

SOLID-STATE HIGH RESOLUTION NMR STUDY ON POLY (2,6-DIMETHYL- 1,4-PHENYLENE OXIDE)

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ABSTRACT

Experiments including ^{13}C spin-lattice relaxation, ^{13}C heteronuclear dipolar dephasing and ^1H spin diffusion are performed on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). The results show that the rotation of the methyl groups in solid PPO is partially restricted, which results in a surprisingly efficient spin diffusion between the aromatic proton and methyl proton characterized by a diffusion time of $150\mu\text{s}$. The results also show that the aromatic ring in solid PPO is rigid and twisted, which causes all aromatic carbons to be chemically unequivalent.

INTRODUCTION

The nuclear spin relaxation and dynamics of the solutions based on poly(2,6-dimethyl-1,4-phenylene oxide) (PPO), have been exclusively investigated in the past decades^[1-8]. A detailed interpretation on the nuclear spin relaxation of PPO solutions was undertaken in terms of four sorts of motions including overall rotatory diffusion, segmental motion, phenyl rotation and methyl rotation^[1-6]. In addition, the miscibility between PPO and other polymers such as polystyrene and polystyrene derivatives has been studied by means of ^1H spin-lattice relaxation in rotating frame measured via the indirect detection of ^{13}C signals in CP/MAS NMR experiments^[9-11]. In this paper, several solid state high resolution NMR experiments including ^{13}C spin-lattice relaxation, ^{13}C dipolar dephasing, ^1H spin-lattice relaxation

and ^1H spin diffusion are performed on PPO with the aim to investigate the dynamics and structure of solid PPO.

EXPERIMENTAL

All experiments are performed on a Bruker MSL-400 spectrometer at room temperature operating at 400.13 MHz for ^1H and 100.6 MHz for ^{13}C respectively.

^{13}C solid-state high resolution NMR spectrum of PPO ($M_n = 6800$) is recorded by means of Cross Polarization (CP) and Magic Angle Spinning (MAS) combined with TOSS sequence [see Fig. 1(a)], which can eliminate the spinning sidebands produced by the aromatic carbons. Normally 1ms contact time and about 4kHz spinning rate are adopted and the spin locking field is 54kHz.

^{13}C spin-lattice relaxation times (T_1^{C}) can be obtained by the CP/MAS inversion-recovery method developed by Torchia^[12]. Here a version modified with TOSS sequence [see Fig. 1(b)] is used, 25 recovery times in the range of 10ms to 50s are employed. T_1^{C} values are listed in Table 1.

^{13}C heteronuclear dipolar dephasing experiments on solid PPO is done by the pulse sequence shown in Fig. 1(c). 20 interrupted times ranged from 5 μs to 400 μs are used. The fast dipolar dephasing time (T_{DD}^{f}) and slowly dipolar dephasing time (T_{DD}^{s}) can be calculated by simulating the resonant intensity as a function of the interrupted time by two Gaussian decays, and the results are listed in Table 1.

^1H solid-state high resolution spectrum of PPO is recorded by the so-called Combined Rotation And Multiple Pulse Spectroscopy (i. e. CRAMPS). The pulse sequence is

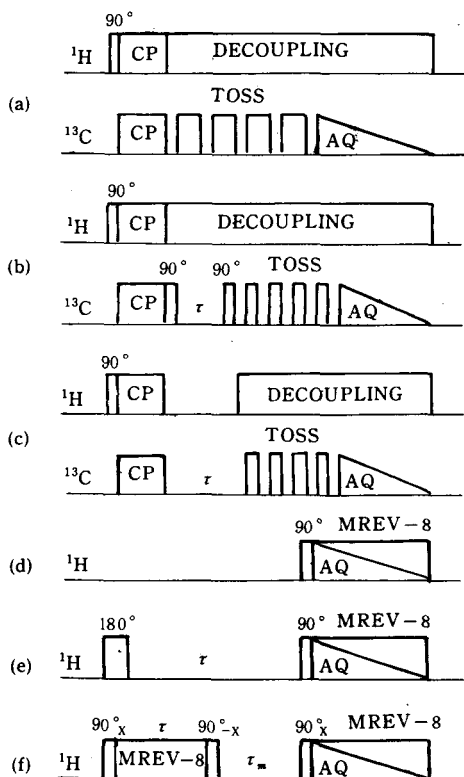


Fig. 1 Pulse sequences

shown in Fig. 1(d). MREV-8 multiple pulse sequence is used to decouple the homonuclear dipolar interaction with $1.95\mu\text{s}$ of 90° pulse width and $48\mu\text{s}$ of cycling time. 1024 data points are acquired with single mode detection.

