

## Solid State NMR Study of PAZO-6 and Related Materials

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(Received August 20, 1995)

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**Abstract :** PAZO-6 is a new combined type liquid crystalline polymers (LCP) which has two types of mesogens combined non linearly. Ordering of branch mesogen, azo group, in PAZO-6 is an important parameter to observe as well as the substitution effect on the backbone. The related small molecules such as monomers as well as the polymer itself are studied by solid state NMR techniques. Preliminary <sup>13</sup>C CP/MAS (cross polarization/ magic angle spinning) spectral results suggest that the azo groups in the monomers are not aligned with themselves. Azo groups in the monomers seem to be poorly ordered between well ordered *p*-phenylene terephthalate moieties. Similar disordering tendency of the azo group in PAZO-6 is deduced from the overall aromatic carbon peak positions which are not much different from those of the monomer.

**Keywords :** Liquid crystalline polymer (LCP), Solid state NMR, Ordering of mesogens in a new combined type LCP

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### 1. Introduction

The polymer which is named as PAZO-6 in our group is composed of poly(*p*-phenylene

terephthalate) backbone and azo groups substituted to terephthalic acid moieties of the backbone *via* flexible alkyl chains. Not only *p*-phenylene terephthalates but also azo groups are mesogens. Thus, PAZO-6 is one

of the new combined type liquid crystalline polymers (LCP) [1] which have two or more types of mesogens combined nonlinearly. Ordering of branch mesogen in a new combined type LCP is an important parameter to observe as well as the substitution effect on the backbone such as changing phase transition temperatures and degrading crystallinities. Structure and dynamics of the LCP can also be affected by photoisomerization of azo group [2] when azo groups are one type of the mesogens of the polymers like PAZO-6.

As the first step to study dynamics and structure of PAZO-6 systematically, not only the polymer itself but also related small molecules such as monomers were studied by solid state NMR techniques. Preliminary  $^{13}\text{C}$  CP/MAS (cross polarization/ magic angle spinning) spectral results are discussed with respect to ordering of each type mesogen.

## 2. Experimental

Synthetic details for the preparation of SC-6, MAZO-6 and PAZO-6 have been reported in the MS thesis by one of the authors [3]. Synthetic procedure of KH-12 will be described in a future publication. The chemical formulas of SC-6, MAZO-6, KH-12,

and PAZO-6 are shown with each  $^{13}\text{C}$  spectrum in Fig. 1. PAZO-6 sample quenched from liquid crystalline state was prepared by heating the PAZO-6 powder in a heating bath upto  $210^\circ\text{C}$  under dry nitrogen gas and then cooling the sample quickly by liquid nitrogen. PAZO-6 is in nematic liquid crystalline state above  $188^\circ\text{C}$  as indicated in Table 1.

$^{13}\text{C}$  CP/MAS NMR spectra of the samples were acquired at room temperature and at an MSL 200 instrument with the carbon Larmor frequency of 50.3 MHz. Typical spinning rate was between 3.0 ~ 4.0 kHz with 7 mm outer diameter rotors. The  $90^\circ$  pulse length for both  $^{13}\text{C}$  and  $^1\text{H}$  was 4.5  $\mu\text{s}$  and repetition time was 5 sec. The contact time was 800  $\mu\text{s}$  for SC-6, MAZO-6, and KH-12 and 1ms for PAZO-6. To get the spinning sideband free spectra, four  $\pi$  TOSS (total suppression of spinning sidebands) pulse sequence [4] was utilized.

