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방향족 코폴리에스테르의 넓은선 핵자기 공명 완화시간에 관한 연구

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Broad Line Nuclear Magnetic Resonance Relaxations of Aromatic Copolyesters

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요 약 : 같은 조성을 갖는 일정서열 코폴리에스테르와 마구잡이 코폴리에스테르를 합성하였고, 이에 대하여 넓은선 핵자기 공명행동을 조사하였다. 마구잡이 공중합체들은 테레프탈산, 디아세톡시나프탈렌 이성질체들과 *p*-아세톡시 벤조산을 각각 1 : 1 : 2의 몰비율로 용융중합하여 얻었으며, 이에 대응하는 일정서열 공중합체는 테레프탈산-*p*-히드록시벤조산-나프탈렌디올-*p*-히드록시벤조산순의 일정서열을 갖도록 합성하였다. 이때 사용된 나프탈렌디올 이성질체들은 1,6-, 2,6-와 2,7-디올이었다. 공중합체의 NMR 스펙트럼은 180~460 K(-93~187℃)의 온도범위에서 6 MHz로 측정하여 얻었다. 2,6-중합체의 스핀-격자 완화시간(T_1)은 직선형의 분자구조 때문에 단위체의 서열에 불구하고 다른 것들에 비해 매우 짧았다. T_1 곡선에서 최소값을 나타낼때의 온도는 시차주사열분석기(DSC)에 의해 결정된 공중합체들의 유리전이온도(T_g)와 잘 일치하였다. 그러나 규칙서열 1,6-중합체의 경우는 포화현상때문에 T_1 값을 측정할 수 없었다. 스핀-스핀 완화시간(T_2)의 값들은 중합체의 구조에 별 영향을 받지 않았다.

Abstract : Broad line nuclear magnetic resonance (NMR) measurements have been made for a series of the random as well as the ordered sequence copolyesters having the same overall compositions. The aromatic, random copolyesters were prepared in melts from terephthalic acid(TERE), diacetoxynaphthalene(DAN) isomers and *p*-acetoxybenzoic acid(ABA) in the mole ratio of TERE : DAN : ABA=1 : 1 : 2. The corresponding ordered sequence copolyesters also were prepared to have a regular sequence in the order of terephthalic acid(TERE)-*p*-hydroxybenzoic acid(POB) -naphthalenediol(NAPH)- *p*-hydroxybenzoic acid(POB) moieties. Naphthalenediol isomers used in this study are the 1,6-, 2,6- and 2,7-derivatives. NMR spectra of copolyesters were obtained at 6 MHz in the tempe-

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rature range of 180~460 K (−93~187℃). Spin-lattice relaxation time(T_1) of 2,6-polymer was significantly shorter than those of the others, regardless of the comonomer sequence, due to its linear molecular structure. The temperatures where minimum in T_1 was observed coincide very well with the glass transition temperatures(Tg) of the respective copolyesters determined by differential scanning calorimetry(DSC). The 1,6-polymer having an ordered sequence was unique in that it did not show any T_1 because of saturation phenomenon. The values of spin-spin relaxation time(T_2), however, were not dependent much on the polymer structures.

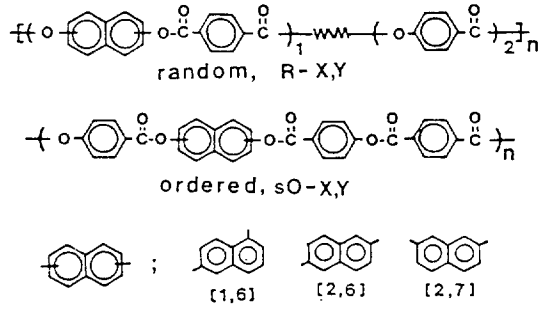
INTRODUCTION

Thermotropic liquid crystalline main chain polyesters have been attracting considerable attention in recent years.[1~6] This is due to their melt processability and expected good mechanical properties, which suggest potential applications in high modulus fibers and molding parts. However, for these types of polymers, not much informations are available in literature on the relationship between polymer structure and molecular motion.[7]

