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On the nature of "functional groups" in non-functionalized hypercrosslinked polystyrenes

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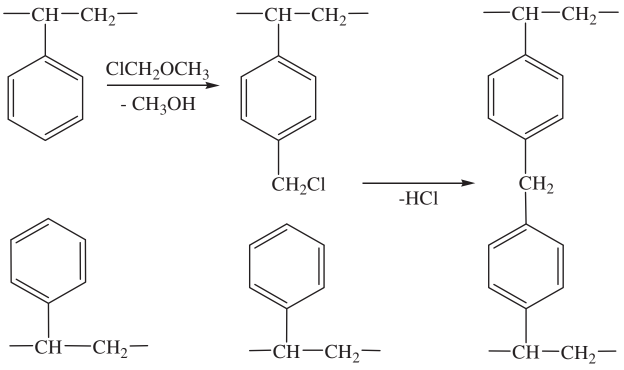
ABSTRACT

The paper discusses the assignment of the absorbance band at 1700 cm^{-1} in FTIR spectra of hypercrosslinked polystyrenes. This band is exceptionally intensive in the spectra of networks obtained by post-crosslinking styrene-0.5% DVB copolymer, swollen in ethylene dichloride, with monochlorodimethyl ether up to the maximum possible crosslinking degrees of 300%, 400% and 500% in the presence of non-oxidizing catalyst $SnCl_4$. Theoretically, in these networks each phenyl ring binds to neighboring phenyls through three, four or five methylene groups, respectively. Elemental analysis of the products seems to be deficient in C and H, thus allowing expectation of a surprisingly high percentage of oxygen. However, the traditional attribution of both the suspected high content of oxygen and the band at 1700 cm^{-1} to aromatic carbonyl groups is incorrect. Treatment of hypercrosslinked polystyrenes with hydroxylamine, sodium bisulfite, ethyl orthoformiate or $LiAlH_4$ do not result in disappearance of the absorbance at 1700 cm^{-1} in FTIR spectra and emergence of corresponding characteristic new bands. Solid state ^{13}C NMR spectroscopy also confirms the absence of C=O moieties in the above hypercrosslinked polystyrenes. The absorbance at 1700 cm^{-1} disappears, while new bands in the range of 1670–1650 cm^{-1} emerge, in the spectrum of the sample with 500% crosslinking degree after the reduction of its benzene rings via Birch reaction. This allows suggesting that the band at 1700 cm^{-1} and its shoulders are caused by hindered vibrations of carbon–carbon bonds and valence angles in the aromatic fragments composing the rigid network with extremely high extent of mutual connectivity.

1. Introduction

During the last decade, the interest of the scientific community and many manufacturers to hypercrosslinked polystyrene adsorbing materials increased steeply, because their advantages over traditional macroporous resins and activated carbons, in terms of higher sorption power and simpler regeneration, have become evident. Hypercrosslinked polystyrene owes its high sorption potential to a specific structure which, in its turn, is determined by the conditions of synthesis. The basic principle of the preparation of hypercrosslinked polystyrene consists in the intensive bridging of highly swollen polystyrene chains with rigid links. In the laboratory practice such bridging is carried out mostly by crosslinking polystyrene chains, swollen in ethylene dichloride (EDC), with monochlorodimethyl ether (MCDE) through Friedel–Crafts reaction:



The reaction proceeds in two steps: at first, chloromethyl groups are introduced into starting polymer chains, which then alkylate phenyl rings of other chains in the presence of $SnCl_4$ (or $FeCl_3$), thus binding them by methylene bridges. To obtain the hypercrosslinked polystyrene adsorbing materials on an industrial scale, a beaded styrene–divinylbenzene (DVB) copolymer is

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subjected to chloromethylation by any method reasonable for technology, and then the copolymer undergoes self-crosslinking in the presence of a Friedel–Crafts catalyst. At an elevated temperature the binding of phenyl rings with methylene groups is accompanied by the intensive release of gaseous hydrogen chloride. Actually, the latter plays a role of a *sui generic* protective medium preventing completely the contact of air oxygen and moisture with the reacting components, so that the resulting network should be composed solely of benzene rings, CH and CH_2 groups. One may expect, of course, the presence in the final product of some residual chloromethyl groups which failed to find a reaction partner for steric reasons. Nevertheless, many publications report the presence in the hypercrosslinked polystyrenes of chemically bound oxygen-containing groups, such as hydroxyls, carbonyls or ethers, which are supposed to arise in the polymers from side-reactions of oxidation.

Streat et al. [1–3] have studied the chemical structure of commercial hypercrosslinked polystyrene Macronet Hypersol™ resins MN-100, MN-150 (both are weak basic anion exchange resins), MN-200 (non-functionalized resin), MN-500 (sulfonate) and MN-600 (carboxyl-containing resin). Elemental analysis of MN-200 sample showed that, beside carbon and hydrogen, the polymer contains 1% residual chlorine and 6.4% oxygen when calculated as O% = 100% – (C% + H% + Cl%). When judging by the intensive absorbance band at 1706 cm^{-1} in Furier transform infrared (FTIR) spectrum of MN-200 resin (as well as in the spectra of all the above products), the authors attributed oxygen largely to the presence of carbonyl functional groups. In their turn, C=O were assigned to a combination of aryl- and alkyl-aryl ketones [2]. The authors see the evidence of aryl ketone functions in "the presence of an absorption band at 1210 cm^{-1}, the phenyl carbon stretch, and several medium intensity bands around 1300 cm^{-1}, due to C—C—C bending and C—CO—C. Similarly, bands at 1304 cm^{-1} and several bands around 1100 cm^{-1} suggest the possible presence of an alkylketone" [2].

