

PHYSICAL STUDIES OF IONICALLY-TERMINATED POLYTETRAHYDROFURAN POLYMERS—III. NMR RELAXATION TIME STUDIES

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Abstract—From ^{13}C -NMR relaxation time studies it was confirmed that the introduction of ionic end groups in polytetrahydrofuran (PTHF) polymers affects the hydrodynamic behaviour of these ionically-terminated PTHF polymers. This phenomenon only occurs in solvents with low dielectric constant.

INTRODUCTION

^{13}C nuclei are chemically isolated from one another by their low natural abundance of about 1% [1]. They do not effectively exchange energy via spin diffusion with protons because of the differences in resonance frequencies. The ^{13}C spin-lattice relaxation time, T_1 , can therefore, be used to differentiate resonances resulting from methine, methylene, methyl and non-protonated carbons [2]. Data derived from such measurements can give interesting information on local molecular motions in polymers. The width of the NMR absorption line is affected by nuclear dipole-dipole interactions. The magnitude of these is revealed in the value of the spin-spin relaxation times, T_2 , which are, in principle, obtainable from line widths.

Nuclear magnetic resonance spectra of PTHF polymers have been reported [3]. While ^{13}C chemical shifts and ^{13}C - ^1H coupling constants provide powerful tools for the solution of structural problems, increasing interest is being shown [4] in ^{13}C spin-lattice relaxation times as structural parameters. They reflect the inter- and intra-molecular mobility of a molecule, and, thus, complement the results of temperature-dependent NMR spectroscopy. The T_1 differences within a molecule show, for instance, whether the molecular motion is anisotropic in solution; whether the internal motion is subject to steric hindrance; the extent to which strong inter-molecular or inter-ionic interactions affect the flexibility of the molecule, and which parts of the molecule are rigid and which are flexible. Finally, differences between the T_1 values measured for the ^{13}C nuclei of a molecule frequently provide a reliable aid in the assignment of signals in ^{13}C -NMR spectra, particularly in cases of signal crowding and multiplet overlapping.

Relaxation time studies of PTHF polymers were used in this work to investigate the effect on solution dynamics of introducing ionic groups on the PTHF chain ends. This introduction is thought to affect the

interaction between the ion-containing polymer chains in solution, resulting in associations of their chains forming through their ionic ends in certain solvents. Measurements of the relaxation time, T_1 , of various ^{13}C sites for the methoxy-terminated (PTHF-OMe) and pyridinium bromide-terminated (PTHF-Py) polytetrahydrofuran polymers, and the comparisons of relaxation time values for both series of PTHF polymers provide a useful good technique for understanding the structural difference between the two series.

The relaxation time, T_1 , values pass through a minimum as the mobility is varied. As the mobility increases therefore, T_1 may increase or decrease depending on the motional regime. In the poly(THF) systems, which give narrow lines and NOE values close to the maximum, the backbone mobility does lie in the extreme narrowing regime where a decrease in mobility leads to a decrease in T_1 .

The value for the relaxation time, T_1 , reflects the ease of dissipation of the excitation energy with time, so that if there was any association of the chains of the PTHF-Py polymers, in some solvents, through the pyridinium ends of two chains, then this association will be at the centre of gravity of the new dimeric species with the two molecules associated through their pyridinium ends. The T_1 values for carbons in the pyridinium groups, in this case, should be short because when in the middle of the dimeric system they are closely involved with the molecular lattice system and can, therefore, lose excitation energy readily. In solvent systems where no association occurs, the T_1 relaxation times for the pyridinium group, which now resides at the end of the polymer chain, would be longer because the chain end to which the pyridinium group is attached has relatively independent motion. The study reported here seeks to determine if the relaxation times show molecular structural change, i.e. association of the PTHF-Py in certain solvents.

EXPERIMENTAL PROCEDURES

The PTHF polymers used in this work were synthesized by anionic polymerization using a procedure already detailed [5] in the literature. The PTHF-OMe and PTHF-Py series exhibit a relatively wide range of molecular weight, and full characterization data have already been published [6].