In order to understand the effect of chemical structure on the molecular motion, it is essential to study the relaxation behavior of the polymers. The molecular motion and relaxation behavior have been studied by broad line NMR, dielectric dispersion and ESR studies.[8,9] In particular, broad line NMR spectroscopy is a useful tool to observe molecular motion in solid polymers.[10~12] NMR measurements are sensitive to microscopic motions. Therefore, over the past few decades there has been considerable interest in using NMR to define and quantify the motional processes which occur in bulk polymers below the glass transition temperature, T_g.[13] At temperatures greater than T_g, a polymer chain may undertake a wide variety of motions.

In this paper discussions will be made on the line width, spin-lattice relaxation time (T_1) and spin-spin relaxation time (T_2) of a series of aromatic copolyesters studied by broad line NMR spectroscopy. A couple of recent articles by Japanese workers describe NMR studies on thermotropic copolyesters.[14,15]

The random copolyesters were prepared in melts from terephthalic acid(TERE), diacetoxynaphthalene(DAN) isomers and *p*-acetoxybenzoic acid(ABA) isomers in the mole ratio of TERE : DAN : ABA = 1 : 1 : 2.[16] The corresponding, sequentially ordered copolyesters also were prepared to have a comonomer sequence in the order of terephthalic acid (TERE) -*p*-hydroxybenzoic acid (POB)- naphthalenediol (NAPH) -*p*-hydroxybenzoic acid(POB) moieties.[17] Naphthalenediol isomers used in this study are the 1,6-, 2,6-and 2,7-derivatives.



For the sake of convenience, the copolyesters will be described as R- or s O-X,Y. R stands for a random copolyester and s stands for solution polymerization and O for the ordered sequence. X and Y are the substituent positions on naphthalene rings.

EXPERIMENTAL

Synthesis of Polymers

Detailed polymerization method can be found in our previous papers.[16,17] The structures were confirmed by elemental analysis and by IR and NMR

spectra. The purity of the intermediate compounds was checked by TLC and liquid chromatography.

NMR Measurements

The equipment used for NMR measurements was a Varian model WL-112 wide line spectrometer(3-35 MHz). In this experiment, the spectra were obtained at 6 MHz. The magnetic field was supplied by an electromagnet (30.5cm in diameter and 4.50cm in pole gap) up to the maximum field strength of 1.8 Tesla. The sample temperature was varied from 180 K to 460 K(−93~187℃). The polymers were ground to powders and were placed in a 5mm diameter pyrex tube, with a copper-constantan thermocouple directly dipped inside the sample for the precise temperature measurement. In this experiment, two types of sample compartment were used(Fig. 1(a) and (b)). For low temperature experiments, a small Dewar vessel was installed in the spectrometer probe. Dewar vacuum pressure was maintained at 10^{-4} torr between the double walls. Inner part of the vessel could contain about 500ml of liquid nitrogen. The low temperatures were obtained by pouring liquid nitrogen into the Dewar vessel. On the other hand, for high temperature experiments, the temperature was controlled by blowing up the dry nitrogen gas heated by a home-made nichrome heater heating the sample tube.

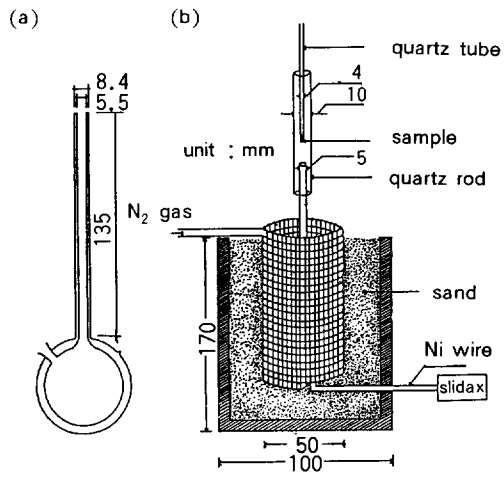


Fig. 1. Cell compartments used (a) for low temperature and (b) for high temperature experiments.

