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NMR and DSC Observation of Thermotropic Nematic Liquid-Crystalline Polymer with Cyanobiphenyl Group in The Side Chain

Yutaka Tanaka [a] , Ryoichi Kishi [a] & Hisao Ichijo [b]

[a] Department of Materials Science and Engineering, Faculty of Engineering, Fukui University, Bunkyo, Fukui, 910-8507, Japan

[b] Department of Polymer Engineering, National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki, 305-8565, Japan

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NMR and DSC Observation of Thermotropic Nematic Liquid-Crystalline Polymer with Cyanobiphenyl Group in The Side Chain

YUTAKA TANAKA[a*], RYOICHI KISHI[a] and HISAO ICHIJO[b]

[a]Department of Materials Science and Engineering, Faculty of Engineering, Fukui University, Bunkyo, Fukui 910–8507, Japan and [b]Department of Polymer Engineering, National Institute of Materials and Chemical Research, 1–1 Higashi, Tsukuba, Ibaraki 305–8565, Japan

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The proton NMR spectra and DSC thermograms were observed with raising temperature for side chain type thermotropic liquid-crystalline polymer, poly(6-(4′-cyanobiphenyl-4-yloxy) hexylacrylate (PCBA). A pronounced variation was found for the NMR spectra and DSC heating curve depending on the thermal history applied on PCBA before the measurements. In the case of gradual cooling from the isotropic state to the solid state, DSC heating curve showed endothermic peak at the glass transition temperature. The line widths was taken as the parameter characterizing the NMR spectra and their temperature dependence was discussed. A qualitative interpretation on the observed NMR spectra was given in relation to the orientation of mesogenic group. The obtained endothermic peak was considered to come from the change in orientational behavior caused by the gradual cooling to the solid state.

Keywords: liquid-crystalline polymer / thermal properties / DSC / proton NMR

INTRODUCTION

There has been substantial interests in synthesizing thermotropic liquid crystalline polymer in response to a need for new compounds for functional devices. Previously we have demonstrated electrical – mechanical energy conversion system using thermotropic liquid-crystalline mixture which consists of thermotropic liquid-crystalline elastomer and low molecular weight liquid crystal [1]. The

* Correspondence Author.

elastomer was prepared by cross-linking poly(6-(4′-cyanobiphenyl-4-yloxy) hexylacrylate (PCBA), having the structural formula of Figure 1. It undergoes solid, nematic and isotropic phase transition according to a change in temperature.

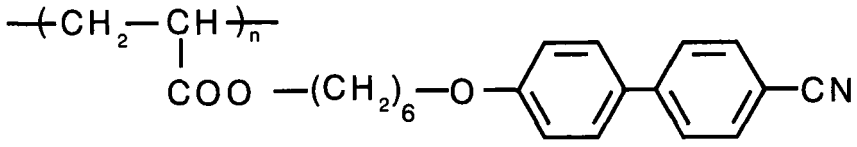

FIGURE 1 The structural formula of poly(6-(4′-cyanobiphenyl-4-yloxy) hexylacrylate (PCBA)

It is important to make a high orientation of mesogenic elements of cyanobiphenyl groups in the side chains while cross-linking, in order to make high efficiency for electrical – mechanical energy conversion. So we put an attention on the thermal history for PCBA and its effect on the orientation of mesogenic elements.

This paper is concerned with the proton NMR and DSC observation for PCBA after different thermal treatments. A remarkable variation was found for the proton NMR spectra and DSC heating curve depending on the thermal history applied on PCBA.

NMR studies for liquid crystals have been widely carried out and they showed it is a powerful method for obtaining structural information including the orientation of mesogenic elements. Although the discussion on the detailed molecular orientation could not be developed presently, a qualitative interpretation on the observed NMR spectra was briefly reported.

EXPERIMENTALS

The weight-average molecular weight of PCBA was 6.5×10^4, (average degree of polymerization was 180). Other characterization of PCBA as well as synthesis were reported elsewhere. [2] The prepared sample was purified by repeated precipitation from tetrahydrofuran solution into methanol, then the sample were dried in vacuum. Powdered PCBA was poured into a normal NMR glass tube which was introduced into the NMR spectrometer.

