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^{1}H- and ^{13}C-NMR of Tactic Polymethallylalcohols and Polymethallylurethanes

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Summary

The reduction of syndiotactic or isotactic polymethylmethacrylate yields the tactic polymethallylalcohols. Degree of conversion and tacticity can be determined by ^{1}H-and ^{13}C-NMR. The polymethallylalcohols are reacted with isocyanates to obtain the corresponding polymethallyl urethanes whose ^{13}C-NMR spectra are also studied.

Introduction

The preparation of syndiotactic or isotactic polymers of high tactic purity is often difficult or impossible by polymerisation, particularly if monomers with reactive functional groups are involved. However, the chemical transformation of a tactic polymer to another polymer or copolymer with unchanged configurational order may considerably extend to range of tactic polymers available.

Of a large number of papers on the reduction by complex metal hydrides only few deal with polymers. For instance, atactic polymethylacrylate and polymethylmethacrylate (PMMA) have been reduced by lithium aluminium hydride in THF to the corresponding polyallylalcohols , HOUEL (1958) and PETIT and HOUEL (1959). Elementary analysis and saponification of the acetate prepared from the polymethallylalcohols pointed to a loss of 10 % of the hydroxyl groups by etherification. SCHULZ et al (1959) also reduced atactic polymethylmethacrylate by $LiAlH_4$ in THF. COHEN and MINSK (1959) and COHEN et al (1960) introduced as the reaction solvent N-methylmorpholine which easily swells the insoluble polymer-hydride complex and which allows a higher reduction temperature. They also introduced hydrolysis of the complex by aqueous sodium-potassium tartrate to remove the complexed inorganic salts from the polyallylalcohols. In the present work tactic polymethylmethacrylates were reduced by using the pro-

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cedure of COHEN et al(1959,1960) with some modifications and characterizing the polymer by NMR.

The tactic polymethallylalcohols were reacted with isocyanates to yield polymethallylurethanes by procedures analogous to those for preparing low molecular weight urethanes and polyurethane foams (BAKER and HOLDSWORTH (1947), LOEW and HÖRL (1960), HOSTETTLER and COX (1960)). Complete conversion of the polymethallylalcohols could be obtained with the catalysts N-methyl morpholine, triethylenediamine and dibutyltindilaurate, if an 100 % excess of the isocyanates was employed.

Results and Discussion

In Fig. 1 the ^{1}H-NMR spectra of syndiotactic (trace I) and isotactic (trace II)polymethallylalcohols are seen. The configurational diads and triads are observed in the β-CH_2- and α-CH_3 resonances, respectively. The differences in chemical shift between the syndiotactic , heterotactic and isotactic triad is not large, but suffice to show that configurational integrity is preserved during reduction.

Fig. 2 gives the ^{13}C-NMR spectra of the polymethallylalcohols. The assignments of the four different carbon atoms could be confirmed by off-resonance decoupling, whereby tripletts could be observed for the -CH_2-O- and -CH_2- groups and a quartett for the α-CH_3 group. The atactic polymethallylalcohol in trace I shows a splitting of the α-CH_3 carbon in a syndiotactic and a heterotactic triad. The isotactic triad of the isotactic polymethallylalcohol in trace II is still further removed upfield. More than two lines expected for the two tactic diads appear in the β-CH_2- resonance of the atactic polymethallylalcohol (trace II). This is probably due to an influence of tetrads on chemical shift which cannot be seen in highly tactic homopolymers. In the syndiotactic polymethallylalcohol (trace III) small peaks immediately adjacent to the main signals are caused by a small amount of tactic impurity (8 % heterotactic triads) which is present already in the PMMA. A similar observation may be made with respect to the spectrum of trace I, Fig. 1.