## 3. Results and Discussion

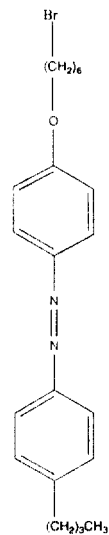
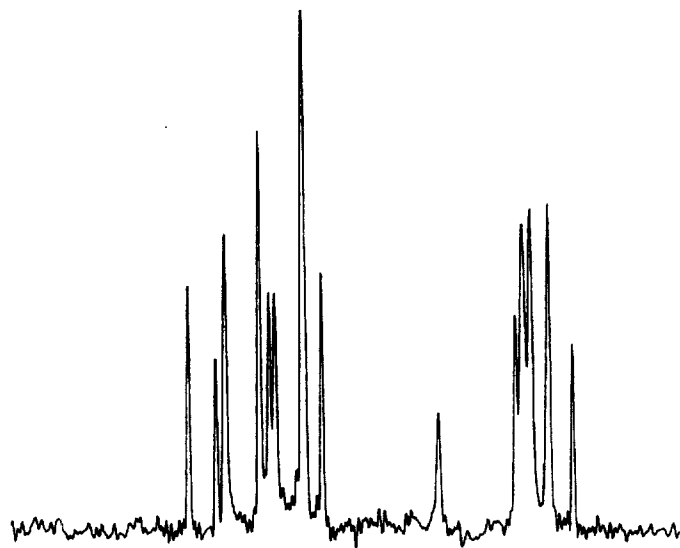
Representative  $^{13}\text{C}$  CP/TOSS spectra of SC-6, MAZO-6, PAZO-6, and KH-12 are shown in Fig. 1. Spectra of KH-12 and SC-6 have relatively narrow peaks implying crystalline property. MAZO-6 has both narrow peaks and a broad feature underneath.

Table 1. Phase transition temperatures obtained by DSC

Sample	$T_g$ ( $^\circ\text{C}$ )	$T_m$ ( $^\circ\text{C}$ )	$T_i$ ( $^\circ\text{C}$ )	Liquid Crystal
SC-6	---	66	86	nematic
MAZO-6	---	101	145	nematic
PAZO-6	~ 53	188	> 300	nematic
KH-12	---	111	120	nematic

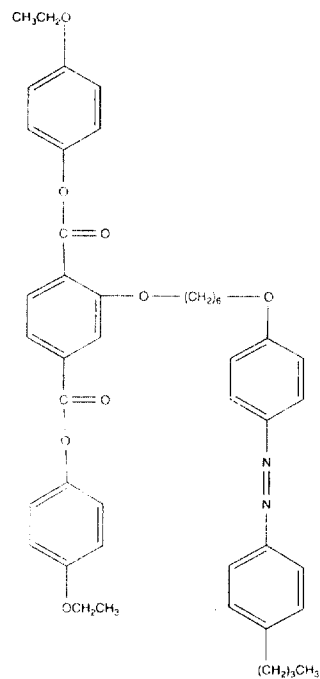
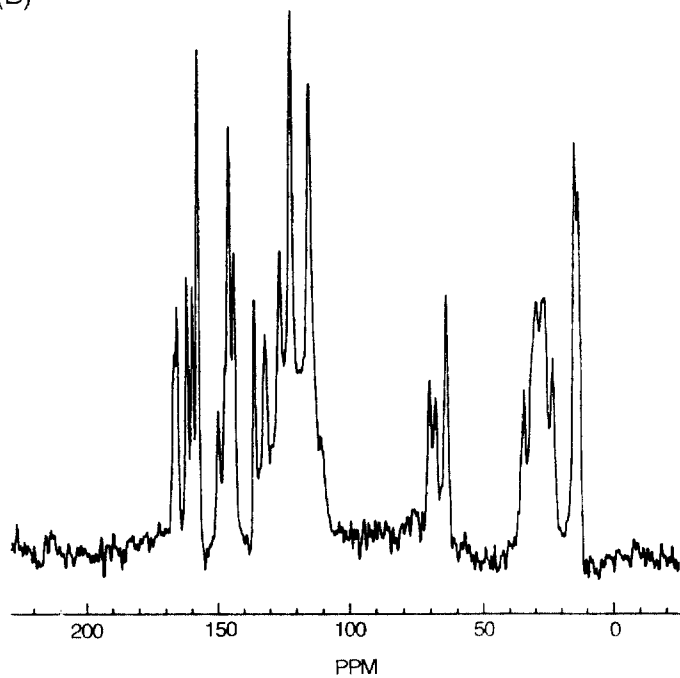
(A)

