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Insertion of Cl- and CCl_3-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 ^{13}C-enriched tetrachloromethane.
Surprisingly, although the Cl- and CCl_3-radicals were simultaneously produced, it was almost entirely the Cl-radical that was built into the polymer.
The detection was carried out by $^{13}CNMR$-spectroscopy and elementary analysis.
Phosgene was detected as an oxidation product of tetrachloromethane.

INTRODUCTION

The radical chain decomposition of 1,4-cis-polyisoprene in CCl_4, 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 CCl_4 in more detail.

There are numerous publications which deal with the addition of CCl_4 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 CCl_4 and polyisoprene through addition of a radical initiator.

This paper deals with the quantitative determination of the inserted Cl- or CCl_3-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	CCl_4
	0.06 g	azodiisobutyric acid dinitrile (radical initiator)
2nd series of experiments:	50.0 g	$^{13}CCl_4$ (^{13}C 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 CCl_4 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 ^{13}CNMR-spectroscopy as well as by Cl- and O-analysis.
The broadband decoupled ^{13}CNMR-spectra were recorded on a Varian XL 200 spectrometer under the following conditions: solvent C_6D_6 with addition of Tetramethylsilane (TMS) as internal standard and chromium acetylacetonate as relaxation reagent; Pulse-delay: 5s. The quantification of the inserted CCl_3-groups was carried out in the second series of experiments by addition of $^{13}CCl_4$ 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.

Determination of phosgene content
Volatile phosgene as well as phosgene which had remained in the reaction flask was derivitized to bis-n-octylurea. The quantification was carried out by thin-layer chromatography in a linear chamber from Camag by reflection measurements at 190, 200 and 220 nm using dichloromethane as the carrier.
A chloride analysis (titration with a titroprocessor 636 from Metrohm) was completed due to the high reactivity of phosgene.
Spectroscopic Data:

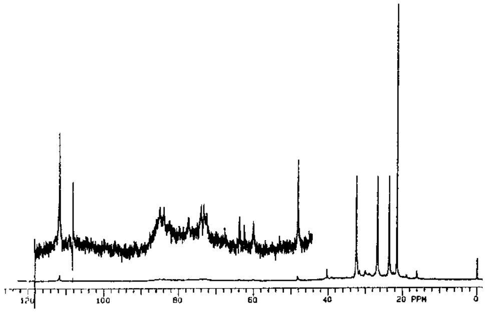

fig. 1 : ^{13}CNMR spectrum decomposition product of experiment 1.1

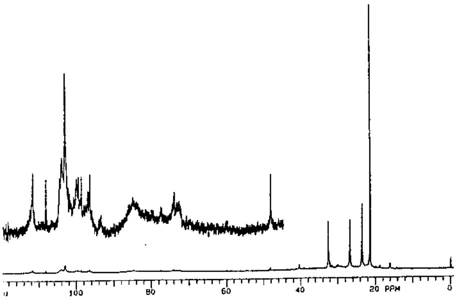

fig. 2 : ^{13}CNMR spectrum decomposition product of experiment 2.1

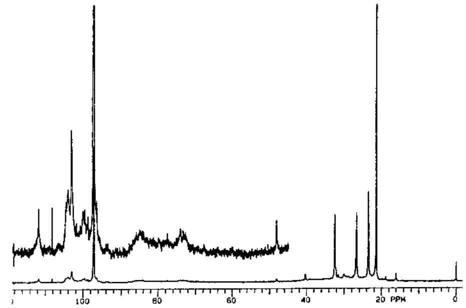

fig. 3 : ^{13}CNMR spectrum decomposition product of experiment 2.1 with $^{13}CCl_4$ as int. integration standard

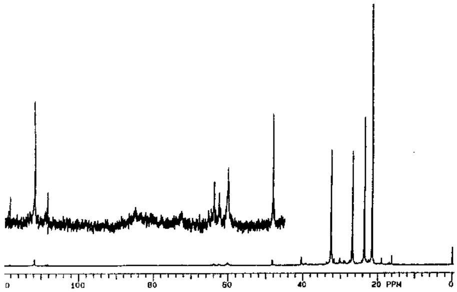

fig. 4 : ^{13}CNMR spectrum decomposition product of experiment 3.1

Figures 1 - 4 show the ^{13}CNMR-spectra of the polyisoprene samples decomposed in experiments 1 - 3. The signal assignments were made with the help of the C-Search-Data collection (9). The expectation for the chemical shift of $R\underline{C}CL_3$ (i.e. insertion of CCl_3-groups) ranges between 95 and 105 ppm and for the chemical shift of $R\text{-}R'_2\underline{C}Cl$ (i.e. insertion of Cl-groups) between 40 and 85 ppm.