The syndiotactic polymethallylalcohol was reacted with phenylisocyanate, benzylisocyanate and (S)-(-)-1-phenylethylisocyanate to yield poly-N-phenylmethallylurethane, poly-N-benzylmethallylurethane, and poly-(S)-N-1-phenylethylmethallylurethane (PMAU). Fig. 3 presents the ^{13}C-NMR spectra of these polymethallylurethanes. With all polymers the >c=o resonance appears at lowest field. For the poly-N-phenylmethallylurethane (trace I) the aromatic C-atoms were assigned in analogy

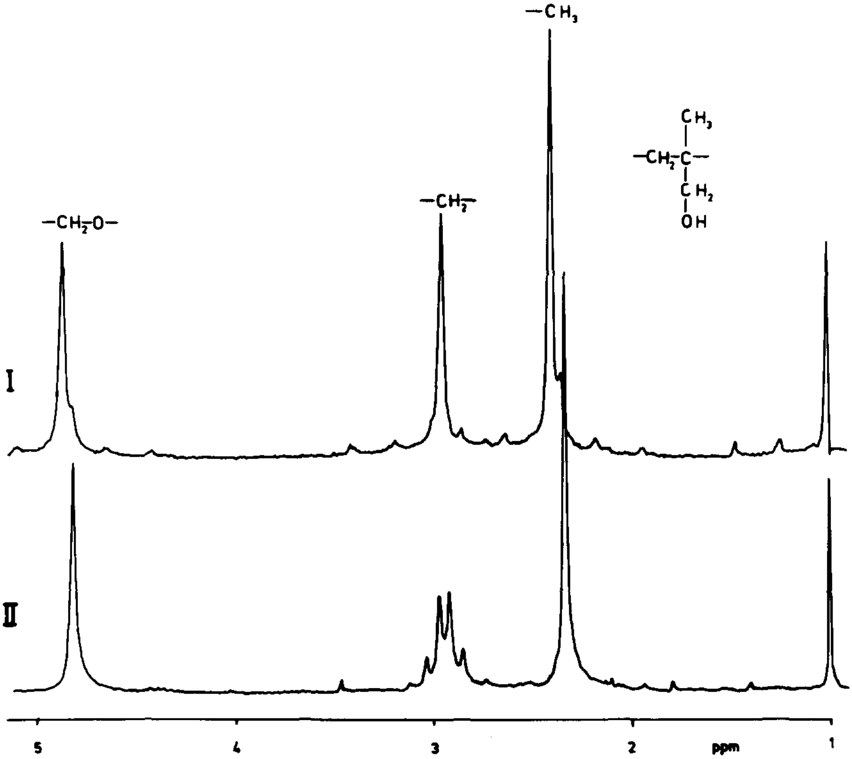

Fig. 1 ^{1}H-NMR spectra of syndiotactic (trace I) and isotactic (trace II) polymethallylalcohol in pyridine-d_5

to aniline (LE ROY and JOHNSEN (1972)). Of the aliphatic carbons in this polymer the $-CH_2-O-$ group is at lowest and the α-CH_3 group at highest field. The assignment of the $-CH_2$-group and of the quaternary carbon is analogous to polymethallylalcohol and polymethylmethacrylate.

For poly-N-benzylmethallylurethane (trace II) one obtains an additional signal for the $-CH_2$-group bound to the aromatic ring. The assignment of the aromatic C-atoms is made according to that of toluene (LE ROY and JOHNSEN (1972)). The spectrum of poly-(S)-N-1- phenylethylmethallylurethane(PMAU) (trace III) possesses another additional signal, i.e. that of the $-CH_3$ group