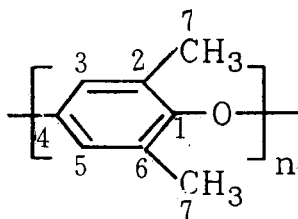
^1H spin-lattice relaxation times (T_1^{H}) can be measured by inversion-recovery method in CRAMPS experiments [see Fig. 1(e)]. The values are listed in Table 2.

^1H spin diffusion time between the methyl proton and aromatic proton is measured by the proposed pulse sequence shown in Fig. 1(f) by setting $\tau = \pi/\omega_{ij}$, where $\omega_{ij} = 2^{0.5}(\sigma_i - \sigma_j)/3$ and $(\sigma_i - \sigma_j)$ is the frequency difference in ^1H CRAMPS spectrum under MREV-8 which is scaled by a factor of $2^{0.5}/3$. Thus inversion in z axis for the methyl proton spins and the phenyl proton spins is obtained (the phenyl proton spin is at $-z$ axis and the methyl proton spin is at $+z$ axis). The spin magnetization is monitored under MREV-8 multiple pulse decoupling after a period of diffusion time τ_m .

Table 1 ^{13}C chemical shifts, spin-lattice relaxation times and dipolar dephasing times of solid PPO

Sample ^c	Chem. shift	T_1^{C} (s)	$T_{\text{DD}}(\mu\text{s})$	
No.	(ppm)		T_{DD}^{f}	T_{DD}^{s}
1	144.7	10.6	72(0.19) ^c	838(0.81) ^c
2	131.4	9.3	68(0.33)	568(0.67)
3	110.8	8.4	24(1.00)	— —
4	154.7	9.8	70(0.29)	538(0.71)
5	116.4	9.2	22(1.00)	— —
6	133.0	9.3	68(0.33)	568(0.67)
7	16.0	1.6 ^b (0.25)	46(0.64)	392(0.36)
		7.1 ^b (0.75)		

a: The structure of PPO is



b: The experimental data can not be best-fitted with single exponential decay but can be best-fitted with two exponential decays

c: The data in brackets indicate the molar fraction

Table 2 ^1H chemical shifts, spin-lattice relaxation times and spin diffusion time of solid PPO

	Phenyl proton	Methyl proton
Chem. shift (ppm)	6.8	2.2
$T_1^H(\text{ms})^a$	360	360
$T_1^H(\text{ms})^b$	360	360
Spin diffusion time (μs) ^c	150	150

a: Obtained by the pulse sequence shown in Fig 1(e)

b: Obtained by using the data for $\tau_m > 1\text{ms}$ in spin diffusion experiments

c: Obtained by using the data for $\tau_m < 1\text{ms}$ in spin diffusion experiments

RESULTS AND DISCUSSION

The ^{13}C CP/MAS NMR spectrum of solid PPO is shown in Fig. 2(a). The aromatic carbons have six distinguished resonant peaks which corresponds to the six aromatic carbons and four resonant peaks in liquid spectrum shown in Fig. 2(b). This fact shows that the carbon 3 and 5 and the carbon 2 and 6 are chemically equivalent in PPO solution. The resonant peaks for the carbon 3 and 5 in the CP/MAS NMR spectrum are well-resolved, but the resonant peaks for the carbon 2 and 6 are partially resolved. However, only partially resolved peaks for the carbon 3 and 5 were observed by Schaefer et al. [13]. These results clearly demonstrate that the aromatic ring in solid PPO is rigid and twisted, which causes the carbon 2 and 6 and the carbon 3 and 5 to be chemically unequivalent. Furthermore, our two-dimension spin exchange experiments and CP/MAS varied-temperature experiments (up to 343K) show that there is no evidence to indicate that the aromatic ring in solid PPO rotates around 1-4 axis.

The carbons in solid PPO have approximately the same T_1^C ($T_1^C \approx 10\text{s}$) except the methyl carbon. This shows that the methyl groups is the relaxation center which dominates the spin relaxation of the other carbons. But the T_1^C of about 75% methyl groups approaches those of the aromatic carbons. This shows that 75% methyl groups have poor mobility, but only 25% methyl groups have good mobility ($T_1^C = 1.6\text{s}$), and these methyl groups are really relaxation centers.