SC-6



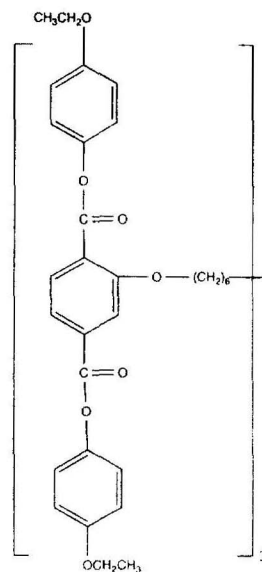
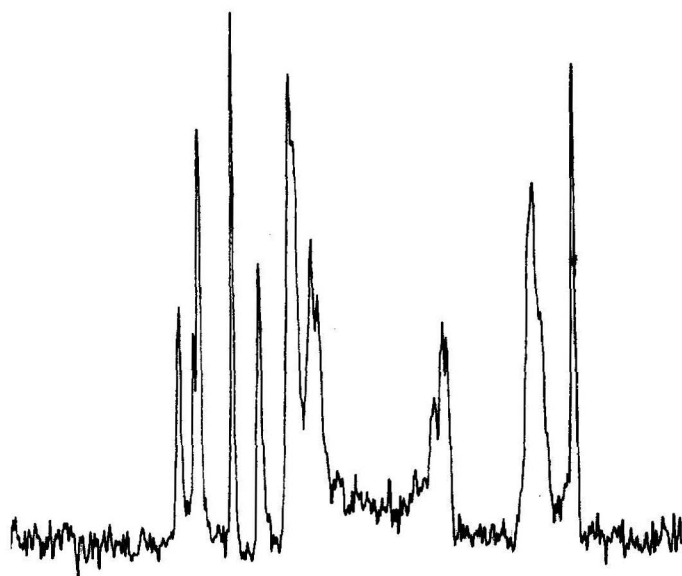
(B)

MAZO-6



(C)

KH-12



(D)

PAZO-6

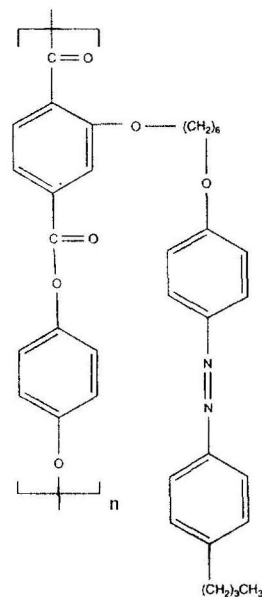
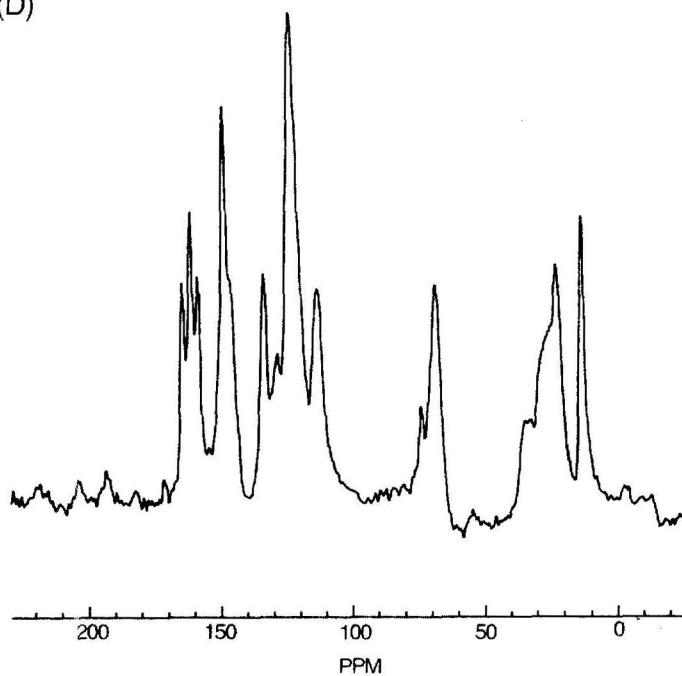


Fig. 1 : 4.7 T  $^{13}\text{C}$  CP/TOSS spectra of (A) SC-6 at 3.8 kHz, (B) MAZO-6 at 3.6 kHz, (C) KH-12 at 3.0 kHz, and (D) PAZO-6 at 3.5 kHz.