RESULTS AND DISCUSSION

The line widths of NMR curves are known to be much dependent on the temperature and molecular geometry of the polymer chains.[18] The NMR signals of the present polymer samples consist of comparatively broad lines especially when the temperature is below their glass transition temperatures(Tg). Such a broadening of the NMR peaks is caused by the local magnetic fields of the protons in the samples. In the solid state the freedom of thermal motion of the molecules is strongly limited, so that the exchange of energy between the spin and molecular system is hampered. Therefore, in many cases, solid may be regarded as a rigid system of immobile magnetic moments.

The dependence of line width defined by the peak-to-peak distance of the derivative NMR lines are shown for R- and sO-X,Y copolyesters in Figs. 2 and 3. The line widths of random copolymers are in the range of 8-9 gauss at 180 K, whereas those of the corresponding ordered sequence ones are a little lower, about 6 gauss. But their values become more or less the same at about 400 K, which is close to the polymers' Tg's. The line width of the copolyesters decreased rapidly at the temperatures

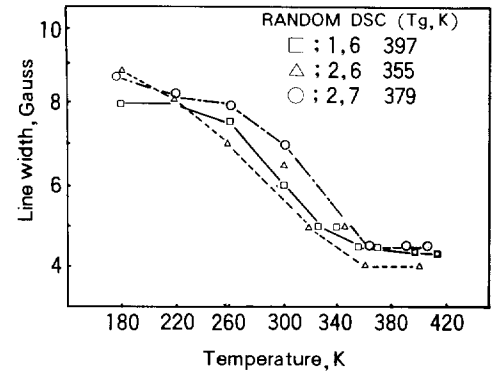
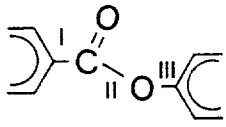


Fig. 2. Line width of R-X,Y-copolyesters as a function of temperature.

between 220 K(−53℃) and 360 K(87℃), and then the decrease slowed down beyond 360 K (87℃).

In general the decrease is more rapid for the random polymers than the ordered ones. This indicates that the formers experience much more enhanced thermal contact as temperature is increased than the latters. This difference can be ascribed to the higher degree of structural regularity in the latters than in the formers. This point will be further discussed later. The decrease of the line width between 220 K and 360 K appears to be caused by the onset of such motions as large oscillations of the benzene rings and of the ester bonds in the chain linkages.[19]

Structural models of the polymer chains show that the carboxyl groups cannot move without accompanied motions of adjacent phenylene units. The three links, I, II, and III, in the ester group



are not equivalent in terms of their rotational barriers ; in fact, because of the noticeable double-bond character, the ester linkage II has a potential barrier to rotation of about 17 kcal/mol,[20] which is much higher than those of the other two. Therefore, motion about this bond is most unlikely, at least at low temperatures, and its contribution to the motion of the carboxyl groups can be neglected. Thus, any mobility of the ester group can be brought about only by motion about the ϕ-CO and O-ϕ bonds.

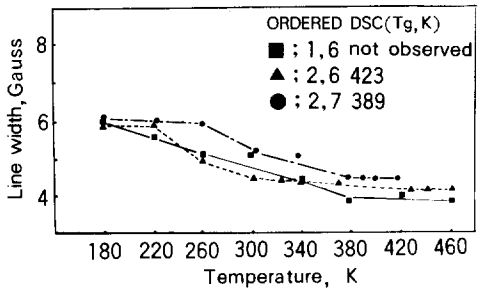


Fig. 3. Line width of sO-X,Y-copolyesters as a function of temperature.

