

A STUDY ON CONFORMATIONAL STRUCTURE OF MODEL COMPOUND OF NOVEL SIDE CHAIN LIQUID CRYSTALLINE POLYMER BY USING HIGH RESOLUTION SOLID STATE ^{13}C -NMR

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ABSTRACT

^{13}C -NMR chemical shifts of model compound of a novel side chain liquid crystalline polymer, poly 2,5-bis(4-alkoxybenzoyloxy) styrene, have been assigned in this study. Moreover, by using high-resolution solid-state CP/MAS (cross polarization/magic angle spinning) technique, the spectrum shows that in the crystalline state the ester linkage has a conformation nearly perpendicular to the either side of ring planes, and that the alkoxy groups are not fully in zigzag form. The possible conformational changes around the mesogens from the solid state to the mesophase are discussed.

INTRODUCTION

Side chain liquid crystalline polymers have been a subject of intensive studies in recent years^[1, 2]. It is well-known that the systematic realization of liquid crystalline side-chain polymers requires a flexible linkage of the rigid mesogenic moieties to the polymer backbone via a flexible spacer^[1]. However, Zhou et al. have prepared new side chain polymers with only very short spacer^[3] or even without a flexible spacer which still show liquid crystal character^[4].

The mesogenic moiety used in the novel side chain liquid crystalline polymer is a kind of aromatic ester compound. Its chemical structure is shown in Fig. 1. This big moiety was found to have a stereo hindered effect that interchain interaction of the polymer occurs among the side chain mesogenic moieties instead of the main chain backbone^[5]. Generally, through phase transitions, the polymer chain should undergo a series of variation of interaction environments.

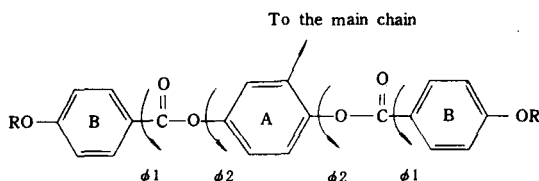


Fig. 1. Chemical structure of side-chain mesogenic moiety of the novel polymer

Conformation of the mesogenic moiety may change with the various interchain interactions. Therefore, the conformational alteration of the big moiety in different phases is an interesting point to be understood.

General methods of characterizing compounds such as DSC and Optical Microscope cannot offer message about the molecular conformation. Recently, high-resolution CP/MAS (cross polarization/magic angle spinning) NMR has become a powerful tool for characterizing molecular packing, molecular order, molecular motion and conformational structure^[6-8]. In the present work, the thermotropic aromatic ester as shown in Fig. 2 as a model compound of the novel polymer has been investigated by CP/MAS NMR in order to understand whether any conformational change could happen to the big mesogenic moiety during phase transitions.

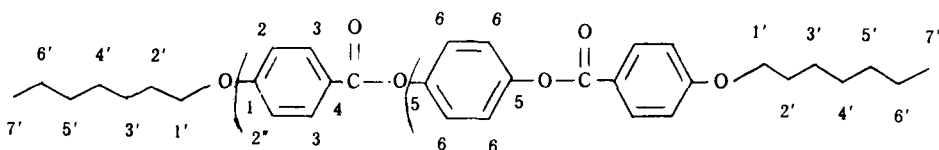


Fig. 2 Chemical structure of the model compound.

EXPERIMENTAL

1, 4-bis[4-(heptyloxybenzoyloxy)]-benzene was the product of Shanghai Third Chemical Reagent Factory. The ^{13}C solid-state NMR spectra were recorded on a Bruker 400(^{13}C Frequency 100MHz) spectrometer with a CP/MAS unit. The solid-state NMR measurements were performed at room temperature. The spinning rates were about 4KHz. Contact time was 1ms. Conventional and TOSS pulse sequences were used for measurements. Spectra were accumulated 400 scans.

The solution ^{13}C spectra of aromatic ester were recorded on the Varian XL 300 spectrometer at 75MHz at room temperature and low temperature (-45°C) in about 10% (w/v) CDCl_3 solvent. The peak of CDCl_3 was used as internal standard.

RESULTS AND DISCUSSION

The solid-state CP/MAS spectrum of the model compound free of spinning sidebands was obtained by using TOSS pulse sequence at room temperature as shown in Figure 3A. The solution spectra of the compound in CDCl_3 at room temperature and at low temperature (-45°C) are shown in Figure 3B and 3C. To authors' knowledge little work has been published on the ^{13}C NMR peak assignment for the compound. Therefore, some parameters were needed to estimate every chemical shift of the compound and to confirm the assignment first. Based on chemical shifts of a substituted benzene, $\text{RO}-\text{C}_6\text{H}_4\text{COOC}_6\text{H}_5$, from Sadlter ^{13}C Standard Spectra Data, the parameter for the substituent on benzene was obtained to be 128.5ppm, which was used as a standard value in handling the overall assignment. Combining useful information from the off resonance ^1H decoupling technique, as a result, ^{13}C resonances of the model compound could be interpreted unambiguously. In Table 1 and Table 2 are given the chemical shift

assignments for each carbon of the model compound, together with calculated values from our parameters that are in good agreement with those observed.