Proton NMR spectra were recorded as a function of temperature over the solid, nematic and isotropic phases, using Varian AC-200 spectrometer working at the field strength of 47kGauss, equipped with a temperature-regulating unit which

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was calibrated by measuring the proton chemical shift difference in ethylene glycol. [3]

DSC measurement was carried out using SEIKO DSC-120 thermal analyzer at the heating rate of 5°C/min. The polarizing microscope of Olympus BH-2 equipped with a hot stage was used to observe the textures of PCBA.

RESULTS AND DISCUSSION

Figure 2 shows the heating DSC curve for PCBA at different thermal histories. One was DSC measurement after rapid cooling and the other was that after gradual cooling; that is, PCBA melted at 180°C was cooled to 0°C at a rate of −30°C/min (rapid cooling), then heating DSC measurement was carried out and the result was shown in curve I. On the other hand, the same sample melted at 180°C was left inside the DSC apparatus and cooled to room temperature (gradual cooling), then the measurement was carried out and the result was shown in curve II.

Curve I showed a discernible shoulder at 44°C (T_g) which was the typical feature of an amorphous polymer with a glass transition, and an endothermic peak at 129°C which reflects the phase transition to the isotropic melt (T_{NI}). The nematic – isotropic phase transition at T_{NI} was also confirmed by the polarizing microscopic observation. PCBA displayed schlieren textures characteristic of the nematic liquid-crystalline phase below T_{NI}.

Curve II showed two peaks, one was in the same temperature as T_g, and the other in the same as T_{NI}. The difference between the shoulder in Curve I and the peak in Curve II at T_g appeared with good reproducibility according to the thermal history before the DSC measurement. The fact that an endothermic peak obtained at $T_g$in Curve II indicates some ordered structure of PCBA in the solid phase after gradual cooling.

Figure 3 shows the NMR spectra measured with raising temperature (T) for PCBA; the sample was melted at 140°C and then cooled by soaking the NMR glass tube into liquid nitrogen (rapid cooling). The line shape at T=22°C was a mixed form which appeared to be a combination of a broad line with a narrow component in the center. The broad line became narrow with raising temperature as shown in the spectrum at T=77°C, whereas it clearly split out with keeping the narrow component at T=83°C. Further raising in temperature brought about an extreme narrowing as seen in the spectrum at T=134°C.

After the NMR measurement the sample was taken out and gradually cooled to room temperature outside the NMR magnetic field using thermostatic bath. Then the measurement was repeated with raising temperature. The split broad line with

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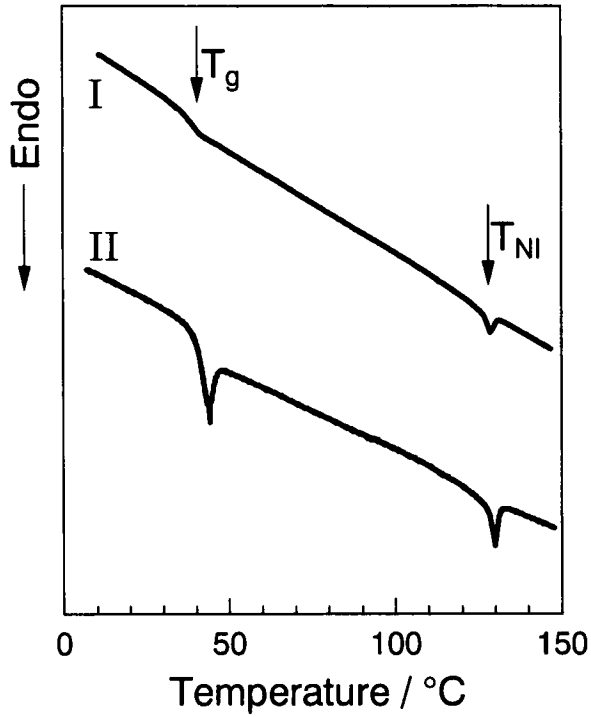

FIGURE 2 Heating DSC thermograms of PCBA at different thermal histories. I: measured after rapid cooling. II: measured after gradual cooling. The heating rate is 5°C/min

the narrow component in the center appeared at lower temperature region as shown in the spectrum at T=30°C in Figure 4. It is noteworthy that the line width increased when comparing the spectrum measured after gradual cooling with that measured after rapid cooling at same temperature. The split broad line narrowed without any change in the line shapes as raising temperature as shown in Figure 4. After the temperature was raised to T=134°C the measurement was continued with lowering temperature, which resulted in the broadening of the line shape reverse to the behavior observed after the gradual cooling treatment. The change in line shapes according to the thermal history previous to the NMR measurement was observed with good reproducibility.