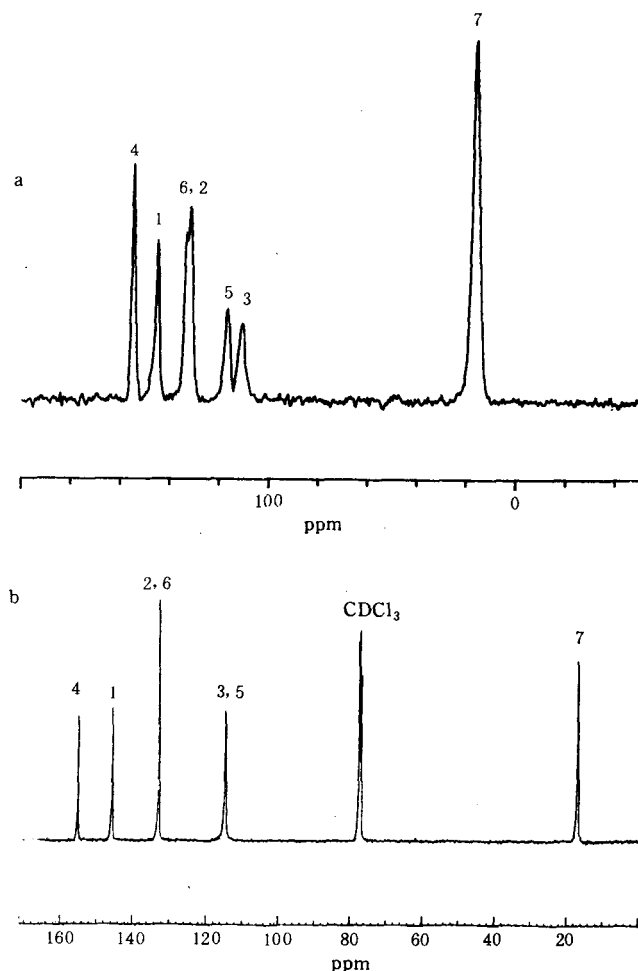


Fig. 2 The ^{13}C NMR spectra of PPO (a) the CP/MAS Spectrum, (b) the liquid NMR spectrum
Theoretically, T_1^{C} can be expressed as [14]

$$1/T_1^{\text{C}} = 0.1\gamma_{\text{C}}^2\gamma_{\text{H}}^2h^2r^{-6}[J_0(\omega_{\text{H}}-\omega_{\text{C}}) + 3J_1(\omega_{\text{C}}) + 6J_2(\omega_{\text{H}}+\omega_{\text{C}})]$$

where γ is the magnogyric ratio, ω indicates the angle resonant frequency, r is the length of C—H vector, and J represents the spectral density function. For the methyl groups rapidly rotating, it can be obtained that [14]

$$J_m(\omega) = 2/3k_m(\sin^2 2\Delta + \sin^4 \Delta)\tau/(1 + \omega^2\tau^2)$$

Therefore, the rotational correlation times of the methyl groups in solid PPO are calculated as about 10^{-8}s for $T_1^{\text{C}} = 1.6\text{s}$ and 10^{-7}s for $T_1^{\text{C}} = 7.1\text{s}$ respectively. These results illustrate that 75% methyl groups are impeded, while only 25% methyl groups are relatively mobile. This conclusion can also be certified by ^{13}C dipolar dephasing experiments.

^{13}C dipolar dephasing technique provides an efficient way to monitor the ^1H - ^{13}C heteronuclear dipolar interaction. The basic idea is that the signal intensities of the carbons which are strongly coupled to protons such as the carbons in CH , CH_2 , and CH_3 groups are rapidly decaying with increasing the dephasing time in a dephasing experiment, while the signal intensities of the carbons which are weakly coupled to their adjacent protons are decaying much more slowly. It is known from Table 1 that the dephasing times for the two protonated aromatic carbons are 22–24 μs , a typical value for this kind of carbons. However, about 64% methyl groups have a dephasing time of 46 μs which is much smaller than that expected for a methyl group in an ordinary organic solid such as amino acids. This demonstrates that the rotation of 64% methyl groups can not efficiently average the heteronuclear dipolar interaction. The slowly decaying part (about 36%) with a dephasing time of 392 μs should correspond to the methyl groups relatively mobile. This result is basically in accordance with that from T_1^{C} .

The solid-state high resolution proton spectrum of PPO is shown in Fig. 3, which contains two well-resolved resonant peaks corresponding to the methyl protons and aromatic protons respectively. The peak intensities of both the methyl protons and the aromatic protons as a function of the diffusion time τ_m are shown in

