Chemical reactions of terminal groups in polyurethane foams

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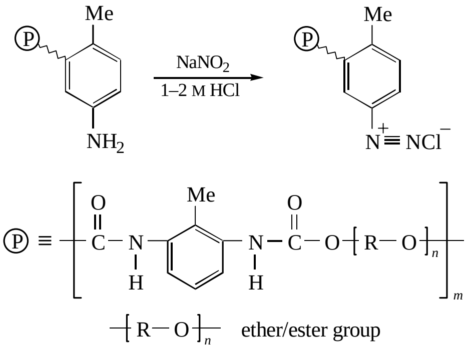
The terminal toluidine groups of polyurethane foams can undergo reactions typical of monomeric aromatic amines, and these reactions may be used in chemical analysis.

Chemical reactions of polymers[1] containing highly reactive surface groups are of most interest to the chemical modification of polymers[2] and to organic synthesis.[3,4] We report here on the heterogeneous chemical reactions of terminal toluidine groups in polyurethane foams (PUFs). PUFs are prepared by the polycondensation of polyhydric alcohols with tolylene diisocyanates. The preparation conditions are responsible for the presence of tolylene diisocyanate groups, which can be hydrolysed to form terminal toluidine groups. We supposed that amino groups that are constituents of terminal toluidine groups can undergo diazotization, azo coupling and other reactions typical of monomeric aromatic amines.

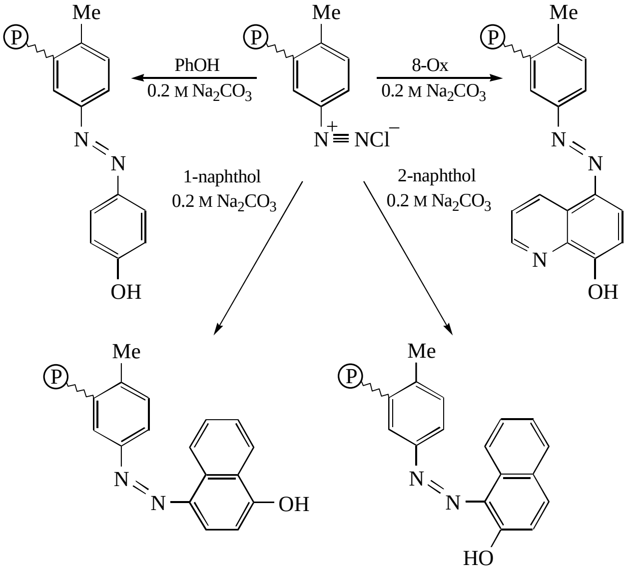
Commercial polyether (5-30 and M-40 brands) and polyester (2200 and 35-08 brands) foams from Radikal (Ukraine) were used in this study. PUFs were cut as tablets (16 mm in diameter and 5 mm in thickness) of mass 0.04±0.005 g and purified as described earlier.[5] The interactions between PUFs and aqueous sodium nitrite, 4-nitrophenyldiazonium tetrafluoroborate, free active chlorine and formaldehyde solutions were studied as described below. A PUF tablet was placed in a closed vessel containing 25 ml of the test solution. Air bubbles were removed using a glass rod. The vessel was shaken until the completion of the reaction (15–60 min). Then, the tablets were removed and dried between filter paper sheets. The yields of reaction products were found using diffuse-reflectance spectroscopy. Diffuse-reflectance spectra were measured on a Spectroton colorimeter (NPO Khimavtomatika, Uzbekistan) and treated in terms of the Kubelka–Munk equation.

Amino groups incorporated into the terminal groups of PUFs readily react with aqueous sodium nitrite solutions to form a polymeric diazonium cation (Scheme 1). Note that the diazotization occurred at room temperature. In contrast to monomeric diazonium chloride, which is extremely unstable and can be retained for a short time in aqueous solutions at 0 °C, solid polymeric diazonium chloride is stable in storage in air during one hour.



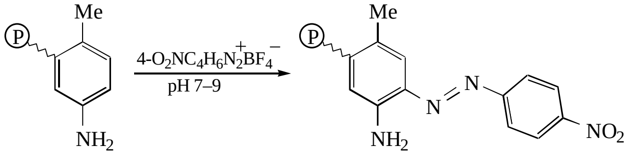
Scheme 1

The diffuse-reflectance spectrum of diazotised PUF exhibits a wide band with λ_{max} = 390 nm (Figure 1, curve *2*). A maximum yield of diazotised PUF was attained in 30 min on contact between PUF tablets and an aqueous solution containing sodium nitrite and 1–2 M HCl. The Kubelka–Munk function linearly depends on the nitrite ion concentration in the aqueous solution.



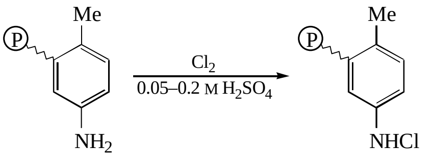
Scheme 2

The concentrations of terminal toluidine groups calculated from the chemisorption isotherms of nitrite ions on all sorbents were equal to 8.7±0.6, 9.3±0.2, 8.4±0.5 and 9.5±0.9 mmol g^{-1} for 5-30, M-40, 2200 and 35-08 PUFs, respectively. Diazotised PUFs may enter into the subsequent azo coupling reaction with phenol, 8-hydroxyquinoline, 1-naphthol and 2-naphthol (Scheme 2). This is accompanied by a colour change and the appearance of new bands with λ_{max} = 420, 480, 510 or 520 nm, respectively. Moreover, the polymeric azo compounds formed are stable and do not degrade even after contact with 5 M HCl, 2 M NaOH and organic solvents such as acetone, ethanol and chloroform.



