Polymer Bulletin 3, 521-528 (1980)

Polymer Bulletin

^{13}C-NMR Relaxation and Circular Dichroism of Tactic Polymethallylalcohol and Polymethallylurethane

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Summary

^{13}C-NMR spin-lattice relaxation (T_1) measurements on syndiotactic and isotactic polymethallylalcohols and poly-(S)-N-1-phenylethylurethanes demonstrate a lack of dependence of T_1 on tacticity. On the other hand, the T_1-values show a hindered motion of the $-CH_2OH$ side chain, which is explained by hydrogen bonding. In an Arrhenius type plot the enthalpy of motion is found to to be verysimilar for the different groups of polymethallylalcohols,pointing to a common set of motions. The circular dichroism of the polymethallylurethanes is similar to the model compound (S)-N-1- phenylethylneopentylurethane, indicating a lack of conformational restrictions of the outer part of the side chains by a polymer effect.

Introduction

In a previous communication (LENK and KLESPER,1980) the preparation of syndiotactic and isotactic polymethallylalcohols and polymethallylurethanes and their characterization by ^{1}H- and ^{13}C-NMR has been discribed. In this communication the ^{13}C-NMR spin lattice (T_1) measurements of both types of polymers and the CD-spectra of poly-(S)-N-1- phenylethylmethallylurethanes are discussed.

For polystyrene (SCHÄFER and NATUSCH, 1972), polyacrylonitrile, polyvinylchloride and polyvinylalcohol (INOUE et al, 1973) no dependence of ^{13}C-NMR T_1 on tacticity was found for a given carbon atom. However, the T_1 were obtained on atactic polymers, determining the T_1 of different triads. It does,however,not necessarily follow that the pure tactic forms of a polymer also do not show any dependence on tacticity, since a homotactic sequence which is longer than a triad may show a different conformational behavior than the homotactic triad itself. The predominantly tactic

0170-0839/80/0003/0521/$01.60

TABLE 1
Temperature dependence of T_1 for synd.polymethallylalcohol in pyridine.d_5 (exp.error ± 10 %)

	T_1/sec.				
T/°K	$-CH_2O-$	$\beta-CH_2$	$-\overset{\vert}{\underset{\vert}{C}}-$	$\alpha-CH_3$	V
303	0,034	0,034	0,396	0,089	0,91
313	0,031	0,033	0,442	0,099	1,14
323	0,042	0,039	0,472	0,123	0,88
333	0,045	0,047	0,568	0,150	0,99
343	0,046	0,053	0,641	0,181	1,09
353	0,056	0,062	0,758	0,204	1,06
363	0,064	0,066	0,862	0,263	1,06
368	0,092	0,090	1,090	0,331	0,93
373	0,097	0,114	1,126	-	0,91

TABLE 2
Temperature dependence of T_1 for isot.polymethallylalcohol in pyridine.d_5 (exp. error ± 10 %)

	T_1/sec.				
T/°K	$-CH_2O-$	$\beta-CH_2-$	$-\overset{\vert}{\underset{\vert}{C}}-$	$\alpha-CH_3$	V
303	0,035	0,035	0,432	0,097	0,97
313	0,033	0,033	0,419	0,119	1,00
323	0,042	0,039	0,500	0,144	0,93
333	0,048	0,049	0,575	0,171	0,94
343	0,054	0,055	0,667	0,205	0,97
353	0,074	0,071	0,806	0,254	0,85
363	0,080	0,082	0,977	0,325	0,96
373	0,109	0,096	1,214	0,443	0,87

polylalkylmethacrylates have been repeatedly investigated (INOUE and KONNO, 1978 ; HATADA et al, 1977;HATADA et al, 1978) and a strong dependence on tacticity has been found. The ^{13}C-NMR T_1-values were considerably longer for the isotactic than for the syndiotactic polymers.