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Relaxation time measurements using ^{13}C -NMR spectroscopy

Several methods are available for measuring T_1 values [7–12]. The most important routine methods of Fourier-transform ^{13}C -NMR spectroscopy in present use are the “progressive saturation” and “inversion recovery” methods. The procedure adopted for this work is the progressive saturation technique [8] in which the signal is sampled after equally spaced 90° pulses, and the procedure is repeated a number of times for different values of t , the pulse interval. Signal summation should be commenced only after a steady-state regime has been obtained. There are three basic conditions which should be satisfied.

- Sufficient dummy pulses must be made for the steady-state condition to be properly established before data acquisition commences.
- Negligible transverse components of magnetization should remain when the next pulse in the sequence is applied. This is not ensured by field inhomogeneity alone since this tends to be refocused by the effect of the pulses, as in the spin echoes described by Hahn [13]. Noise coupling is very effective in preventing refocussing, and a “homogeneity spoiling” pulse can be included in the pulse sequence to remove residual transverse magnetization after each data acquisition.
- The 90° pulse length must be correctly calibrated, and be sufficiently short so that off-resonance effects can be neglected. This ensures that z -axis magnetization immediately following the pulse is negligible.

When these three conditions are satisfied, the signal strength, S_t , observed with a pulse interval, t -seconds, is related to the asymptotic signal S_∞ that is observed when the pulse interval is “infinitely” long compared with the relevant relaxation time, by the equation

$$S_\infty - S_t = S_\infty \exp(-t/T_1). \quad (1)$$

Thus, by determining the individual signal intensities in the transformed spectra as a function of the pulse interval t , the characteristic spin-lattice relaxation times can be obtained graphically. Let the two measurements for two values of t

be represented by S_a and S_b , and suppose that time a is always shorter than time b .

Then, from equation (1),

$$R = S_a/S_b = 1 - \exp(-a/T_1)/1 - \exp(-b/T_1). \quad (2)$$

The ratio of signal intensities thus derived is uniquely related to the spin-lattice relaxation time T_1 , and can be displayed graphically as a family of curves for various pairs of times a and b . For molecules exhibiting T_1 values over extended ranges, accurate estimates for this parameter can often be obtained using only 3 t values, giving two complementary pairs of a and b in equation (2).

^{13}C -NMR spectra were obtained at 25.05 MHz with a pulsed Fourier-transform NMR spectrometer. The spectra were obtained in a variety of solvents, using proton noise decoupling and with external deuterium locking using D_2O contained within a capillary tube. Spin-lattice relaxation times were obtained by the progressive saturation technique; the 90° pulse width was *ca* 15 μsec .

RESULTS AND DISCUSSION

From earlier hydrodynamic studies of the PTHF polymers [6, 14], it was clear that the PTHF-Py polymers associated in solvents with low dielectric constant; for example cyclohexane and carbon tetrachloride. In order to confirm the above results a different experimental technique, i.e. determination of ^{13}C T_1 values, was employed for the same polymers. The comparison of relaxation time values for both the PTHF-OMe and the PTHF-Py polymers provide data for understanding the structural differences between the materials. Spectra for the PTHF-OMe polymer in the solvents deuterio-chloroform, deuterio-benzene and carbon tetrachloride, and the PTHF-Py polymer in the same solvents, plus cyclohexane, were obtained. Figure 1 shows the spectrum of PTHF-OMe polymer in chloroform, and the PTHF-Py polymer in carbon tetrachloride is given in Fig. 2.