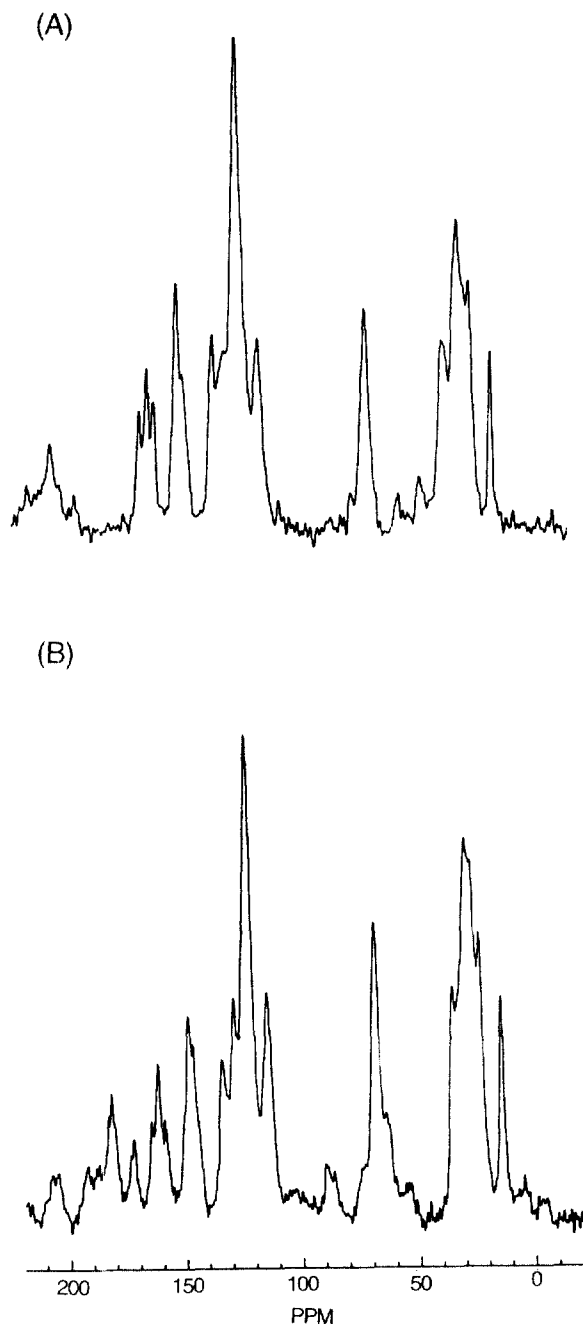


Fig. 2: 4.7 T  $^{13}\text{C}$  CP/MAS spectra of (A) PAZO-6 at 4.0 kHz, (B) PAZO-6 quenched from liquid crystalline state at 3.0 kHz taken at room temperature.

