Molecular Mobilities of Individual Constituent Carbons of Solid Polyesters above T_g As Studied by Carbon-13 Nuclear Magnetic Resonance Spectroscopy

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ABSTRACT: High-resolution ^{13}C spectra and spin–lattice relaxation times T_1 have been measured for solid terephthalic acid polyesters $[-COC_6H_4COO(CH_2)_mO-]_n$ (m = 2, 3, 4, 6, and 10) and succinic acid polyesters $[-COC_2H_4COO(CH_2)_mO-]_n$ (m = 2 and 4) over a wide range of temperatures above T_g by the ^1H scalar-decoupling technique. The high-resolution lines of the individual carbons of the terephthalic acid polyesters appear at different temperatures, T_a, indicating that the carbons differ greatly in molecular mobility. According to the results, they are divided into three groups: terephthaloyl residues, terminal CH_2 groups directly attached to the ester bond, and other central CH_2 groups in the glycol residues. The molecular mobilities of these groups are strongly dependent on the number m of CH_2 groups: for m = 2 and 3, terephthaloyl residues are more mobile than CH_2 groups, regardless of the existence of two kinds of CH_2 groups for m = 3. For $m \geq 4$ central CH_2 groups become most mobile, whereas terminal CH_2 groups are still highly restricted in motion. Similar results have been obtained from the measurements of the temperature T_{min}, at which T_1 has a minimum value and the segmental motion is described by a shorter correlation time (about 5×10^{-9} s) than at T_a. On the other hand, all CH_2 groups of succinic acid polyesters are almost equally mobile. On the basis of these results the molecular motions of the terephthalic acid polyesters are discussed.

Introduction

Molecular motions of solid polymers have been extensively investigated by measuring dynamic mechanical relaxation, dielectric relaxation, nuclear magnetic relaxation, and other relaxation phenomena. Several relaxation processes such as α, β, and γ processes have been found in amorphous and semicrystalline polymers and assigned to different modes of motion for backbone chains or side groups.[1] However, it is not yet clear how the individual carbons in the molecule contribute to these relaxation processes. Variable-temperature ^{13}C high-resolution NMR in solids will be useful for such analyses of relaxation processes because relaxation parameters can be measured for each carbon by combining the techniques of cross polarization, high-power proton decoupling, and magic-angle sample spinning.[2] Some attempts[3-5] have been already reported using a home-built temperature-controlling system.

On the other hand, well above the glass transition temperature T_g, ^{13}C high-resolution spectra are obtainable for solid polymers even by conventional NMR spectrometers used for liquids owing to the reduction of ^{13}C–^1H dipolar interactions by rapid molecular motions.[6-12] In this paper, we report a study of molecular motions of each constituent carbon in different polyesters above T_g by conventional ^{13}C NMR spectroscopy. The polyesters used are terephthalic acid polyesters $[-COC_6H_4COO(CH_2)_mO-]_n$, m = 2, 3, 4, 6, and 10 (subsequently referred to as C_mT), and succinic acid polyesters $[-COC_2H_4COO(CH_2)_mO-]_n$, m = 2 and 4 (subsequently referred to as C_mS). These samples were isothermally crystallized from the melt under well-controlled conditions in order to avoid an annealing effect during NMR measurements. Therefore, a definite amount of crystalline component coexists with a noncrystalline component, which has been confirmed by ^1H broad-line analysis.[13-17] This paper, however, deals with only the rubbery, noncrystalline component.

Experimental Section

Samples. Terephthalic acid polyesters C_2T, C_3T, C_4T, and $C_{10}T$ were obtained from commercial sources and C_6T was prepared by polycondensation of terephthaloyl chloride and hexamethylene glycol.[18] As aliphatic polyesters, poly(ethylene succinate) (C_2S) and poly(tetramethylene succinate) (C_4S) were prepared by direct polycondensation of succinic acid and the corresponding glycols.[19] All the samples were purified by precipitation from o-chlorophenol or chloroform solution into methanol.

