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Analysis

Functionalization of Soluble Polymers

5. ^{13}C-NMR Studies of Poly(Oxyethylene) Derivatives

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Summary

Twelve poly(oxyethylene)derivatives were characterized by their ^{13}C-NMR spectra and compared in terms of their chemical shifts. Substituent effects of the halogen series, of various ethers, nitrogen terminated compounds and some other derivatives were investigated. ^{13}C-NMR spectroscopy is discussed as control method for functionalization reactions.

Introduction

Polymers based on poly(oxyethylene) are of considerable interest for practical application because of their hydrophilic properties and as soluble support for the liquid phase peptide synthesis (BAYER and MUTTER 1972). A great number of reports on synthesis and application of such polymers have been published, however, relatively few papers deal with the analytical characterization by NMR-spectroscopy of poly(oxyethylene) derivatives (ANZINGER and MUTTER 1982, BARELLE et al. 1982). The ^{13}C-NMR data of amino and hydroxy poly(oxyethylene) (ZIEGAST and PFANNEMUELLER 1981) and of oxygenated derivatives of poly(oxyethylene) (BARELLE et al. 1982) have been reported. ^{13}C-NMR spectroscopic studies of poly(oxyethylene)-bound peptides have found interest in liquid-phase method for step-wise control during synthesis of the peptide (SCHOKNECHT et al. 1982).

To provide more information on this important analytical aspect of polymer functionalization, we now present ^{13}C-NMR data of a number of poly(oxyethylene) derivatives of which many are basis polymers for further modification reactions.

Results and Discussion

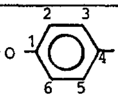
In this study, the functionalization products of poly(oxyethylene) 1-12 were characterized by ^{13}C-NMR spectroscopy. The chemical shifts of all derivates are summarized in Table 1 and 2.

Table 1: ^{13}C-NMR Chemical Shifts of Poly(oxyethylene) Derivatives 1-6 (in ppm; solvent: $CDCl_3$). $X-\underset{\alpha}{CH_2}-\underset{\beta}{CH_2}-O-(CH_2-CH_2-O-)_n-\underset{\beta}{CH_2}-\underset{\alpha}{CH_2}-X$

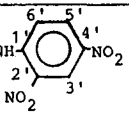
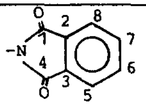
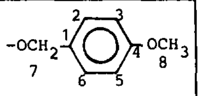
Compound	1	2	3	4	5	6
X	OH	Cl	Br	J	NH_2	$-O-\underset{1}{CO}-\underset{2}{CH_2}-NH\underset{3}{COO}-\underset{4}{C}(\underset{5}{CH_3})_3$
n-CH_2	70.5	70.5	70.4	70.1	70.5	70.7
C_β	72.5	71.2	71.5	71.5	73.1	68.8
C_α	61.6	42.6	30.2	2.9	41.6	64.3
C-1	-	-	-	-	-	170.4
C-2	-	-	-	-	-	41.7
C-3	-	-	-	-	-	155.1
C-4	-	-	-	-	-	79.7
C-5	-	-	-	-	-	28.4
$\bar{n}$	33	33	33	66	33	66
MHz	20.115	20.115	20.115	22.628	22.628	22.628

Table 2: ^{13}C-NMR Chemical Shifts of Poly(oxyethylene) Derivatives 7-12 (in ppm). Solvents: $CDCl_3$ (7-11), D_2O (12); $\bar{n}$ = 33 (7-11), $\bar{n}$ = 66 (12).

$\ldots -(CH_2-CH_2-O)_n-\underset{\beta}{CH_2}-\underset{\alpha}{CH_2}-X-R$

X = −O 

(7-10)

