Proton NMR Relaxation Study of Thermotropic Copolyesters

Kazuo SATO, Shun-ichi SUZUKI, Nobuyuki INABA,
and Hideya MURAI

*Polymer Research Laboratory, Idemitsu Petrochemical Co., Ltd.,
Anesakikaigan, Ichihara, Chiba 299-01, Japan*

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ABSTRACT: *p*-Hydroxybenzoic acid/poly(ethylene terephthalate) (PHB/PET) and *p*-hydroxybenzoic acid/6-hydroxy-2-naphthoic acid (PHB/PHN) thermotropic copolyesters were investigated in the temperature range from -120 to 180°C by observing the proton magnetic relaxation times T_1 , $T_{1\rho}$, and the line width. In the temperature dependence of $T_{1\rho}$ of PHB/PET two minima of the relaxation times were observed. The one at higher temperature corresponds to the glass transition, and the other at lower temperature (40°C) is considered to result from the phenylene group motion. For PHB/PHN, the transition similar to the low temperature one of PHB/PET was observed. The transition temperature of PHB/PHN is higher by $30\text{--}40^{\circ}\text{C}$ as compared with PHB/PET due to the rigid structure. From analysis of line width, it was found that there are two motional regions for both copolyesters, and the activation energies could be obtained. The T_1 minimum associated with the glass transition was observed in the T_1 experiment. The mesophase formation seems to narrow the distribution of the correlation times of motion.

KEY WORDS Liquid Crystalline Polymer / Molecular Motion / ^1H Nuclear Magnetic Relaxation / Thermotropic Copolyester /

Recently, much attention has been focused upon thermotropic copolyesters which provide a potential for developing high modulus materials. Since the pioneering work of Jackson and Kuhfuss¹ was reported, there have been many activities in the synthesis of thermotropic main chain copolyesters. Physical properties of their copolyesters have been investigated in most cases by thermal analysis and morphological observations.² To understand the high dynamic modulus resulting from self-reinforcing property of such thermotropic copolyesters, it is essential to investigate the effect of liquid crystal formation on molecular motions. The molecular motion and relaxation have been studied by dielectric dispersion,³ ESR spin probe,⁴ and broad line NMR⁵ etc. However, information is limited, and further study is needed. We investigated thermotropic copolyesters by observing ^1H NMR relaxation times, T_1 , $T_{1\rho}$, and T_2 in the

temperature range from -120 to 180°C . Copolyesters studied were *p*-hydroxybenzoic acid/poly(ethylene terephthalate) (PHB/PET), and *p*-hydroxybenzoic acid/6-hydroxy-2-naphthoic acid (PHB/PHN) copolyesters. The mole fractions of PHB in PHB/PET copolyester were 30, 60, and 80%. PHB/PHN copolyester contains 73 mol% PHB. These copolyesters are, hereafter, denoted by PHB/PET30, PHB/PET60, PHB/PET80, and PHB/PHN, respectively. These copolyesters except PHB/PET30 are known to show nematic liquid crystalline behavior. We reported the quite high orientational order of the mesogen in the fiber and film of PHB/PET60 by observing the proton dipolar splitting.⁶ In addition to knowledge about the molecular orientation, information concerning the molecular motion is expected to give insight into the nature of liquid crystalline copolyesters.

EXPERIMENTAL

Materials

PHB/PET copolyesters were copolymers based on poly(ethylene terephthalate) modified with *p*-hydroxybenzoic acid of 30, 60, and 80 mol%. PHB/PHN copolyester was a commercial product.

NMR Measurement

The instrument used was Bruker CXP-90 operating at 90 MHz and equipped with a temperature variable unit B-VT1000. Temperature of the sample was varied from -120 to 180°C . Pellets of a sample were packed into NMR tube, degassed under vacuum and then sealed off. Spin-spin relaxation was estimated as the line width at half height of the absorption spectrum obtained by Fourier transformation of FID. Spin-lattice relaxation times T_1 and $T_{1\rho}$ in static and rotating frames were measured by the usual inversion recovery (180° - τ - 90° pulses) and $90^{\circ}(x)$ - 90° phase shifted locking pulse methods, respectively. The locking field in $T_{1\rho}$ experiment was 10 Gauss.