Table I
Crystallization Conditions, Intrinsic Viscosity Number, and Melting Temperature for Different Polyesters

sample	crystallization conditions: temp/°C	time/h	$[\eta]^a$/ $g^{-1}\cdot dL$	$T_m{}^b$/°C
C_2T	240	4	0.718[c]	263
C_3T	215	24	0.775	234
C_4T	200	4	0.887	224
C_6T	142	5	0.404	157
$C_{10}T$	120	24	1.222	134
C_2S	90	24	0.367	108
C_4S	97	24	0.458	119

[a] $[\eta]$'s were measured at 25 °C in 1/1 tetrachloroethane/phenol for C_mT and in chloroform for C_mS, respectively. [b] Measured with a Perkin-Elmer DSC 1-B at a scan rate of 10 °C/min. [c] This value corresponds to $\overline{M}_v$ = 20 400.[14]

Each of these specimens was melted in a 10-mm NMR tube under vacuum or sometimes in an argon atmosphere at a temperature at least 50 °C higher than the melting temperature; after sealing it was crystallized for 4 or 24 h in a thermostat controlled at a given temperature and quenched in ice water. In each case the crystallization temperature was chosen so that the crystallization started within 10–30 min. The crystallization conditions are summarized in Table I together with the limiting viscosity number $[\eta]$, measured in o-chlorophenol or chloroform at 25 °C, and melting temperature T_m, which was determined as a final temperature of the endothermic melting curve measured with a Perkin-Elmer DSC 1-B at a scan rate of 10 °C/min.

It is noted here that the T_m for C_4S obtained by us is much higher than the value cited in ref 20. Since the latter was measured with a polarizing microscope, it should not be cited as T_m.

NMR Measurements. Natural-abundance ^{13}C NMR spectra were obtained for the samples directly crystallized in NMR tubes

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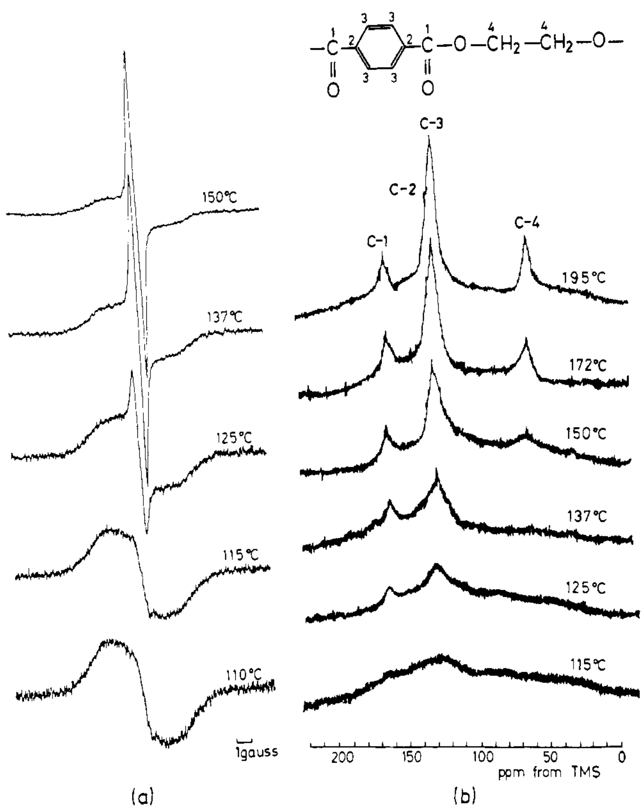

Figure 1. ^1H broad-line first-derivative NMR spectra (a) and ^1H scalar-decoupled ^{13}C NMR spectra (b) of solid poly(ethylene terephthalate) (C_2T) at different temperatures.

at 25.1 MHz with a JEOL JNM-FX100 pulse FT NMR spectrometer under conditions of proton noise decoupling. The field strength $\gamma_H H_{1H}/2\pi$ of the decoupling was 6.5 kHz. A ^2H external lock unit was used as a frequency lock. Ordinary spectra were obtained with a pulse width of 6 μs, corresponding to a flip angle of 45° and a repetition time of 2.5 s, employing 8K data points over a 6024-Hz frequency range.