Table 1 ¹³C Chemical shifts of aromatic ring carbons of the model compound in the solid state and in the solution

	1	2	3	4	5	6	C=O
Solid	162.9	111.1 118.0	132.6	123	147.9	122.5	164.1
Solution	{ R. T	114.2	132.4	121.3	148.3	122.5	164.6
	{ L. T(-45 °C)	114.6	132.5	120.5	147.9	122.7	164.8
Calculated value	164.3	114.6	130.9	121.4	148.8	122.6	
Chemical shifts difference *	- 0.4	- 3.1 3.8	0.2	1.7	- 0.4	0	- 0.5

* Chemical shift difference between the assigned peaks in solution state and the solid state.

Table 2 ¹³C chemical shifts of alkyl carbons of the model compound in the solid state and in the solution

	1'	2'	3'	4'	5'	6'	7'
Solid	66.1	32.9	27.0	32.9	32.9	24.2	16.8 14.3
Solution	{ R. T	28.9	25.72	28.8	31.25	22.4	13.9
	{ L. T(-45 °C)	29.03	25.9	28.96	31.71	22.5	14.02
Calculated value	68.2	28.5	25.7	29.0	31.7	22.5	13.7
Chemical shifts Difference *	- 2	1.4	1.3	4.1	1.7	1.8	2.9 0.4

* Chemical shift difference between the assigned peaks in the solution state and the solid state.

Comparison of the solid-state spectrum with the solution spectra gives us information concerning the different conformational structures of the compound in different molecular environments.

Among the chemical shifts in Table 1, the resonance of the aromatic carbons ortho to the alkoxy group is located at 114.2ppm in solution. In the solid state, this peak is separated into a doublet by 6.9ppm, that is, resonances of C₂ and C₂' at 111.1 and 118.0ppm, respectively. This splitting can be interpreted as a nonequivalency of the carbons, like the same phenomena in the case of p-alkoxybenzoic acids investigated by Hays^[9]. Therefore, in the solution of our sample, the ortho carbons are equivalently to be shielded since the alkoxy group can freely rotate about the axis of the oxygen-aromatic carbon to which the alkoxy group is attached. However, the motion of the substituents is frozen in one position when the system is condensed to the crystalline state, indicating a fixed orientation of the alkoxy group with respect to the benzene ring in the solid state. Taking into account of X-ray observation^[10], the two groups in the fixed conformation should be of coplanarity.

The observation of other two carbons in the ring B(Fig.2) ortho to the ester linkage gave rise to a well-resolved and narrow peak in the solid state spectrum. This resonance reveals that the ortho carbons are completely equivalent. In the crystalline state, the equivalency confines the spatial position of the carbonyl group. In other words, it is reasonable that the ester linkage has a conformation nearly 90 ° to the plane of ring B.

It is a well known factor that 'carbonyl group has a stable conformational state when it is in the same plane with phenylene ring. Stable conformational structure of the model compound was calculated as that the carbonyl orients in the same plane with ring B and almost perpendicular to the ring A^[11]. But our findings here show the difference. It is much similar to another observation obtained by Uryu et al. in bis(4-butoxyphenyl) terephthalate^[6], where the conformation of carbonyls was also perpendicular to the connected phenylene ring. The existence of this unusual conformation in the crystalline state may be attributed to the

