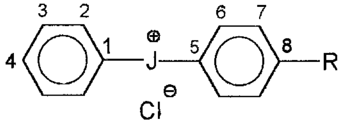
The present paper deals with the synthesis of these side chain polymers, their photolysis, and the identification of the decomposition products. We examined the formation of HCl and the photolytical products by GC-MS analysis. Besides we used model substances with the chloride anion for the better detection of the polymeric iodonium salts.

Experimental part

A general preparation for the synthesis of unsymmetrical iodonium salts (4)

A mixture of 15.5 mmol of iodosobenzene diacetate, 6.5 ml of acetic anhydrid and 72 ml of glacial acetic acid was placed in a 150 ml 4-necked flask equipped with a reflux condenser, a stirrer, thermometer and addition funnel. 15.5 mmol of the coupling compound was added. The mixture was cooled to 10°C (ice/ salt mixture). 1 ml sulfuric acid was introduced into the solution. The system was allowed to warm up to room temperature and 15.5 mmol of NH_4Cl or NaCl dissolved in a little amount water was added. To cover with a layer ether or recristallisation from ethanol gave the crystalline product. The sodium decomposition analysis showes that the compound does not contain sulphur. The yield is 60-80 % of the theory.



R = OCH_3 1
$C(CH_3)_3$ 2
OC_8H_{17} 3

p-Methoxydiphenyliodoniumchloride 1

m.p.: 195°C ; λ_{max}= 246 nm (EtOH);
$C_{13}H_{12}ClJO$ (345.45 g•mol^{-1}) calc: C 45.18 H 3.50
found: C 44.08 H 3.48
^{13}C NMR (50 MHz; d^6-DMSO):120.66 C_1; 134.45 C_2; 131.15 C_3; 130.92 C_4; 109.51 C_5; 136.75 C_6; 116.95 C_7; 161.23 C_8
MS(70 eV): M^+-peak 347 not; 310, 234, 204, 127, 112, 77

p-tert.Butyldiphenyliodoniumchloride 2

m.p.: 180°C ; λ_{max}= 234 nm (MeOH);
$C_{16}H_{18}ClJ$ (372.654 g•mol^{-1}) calc: C 51.56 H 4.86
found: C 51.11 H 4.80
^{13}C NMR(50 MHz; $CDCl_3$): 120.08 C_1; 134.66 C_2; 131.33 C_3; 130.93 C_4; 116.34 C_5; 134.22 C_6; 128.43 C_7; 154.39 C_8
MS(70 eV): M^+-peak 372 not, 260, 245, 204, 127, 77

p-Octyloxydiphenyliodoniumchloride 3

m.p.: 145°C; λ_{max}= 247.6 nm (EtOH);
$C_{20}H_{26}ClJO$ (444.748 g•mol^{-1}) calc: C 54.01 H 5.89
found: C 52.25 H 5.70

^{13}C NMR(50 MHz; $CDCl_3$): 120.37 C_1; 134.28 C_2; 131.02 C_3; 130.48 C_4; 108.60 C_5; 136.86 C_6; 116.92 C_7; 161.270 C_8
MS(70 ev): M^+-peak 445 not, 408, 332, 219, 204, 127, 77

Polymers

Anisole-polystyryliodoniumchloride 4

Iodinated Polystyrene (0.01 mol) was dissolved in CH_2Cl_2.The mixture was cooled to - 10 °C. To this solution a surplus of peracetic acid was added dropwise .The system was allowed to warm up to room temperature and then p-toluenesulfonic acid was added. After stirring for 30 min anisole was introduced into the solution. The polymer solution was kept overnight at room temperature and NH_4Cl or NaCl dissolved in a little amount water/methanol were added. The polymer was isolated by filtration and was washed with water and methanol. It was redissolved in $CHCl_3$ and was precipitated in n-hexane.
Octylphenylether-polystyryliodoniumchloride 5 was prepared in the same way.

Photolysis of polymers - Determination of HCl

A solution of a definite concentration of the polymeric salt in dioxane or chloroform was droped on a quartz glass. After drying the quartz glass was irradiated with the light of a high pressure mercury lamp (250 W, 254 nm) for 6 h in a closed quartz tube. The quartz tube contains a solution of 2 ml 0.05 n KOH and 12 drops of a saturated hydrazine sulphate solution for the absorption of eliminated HCl. The Cl-content was determined by potentiometric titration with $AgNO_3$.

Characterization

^{13}C NMR spectra were recorded on a WP 200 (BRUKER). UV spectra were obtained by means of an spectrophotometer SPECORD UB 80 (Carl Zeiss Jena). The GC-MS spectra were recorded on a SSQ 710 (FINNIGAN).