Experiment 1 (fig. 1) revealed the first hints that CCl_3-groups are inserted only in a subordinate amount because even at a high signal enhancement, no resonances in the expectation range could be observed. In the range from 70 to 90 ppm however signals are clearly seen. A quantification could not be carried out because of superposition of signals from the oxidation products (hydroxides, hydroperoxides). This was shown again in Fig. 4 for the ^{13}CNMR spectrum of the polyisoprene decomposed in toluene.

In the ^{13}CNMR spectrum from the second series of experiments (decomposition reaction in $^{13}CCl_4$, fig. 2) CCl_3-groups can definitely be recognized. The signals appear in the range between 92 and 108 ppm and extend over the entire expectation range.

With the addition of a known amount of ^{13}C-enriched CCl_4 as internal integration standard, a quantification of the inserted CCl_3-groups is possible (fig. 3). The results are summarized in table 2. In both determinations an excellent conformity exists between the insertion rate of Cl- and CCl_3-groups in spite of the clearly different amount of total chlorine content (6.2 % versus 5.1 %).

RESULTS AND DISCUSSION

In table 1 the experimentally determined amounts of inserted oxygen and chlorine are listed.

Table 1: elementary analysis of the decomposition products (determination of O and Cl)

experiment		1.1	1.2	2.1	2.2	3.1	3.2
oxygen	weight-%	14.5	14.3	14.0	13.0	17.3	17.8
chlorine	weight-%	6.7	6.6	6.2	5.1	-	-

The total chlorine insertion rate is about a factor of 10 higher in comparison to the industrial product. This effect is caused by the high concentration of radical initiator chosen.
Table 2 shows that in both determinations of experiment 2 approximately 20 weight-% of the analytically registered chlorine are due to CCl_3-groups and approximately 80 weight-% are due to Cl-groups. Accordingly of the total chlorination, approximately 8 mole-percent is due to CCl_3-groups and 92 mole-percent comes from Cl-groups.

Table 2: chain insertion of Cl- and CCl_3-groups

experiment		2.1	2.2
total chlorine	weight-%	6.2 (= 100 %)	5.1 (= 100 %)
chlorine of Cl	weight-%	4.9 (79 %)	4.2 (82 %)
chlorine of CCl_3	weight-%	1.3 (21 %)	0.9 (18 %)
CCl_3-groups	mole-percent*	8	9
Cl-groups	mole-percent*	92	91

* data related to the inserted groups

Phosgene was detected as a further reaction product of CCl_4. Chlorine balances were carried out for the observed reactions of CCl_4: chain insertion, oxidation to phosgene and formation of chloride (e.g. by hydrolysis of phosgene). The initial quantity of CCl_4 serves as reference amount.
The values are listed in table 3.

Table 3: Balance of chlorine for the reactions of the solvent CCl_4
(data in weight-% related to the initial quantity of CCl_4)

experiment	1.1	1.2	2.1	2.2
polyisoprene-chlorine	0.43	0.42	0.38	0.31
phosgene-chlorine	0.47	0.41	0.71	0.78
chloride *	0.74	0.53	1.15	1.25
sum of chlorine	1.17	0.95	1.53	1.56
=> chemically converted CCl_4	1.26	1.02	1.66	1.69

* includes phosgene-chlorine

Depending on the experimental conditions up to 1.7 % of the used solvent is "consumed" by the chemical reactions mentioned above.
It is a known fact that in the presence of moisture the decomposition of CCl_4 is accelerated. The increased phosgene- and chlorine-quantities in experiment 2 compared with those of experiment 1 can be attributed to this fact.

REFERENCES

(1) Derouet D, Brosse JC Eur. Polym. J. 19, 697 (1983)
(2) Derouet D, Brosse JC Eur. Polym. J. 21, 1053 (1985)
(3) Derouet D, Brosse JC Eur. Polym. J. 26, 739 (1990)
(4) Derouet D, Brosse JC Eur. Polym. J. 26, 753 (1990)
(5) Okamoto H, Adachi S, Iwai T J Makromol Sci, Chem. 11, 1949 (1977)
(6) Okamoto H, Adachi S, Iwai T J Polymer Sci, Polym. Chem. Ed. 17, 1279 (1979)
(7) Okamoto H, Adachi S, Takada K, Iwai T ibid 17, 1279 (1979)
(8) Rosin H, Asscher M J Appl. Polym. Sci. 13, 1721 (1969)
(9) Kalchhauser H, Robien W, J. Chem. Inf. Comput. Sci. 25, 103 (1991)

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