The quantitative determination of oxygen-containing groups in MN-100, MN-150 and MN-200 using the so-called Boehm titration [4,5] revealed no strongly acidic and weakly acidic groups; the capacities were less than 0.03–0.06 and 0–0.05 meq/g, respectively. The concentration of phenolic functionalities proved to be vanishingly small, 0–0.01 meq/g, while the concentration of carbonyl groups was found to be somewhat larger, 0.10–0.13 meq/g [6]. At the same time the solid state ^{13}C MAS NMR studies did not unambiguously reveal carbonyl groups in the commercial hypercrosslinked resins MN-200 and MN-270 [7,8]. X-ray photoelectron spectroscopy also failed to advance direct arguments confirming reliably the presence of C=O groups in MN-150 and MN-600, because the spectrum of C1s orbital completely masked the area of C=O signal [1,2].

Strictly speaking, one may expect the formation of a certain portion of oxygen-containing groups in commercial hypercrosslinked products during the steam stripping of final polymers after the bridging process. Steam, oxygen in it, a trace catalyst and a fairly high temperature may facilitate the hydrolysis and oxidation of residual chloromethyl groups to hydroxymethyl groups or aldehyde functions or even the oxidation of methylene bridges with the formation of benzophenone-type fragments. What is really interesting, is the presence of an intensive absorbance band at 1700 cm^{-1} not only in the infrared spectra of various commercial hypercrosslinked polystyrenes [9–12], but also in the spectra of in-house made samples [13–17] which were subjected to mild washing and drying, rather than steam treatment. For the first time, Grassie et al. [18] have found this band in the IR spectrum of the product of self-condensation of α,α'-dimethoxy xylene via Friedel–Crafts reaction and also explained its appearance by the side-reaction of oxidation. Somewhat later we observed the same absorbance at 1700 cm^{-1}, too, in the IR spectrum of the hypercrosslinked product of crosslinking linear polystyrene with methylal in the presence of $SnCl_4$ [19]. However, we have questioned the hypothesis of oxidation because the crosslinking of linear polystyrene with methylal in an inert atmosphere did not eliminate the band of interest in the spectrum of the resulting network.

Recently, we described the hypercrosslinked polystyrene resins with maximum possible crosslinking degrees of 300%, 400% and 500% [20]. In FTIR spectra of these materials the band at 1701 cm^{-1} is exceptionally intensive and so we have attempted to ascertain the possible origin of this band. For this purpose we exploited various characteristic chemical reactions converting C=O functionalities into other chemical groups which can be easily detected by FTIR spectroscopy. Also, we appealed two instrumental methods, solid state ^{13}C NMR and X-ray photoelectron spectroscopy, as the independent methods of identifying functional groups in the above-mentioned polymers.

2. Experimental

2.1. Chemicals

Monochlorodimethyl ether (carcinogenic agent) with boiling temperature of 57–61 °C was used as a crosslinking agent. The reaction solvent, ethylene dichloride, was boiled over P_2O_5 and distilled. Hydroxylamine hydrochloride, stannic tetrachloride and other chemicals were used as received from Reakhim, Russia.

2.2. Syntheses of networks and chemical reactions

2.2.1. Synthesis of hypercrosslinked polystyrene networks

The beads of largely 0.3–0.5 mm in diameter of gel-type styrene-0.5% divinylbenzene (DVB) copolymer, pre-swollen within 1.5 h in the mixture of ethylene dichloride and a required quantity of monochlorodimethyl ether, were cooled down to 8–9 °C. At stirring, stannic tetrachloride (one mole per mole of the ether) was added dropwise so that the temperature of reaction mixture did not exceed 18–20 °C. The reaction was conducted at 80 °C for 10–12 h at constant agitation. After accomplishing the reaction, the beads of the crosslinked product were filtered and washed with acetone, 0.5 N HCl and excess distilled water. The beads were dried in an oven at 80 °C.

2.2.2. Synthesis of hypercrosslinked network incorporating aldehyde groups

The synthesis was carried out in three stages. First, chloromethyl groups were introduced in the hypercrosslinked polystyrene network with the crosslinking degree of 100%. To this end, 10.4 g (0.1 mol) of the polymer were placed in 100 ml conical flask and the solution of 26.8 ml (0.35 mol) MCDE in 35 ml EDC was added. In 1.5 h 3.5 ml (0.03 mol) $SnCl_4$ were added in the flask, the reaction mixture was agitated manually and the chloromethylation reaction was allowed to proceed for 6 h at room temperature. Afterwards, the beads of chloromethylated product were filtered, washed with acetone, 0.5 N HCl, excess distilled water and dried in an oven at 70 °C. Thus obtained polymer contained 7.8% Cl.

At the second stage, the chlorine atoms were replaced with iodine atoms, for which the above polymer was placed in a three-necked round bottom flask and covered with a solution of 1.85 g NaI in 80 ml acetone. The reaction mixture was agitated for 4 h at 50 °C. The beads together with precipitated NaCl were filtered, washed with 200 ml acetone, 100 ml ethanol and 50 ml of dimethyl sulfoxide (DMSO).