RESULTS AND DISCUSSION

PHB/PET Copolyester

Typical spectra of PHB/PET60 are shown in Figure 1. At higher temperature, similar spectra to those reported by McFarlane *et al.*⁷ were observed. The dipolar splitting is due to the liquid crystalline nature of this copolyester, and the spectra correspond to powder spectra. The central narrow line appearing above about 120°C is attributed to the isotropic mobile protons, the fraction of which increases with rising temperature. This result is in agreement with that obtained by McFarlane *et al.*

Temperature dependence of the line width at half height of PHB/PET60 is shown in Figure 2. At higher temperatures where a narrow line appears, the line width of the broad component is taken as the line width of the spec-

Figure 1. ^1H NMR spectra of PHB/PET60 copolyester measured at indicated temperatures.

trum. The line width is about 29 KHz at low temperature, and gradually decreases with increasing temperature. The line width decreases rapidly at the temperatures between -40 and 80°C , and then decreases gradually above 80°C . The effect of motion on the line width can be analysed using the following phenomenological equation for motional narrowing in solids,⁸

$$\ln(1/W - 1/A) = -E_a/kT + \ln(1/B - 1/A) \quad (1)$$

where, W is the line width at temperature T , E_a is the motional activation energy, and A and B are the limiting values of the line width at low and high temperatures, respectively. The advantage in using eq 1 is that the temperature dependence of the line width can be analysed even when the value of B cannot be easily defined and that the activation energy is estimated without being influenced by the distribution of correlation times of motion. Figure 3 shows experimental line widths of PHB/PET60 together with PHB/PET30 plotted as a function of the inverse of temperature according to eq 1. Two distinct motional regions are observed above and below 70°C . This temperature corresponds to the glass transition temperature of PHB/PET60 determined by

Figure 2. Line width at half height of the broad component of PHB/PET60 copolyester as a function of temperature.

Figure 3. Plot of line width as a function of the inverse of temperature according to eq 1. The line width at -120°C was taken as A in eq 1. $\circ$, PHB/PET60; $\triangle$, PHB/PET30.

dynamic mechanical measurements. The motional process which causes the narrowing of the line width is considered to be different above and below T_g . The activation energies in the low and high temperature regions are 4.70 and 2.02 kcal mol $^{-1}$, respectively. In the case of PHB/PET30, two motional regions are also observed; however, the high temperature region is obscure probably due to higher glass transition temperature, 90°C , determined by dynamic mechanical measurements. The acti-

Figure 4. Plot of spin-lattice relaxation time T_1 of PHB/PET copolyesters as a function of temperature. $\bullet$, PHB/PET80; $\circ$, PHB/PET60; $\triangle$, PHB/PET30.

vation energy 4.60 kcal mol $^{-1}$ in the low temperature region agrees with that of PHB/PET60, indicating the motional process not to depend upon whether a liquid crystalline mesophase exists or not.

Temperature dependences of spin-lattice relaxation times of PHB/PET30, 60, and 80 are shown in Figure 4. In the whole temperature range studied, the magnetization recovery was exponential and single T_1 value was obtained. This may result from the effective spin diffusion. T_1 minima observed at 120°C for PHB/PET60 and 80 and 150°C for PHB/PET30 correspond to the glass transition of respective copolyesters. It is of interest to note that T_1 minimum of PHB/PET30 is broad compared with those of PHB/PET60 and 80. It is reasonable to consider that this phenomena is attributed to the broad distribution of correlation times of PHB/PET30. The ordered mesophase formation in PHB/PET60 and 80 may result in the narrow distribution of correlation times and the sharp minimum of T_1 .

We would like to discuss the results of the $T_{1\rho}$ experiment in the following. Figure 5 shows the temperature dependence of $T_{1\rho}$ of PHB/PET copolyesters. At low temperatures below -30°C , two $T_{1\rho}$'s were observed, indicating the spin diffusion does not act effec-

Figure 5. Plot of spin-lattice relaxation time $T_{1\rho}$ in the rotating frame ($H_1 = 10$ Gauss) of PHB/PET copolyesters as a function of temperature. ●, PHB/PET80; ○, PHB/PET60; △, PHB/PET30.

tively in $T_{1\rho}$ time scale. The fraction of component with long $T_{1\rho}$ increases with increasing PHB content. Therefore, it is reasonable to attribute the long $T_{1\rho}$ component to the rigid aromatic constituent. The long $T_{1\rho}$ decreases with rising temperature and above -20°C the magnetization decay in the rotating frame becomes exponential and single $T_{1\rho}$ was obtained. The $T_{1\rho}$ minimum observed at 120°C for PHB/PET30 and the $T_{1\rho}$ shoulder at 90°C for PHB/PET60 correspond to the respective glass transition temperatures of these copolyesters. The $T_{1\rho}$ minimum indicating a molecular relaxational motion was observed at 40°C , which is considered to be the low temperature motion observed in the line width study. It is interesting to note that this relaxation was not detected by the T_1 experiment. In the T_1 experiment, molecular motion with a correlation frequency of 10^7 – 10^8 Hz influences effectively nuclear relaxation; on the other hand, in the $T_{1\rho}$ experiment, motion with correlation frequency 10^4 – 10^5 Hz is much effective.⁹ Therefore, we consider the relaxation at 40°C to be due to the relatively slow motion.