^{13}C spin–lattice relaxation times T_1 were measured only for protonated carbons by the inversion–recovery method, using homogeneity spoiling. Intervals τ between 180° and 90° pulses ranged from 10 to 400 ms and the repetition times were 7–10 times T_1. Longitudinal decay curves obtained were not always exponential but the deviation was not great. Therefore, all T_1 values were determined from the initial slope in the region of $\tau < 200$ ms. Estimated accuracy of the T_1's was mostly ±10% but sometimes fell to ±20% below the temperature at which the minimum value for T_1 was observed.

^1H broad-line first-derivative NMR spectra were also obtained for the same samples used in the ^{13}C NMR measurements with a JNM-PW-60 NMR spectrometer (JEOL) at a frequency of 60 MHz. The magnetic field was modulated at 35 Hz and an amplitude of 0.05–0.08 mT.

The sample temperature was regulated to ±0.5 °C and monitored by a JEOL variable-temperature unit. The temperature was calibrated by using a copper–constantan thermocouple buried in a polymer block in an NMR tube, which was placed in the probe in the same fashion as for NMR measurements.

Results

A. Aromatic Polyesters. Figure 1 shows ^1H broad-line first-derivative and ^{13}C high-resolution NMR spectra for C_2T at different temperatures. Both kinds of spectra are very broad and seem to be almost structureless below 115 °C. At 125 °C, however, a narrow line appears in the ^1H broad-line spectrum and the intensity increases with increasing temperature. This narrowing is associated with the onset of segmental motions with the order of correlation time 10^{-4}–10^{-5} s as discussed later. Detailed contributions of the respective carbons to this narrowing can be distinctly observed in the ^{13}C NMR spectra shown in Figure 1b. In accord with the narrowing of the broad-line spectrum, the ^{13}C spectrum shows sharp lines at about 130 and 165 ppm at 125 °C and another line appears at about 65 ppm at 150 °C; they increase in intensity and in resolution at higher temperatures.

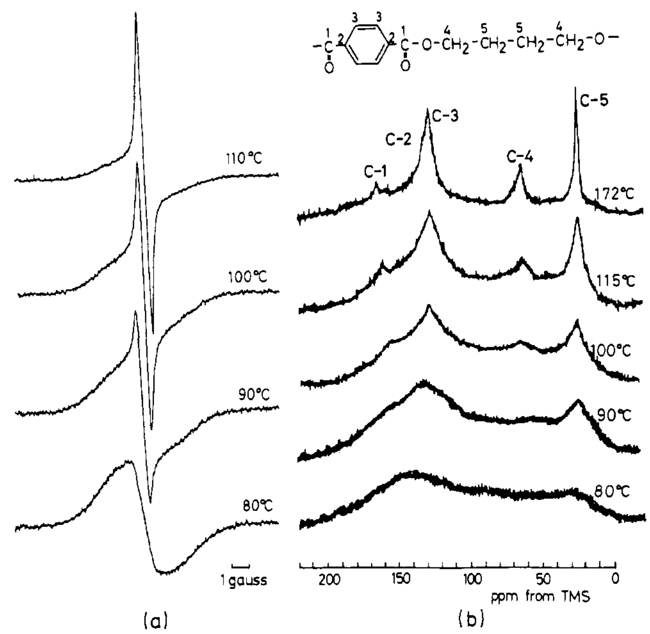

Figure 2. ^1H broad-line first-derivative NMR spectra (a) and ^1H scalar-decoupled ^{13}C NMR spectra (b) of solid poly(butylene terephthalate) (C_4T) at different temperatures.

The chemical shifts of the ^{13}C lines observed here are in good agreement with those measured for its *o*-chlorophenol solution. Hence, the lines at 165, 130, and 65 ppm are assigned to carbonyl carbon (C-1), quaternary aromatic carbon (C-2) and protonated aromatic carbon (C-3) (though they are not well resolved even at 195 °C), and CH_2 carbon in the glycol unit (C-4), respectively. On the basis of this assignment, it is evident that the terephthaloyl residues (C-1, C-2, and C-3) are more mobile than CH_2 groups (C-4), as will be discussed in detail in the next section.