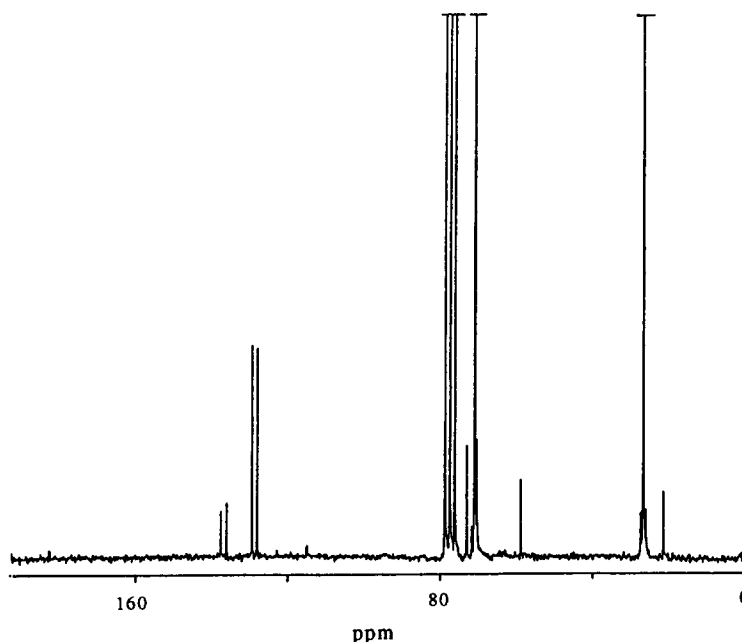


Fig. 1. 25.05 MHz ^{13}C -NMR spectrum of the methoxy terminated polytetrahydrofuran polymer [12.4% (w/v)] in chloroform.

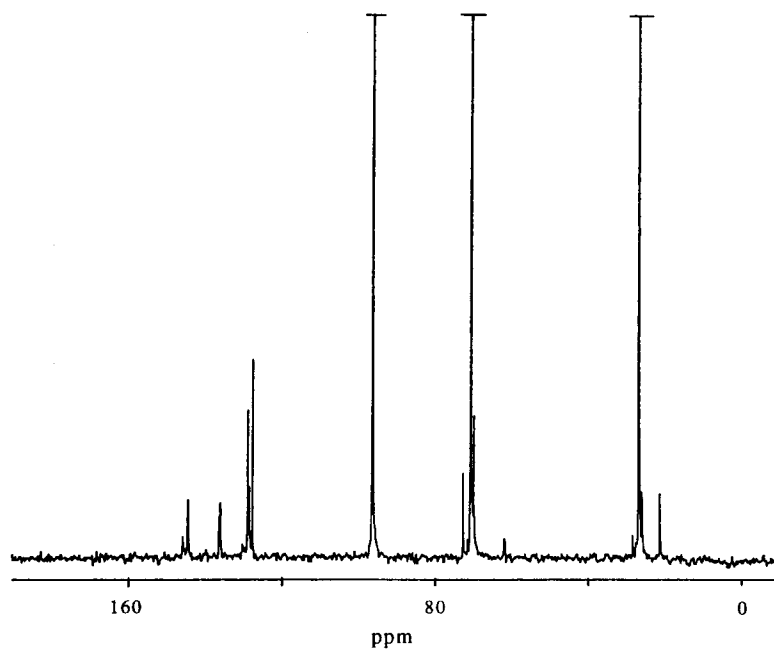


Fig. 2. 25.05 MHz ^{13}C -NMR spectrum of the pyridinium bromide terminated polytetrahydrofuran polymer [12% (w/v)] in carbon tetrachloride.