One of the possible motional mode may be

the phenyl ring π -flip motion about C_1 – C_4 axis. Recently, such a motion has been proposed for polymers containing aromatic groups in the main chain such as polycarbonate,¹⁰ poly(butylene terephthalate)¹¹ and poly(arylene ether sulfones)¹² on the basis of solid state ^2H and ^{13}C NMR studies. It has been found that the phenyl ring flip motions are relatively slow. Jelinski *et al.*¹¹ estimated the activation energy of the π -flip process of poly(butylene terephthalate) to be $5.9 \text{ kcal mol}^{-1}$, comparable to the values obtained in this experiment. The $T_{1\rho}$ minimum of PHB/PET60 is much narrower than that of PHB/PET30, also indicating the narrow distribution of correlation times¹³ in the former. In the ordered state, the mode of motion may be considered to become more simple.

PHB/PHN Copolyester

Figure 6 shows the relationship between the temperature and $T_{1\rho}$ of PHB/PHN copolyester. The temperature dependence is similar to those of PHB/PET copolyesters, but the temperature of $T_{1\rho}$ minimum is higher by 30 – 40°C and the values of long $T_{1\rho}$ at low temperature are larger by about one order. This is attributed to the rigid structure of PHB/PHN. The similar temperature dependence suggests that the relaxation observed in the experiment originates from the molecular motion of the common mesogenic unit rather than different spacer units. The π -flip motion of the phenyl ring may also be the possible motional process in PHB/PHN as in PHB/PET.

The line width of PHB/PHN plotted as a function of temperature according to eq 1 is shown in Figure 7. Two motional regions were also observed above and below 60°C , but this temperature does not correspond to the glass transition of the copolyester, but rather to the temperature of the $T_{1\rho}$ minimum. Activation energies were estimated to be 6.74 and $3.08 \text{ kcal mol}^{-1}$ in low and high temperature regions, respectively. These values are larger than the corresponding values of PHB/PET,

Figure 6. Plot of spin-lattice relaxation time $T_{1\rho}$ in the rotating frame ($H_1 = 10$ Gauss) of PHB/PHN copolyester as a function of temperature.

Figure 7. Plot of line width of PHB/PHN copolyester as a function of the inverse of temperature according to eq 1. The line width at 120°C was taken as A in eq 1.

indicating a rigid structure of PHB/PHN. The high temperature region associated with the high temperature side of the $T_{1\rho}$ minimum has the lower activation energy. At present detailed motional mode is not clear. Motion of terminal groups may be one of the possible modes as suggested by Mitchell and Ishii.⁵ For PHB/PET the high temperature region above T_g is probably due to the quasi liquid like motion of the ethylene group.

CONCLUSIONS

We investigated two thermotropic copolyes-

ters, PHB/PET (PHB: 30, 60, and 80 mol%), and PHB/PHN (PHB: 73 mol%) by observing proton magnetic relaxation times, T_1 , $T_{1\rho}$, and line width in the wide temperature range. By analysis of the line width on the basis of Hendrickson-Bray equation,⁸ it was concluded that the two motional regions exist for both copolyesters. The activation energies in the high and low temperature motional regions of PHB/PHN are larger than those of the corresponding values of PHB/PET, due to rigid molecular structure of the former copolyester. In the $T_{1\rho}$ experiment of PHB/PET copolyesters, two minima indicating the molecular relaxational motions were observed. These two relaxational mode correspond to the high and low temperature motional regions observed in the line width study. The relaxation at high temperature corresponds to the glass transition, and the other at 40°C is considered to be ascribed to the π -flip motion of phenylene group. The T_1 minimum associated with this motional relaxation was not observed, probably because the frequency of the motion is not so high (10^7 – 10^8 Hz) as to dominate the spin lattice relaxation in the static field. The $T_{1\rho}$ minimum ascribed to the π -flip motion was also observed for PHB/PHN, however, the temperature at the minimum becomes higher by 30–40°C compared with PHB/PET. The T_1 and $T_{1\rho}$ minima of PHB60 and 80 were sharper than those of PHB/PET30 which does not exhibit the liquid crystalline nature. The sharp minimum of relaxation means the narrow distribution of correlation times of motion, indicating the ordered liquid crystal formation resulting in the simple motional mode.

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