Compound	7	8	9	10	11	12[a)]
R	-CHO 7	-COOH 7	-CH=N-OH 7	-CH=N-NH-  7	 X = -	 X = -
n-CH_2	70.5	70.6	70.6	70.0	70.6	72.0
C_β	69.4	69.5	69.7	69.0	67.9	71.0
C_α	67.7	67.6	67.6	67.2	37.3	74.8
X,R:C-1	163.7	162.9	160.1	160.7	C1/4 168.1	132.5
C-2/-6	114.8	114.2	114.9	114.6	C2/3 132.1	132.7
C-3/-5	131.7	132.1	128.3	128.8	C5/8 123.2	116.5
C-4	130.1	122.2	132.9	137.1	C6/7 133.8	161.3
C-7	190.5	169.7	149.3	148.2	-	74.2
C-8	-	-	-	-	-	57.8
C-1'	-	-	-	144.3	-	-
C-2'	-	-	-	125.7	-	-
C-3'	-	-	-	122.9	-	-
C-4'	-	-	-	128.5	-	-
C-5'	-	-	-	129.2	-	-
C-6'	-	-	-	116.2	-	-
MHz	20.115	22.628	20.115	100.62	20.115	22.628

a) Data by BERGMANN 1978.

The signals of the terminal C-atoms of the polymer chain were identified for C_α between 2 ppm and 62 ppm and for C_β between 71 ppm and 73 ppm. In general, there is a continuous shift of C_α from 61 ppm over 64 ppm to 68 ppm in the series hydroxy, ester and ether compounds. The nitrogen terminated derivates amino and phthalimido poly(oxyethylene) exhibit a high-field shift to 41 ppm and 37 ppm respectively. In the halogen series there is a high-field shift of C_α from 42 ppm over 30 ppm to 3 ppm for the chlorine, bromine, and iodine derivatives.

Noteworthy is the extreme high-field shift of C_α in 4, which can not be explained completely by classical charge polarisation theory. The signal of C_β in compounds 2-4 is not influenced strongly by different halogen atoms and shows only a small low-field shift.

Interesting is the difference between esters and ethers of poly(oxyethylene): C_α- signals of esters absorb at 65 ppm whereas the C_α-shifts of ethers are dependent on substituents. For instance, the C_α-resonance of benzylether 12 has a chemical shift of 74.8 ppm whereas the C_α-signals of phenylethers 7-10 are in the range of 67-68 ppm. There is no difference between esters and ethers concerning the chemical shift of C_β, both absorb in the same shift range.

A strong high-field shift of C_α is observed for poly(oxyethylene) derivates (5 and 11) terminated by nitrogen, whereas the signal of C_β in 11 is high-field shifted in contrast to the down-field shift in the same range of C_β in 5.

The substituent effects of derivatives 1-12 are summarized in Table 3 and referred to the methylene peak in compound 1. As already mentioned above phenyl

Table 3: Substituent Effects of Poly(oxyethylene) Derivatives 1-12 (values referred to chemical shift of n-CH_2 of 1; Ph = Phenyl)

Compound	Terminal Group	α (ppm)	β (ppm)
1	-OH	- 8.9	+ 2.0
2	-Cl	- 27.9	+ 0.7
3	-Br	- 40.2	+ 1.1
4	-J	- 67.5	+ 1.4
5	$-NH_2$	- 28.9	+ 2.6
6	$-OCO-NHCOO-C(CH_3)_3$	- 6.4	- 1.9
7	-OPh-CHO	- 2.8	- 1.1
8	-OPh-COOH	- 3.0	- 1.1
9	-OPh-CH=N-OH	- 3.0	- 0.9
10	$-OPh-CH=N-NHPh(NO_2)_2$	- 2.8	- 1.0
11	$-N=(CO)_2=Ph$	- 33.3	- 2.7
12	$-OCH_2-Ph-OCH_3$	+ 4.8	+ 0.5

ethers are in general independent of the substituent and have shift increments of -2.9 ± 0.1 ppm for C_α and -1.0 ± 0.1 ppm for C_β. The same shift direction of C_α was found for the methoxy group (BARELLE et al. 1982). The substituent effects of the amino compound are in the same range as the chlorine derivative. On the basis of the increments described it is possible to determine the type of bonding of the poly(oxyethylene) derivative.

For instance, Fig. 1 shows the ^{13}C-NMR spectrum (100.62 MHz) of compound 10 in $CDCl_3$ ($c = 300$ mg·cm^{-3}). The content of unfunctionalized compound can be estimated to about 2 % by the signal of C_α(OH) of compound 1 at 61.6 ppm.