Results and discussion

Tables 1 and 2 show the ^{13}C-NMR T_1 data of different carbons of syndiotactic and isotactic polymethallylalcohol in pyridine d_5 in dependence of temperature. Within an error of 10 % for the individual measurement, there is no difference in T_1 between the two tactic polymers for a given carbon atom. Considering the finding (not shown) that the areas of the peaks for all carbons in the same spectrum are the same, the Nuclear Overhauser Effect(NOE) should also be equal. This includes even the quaternary carbon atom. The equal NOE in turn points to a spin-lattice relaxation mechanism which is dominated by $^{13}C-^1H$ dipole-dipole interaction (DODDRELL et al.1972). Assuming furthermore isotropic segmental motion and the extreme narrowing limit$(\omega_C + \omega_H)^2 \tau_c^2 <<1$, the spin lattice relaxation time is given by

$$1)\qquad \frac{1}{T_1} = \hbar^2\,\gamma_C^2\,\gamma_H^2\,\tau_C \sum_i r_i^{-6}$$

or

$$2)\qquad \tau_C = \frac{\text{const.}}{T_1 \sum_i r_i^{-6}}$$

whereby $\hbar$ is Planck's constant divided by 2π, γ_C and γ_H are the gyromagnetic ratios of the carbon and hydrogen nuclei, r_i is the bondlength between the carbon atom of interest and the i-th neighboring hydrogen atom, τ_C is the correlation time describing the segmental motion , and ω_C and ω_H are the resonance frequencies of C and H. Because τ_C depends on the inverse sixth power of r_i, only the two directly bound hydrogens of the β-CH_2 group, the three directly bound hydrogens of the α-CH_3 group, and the nine next neighboring protons of the quaternary C-atom contribute to the dipole-dipole relaxation of the respective carbon atom. The ratio of the products $T_1 \sum r_i^{-6}$, for the β-CH_2- and the quaternary C-atom amounts to nearly 1 at all temperatures as seen from Tables 1 and 2 (column V), thereby the values for $\sum r_i^{-6}$ of 1.13 $10^{48} cm^{-6}$ for β-CH_2-, 1.69 $10^{48} cm^{-6}$ for α-CH_3, and 0,08865 $10^{48} cm^{-6}$ for quaternary C have been taken (INOUE and KONNO, 1978). This ratio of 1 holds also for DMSO.d_6 as a solvent over the range of temperature (30° to 110°C).Thus it is likely that the set of segmental motions is equal for β-CH_2- and quaternary C. Moreover, the set can be described by a single effective correlation time.

Turning to pending groups,the α-CH_3 carbon possesses a longer T_1 than would be expected on account of its three hydrogens and the correlation time of the chain backbone. This is a consequence of the additional free rotation of the α-CH_3 group. Thus the measured correlation time of the α-CH_3 group is composed of two terms which may be approximated as

$$3)\qquad \frac{1}{\tau_{CH_3}} = \frac{1}{\tau_C} + \frac{1}{\tau_{r,CH_3}}$$

with τ_C being the backbone correlation time and $\tau(r,CH_3)$ the correlation time for the additional rotation of the α-CH_3 group. Calculating τ_C by eq. 1 yields 0.73 10^{-11}sec. for 30°C in pyridine.d_5.Likewise $\tau(CH_3)$ is 0.19 10^{-11}sec. by eq.1. Employing eq. 3 yields $\tau(r,CH_3)$= 0,26 10^{-11}sec.

The T_1 for the -CH_2O-group is within error of determination the same as for the β-CH_2-group over the range of temperature for both pyridine.d_5 and DMSO.d_6. However, the pending -CH_2O-group might in principle also rotate freely about the C-C bond in analogy to the α-CH_3 group. This additional rotation is apparently suppressed and only the segmental motion imposed by the backbone is prevailing in an at least partially cooperative manner. The suppression of high frequency rotation is probably due to hydrogen bonding via the -OH group. Polyvinylalcohol also shows by ^{13}C-NMR T_1 measurements an immobilization of the tertiary carbon which, however, diminishes above 70°C (INOUE et al,1973). This effect could be due to cyclic intramolecular hydrogen bonding in competition to bonding to the solvent.

Applying an Arrhenius type relation to the temperature dependence of T_1, the enthalpy for attaining Larmor frequency motion of the different groups can be approximately deduced by

4) $\ln T_1 = - \Delta H/RT + \text{const.}$

where ΔH is the enthalpy and T the absolute temperature. In Figs. 1 and 2 the plots of ln T_1 versus T^{-1} are presented for the tactic polymethallylalcohols in DMSO.d_6 as a solvent. The plots are very similar for the syndiotactic and the isotactic polymethallylalcohol, demonstrating again the lack of dependence on tacticity. The suppression of the additional rotation of the $-CH_2O-$ group is obvious from the fact that the T_1 for $-CH_2O-$ and β-CH_2-trace out the same line. The rapid additional rotation of the α-CH group, however, leads to considerably longer T_1. Also the similar slopes of all curves are noteworthy, pointing to the same enthalpy of motion for all groups. This confirms a similar