Figure 2 shows ^1H broad-line and ^{13}C high-resolution spectra above 70 °C for C_4T, which contains two more CH_2 groups than C_2T. In this case sharp ^{13}C lines appear also in accord with the appearance of a narrow line in the ^1H broad-line spectra. However, the appearance order of each ^{13}C line is different from the case of C_2T; first the line for the central CH_2 carbons (C-5) in the glycol units (hereafter referred to as central CH_2) appears at about 90 °C and then successively at 100 °C the lines for terephthaloyl residues (C-1, C-2, and C-3) and terminal OCH_2 carbons (C-4) in the glycol units (hereafter referred to as terminal CH_2) appear.

Such high-resolution lines could be also observed for other polyesters, though for $C_{10}T$ central CH_2 carbons were not well resolved even in the molten state. In Figure 3, the temperatures T_a at which sharp ^{13}C lines appear are plotted against the number m of CH_2 groups for the three kinds of protonated carbons. The temperatures T_n, at which a narrow line appears in the ^1H broad-line spectra, are also shown in this figure. The T_a's of those carbons decrease with increasing m but the mode of the dependency of T_a on m differs among the carbons. The T_a of CH_2 is higher than that of aromatic CH for $m = 2$. This is the same for $m = 3$, where two kinds of CH_2 groups have the same T_a. For $m = 4$, however, the T_a of central CH_2 is lower than that of terminal CH_2 so that the former

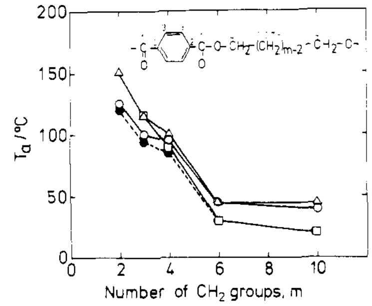

Figure 3. Plots of T_a vs. the number of CH_2 groups in the glycol residues for terephthalic acid polyesters: (○) aromatic CH (C-3); (△) terminal CH_2 (C-4); (□) central CH_2 (C-5, -6, -7, and -8). Filled circles indicate T_n's at which a narrow line appears in ^1H broad-line NMR spectra.

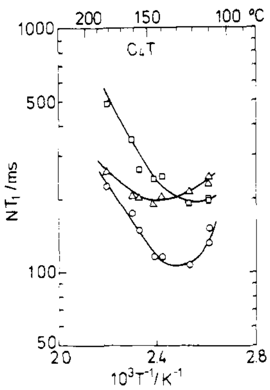

Figure 4. Semilogarithmic plots of ^{13}C NT_1 vs. the reciprocal of absolute temperature for C_4T: (○) C-3; (△) C-4; (□) C-5.

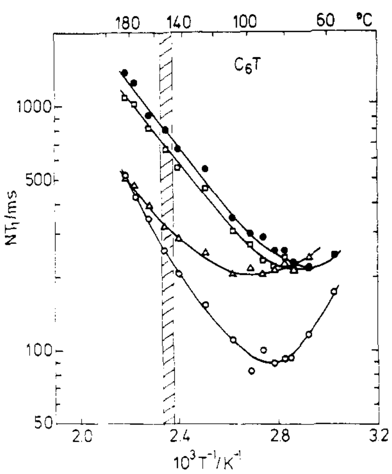

Figure 5. Semilogarithmic plots of ^{13}C NT_1 vs. the reciprocal of absolute temperature for C_6T: (○) C-3; (△) C-4; (□) C-5; (●) C-6. The hatched zone in the figure indicates the melting temperature range of the polymer determined by DSC.

becomes lower than the T_a of aromatic CH, whereas the latter is still higher than it. When $m > 4$, such a difference in T_a between two CH_2 carbons gradually increases with increasing m, though the difference between terminal CH_2 and aromatic CH seems to disappear.