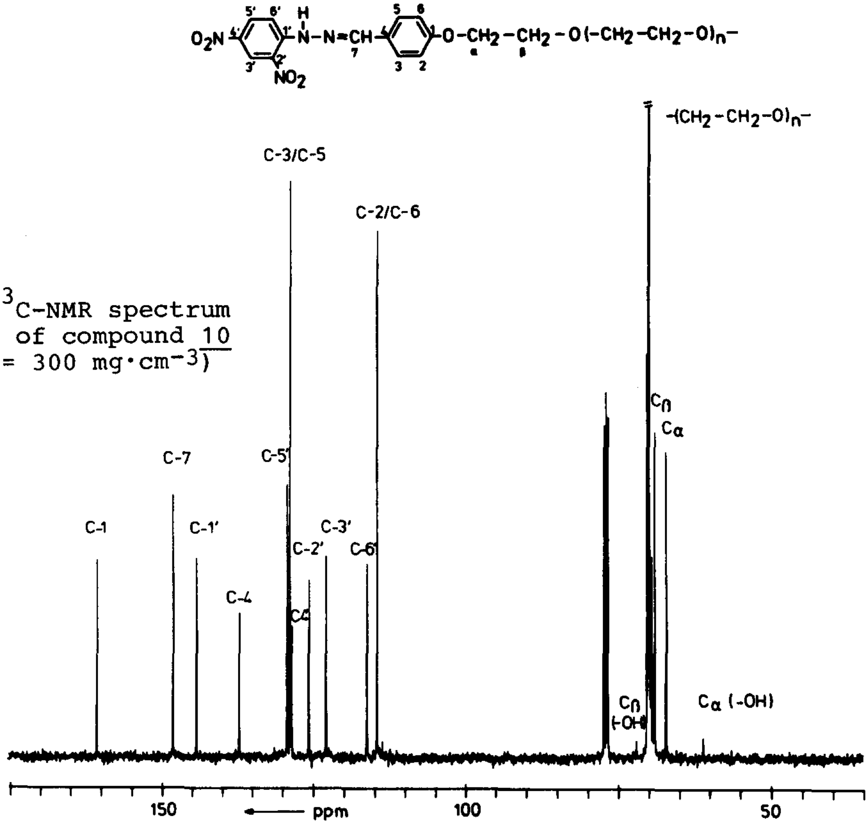


Figure 1: ^{13}C-NMR spectrum (100.62 MHz) of compound 10 in $CDCl_3$ ($c = 300$ mg·cm^{-3})

It can be stated that the signal of C_β is not very significant for derivatization reactions whereas the C_α-resonance is an indicator for the substitution of such macromolecules. In comparison, ^{1}H-NMR spectroscopic substituent effects are much smaller. Therefore, ^{13}C-NMR spectra are more advantageous for the characterization of substituted telechelics.

In conclusion, ^{13}C-NMR spectroscopy represents an excellent tool in the structural characterization of functionalized soluble polymers. Moreover, in spite of its low sensitivity, this spectroscopic method is a suitable control of conversion of functionalization reactions in telechelics.

Experimental

^{13}C-NMR spectra were taken on Bruker WP 80 (20.115 MHz), Bruker WH 90 (22.628 MHz), and Bruker WM 400 (100.62 MHz) NMR spectrometers.
The chemical shifts were referred to TMS as standard and sample tubes of 10 mm were used, compounds 1-11 were measured in $CDCl_3$ and 12 in D_2O; concentration was about 0.5 g · ml^{-1}. At T = 303 K interferograms of 5-50 · 10^3 depending on sensitivity of the apparatus were accumulated by ^{1}H-broadband decoupling. The substituent effects α and β were calculated on the basis of the methylene peak of 1.
The syntheses of the derivatives are described elsewhere (KÖSTER 1972, BERGMANN 1978, GAEDE 1978, MUTTER 1978, GECKELER 1979, GECKELER and BAYER 1980, BAYER et al. 1982, SCHOKNECHT et al. 1982).
Poly(oxyethylene) (from Fluka Feinchemikalien GmbH, Neu-Ulm) was purified as described in preceding papers and had an average molecular mass of 1500 and 3000 g · mol^{-1}.

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