There were so far several studies about nematic liquid crystal compounds using NMR technique from the viewpoint of molecular orientation. [4–7] According to the studies of Martins *et. al.*, the line width at half-height ($\Delta_{1/2}$) as shown in Figure 3 and 4 should be taken for the parameter characterizing the proton NMR spectra. Figure 5 shows this spectral parameters as a function of temperature.

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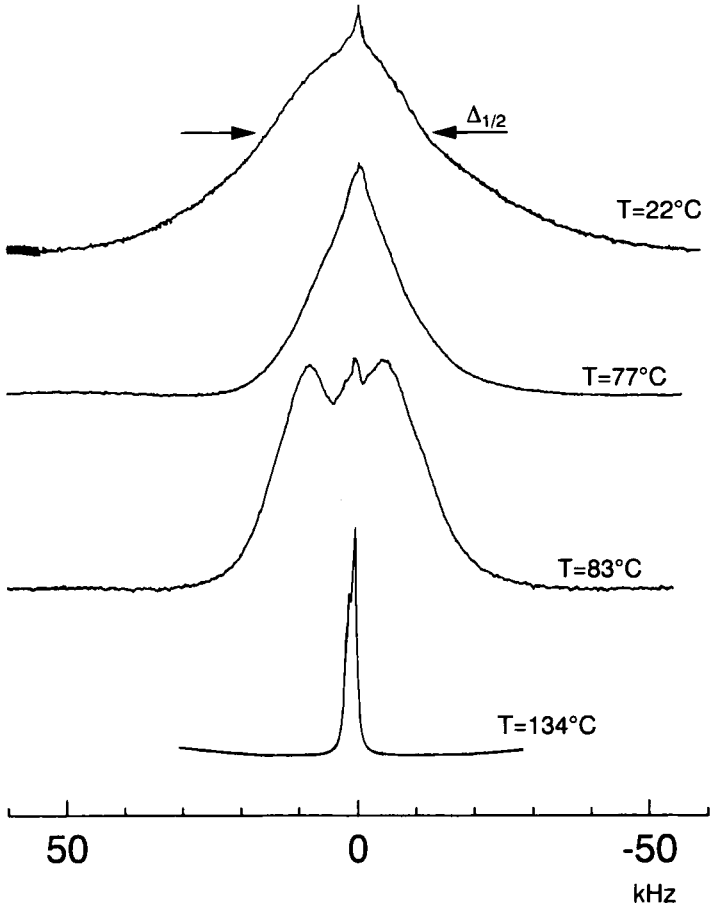

FIGURE 3 Proton NMR spectra measured with raising temperature (T) for PCBA after rapid cooling

Two kinds of temperature dependence of $\Delta_{1/2}$ were observed according to the thermal history of PCBA sample; one was the case of small line width (I) and another was the case of large line width (II). Both in the case I and II $\Delta_{1/2}$ values decreased as the increase in temperature, showing that; as the increase in thermal motion of the polymer the anisotropy of dipole-dipole interaction getting more homogeneous. The conversion from case I to case II was caused by the thermal treatment of gradual cooling or raising temperature above 83°C for PCBA after rapid cooling as shown by the arrow in Figure 5. This behavior indicates the enhancement of dipole-dipole interaction which is assumed to have a relation to the orientation of mesogenic elements. In the case of gradual cooling of PCBA