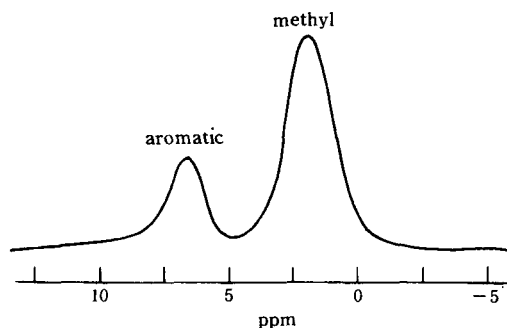


Fig. 3 The solid-state high resolution ^1H spectrum of PPO

Fig. 4, each of which includes two relaxation components, one is the fast relaxation component which is efficient in the period from 0 to 1 ms, and the other is the slow relaxation component which is efficient in the period from 1 ms to seconds. The former is the spin diffusion period during which the spin-lattice relaxation does not take place, while the latter is the pure spin-lattice relaxation period. Therefore, both spin diffusion time and spin-lattice relaxation time can be easily calculated from this measurement. The spin-lattice relaxation times are the same as those measured by inversion-recovery method in CRAMPS experiments. The spin diffusion time is about 150 μs , although these two sorts of protons are separated by four covalent bonds. Following perturbation theory, efficient spin diffusion can lead energy to be

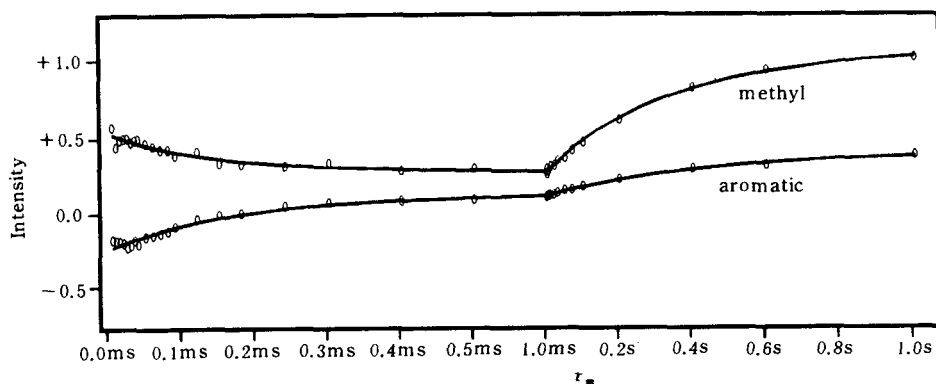


Fig. 4 The peak intensities of both the methyl and aromatic protons of PPO as a function of the diffusion time in a spin diffusion experiment

rapidly averaged among protons before the spin-lattice relaxation actually takes place. Thus only a single relaxation time for both the methyl protons and phenyl protons is obtained. The efficient spin diffusion between the two sorts of protons in solid PPO reflects that their mobility is considerably poor, which is in accordance with the results discussed above.

Briefly, the unequivocal resonant signals of the phenyl carbons in solid PPO are observed, which suggests that the ring is rigid and twisted. The rotation of a large part of the methyl groups is slow and impeded.

Keywords:

Solid-state high resolution NMR; ^{13}C Spin-lattice relaxation; ^{13}C Heteronuclear dipolar dephasing; ^1H Spin diffusion; Poly (2,6-dimethyl-1,4-phenylene oxide)

REFERENCES

- [1] Jones, A. A. and Lubianez, R. P., *Macromolecules*, **1978**, 11, 126.
- [2] Lubianez, R. P.; Jones, A. A. and Bisceglia, M., *Macromolecules*, **1979**, 12, 1141.
- [3] Jones, A. A.; Robinson, G. L.; Gerr, F. E., et al., *Macromolecules*, **1980**, 13, 95.
- [4] Lubianez, R. P. and Jones, A. A., *J. Magn. Reson.*, **1980**, 38, 331.
- [5] Jones, A. A. and Shes, F. P., *J. Polym. Sci., Phys.*, **1982**, 20, 681.
- [6] Jones, A. A.; Lubianez, R. P. and Shostak, S. L., *Polym. Prepr.*, **1978**, 19(1), 470.
- [7] Laupretre, F. and Monnerie, L., *Eur. Polym. J.*, **1975**, 11, 845.
- [8] Macura, S.; Bremer, J. and Brown, L. R., *J. Magn. Reson.*, **1985**, 63, 484.
- [9] Stejskal, E. O.; Schaefer, J.; Sefcik, M. D., et al., *Macromolecules*, **1981**, 14, 275.
- [10] Dickinson, L. C.; Yang, H.; Chu, C. W., et al., *Macromolecules*, **1987**, 20, 1750.
- [11] Feng, H.; Feng Z.; Yuan, H., et al., *Macromolecules* **1992**, 25, 5981.
- [12] Torchia, D. A., *J. Magn. Reson.*, **1978**, 30, 613.
- [13] Schaefer, J.; Stejskal, E. O. and Buchdahl, R., *Macromolecules*, **1977**, 10, 384.
- [14] Yan, X., Ph.D. Thesis, Wuhan Institute of Physics, The Chinese Academy of Sciences, **1990**.