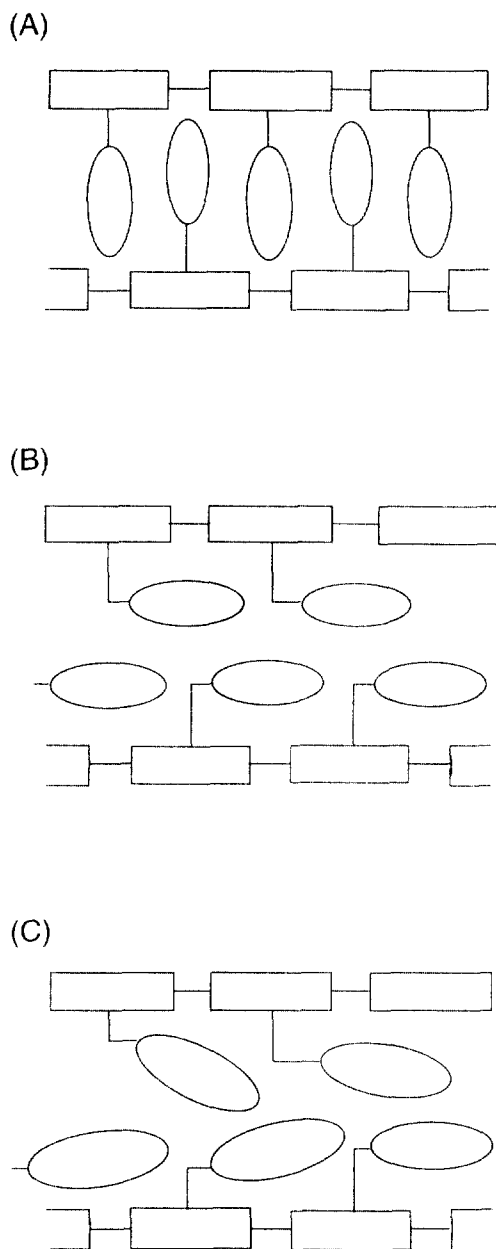


Fig. 3: Schematic presentation of three possible ordering of azo groups in PAZO-6. Azo groups are (A) aligned by themselves between poly(*p*-phenylene terephthalates) backbone of PAZO-6, (B) regularly parallel, and (C) relatively parallel with the poly(*p*-phenylene terephthalates) backbone. Azo groups and *p*-phenylene terephthalates are represented as ellipsoids and rectangles, respectively.

PAZO-6 shows amorphous character with broad and severely overlapped peaks. Amorphous property of PAZO-6 agrees with observed glass transition temperature obtained by DSC (differential scanning calorimetry) as shown in Table 1. Alkyl carbon peaks are between 10 to 40 ppm and the far right peaks among them are from methyl carbons. Alkoxy carbon peaks appear around 65 ppm. More than one of methyl peaks and alkoxy peaks are observed in MAZO-6 and KH-12. Aromatic and carboxyl carbons resonate in a region between 110 and 170 ppm. Since aromatic peaks of azo groups and of *p*-phenylene terephthalate moieties resonate in the same chemical shift region, spectra of SC-6 and KH-12 are utilized to assign peaks. SC-6 and KH-12 are compounds with azo groups only and *p*-phenylene terephthalate moieties only, respectively.

Comparison of the spectra of KH-12 and MAZO-6 indicates that aromatic carbons of *p*-phenylene terephthalate moieties in both samples have the same chemical shifts and linewidths. On the other hand, dramatically different resonances of the azo group aromatic carbons in the spectra of SC-6 and MAZO-6 are observed. Most protonated aromatic carbons of azo group in MAZO-6 lose sharpness of the peaks and appear as a broad component covering from 110 to 130 ppm in the spectra. This observation suggests that azo groups in SC-6 and MAZO-6 are in very different microscopic environments. Azo groups in MAZO-6 do not seem to be aligned with themselves as in SC-6 and are probably poorly ordered between well ordered *p*-phenylene terephthalate moieties. Similar disordering tendency of the azo group in PAZO-6 is deduced from the overall aromatic carbon peak positions, considering much broader linewidths, which are not much different from those of MAZO-6. However, backbone chains in PAZO-6 is expected to

have relatively regular spacing from close similarity of main peaks in the  $^{13}\text{C}$  CP/MAS spectra of PAZO-6 quenched from liquid crystalline state (Fig. 2B) and the amorphous PAZO-6 (Fig. 2A). Peak position changes, especially over 170 ppm and minor line shape difference of the spectra are due to different magic angle spinning rates (4.0 kHz and 3.0 kHz) of the two samples rather than due to difference of the samples. When a spinning rate is changed, spinning side band peaks move their positions and can be overlapped with main peaks, the positions of which are not affected by the spinning rate [4]. Thus, the relative orientation of azo group and backbone of PAZO-6 can be summarized as in Fig. 3C rather than as in Fig. 3A or 3B.

#### Acknowledgment

This work was partially supported by the Korean Ministry of Science and Technology. J.-I. Jin would like to acknowledge the support of this work (BSRI-95-3406) by the Korea Ministry of Education through the Basic Science Research Institute of Korea University. The authors also acknowledge Mr. K. S. Hong for technical support in NMR experiments.

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