The temperature T_n is in good accord with the lowest value of T_a for each m, i.e., with the T_a of aromatic CH for $m \leq 3$ and with the T_a of central CH_2 for $m \geq 4$. This means that the narrow component appearing near T_n in the ^1H broad-line spectra is composed of aromatic CH protons for $m \leq 3$ and central CH_2 protons for $m \geq 4$.

In Figures 4–6, NT_1's of aromatic CH, terminal CH_2, and central CH_2 carbons are plotted against the reciprocal of absolute temperature for C_4T, C_6T, and $C_{10}T$, respectively.

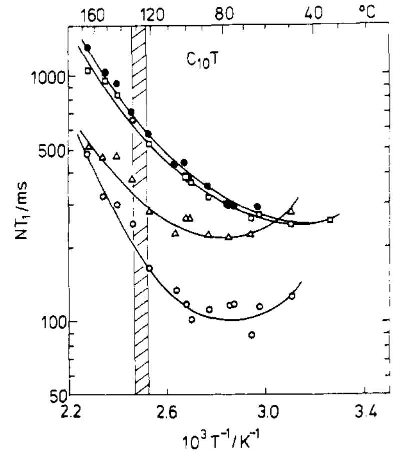

Figure 6. Semilogarithmic plots of ^{13}C NT_1 vs. the reciprocal of absolute temperature for $C_{10}T$: (○) C-3; (△) C-4; (□) C-5 and C-6; (●) C-7 and C-8. The hatched zone indicates the melting temperature range of the polymer.

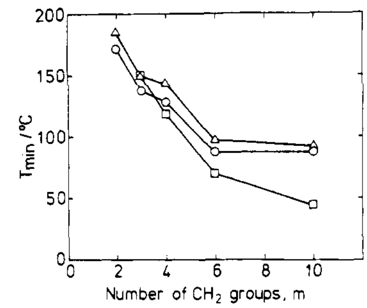

Figure 7. Plots of T_{min} vs. the number of CH_2 groups in the glycol residues for terephthalic acid polyesters: (○) aromatic CH (C-3); (△) terminal CH_2 (C-4); (□) central CH_2 (C-5, -6, -7, and -8).

Table II
T_a and T_{min} Values for CH_2 Carbons of Succinic Acid Polyesters

sample	T_a/°C	T_{min}/°C
C_2S	30	61
C_4S	−10	28

Here, NT_1 is the product of T_1 and the number N of protons directly attached to the carbon. As expected by the single-correlation-time theory,[21] with increasing temperature each T_1 initially decreases, passes through a minimum, and then monotonically increases, even through the melting zone (hatched zone in Figures 5 and 6) of the polymer, without any discontinuity as reported by Mandelkern et al.[11] However, NT_1 at the minimum, $(NT_1)_{min}$, is much greater than the value ($(NT_1)_{min} = 36$ ms at the resonance frequency of 25.1 MHz) calculated according to the theory.[21] For example, the $(NT_1)_{min}$ values for C_4T are 190 ms for both CH_2 carbons and 107 ms for the aromatic CH. Since similar values were obtained for the corresponding carbons of the other polyesters, their high values of $(NT_1)_{min}$ will reflect unique molecular motions of terephthalic acid polyesters.

The temperature T_{min} at which NT_1 shows a minimum value is also found to be markedly different among those carbons as shown in the figures. Their T_{min} values are plotted against m in Figure 7. Although each T_{min} shifts to a higher temperature in comparison with the corresponding T_a, the dependence of T_{min} on m is very similar to the case of T_a.

B. Aliphatic Polyesters. In Figure 8, the NT_1's of CH_2 carbons for C_4S are plotted against the reciprocal of absolute temperature. As clearly seen, the T_{min}'s of all CH_2

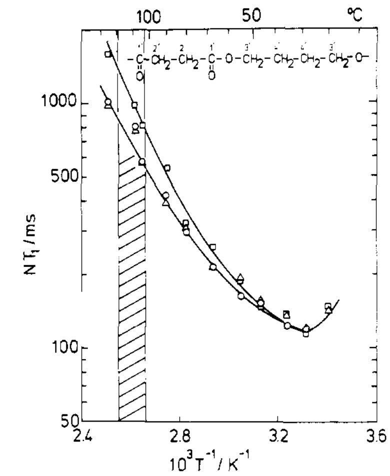

Figure 8. Semilogarithmic plots of ^{13}C NT_1 vs. the reciprocal of absolute temperature for C_4S: (○) C-2′; (△) C-3′; (□) C-4′.

carbons are in good accord with each other. Since there is no difference in T_a as well as T_{min} of each carbon of the aliphatic polyesters, their common values are summarized in Table II.