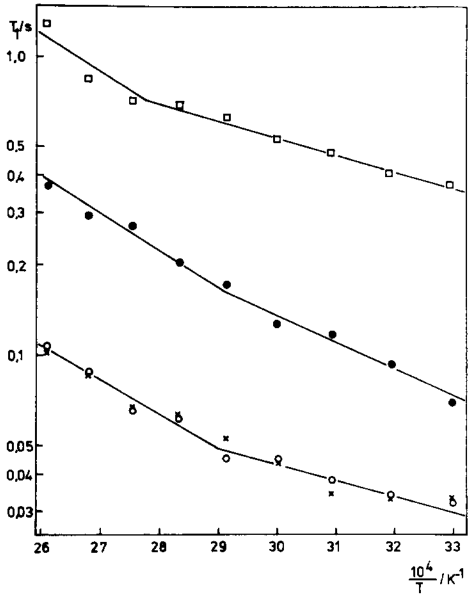

Fig. 1 Temperature dependence of T_1 for syndiotactic polymethallylalcohol in DMSO.d_6. Symbols: (o)= β-CH_2-; (x)= $-CH_2O-$; (●)= α-CH_3; (□):quaternary carbon

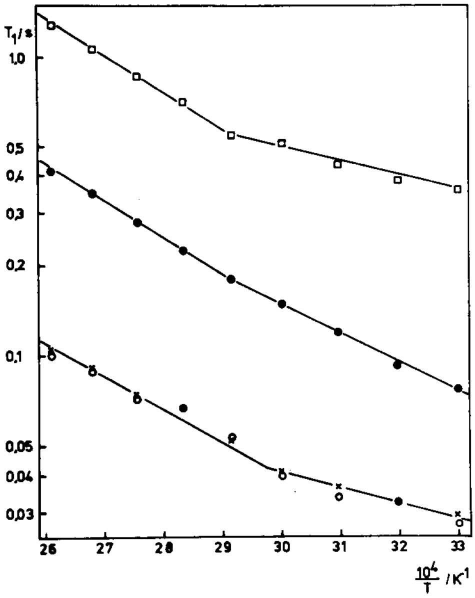

Fig. 2 Temperature dependence of T_1 for isotactic polymethallylalcohol in DMSO.d_6. Symbols: (o) = β-CH_2-; (x) = -CH_2O-; (●) = α-CH_3; (□) = quaternary carbon

set of motions. Nearly the same curves are obtained with pyridine.d_5 as the solvent, if the data of Tables 1 and 2 are plotted, with the qualification that the T_1 are slightly smaller for DMSO.d_6. The similarity between the temperature dependence of α-CH_3 on one hand and the β-CH_2 and quaternary carbons on the other hand, underlines the cooperativity of the motion between pending α-CH_3 and the backbone. A similar slope will prevail if, for instance, the additional rotation about the C-C bond contributes little to the enthalpy of activation deduced by eq. 4.

The curves show a decreasing slope at higher temperatures, indicating that further ways of motion are activated. Due to the error in T_1 and the questionable accuracy of eq. 4 it is, however, not certain that the curves can be divided in two straight line portions (as is tentatively shown).

With respect to the same T_1 for syndiotactic and isotactic polymethallylalcohol it must be pointed out that different conformations are likely for the syndiotactic and the isotactic polymethallylalcohol, but the rotatory motions of the C-H bonds are apparently not affected by different conformations.

T_1measurements on tactic poly-(S)-N-1-phenylethylurethane $\{ CH_2-C(CH_3)(CH_2OCONH\ CH(CH_3)(C_6H_5)\}_n$ resulted also not in differences between syndiotactic and isotactic polymer (TABLE 3). Compared to the tactic polymethallylalcohols (TABLES 1 and 2) little change is noticed with respect to the backbone carbons, but the additional rotation of the α-CH_3 around the C-C bond seems to slowed. Along the pending urethane group the NT_1 values (N= number of equivalent hydrogen atoms) increase, as expected for increasing mobility of the side chain in this direction. The $-CH_2O$-group possesses, however, about the same value as the β-CH_2-group.

