Insertion of Cl- and CCl3-groups during the free radical initiated chain decomposition of 1,4-cis-polyisoprene in tetrachloromethane

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SUMMARY

The free radical initiated chain decomposition of 1,4-cis-polyisoprene was carried out in 13C-enriched tetrachloromethane. Surprisingly, although the Cl- and CCl3-radicals were simultaneously produced, it was almost entirely the Cl-radical that was built into the polymer. The detection was carried out by 13CNMR-spectroscopy and elementary analysis. Phosgene was detected as an oxidation product of tetrachloromethane.

INTRODUCTION

The radical chain decomposition of 1,4-cis-polyisoprene in CCl4, initiated by azodiisobutyric acid dinitrile in an air atmosphere, is carried out in industry to degrade commercial polyisoprene from a molecular weight of approximately 1 million to approximately 100 000. The decomposition products are used in the production of chlorinated rubber. It has been discovered that during the chain decomposition stage up to 0.5 % chlorine with respect to the polymer is built into the chain. We used this as the basis to examine the reactions of CCl4 in more detail.

There are numerous publications which deal with the addition of CCl4 to 1,2-polybutadiene (1 - 7) and 1,4-polybutadiene (8). However, to the best of our knowledge, there is no paper which discusses the reaction between CCl4 and polyisoprene through addition of a radical initiator.

This paper deals with the quantitative determination of the inserted Cl- or CCl3-groups and the analysis of phosgene. Decomposition reactions on a laboratory scale are carried out for analysis.

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EXPERIMENTAL

The chain decomposition was carried out in three series of experiments (2 determinations each).

In addition to 2.5 g polyisoprene, the following educts were used:

1st series of experiments: 50.0 g CCl₄
0.06 g azodiisobutyric acid dinitrile
(radical initiator)

2nd series of experiments: 50.0 g ¹³CCl₄
(¹³C isotope content: 80 %)
0.06 g azodiisobutyric acid dinitrile

3rd series of experiments: 50.0 g toluene
0.06 g azodiisobutyric acid dinitrile

General method
The educts were mixed and heated while stirring under reflux for 16 hours at 74°C. In addition, dried air was passed into the solution at a flow rate of 1 l/h. Downstream of the reflux condenser the gas stream was passed into a wash bottle filled with a solution of n-octylamine in toluene in order to allow the volatile phosgene to react and form the corresponding urea derivative.

Analysis of the decomposed polyisoprene
After the decomposition reaction, the solvent CCl₄ was removed to a residual content of < 5 ppm by repeated concentrating with toluene. Complete evaporation to dryness could not be carried out because of the formation of insoluble products. The analyses were carried out in a solution of 50 % concentration in toluene. The characterization of the decomposed polyisoprene was carried out by ¹³CNMR-spectroscopy as well as by Cl⁻ and O-analysis. The broadband decoupled ¹³CNMR-spectra were recorded on a Varian XL 200 spectrometer under the following conditions: solvent C₆D₆ with addition of Tetramethylsilane (TMS) as internal standard and chromium acetylacetonate as relaxation reagent; Pulse-delay: 5s. The quantification of the inserted CCl₃-groups was carried out in the second series of experiments by addition of ¹³CCl₄ as internal standard for integration. The oxygen content was determined from the solvent-free polymer using the Elemental Analyzer 1106 from Carlo Erba. The organic bound chlorine content was determined after a Wurzschmitt decomposition with a Titroprocessor 636 from Metrohm. Chloride was analyzed before the hydrolysis and taken into account for the calculation of the organic bound chlorine.