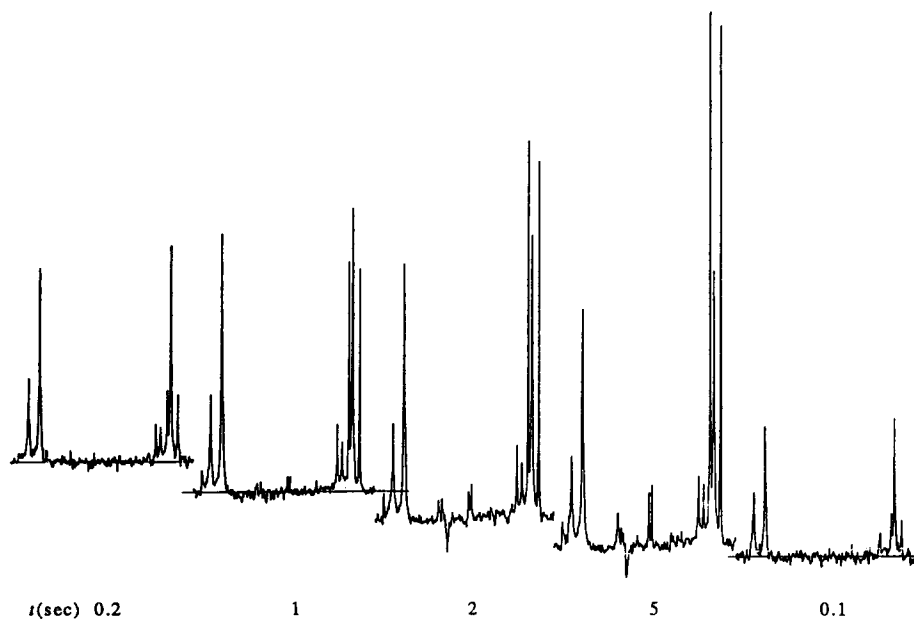


Fig. 3. 25.05 MHz ^{13}C -NMR spectra of the pyridinium bromide terminated polytetrahydrofuran polymer [12% (w/v)] in carbon tetrachloride used in spin-lattice relaxation time measurements.

Table 1. Values of spin-lattice relaxation time (T_1) measured by partially relaxed Fourier-transform ^{13}C -NMR in several solvents (25°C)

Series	M_n	Solvent	T_1 (sec)		
			$-\text{O}-\text{CH}_2-$	$-\text{O}-\text{CH}_2-\text{CH}_2-$	Aromatic ring
PTHF-OMe	1500	CDCl_3	0.29	0.36	5.00
		C_6D_6	0.54	0.57	—
		CCl_4	0.33	0.37	1.00
PTHF-Py	1600	CDCl_3	0.64	0.62	0.89
		C_6D_6	0.97	0.79	0.95
		CCl_4	0.23	0.23	0.14
		C_6H_{12}	0.24	0.30	0.12

Figure 3 shows representative spectra of the PTHF-Py polymer used for T_1 measurements.

Table 1 shows the relaxation times for the PTHF-OMe and the PTHF-Py polymers determined via progressive saturation measurements.

The relaxation times, T_1 , were obtained for carbons in three main locations in the polymer chains. These are the methylene group next to the oxygen in the tetrahydrofuran unit ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$), the internal methylene group ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$) and those in the aromatic residue. T_1 values were calculated for all the solvents used with one exception. The benzene ring of the *p*-methylbenzyl aromatic group arising from the initiator [5] is at the opposite end of the molecule to the methoxy end of PTHF-OMe polymers. The absorption peaks of this and the deuterio-benzene solvent overlapped.

From the study of the hydrodynamic properties of PTHF polymers in several solvents it was concluded [6, 14], that in low dielectric constant solvents, such as toluene, cyclohexane and carbon tetrachloride, the PTHF-Py polymers tended to associate through the ionic ends of the polymers and form a cluster of two to three chains. Table 1 shows that T_1 values for both the methylene groups ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$) of the PTHF-OMe polymers in chloroform, benzene and carbon tetrachloride are similar, while T_1 values for the aromatic group (i.e. the benzene ring at the opposite end of the polymer to the methoxy group) in chloroform and carbon tetrachloride are long. The latter indicate that the relaxation for this group is inefficient. Therefore, the PTHF-OMe polymers are free from any kind of association in chloroform and carbon tetrachloride.

The T_1 relaxation times of the pyridinium ring of PTHF-Py polymers in carbon tetrachloride and cyclohexane are short compared with these T_1 values in chloroform and benzene. This is attributed to the fact that PTHF-Py polymers in chloroform and in benzene are free from any association of their pyridinium groups. Thus, T_1 relaxation times for this site at the end of the polymer are long because of chain end mobility. In the other solvents, carbon tetrachloride and cyclohexane, there is a possibility of

association of pyridinium ends from two chains. This association will be in the centre of the new dimeric species. T_1 values of the pyridinium group, in this case, are short because the pyridinium groups now in the middle will lose the excitation energy readily.

The ratio of the T_1 relaxation times of the pyridinium ring to the methylene groups ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$) of PTHF-Py sample is an important factor insofar as the pyridinium end-group association is concerned. A significant variation of this ratio is noted (Table 1) for the PTHF-Py sample with different solvents.

It is thus confirmed from ^{13}C -NMR relaxation time studies that the introduction of ionic groups at the ends of the PTHF polymers does affect the hydrodynamic behaviour of the ion-containing PTHF polymers when they are dissolved in solvents with low dielectric constant.

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