The direct estimation of the spin-spin relaxation time T_2 is performed using the following equation :

$$T_2 = 2/(\triangle\omega_G^{(1)})_{p\text{-}p}$$

where $\triangle\omega$ is angular frequency and $(\triangle\omega_G^{(1)})_{p\text{-}p}$ is the distance between the maximum and minimum points in the first derivative of NMR peaks of the Gaussian shape.[18] Therefore, the relaxation time T_2 has an inverse relation to the line width.[21] And the spin-lattice relaxation time T_1 can be written as

$$T_1 = 1/T_2 B_1^2 \gamma^2$$

where B_1 and γ are high frequency magnetic field and gyromagnetic ratio of proton, respectively. Therefore, T_1 values can be estimated from the known quantities of T_2, B_1 and γ.

Of the two types of copolymers in Fig. 4, the copolymers with ordered sequences exhibit only a slight decrease in T_1 up to certain temperatures (about 300 and 260 K for sO-2,6 and sO-2,7 polymers, respectively). And then, as the temperature is further increased, after reaching a minimum point, it rises back up with temperature. In con-

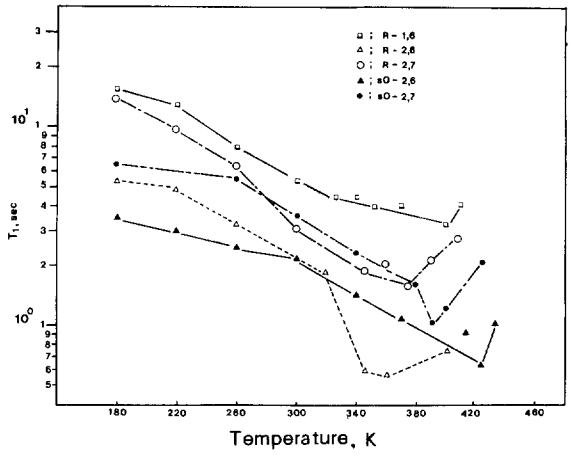


Fig. 4. Plot of spin-lattice relaxation time, T_1, of R- and sO-X,Y-copolyesters as a function of temperature.

trast with the ordered sequence copolymers, the random copolymers show continuous drop in T_1 with temperature down to a minimum value. This is an indication that the ordered sequence polymers definitely favor more efficient molecular packing than the random sequence polymers in the solid state, which, in turn, restrict molecular motions. For the sO- and R-2,6 polymers, the values of T_1 including the minimum point values are relatively short when compared with those of the others. This can be interpreted in terms of its more efficient molecular thermal contact with environment due to its linear molecular shape(see Fig. 5).

The minimum values in T_1(Fig. 4) are observed at about 400, 360, 375, 425 and 400 K, respectively for R-1,6, R-2,6, R-2,7, sO-2,6 and sO-2,7. Surprisingly, these temperatures coincide very well with the glass transition temperatures(Tg) of copolyesters determined by DSC analysis(Table 1). But in the case of sO-1,6 polymer, we could not measure T_1 values by NMR owing to easy saturation phenomenon. It also did not exhibit any glass transition on DSC analysis. The T_1 values for R-2,7 and sO-2,7 copolyesters are 3.1 sec and 3.7 sec at 300 K, respectively, which are a little longer than that the T_1 value of 0.4 sec reported for polystyrene.[22] This means that copolyester chains experience a little poorer thermal contact with environment.

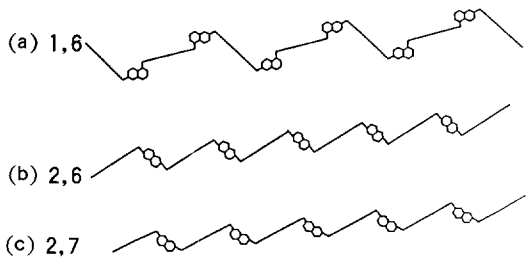


Fig. 5. Molecular geometries of sO-X,Y-copolyesters.

Table 1. Comparison of Tg Values Obtained by DSC and NMR Analyses

Polymer	Tg, K	
	DSC Method	T_1 Measurement
R-1,6	397	400
R-2,6	355	360
R-2,7	379	375
sO-1,6	n.o.[a]	saturation
sO-2,6	423	425
sO-2,7	389	400

[a]not observed.