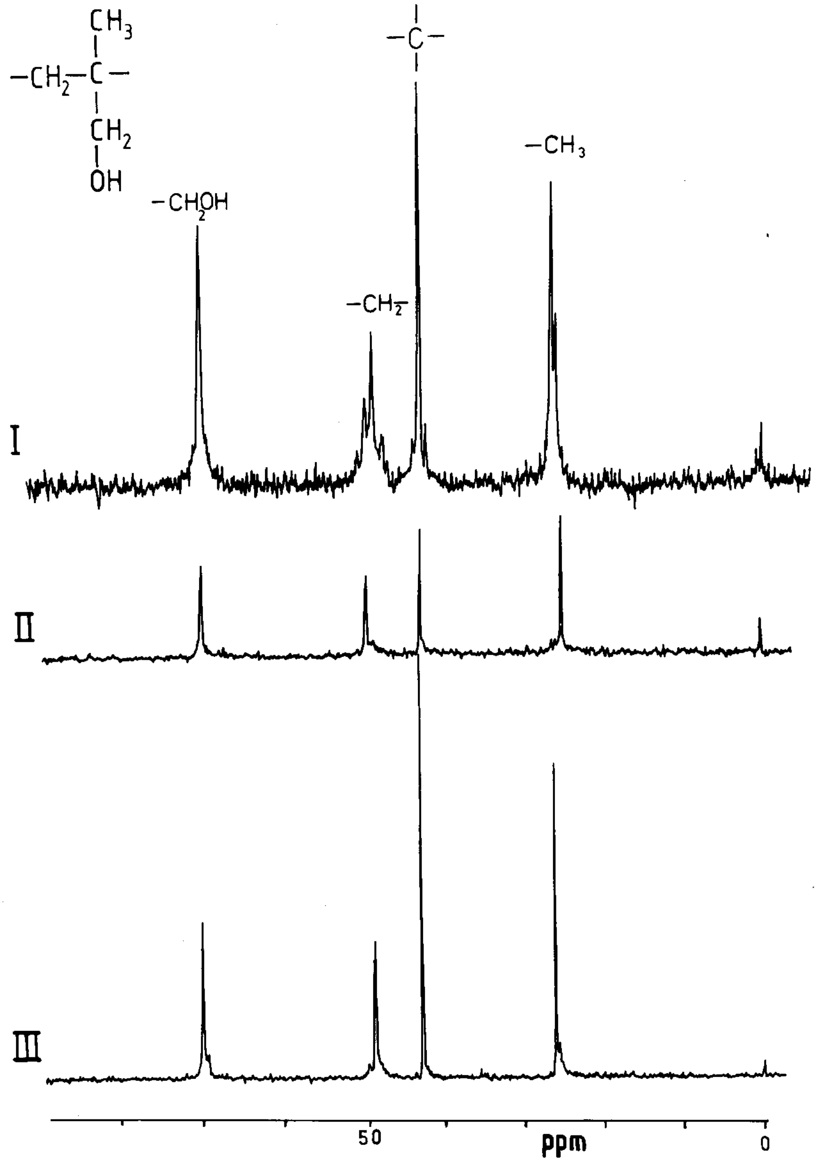

Fig. 2 ^{13}C-FT-NMR spectra of atactic (trace I), isotactic (trace II) and syndiotactic (trace III) polymethallylalcohol in pyridine-d_5

