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^{1}H-NMR/^{13}C-NMR Studies of Branched Structures in PVC Obtained at Atmospheric Pressure

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SUMMARY

The ^{1}H-NMR-spectra of raw poly (vinyl chloride)obtained at atmospheric pressure (U-PVC) have revealed the presence of high concentrations of branches. The content of labile chlorine was determined by reaction with phenole in order to estimate the branch points with tertiary chlorine. The branch length of reductively dehalogenated U-PVC by ^{13}C-NMR analysis have provided evidence for both short chain branches including chloromethyl groups and 2.4-dichloro-n-butyl groups and long chain branching. For a number of U-polymers the total amount of branching ranges from 7.5 to 13.5/1000 C. The ^{13}C-NMR measurements point to a ratio of methyl/butyl branches of 1 : 1 and short chains/long chains of 6 : 1.

Introduction

PVC was prepared by an emulsion type polymerization without emulsifier below the vapour pressure equilibrium of the monomer at constant temperatures. This type of polymerization is termed polymerization at subsaturation pressure or U-polymerization and results in polymer structures different from those which were obtained by normal VC-polymerization. Most of the limited information pertaining to this process has appeared in the patent literature, (W. Heuer, 1939, Holl.Pat.,) but there exist investigations of O'Hara and Prutton (1950), who polymerized various monomers such as vinyl chloride, ethylenoxide or butadiene in this way. The results of these authors were in some agreement with our investigations (D. Braun, G. Holzer, manuscript in preparation) leading to the conclusion that because of rather low rates of polymerization this process is only suitable for special applications. Sörvik and Hjertberg (1977, 1978) studied the polymerization of VC at subsaturation pressure in the presence of different types of seed polymers with monomer and water soluble initiators, respectively. Using such polymerization conditions, polymers with broad molecular weight distribution (MWD),

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substantial branched structures and reduced thermal stabilities occurred. Therefore the polymerization of VC at atmospheric pressure represents a method to produce PVC with high amounts of structural defects influencing its thermal stability. Besides, these polymers were suitable for the investigation of structural irregularities, which act as labile defects for the dehydrochlorination, because U-polymerization also simulates conditions in ordinary VC-polymerization after the pressure drop.

In this work the branched structures of the U-PVC were studied by means of ^{1}H-NMR and ^{13}C-NMR spectroscopic investigations.

Results and Discussion

The possibility of measuring branch points in U-polymers which where not reductively dehalogenated is based in the special structure of the products. Contrary to commercial PVC-samples, the 100 MHz-spectrum (Fig. 1)

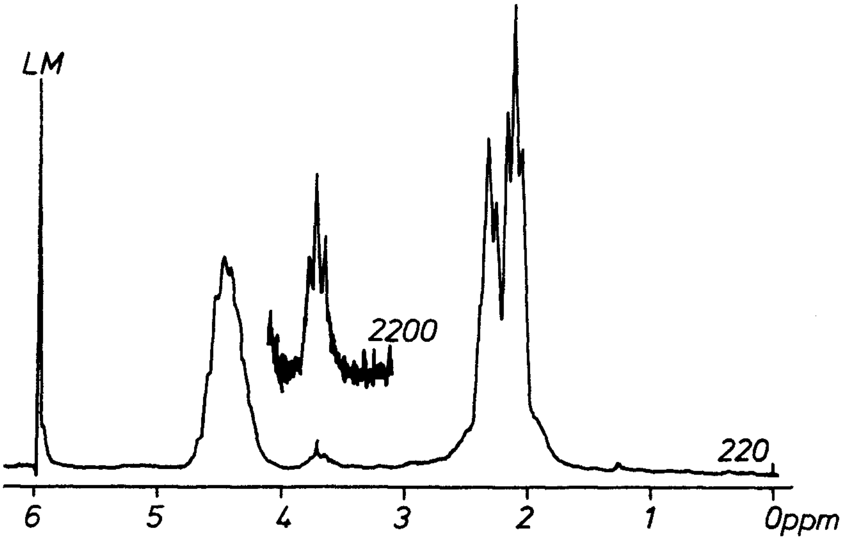

Figure 1 ^{1}H-NMR spectrum (100 MHz) of U-PVC in $C_2D_2Cl_4$ at 100° C; Scan accumulations: 1000; Amplification: 220, 2200.