The V-shape of the T_1 vs. temperature curve results from the much enhanced segmental motions of polymer chains at the temperatures higher than Tg's. The similar results were reported for other thermotropic polyesters by Sato et al..[15] The absolute values of and temperature dependences of T_1's of p-hydroxybenzoic acid(PHB) modified poly(ethyleneterephthalate)s (PET) (PHB content ; 30, 60 and 80 mole %) were reported to be about the same as observed for the present systems.[16,17]

Another interesting observation is that sO-2,6 and sO-2,7 polymers reveal sharper minimum temperatures in T_1 values than the random counterparts as can be seen in Fig. 4. This can be ascribed to the regular chain structures of the ordered sequence samples that would cause a sharper glass transition within a narrower temperature range. In contrast, the random copolymer chains contain chain segments of a broad distribution in the length of consecutively linked p-oxybenzoyl units. Such a structural irregularity is expected to bring about glass transition over a wider temperature range, which would appear as a dull minimum in the T_1-temperature curve as shown in Fig. 4.

According to Fig. 5 the extent of bending in the structure of the 1,6-polymer is significantly severer than those of the 2,6-and 2,7-polymers in both random and sequentially ordered cases. For that reason, T_1 of the 1,6-polymer is the longest because of poorer thermal contact with the lattice. And owing to linear molecular structure the T_1 values of 2,6-polymers, regardless of their sequences, are shorter than those of the corresponding 2,7-polymers. Also, it is of interest to note that the minimum T_1 values of ordered sequence polymers are

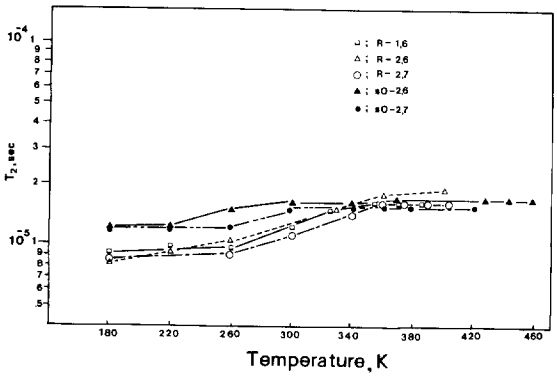


Fig. 6. Plot of spin-spin relaxation time T_2 of R- and sO-X,Y-copolyesters as a function of a temperature.

located in the high temperature region compared with that of random polymers. The probable reason for this is that, as already pointed out above, the sO-polymers possess significantly higher degrees of chain orders than those of random polymers.

A plot of spin-spin relaxation times, T_2, of the copolyesters vs. temperature is shown in Fig. 6. The absolute values of T_2 are in the order of 10^{-5} sec and much shorter than those of T_1. As the temperature rises, the T_2 values increase very slightly and then, after about 350 K, they remain almost constant regardless of the structure of polymers. This signifies that spin-spin energy transfer is rather insensitive to the detailed structural differences in the polymers of the same type. This may be one of the major reasons why very little literature reports can be found on the study of T_2 of polymers.

CONCLUSIONS

It has been shown that valuable informations about the relationship between molecular motions and the structure of aromatic copolyesters are obtained from line widths and relaxation times studied by the broad line NMR spectroscopy.

The following conclusions are drawn from the present work :

1. The line width decreases rapidly at the temperatures near the glass transition temperatures.
2. Spin-lattice relaxation time, T_1, decreases with increasing temperature.
3. The T_1 values of R- and sO-2,6-polymers are the lowest due to their linear molecular structure.
4. The temperatures where the minimum values in T_1 are observed on broad-line NMR spectroscopy coincide with the Tg values of the copolyesters determined by DSC.
5. The ordered sequence copolymers reveal sharper minima in T_1–temperature curves than the random counterparts. This difference can be explained on the basis of structural regularity along the chains.
6. The T_2 values are rather insensitive to the structure of polymers and to the temperature.

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