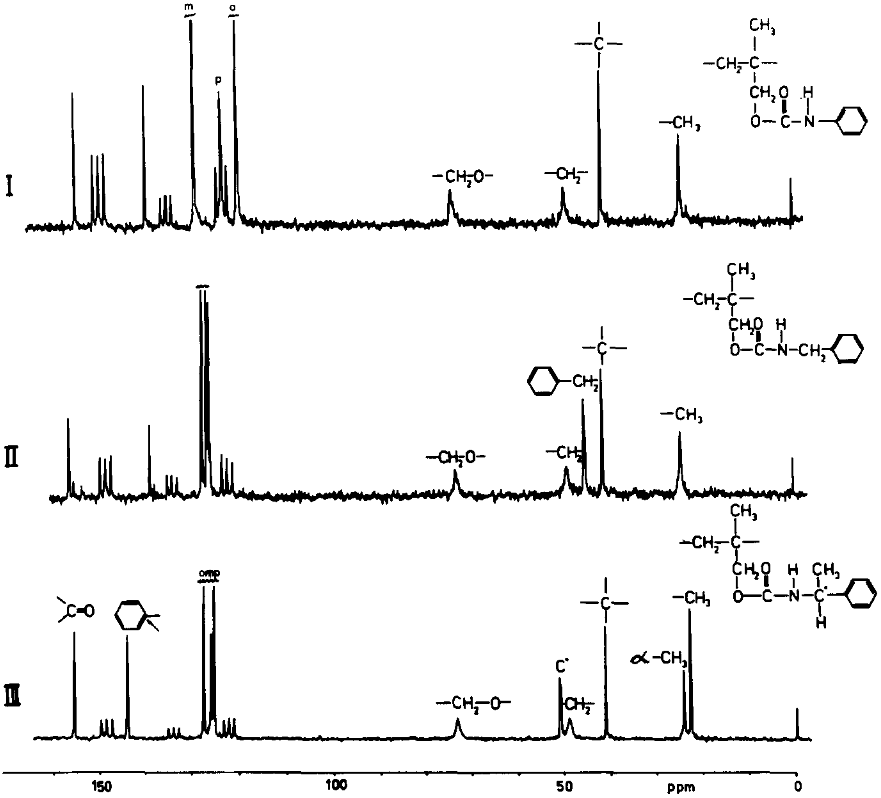

Fig. 3 ^{13}C-NMR-spectra of syndiotactic poly-N-phenylmethallylurethane (trace I), syndiotactic poly-N-benzylmethallylurethane (trace II) and syndiotactic poly-N-(S)-(-)-1-phenylethylmethallylurethane (trace III) in pyridine d_5.

bound to the asymmetric carbon, which appears to highest field. Partial decoupling confirms the comparative assignment of the three polymethallylurethanes. The expected multiplicity of each resonance is observed, although by partial decoupling the two $-CH_3$ groups in trace III cannot be differentiated.

Comparison of the spectra of syndiotactic and isotactic PMAU shows some chemical shift differences (table 1) which are apparently due to tacticity. Specifically the α-CH_3 resonance shows a considerable shift difference, which should allow to measure the triad statistics of atactic samples. With the present samples of PMAU the configuration of the parent polymethallylalcohols was apparently retained, as is to be expected in view of the distance of the reacting -OH group from the quaternary carbon of the backbone.

TABLE 1

^{13}C chemical shifts of tactic poly-(S)-N-1-phenylethylmethallylurethanes

	syndiotactic	isotactic
c=o	157,04	156,74
	145,55	145,22
o	128,92	128,68
m	127,30	127,06
p	126,66	126,39
$-CH_2-O-$	73,60	72,55
c*	51,48	51,19
$-CH_2-$	48,94	49,70
$-\overset{\vert}{\underset{\vert}{c}}-$	41,45	41,36
$\alpha-CH_3$	24,45	25,61
$-CH_3$	23,04	22,75

Less certain is the retention of configuration with respect to the asymmetric carbon in the side chain.The optical antipode could appear in the polymer because (1) the starting (S)-1-phenylethylamine is optically impure, (2) a partial change of configuration takes place during the conversion to isocyanate, or (3) during conversion to urethane. To detect the presence of the optical antipode, a model reaction leading to diastereomeric ureas was carried out. (S)-1-phenylethylamine was converted to (S)-1-phenylethylisocyanate and then reacted with (R)-or (S)-1-phenylethylamine to the diastereomeric ureas (S,S)- and (S,R)-(N,N')-di(1-phenylethyl) urea. The ^{1}H-NMR spectra of the diastereomers showed a chemical shift difference of 0,035 ppm for the $-CH_3$group. In Fig. 4 the ^{1}H-spectra of the compounds are shown. The ^{13}C-spectra did, however, not show a resonance with sufficient chemical shift difference for the diastereomers. The peak areas led to 6,9 % of the other diastereomer to be present in either of the diastereomers. This is also the level of razemization, but only half of this applies if the optical impurity is already present in the starting 1-phenylethylamine, since the amine is represented twice in the urea.