of a PVC obtained in aqueous emulsion at atmospheric pressure indicates a signal at δ = 3.75 ppm, which appears as a triplet with a coupling constant of I_{AX} =

6 Hz. According to position and spin-coupling this signal can be assigned to the following structure:

$$... CH_2-CH_2Cl \quad (1)$$

This structure can be a saturated chain end in a linear chain or the end group of a short or long branch. In the latter case it is not possible to obtain information about the length of the side chain or about the structure of the branch point, i.e. if a chlorine or a hydrogen is attached to the branch carbon. Branching with $-CH_2CH_2OH$ ends can be neglected, because the reduction with $LiAlH_4$ and Bu_3SnH results in a complete disappearance of the signal at $\delta = 3.75$ ppm. Methyl protons, which normally appear at $\delta = 1$ ppm and which would indicate the presence of methyl groups were absent. If the molecules are assumed to be linear and one of the end groups to have a $-CH_2CH_2Cl$ structure, the $\bar{M}_n$ of these U-polymers (ca. 30000) would imply about one $-CH_2CH_2Cl$ group per 1000 C. However, the content of such structures is much higher, which points to an unusual high content of branch points. The results are summarized in Table 1.

Table 1

Concentration of branching and labile chlorine in U-PVC

Sample	Poly. temp. °C	Branching per 1000 C	Labile chlorine per 1000 C
1	0.5	7.5	2.8
2	6	9	3.3
3	11	10.5	3.3
4	16	13.5	3.5

The branching varies with increasing polymerization temperature corresponding to a decreasing monomer concentration in the water phase from 7.5 to 13.5 per 1000 carbon atoms. It is not possible to decide by ^1H-NMR-spectroscopy between tertiary Cl-atoms or H-atoms at the branch points. However, it is known from literature (Robila et al. 1977) that the reaction of phenole with PVC represents a method of quantitative determination of labile chlorine including allylic structures and tertiary chlorine structures. The method is based on the reaction of phenole with labile chlorine atoms in PVC and the analysis of the p-substituted products by UV-spectroscopy. In this work the quantitative determination of the chlorine substitution was performed by elucidation of the signal from the aromatic protons at $\delta = 6.6 - 7.6$ ppm in the ^1H-NMR spectrum of the phenolyzed material. The concentrations of these irregularities are summarized in Tab. 1. The method results in values for labile chlorine of about 3/1000 C. Thus branch points do not completely consist in tertiary carbon atoms with chlorine. The exact amount of this structural defect is only detectable in connection with quantitative measurements of allylic chlorine atoms. The ^{1}H-NMR-spectroscopic investigations of U-PVC as raw material provide evidence of high concentrations of branched structures, partly with tertiary Cl-atoms. The length of side chains still remains unknown. The investigations of the low molecular weight fractions gave detailed information of the microstructure of the polymers. Contrary to the ^{1}H-NMR-spectrum of a raw material, the proton spectrum of a fractionated sample of $\bar{M}_n$ ca. 1000 indicates a signal at $\delta = 3.75$ ppm, which appears as a multiplet consisting of a triplet and a dublet. Presumably this dublet is concerned with structure $>CH{-}CH_2Cl$ (2), for both structures $-CH_2CH_2Cl$ and $>CHCH_2Cl$ should appear at the same position. Structure (2) is a rather abundant branch structure in ordinary PVC and the formation is described by several authors (Rigo et al. 1972, Park 1977). The correct mechanism for the formation of chloromethyl groups was identified by Starnes et al. (1979 a,b) inspecting the ^{13}C-NMR spectrum of $LiAlH_4$-reduced PVC-α-d. Their results confirm the mechanism of Rigo et al.:

