Abstract

The aim of this thesis was the synthesis of reversion-stable crosslinkers for diene-rubbers generating oligothio-1,4-phenylene-bridges in the vulcanizates. First, the synthesis of 1,4-dimercaptobenzene from 1,4-dichlorobenzene and sodiumisopropylthiolate was optimized. 1,4-Dimercaptobenzene was used as an educt in the synthesis of the efficient crosslinkers poly(tetrathio-1,4-phenylene) and zinc(II)benzene-1,4-dithiolate. Due to some disadvantages of this reaction, bis(chlorodisulfanyl-1,4-benzene) was chosen as alternative starting compound. A novel synthesis for 1,4-bis(chlorodisulfanylbenzene) by aromatic substitution of benzene with dichlorodisulfane was developed using the catalysts Montmorillonite KSF and a new compound made from silica and aluminiumtrichloride. Under slightly modified conditions this reaction also directly produces poly(dithio-1,4-phenylene).

Through the reduction of 1,4-bis(chlorodisulfanyl)benzene with lithiumaluminiumhydride, a convenient synthesis of 1,4-dimercaptobenzene in high purity and good yields was introduced. The reduction with lithiumaluminiumhydride was also applied in the characterization of poly(oligothio-1,4-phenylene)s and aromatic chlorosulfanes. Poly(dithio-1,4-phenylene) was obtained by heating 1,4-bis(chlorodisulfanyl)benzol in vacuo. However, poly(dithio-1,4-phenylene) gained from different reactions did not show good crosslinking abilities.

Furthermore, a new class of crosslinkers with the general formula $X\text{-}S_2\text{-}C_6H_4\text{-}S_2\text{-}X$, where X is a primary or secondary amine, was introduced. The products of the reaction of 1,4-bis(chlorodisulfanyl)benzene with dibenzylamine had only poor crosslinking abilities. The oligomers resulting from the reactions of 1,4-bis(chlorodisulfanyl)benzene and the primary amines benzylamine and cyclohexylamine were excellent crosslinkers. All crosslinkers were investigated in technical rheometer-tests and model-compound vulcanizations with 2,3-dimethyl-but-2-ene as model olefin. The vulcanizates were analysed by GPC, RP-HPLC and NMR-spectroscopy. By a combined GPC and RP-HPLC separation the presence of oligothio-1,4-phenylene-bridges in the model-compound-vulcanizates could be proved.