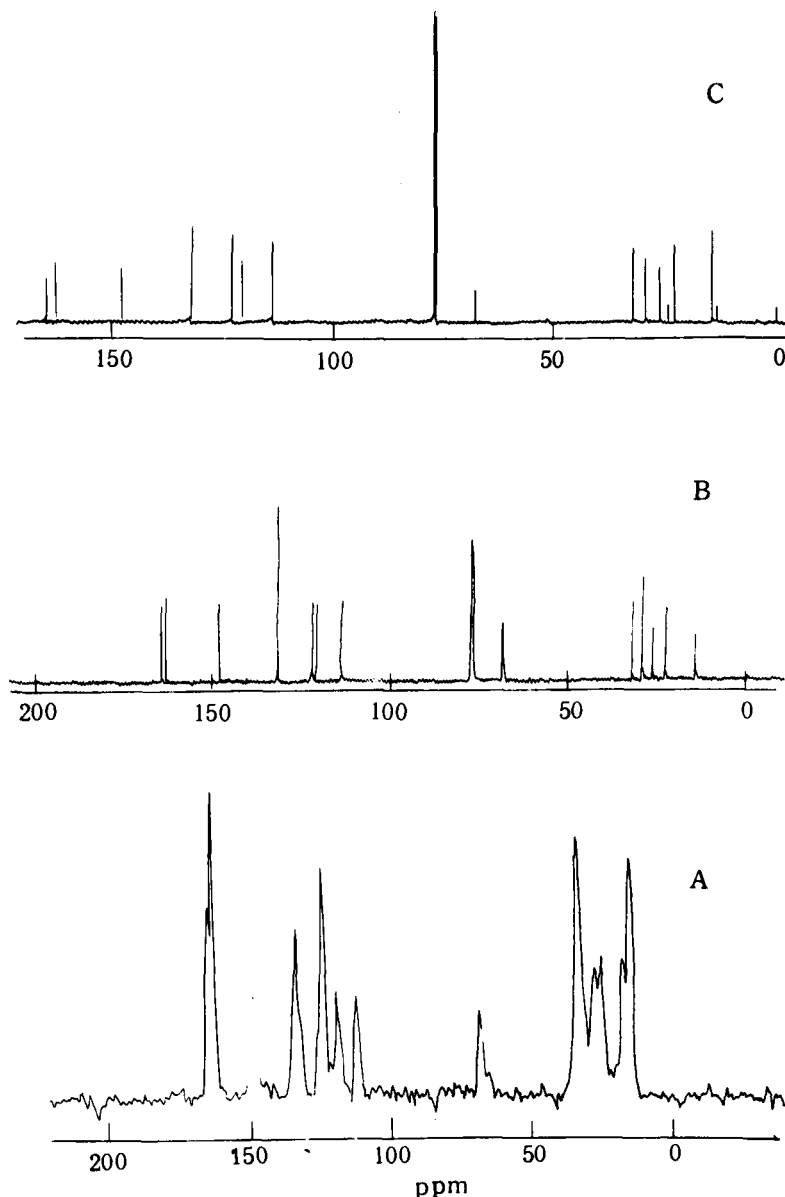


Fig. 3 ^{13}C NMR spectra of the model compound under various conditions:

A. solid-state CP/MAS spectrum; B. solution spectrum at room temperature; C. solution spectrum at -45°C

packing organization of the big mesogenic moiety and the long flexible chains into the lattice. For the ring A, there is no any significant evidence found here to show the four carbons, connecting to hydrogen, being nonequivalent. Thus indicating a stable conformation of the ester linkage to the ring A formed in the crystalline state where the $\Phi_2 = 90^\circ$.

As for aliphatic carbons of the terminal alkoxy group, the resonance of $\text{C}_{2'}$, $\text{C}_{3'}$, $\text{C}_{4'}$, $\text{C}_{5'}$, $\text{C}_{6'}$, and $\text{C}_{7'}$, in the solid state are shifted downfield from those in solution respectively. These chemical shift changes can be explained by the γ gauche effect^[12]. Generally, in the solid state, the alkoxy group is believed to be locked in a planar zigzag conformation, while in solution the conformation changes rapidly and certain populations of gauche-state for each C-C bond exist, which cause averaged upfield chemical shifts. On the contrary, the resonance of $\text{C}_{1'}$, which is next to the oxygen, shows an upfield chemical shift change. This is owing to cessation of a combined effect^[6] after the sample entering the solid state. They are (a) the solvent effect on the oxygen which is next to $\text{C}_{1'}$; (b) the γ gauche effect between $\text{C}_{1'}$ - $\text{C}_{4'}$ by the rotation about the axis of $\text{C}_{2'}$ - $\text{C}_{3'}$; (c) the deshielding effect by the rotation about the axis of $\text{O} - \text{C}_{1'}$. So, upfield change occurs on the chemical shift of $\text{C}_{1'}$. From our observation, the alkoxy chains are not fully in planar zigzag conformation. At least the bond of $\text{C}_{5'}$ - $\text{C}_{6'}$ should be partly in gauche conformation since a splitting happened to the chemical shift of $\text{C}_{7'}$, from 13.9ppm in solution to 16.8 and 14.3ppm in solid state.

On the basis of above results, it is proposed that the mesogenic core of the model compound has a conformation in the solid state depicted in Fig. 4, where $\Phi_1 = \Phi_2 = 90^\circ$. In the weaker intermolecular interaction environment, conformation of the core will thus change. As discussed above, it is reasonably expected that the most popular conformation of the core becomes of $\Phi_1 = 0^\circ$ and $\Phi_2 = 90^\circ$ when the system is in the mesophase or the isotropic phase.

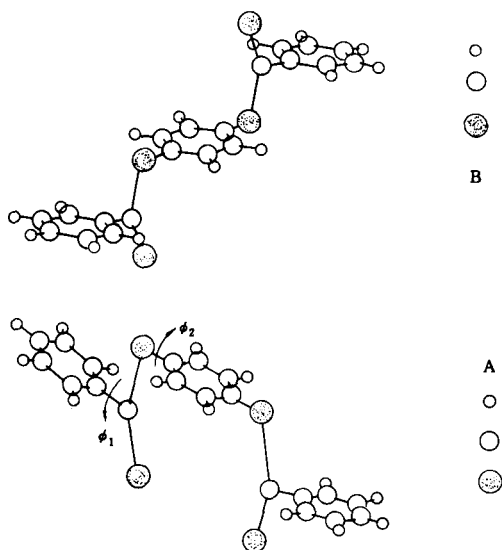


Fig. 4. Proposed conformation of the thermotropic aromatic ester compound in the solid state
A: *cis* conformation ; B: *trans* conformation

Keywords:

Conformation; ^{13}C NMR; Liquid crystal; 1,4-bis[4-heptyloxybenzoyloxy] - benzene

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