$$-CH_2CHCl{-}CH_2CHCl\cdot \longrightarrow -CH_2CHCl{-}CHCl{-}CH_2\cdot$$
$$\xrightarrow{1,2\ \text{shift}} -CH_2CHCl{-}CH{-}CH_2Cl \xrightarrow{VC} >CH{-}CH_2Cl \qquad (2)$$

Recent studies of Starnes et al. (1980, 1981 a,b,c) and Hjertberg (1980) have shown that ^{13}C-NMR specta of reductively dehalogenated PVC samples can provide detailed information of branched structures of the original polymers. As the proton resonance investigations of the raw material shows a high concentration of branching, the ^{13}C-NMR spectroscopy represents a suitable supplementary method to detect side chain length. Samples of U-polymers were reduced with Bu_3SnH; the spectrum is presented in Figure 2. The sample appears to have not been reduced completely, because resonances at $\delta = 63.8$ ppm, $\delta = 39.0$ ppm and $\delta = 26.6$ ppm in the 50.3 MHz spectrum, which can be assigned to the chloromethylen carbon and adjacent CH_2-atoms (Starnes et al. 1981 b, Sörvik and Hjertberg 1981). The residual chlorine content was about 0.5 %. On the basis of the information of the literature (Randall 1973, Bovey et al. 1976, Starnes et al. 1981, Hjertberg and Sörvik 1981) it is possible to state, that short branches such as chloromethyl - groups and 2.4-dichloro-n-butyl groups and long chain branches are present in U-PVC. 2-chloroethyl branches, which were said to be also present in commercial PVC (Starnes et al. 1981 a,b,c) could not be identified. The number of each structure was:

Me-branch: 1.1 - 2.1 per 1000 C

Bu-branch: 1.5 - 2.1 per 1000 C
L-branch: 0.5 - 0.7 " "

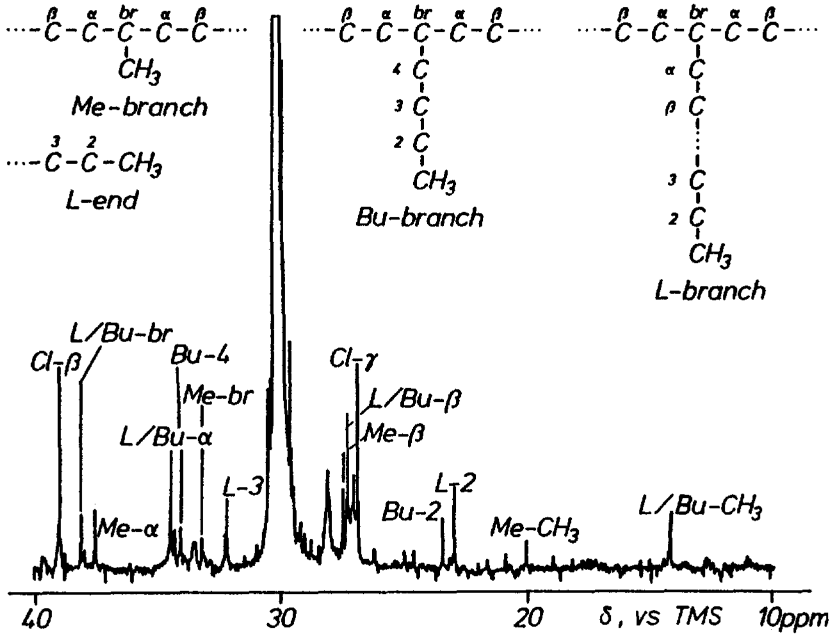

Figure 2 ^{13}C-NMR spectrum (50,3 MHz) of Bu$_3$SnH reduced U-PVC in 1.2.4 trichlorobenzene/benzene-d_6 at 100^o C.