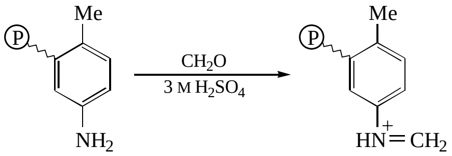
Scheme 3

Using an aqueous solution of 4-nitrophenyldiazonium tetrafluoroborate as an example, we showed that PUFs easily enter azo coupling reactions at pH 7–9 to form a red product (Scheme 3). The diffuse-reflectance spectrum of the product exhibits a wide band with λ_{max} = 510 nm (Figure 1, curve *3*). It is well known that the combination of diazonium compounds with amines can proceed not only at the *para* or *ortho* position to the amino group with the formation of azo compounds, but also at the amino group with the formation of diazo amino compounds. However, diazo amino compounds are extremely unstable in acidic media, whereas the product obtained is stable even in 5 M HCl. In our opinion, the following facts provide support for the formation of an azo compound: the presence of an active diazo component, diazotised 4-nitroaniline; the reaction conditions, the spectral characteristics of the product and its stability.



Scheme 4

In contact between PUF tablets and an aqueous solution of free active chlorine, a yellow product was formed in 10–15 min. This reaction was accompanied by the appearance of a new band at 380 nm in the diffuse-reflectance spectrum (Figure 1, curve *4*). The maximum yield of the product was achieved at an H_2SO_4 concentration of 0.05–0.2 M. We examined the effect of the chemical composition of PUFs on the yield of oxidation products and found that the yield for polyether-based foams was higher than that for polyester-based foams. The F_{380} Kubelka–Munk value increased in the following order: 35-08 PUF < 5-30 PUF < M-40 PUF. The F_{380} value linearly increased as the concentration of free active chlorine in an aqueous solution increased from 0.2 to 6 μg cm^{-3}. We suggested that terminal toluidine groups react with active chlorine according to Scheme 4. Published data[6] on the interaction of chlorine with ammonium salts and amines, as well as the chemical properties of the reaction product (it oxidises potassium iodide to iodine), served as a basis for this suggestion. The elemental analysis confirmed the presence of chlorine in the coloured reaction product. The chlorine content of the product was 3.93% after the reaction between 25 ml of a solution containing about 1.95 mg of active chlorine and 0.042 g of a polyurethane foam.



Scheme 5

In contrast to the above reactions, PUFs slowly react with formaldehyde. A yellow condensation product was formed in contact of a PUF tablet with an aqueous formaldehyde solution containing 3 M H_2SO_4 only after 5–7 days. The diffuse-reflectance spectrum of this product exhibits a broad band at 420 nm (Figure 1, curve *5*). Heating in a water bath shortened the reaction time to 30 min. Based on the published data[7] on the interaction of aldehydes with monomeric primary amines, we believe that the reaction of PUFs with formaldehyde results in the formation imino derivatives of PUFs according to Scheme 5. Salts of the imino derivatives of aldehydes are coloured, whereas free imino derivatives are colourless or coloured only slightly.[8]

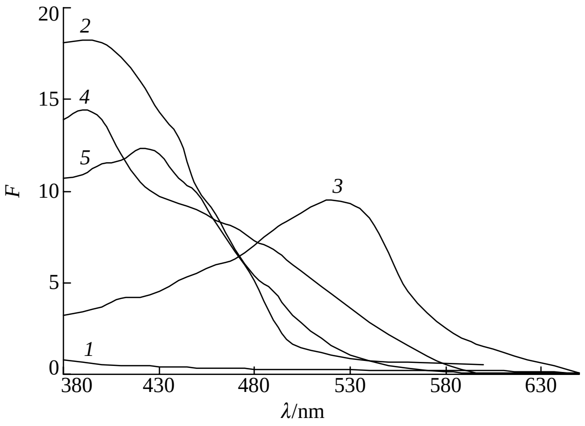


Figure 1 Diffuse reflectance spectra of (*1*) 5-30 polyurethane foam and products of interaction between PUF 5-30 and (*2*) sodium nitrite, (*3*) 4-nitrophenyldiazonium tetrafluoroborate, (*4*) active chlorine and (*5*) formaldehyde.

Like monomeric imino derivatives, a polymeric imino derivative of PUFs becomes colourless in contact with base solutions. An initial yellow colour appears immediately after contact with a 3 M H_2SO_4 solution; this fact is indirect evidence for the high stability of the reaction product.

Thus, we experimentally found that terminal toluidine groups in PUFs are highly reactive towards diazotization, azo coupling, oxidation and condensation reactions with the formation of intensely coloured products. Heterogeneous chemical reactions of PUFs with the above compounds in aqueous solutions rapidly proceed at room temperature and at low solute concentrations. PUFs do not undergo degradation as a result of chemical interactions. The linear response of the Kubelka–Munk function to the solute concentration makes it possible to recommend PUFs as solid polymer reagents for the determination of nitrite ions, free active chlorine and some other compounds.

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