In the past, optical rotations of a number of polyacryl- and polymethacrylesters with optically active side chains have been reported. Generally, a moderate dependence of optical rotation on tacticity was found for poly-L-menthylacrylate and poly-L-bornylacrylate (SCHULZ and HILPERT,1962) poly-L-menthylmethacrylate (KLABUNOWSKI et al,1964; MATSUZAKI et al,1967; SOBUE et al,1964), poly-(S)-2-methylbutylmethacrylate (KLABUNOWSKI et al,1964), and poly-(S)-α-methylbenzylmethacrylate (LIU et al,1967); YUKI et al,1968). The relatively small dependence on tacticity can be explained by the conformational freedom of the ester linkage and the considerable distance of the asymmetric carbon from the backbone of the chain (PINO,1969; PIERONI,1969).

TABLE 3
T_1 for tactic poly-(S)-N-1-phenylethylmethallylurethanes at 30°C in pyridine.d_5 (exp.error ± 10 %)

	T_1/sec					
	$-CH_2O-$	$-CH_2-$	$-\overset{\vert}{\underset{\vert}{C}}-$	α-CH_3	$-CH{<}^{*}$	$-CH_3$
syndiot.	0,033	0,039	0,397	0,058	0,101	0,200
isot.	0,030	0,030	0,366	0,055	0,093	0,203

Fig. 3 shows the CD-spectra of syndiotactic poly-(S)-N-1-phenylethylmethallylurethane as $\Delta\varepsilon$ versus λ in hexafluoroacetone, trifluoroethanol and methylenechloride at 20°C. Only the chirally induced transition of the aromatic ring with vibronic structure is shown. The $\Delta\varepsilon$ increase with decreasing solvent power. No significant difference was found between the syndiotactic and the isotactic polymer. Also, the model coumpound (S)-N-1-phenylethylneopentylurethane did not deviate strongly from the polymers, if the same solvent was employed. The behavior is explained by conformational mobility of the pendent side chain, which is not strongly restricted by a polymeric effect. The asymmetric carbon is apparently too far removed from the backbone, despite the urethane linkage whose carbonyl nitrogen bond may possess partial double bond character and which is capable of hydrogen bonding to neighboring urethane links. Thus the outer portion of the side chain with the bonds on the asymmetric carbon is conformationally unrestricted in a way similar to the model compound. For the inner portion of the side chain the T_1 measurements showed, however, conformational restrictions. For this conformational restriction, the size and mass of the side chains will probably already suffice.

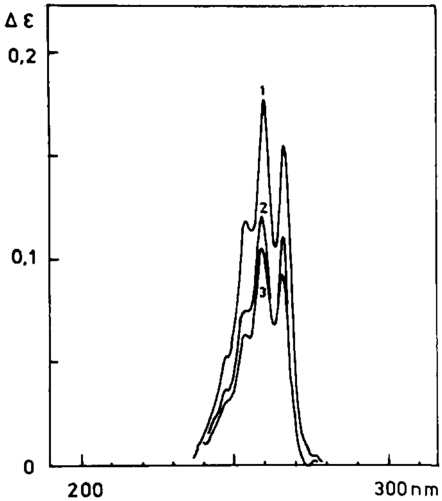

Fig. 3 CD-spectra of syndiotactic poly-(S)-N-1-phenylethylmethallylurethane in methylenechloride (1), trifluoroethanol (2), and hexafluoroacetone (3).

Experimental

The ^{13}C-T_1 were determined by partially relaxed Fourier transform spectra on a Bruker WH-90 at 22.63 MHz,utilizing a 180°-τ-90° pulse sequence. The time difference between the 90° pulses was the five-fold of the longest relaxation time of the carbons in the polymers. The polymer concentration was about 5 %, the solutions were not degassed because the longest relaxation times measured were at or below 1 sec.

The CD-spectra were recorded on a Dichrograph II of Roussel-Jouan, using a 5 mm cell. The concentration was 2.10^{-3} g/cm^3 and the temperature 20°C. The spectra were recorded by one point every nanometer and corrected for the baseline as taken with the pure solvent.

Acknowledgement

Financial support was given by the Deutsche Forschungsgemeinschaft, providing also a Bruker WH-90 FT-spectrometer to the Institut für Makromolekulare Chemie, Universität Freiburg.

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Received November 2/ Accepted November 13, 1980