Results and discussion

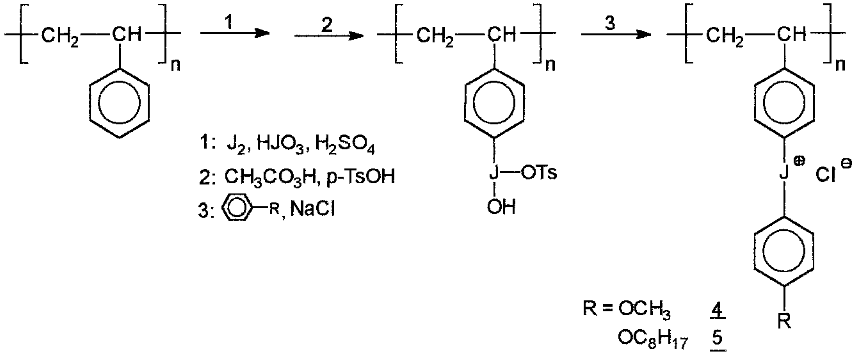
Yamada described the synthesis of polymeric iodonium salts from polystyrene iodosodiacetat and benzene in the presence of conc. sulfuric acid (5). An easier method for the synthesis was developed by Crivello, which was applicable for our compound (4).

For our investigations we synthesized polymeric iodonium salts with anisole and octylphenylether as coupling components. Polystyrene as the starting polymer was iodinated in the first step in para position and afterwards the polymer was treated with peracetic acid and p-toluenesulfonic acid. The resulting polymeric hydroxytosylate derivative was coupled with anisole or octylphenylether directly. The chloride can be obtained by metathesis of the tosylate with NH_4Cl or NaCl. The reaction path is shown in scheme 1.

We found that the solubility of the polymer is influenced by the content of iodine. Polymers with high contents of iodine (iodination of polystyrene 90%) are only soluble in DMF, DMSO or cresol. Nevertheless, anisole substituted polymers are soluble in dioxane or chloroform even with iodine contents of 90%.

The reaction path in scheme 1 is the ideal case.The exact determination of the

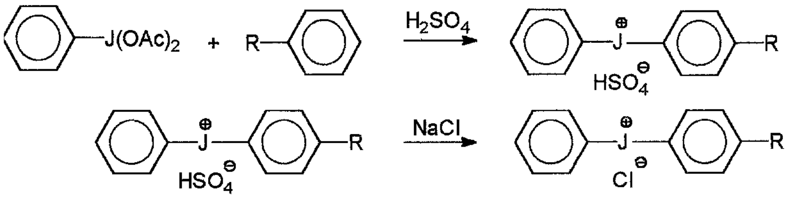
Scheme 1



polymer structure 4 and 5 by elemental analysis is difficult because the obtained polymers consist of units of polystyrene, iodinated polystyrene, and the polymeric iodonium salt.

Therefore, we think that in case of the existence of the iodonium structure, it can be confirmed after photolysis by GC-MS analysis of the decomposition products. For this investigation we irradiated a small amount of the polymeric salt in dioxane with the light of a mercury lamp (250 W). After photolysis for 1h the residue of polymer was precipitated in methanol. The resulting solution was examined by GC-MS analysis. In the GC-MS spectrum of the octylphenylether-polystyryliodoniumchloride 5 we found octylphenylether, p-chlorooctylphenylether and p-iodooctylphenylether as main products.

The polymeric salts are comparable with monomeric iodonium salts. Therefore, we prepared one-sided substituted iodonium salts with a chloride anion . The model substances were synthesized by the shown synthetic pathway (4,5).



(4)

(5)

R = OCH$_3$ 1 , C(CH$_3$)$_3$ 2 , OC$_8$H$_{17}$ 3

The structure of the model compounds can be confirmed with ^{13}C NMR spectroscopy, elemental analysis and MS-analysis. All peaks in the ^{13}C NMR spectrum can be exactly attributed to the structure. In particular the position, of the C-atoms directly bound to the iodonium ion, can be used for the explanation of the ^{13}C NMR spectra of the polymeric iodonium salts. The structure of the monomeric iodonium salts is similiar to the structure of the polymeric iodonium salts. Therefore, the chemical shift of the compounds are comparable. Tab. 1 shows the ^{13}C NMR chemical shifts of the C-atoms directly bound to the iodonium ion in 1, 3, 4 and 5.

Tab. 1: ^{13}C NMR chemical shifts δ of models 1 and 3 and of polymers 4 and 5

compound	C-atom 1 δ in ppm	C-atom 5 δ in ppm
1	120.66	109.51
3	120.37	108.60
4	121.05	114.48
5	120.90	114.98

The photolysis of iodonium salts was exactly investigated (9, 10). For our application it was necessary to know that the polymeric salts eliminate HCl during the irradiation. The HCl-elimination can be detected after photolysis of the iodonium salts by indicators. The monomeric salts were dissolved in ethanol and subsequently irradiated with light of a high pressure mercury lamp (150 W) in the presence of an indicator. An addition of methylorange gave a change of color from yellow to red. The polymers 4 and 5 form good films. From a solution of polymeric salts in dioxane films on glass were prepared. The films are transparent and colorless. Methylorange as indicator is situated on the surface of the polymeric layer. After photolysis for only a few minutes the methylorange change the color. We concluded that the polymeric iodonium salts 4 and 5 release analytical amounts of HCl during the photolysis. The quantity of eliminated HCl we determined after irradiation with a light of a high pressure mercury lamp (250 W, 254 nm) and by potentiometric titration with $AgNO_3$ (experimental part). The content of chloride in the polymers 4 and 5 varyed between 0,7 and 2 per cent. In the ideal case the polymers have a Cl-content between 6-8% (depent on the iodination of polystyrene).

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