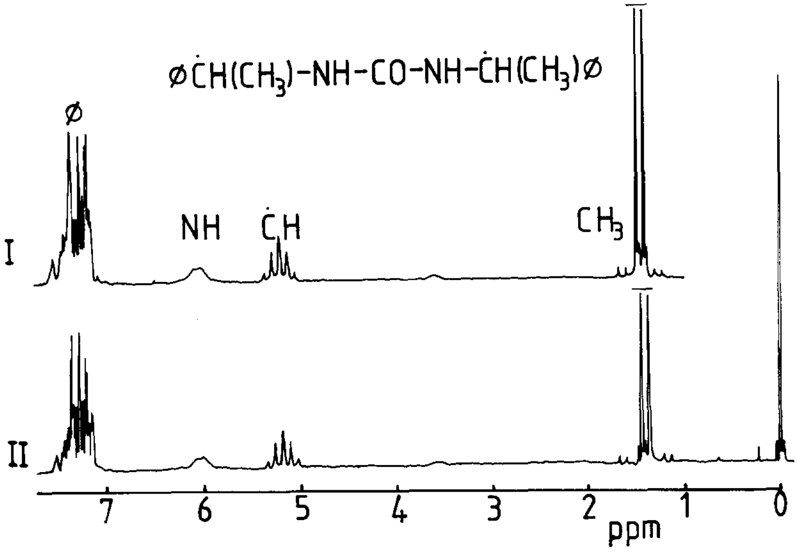

Fig. 4 ^{1}H-NMR spectra of (S,R) - (N,N')-di(1-phenylethyl)urea (trace I) and (S,S)-(N,N')-di(1-phenylethyl)urea (trace II).

In conclusion, both the reduction of tactic polymethylmethacrylate and the reaction of the resulting polymethallylalcohols with isocyanates to yield the polymethallylurethanes can be carried out to complete conversion, without measurable impurities, or change of configuration with respect to the backbone of the chain. With respect to the side chain, a small change in configuration cannot be excluded at present.

Experimental

Syndiotactic polymethylmethacrylate was obtained following ABE (1965) with Ziegler-Natta catalyst in toluene at -78°C, while isotactic polymethylmethacrylate was prepared with $LiAlH_4$ as an initiator in toluene at -78°C according to a procedure of TSURUTA et al (1966).

The reduction of syndiotactic, isotactic and atactic PMMA to polymethallylalcohols has been carried out by dissolving 0.95 g $LiAlH_4$ in 40 ml methylmorpholine by heating. Refluxing, stirring and blanketing with N_2, it was added 2.15 g PMMA dissolved in 25 ml methylmorpholine within 30 minutes. Refluxing and stirring under N_2 was continued for 3 h. Without removing the oil bath, 8 g sodium-potassium tartrate in 35 ml of water was added slowly and then refluxed for another hour. During this time formed a coarse precipitate which was filtered while the solution was still hot. The filtrate was evaporated and the residue dissolved in 40 ml pyridine and precipitated in 3 ltr ether. It was reprecipitated from pyridine solution in 2 ltr of H_2O, adding conc. HCL to obtain 1.5 N HCL. The polymer was filtered, washed with 500 ml dilute NH_3 to remove the HCl, washed with 2 ltr of H_2O to neutrality and dried at 80°C in vacuo.

The polymethallylurethanes were obtained by dissolving 0.2 g polymethallylalcohol in 5 ml pyridine, which had been dried over CaH_2, in an ampoule. A stochiometric excess of 100 % of an isocyanate and 100 mg dibutyltindilaurate was added. The ampoule was blanketed with N_2, sealed and heated for 4 days to 60°C. Precipitation in ether resulted in 80 % yield.

The ^1H-NMR spectra were recorded with a Varian HR-200 c.w. spectrometer at 220 MHz, 100°C and TMS as internal standard. All ^{13}C-NMR were measured with a Bruker WH-90-FT-spectrometer at 80°C with TMS as internal standard.

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References

ABE, H.: Polym.Lett.3 1053 (1965)
BAKER,J.W. and HOLDSWORTH,J.B.:J.Chem.Soc.713(1947)
COHEN,H.L.,BORDEN,D.G.and MINSK,L.M.:J.Org.Chem.26 1274 (1960)
COHEN,H.L., MINSK,L.M. :J.Org.Chem.24 1404 (1959)
HOUEL,B.: Compt.rend. 246 2488 (1958)
LE ROY and JOHNSEN,F.:Carbon-13 NMR Spectra, John Wiley and Sons, London, 1972
PETIT, J. and HOUEL,B.: Compt.rend. 246 1427(1959)
SCHULZ, R.C., ELZER, P.,KERN,W.:Chimia 13 237 (1959)
TSURUTA, T., MAKIMOTO,T. and NAKAYAMA, Y.: Makromol. Chem. 90 12 (1966)

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