The results demonstrate that PVC obtained in aqueous emulsion at atmospheric pressure contains increased concentrations of branches probably due to the polymerization with reduced monomer concentrations. The presence of increased tertiary chlorine content in connection with butyl groups is in agreement with the formation mechanism of the chlorinated n-butyl branches via a "backbiting" reaction (Bovey and Tiers 1962). Such concentrations of tertiary chlorine should also significantly contribute to the thermal instability of PVC. Therefore, these studies point out, that increased branching and consequently increased thermal instability would be expected to occur during the commercial polymerization of VC preferentially after the pressure drop.

Experimental

The polymerizations were carried out in a reaction tube of 1.7 m in length and volume of about 2 litres using the initiator system $K_2S_2O_8/Na_2SO_3/Cu^{2+}$. Phenolysis reactions were performed according to Robila et al. (1977) ^{1}H-NMR spectra were obtained with a 100 MHz Varian XL 100 spectrometer in $C_2D_2Cl_4$ at 100° C. Reductions and ^{13}C-NMR measurements were provided by Sörvik and Hjertberg (1981) from Chalmers University of Technology.

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References

BOVEY, F. A., SCHILLING, F. C., McCRACKIN, F. L. and WAGNER, H. L. : Macromolecules 9, 76 (1976)
BOVEY, F. A. and TIERS, G. V. : Chem. Ind. (London) 1862 (1962)
BRAUN, D. and HOLZER, G.: manuscript in preparation
HEUER, W. : U.S. Pat. 2,179,040 Nov. 7. (1939) Holl. Pat. 46,851
HJERTBERG, Th. and SÖRVIK, E. M.: J. Polym. Sci., Polym. Chem. Ed. 16,645 (1978)
HJERTBERG, Th. and SÖRVIK, E. M.: Preprints, 3rd International Symp. on PVC, Cleveland (1980)
HJERTBERG, Th. and SÖRVIK, E. M.: J. Polym. Sci., Polym. Lett.Ed. in press (1981)
O'HARA, J. B. and Prutton, C. F.: J. Polym. Sci. 5,673 (1950)
PARK, G.: J. Macromol.Sci., Phys. 14, 151 (1977)
RANDALL, J. C.: J. Polym. Sci., Polym. Phys. Ed. 11, 275(1973)
RIGO, A., PALMA, G. and TALAMINI, G.: Macromol. Chem. 153, 219 (1972)
ROBILĂ, G. BURUIANA, E. C. and CARACULACU, A. A.: Eur. Polym. J. 13, 21 (1977)
SÖRVIK, E. M. and HJERTBERG, Th.: J. Macromol.Sci., Chem. A11, 7, 1349 (1977)
STARNES, Jr., W. H., SCHILLING, F. C., ABBÅS, K. B., CAIS, R. E. and BOVEY, F. A.: Macromolecules 12, 556 (1979a)
STARNES, Jr., W. H., SCHILLING, F. C., ABBÅS, K. B., CAIS, R. E. and BOVEY, F. A.: Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem. 20, 653 (1979b)
STARNES, Jr., W. H.,SCHILLING, F. C., PLITZ, I. M, CAIS, R. E., FREED, D. J. and BOVEY, F. A.: Preprints, 3rd International Symp. on PVC, Cleveland (1980)
STARNES, Jr., W. H. : Developments in Polymer Degradation - 3, S. 135 (1981a)
STARNES, Jr., W. H., SCHILLING, F. C., PLITZ, I.M., CAIS, R. E. and BOVEY, F. A. : Polym. Bull. 4, 555 (1981b)
STARNES, Jr., W. H., VILLACORTA, G. M. and SCHILLING, F. C.: Am. Chem. Soc., Polym. Prepr. in press (1981c)

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