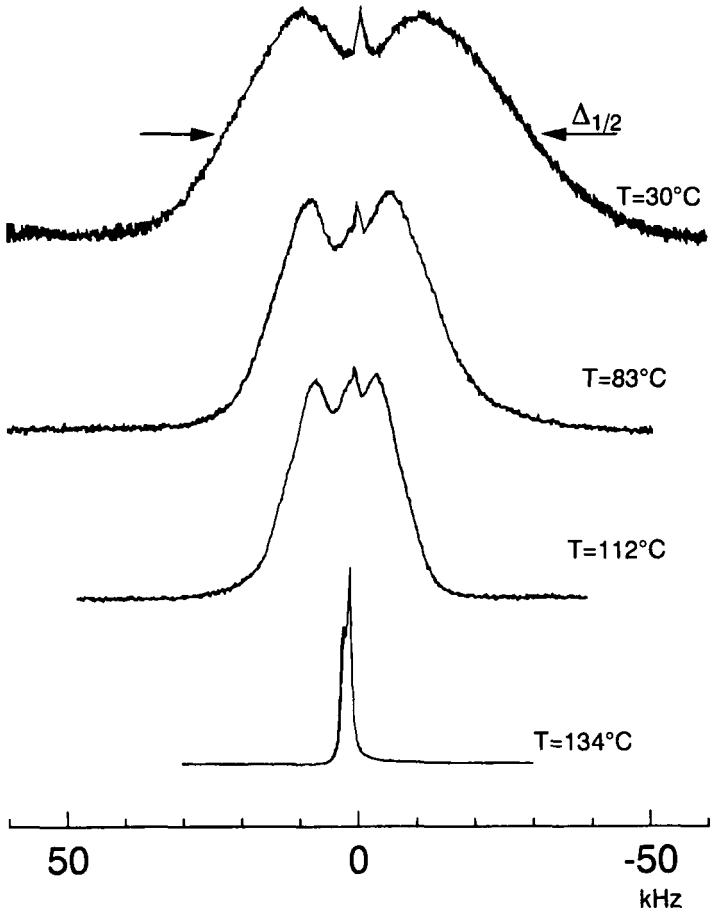

FIGURE 4 Proton NMR spectra measured with raising temperature (T) for PCBA after gradual cooling

melted at 180°C, the polymer was considered to pass the nematic phase and become solid with keeping the alignment of mesogenic unit during cooling, which was detectable by NMR method and led to the fact that the line width increased when comparing the spectrum obtained after gradual cooling with that after rapid cooling in lower temperature region. This result is consistent with the DSC observation that have indicated an endothermic peak for PCBA after gradual cooling.

When comparing $\Delta_{1/2}$ of PCBA measured with lowering temperature with $\Delta_{1/2}$ of PCBA after gradual cooling, line width did not vary, showing that orientation

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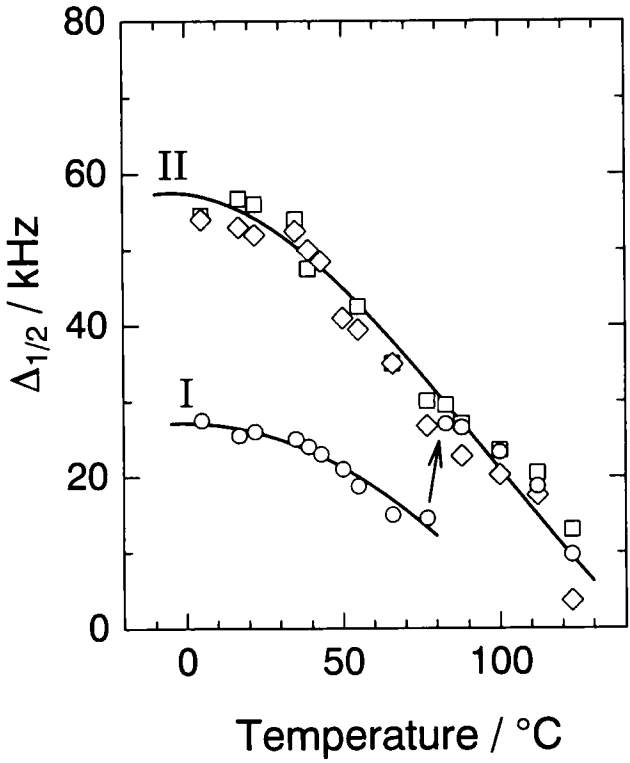

FIGURE 5 Temperature dependence of the spectral parameter $\Delta_{1/2}$. ○: measured for PCBA after rapid cooling, □: measured for PCBA after gradual cooling, ◊: measured with lowering temperature

of mesogenic elements in the NMR magnetic field was not detected. Although we have not analyzed the NMR spectrum in detail, it is confirmed that the degree of orientation of PCBA varies in the solid and nematic phase by thermal treatment.

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