Discussion

A. Relation among T_g, T_a, T_n, and T_{min}. First we discuss the time scale of molecular motions associated with these temperatures. As shown in Figures 1 and 2, the ^1H and ^{13}C NMR spectra are very broad in the solid state, where molecular motions are highly restricted. This is due to the wide distribution of the local field produced around the observed ^1H or ^{13}C nuclei by the neighboring ^1H's. However, this local field will be averaged above T_n or T_a by the pronounced molecular motion. According to Kubo and Tomita's single-correlation-time theory,[22] an NMR line for like nuclei has been assumed to narrow effectively under the condition of $\sigma_0\tau_c < 1$. Here, σ_0 is the square root of the second moment for the line in the rigid state and τ_c is the correlation time representing the isotropic motion of the nuclei. However, the narrowing occurs more markedly at T_n in experiments as shown in Figures 1a and 2a so that the line width decreases to less than $^1/_{10}$, suggesting that the value of $\sigma_0\tau_c$ is much less than 1. Since such a narrow line is theoretically obtained when $\sigma_0\tau_c \leq 0.1$ (see Figure 2 in ref 22), the narrowing condition at T_n should be practically $\sigma_0\tau_c \leq 0.1$. Therefore, τ_c associated with T_n is estimated to be 10^{-4}–10^{-5} s, using the value of $\sigma_0 = 1.4 \times 10^4$ Hz measured for amorphous C_2T.[23]

This estimation may be also valid for T_a, because both of the spectra narrow in the same temperature range. However, some refinement will be necessary for both cases, because the T_a's differ among the individual carbons as shown in Figure 3. Such differences in T_a may not suggest that the individual carbons separately initiate the isotropic motion with $\tau_c = 10^{-4}$–10^{-5} s at different temperatures. It is rather plausible to assume that the segments composed of these carbons cooperatively undergo the isotropic motion. Therefore, the ^1H local field will disappear by the additional effect of inherent inner motions in each carbon, even if the τ_c of the isotropic motion does not attain 10^{-4}–10^{-5} s.

A similar refinement is necessary for the estimation of the τ_c associated with T_{min}, which is assumed to be 5.0×10^{-9} s for a Larmor frequency of 25.1 MHz by the single-correlation-time theory.[21] This value can be also calculated by using different models of molecular chain motions. For example, for the 3-τ model[24] the τ_c's of central CH_2, aromatic CH, and terminal CH_2 of C_6T are 5.2×10^{-8}, 2.1×10^{-8}, and 8.3×10^{-9} s, respectively, as shown later. Though these τ_c values are somewhat changed depending on the models used for the analysis, it is sure that T_a and T_{min} are associated with the onset of the isotropic segmental motions with a somewhat longer time scale than $\tau_c = 10^{-4}$–10^{-5} and 5.0×10^{-9} s, respectively, and shift to lower temperatures by inner motions.

Axelson and Mandelkern[12] have recently found from ^{13}C NMR measurements on nine amorphous and semicrystalline polymers, in which polyesters were not included, that the difference $T_a - T_g$ ranges from about 30 to 100 °C.[26] Though the aromatic polyesters have different T_a's for different backbone carbons, $T_a - T_g$ for the carbons is also in the above-cited range. As discussed by Axelson and Mandelkern,[12] this difference must be explained by the difference in τ_c for the isotropic segmental motion. If τ_c's at T_a and T_g, $\tau_c(T_a)$ and $\tau_c(T_g)$, are assumed to be 10^{-4}–10^{-5} and 10^2 s,[46] respectively, $T_a - T_g$ is estimated as 27–35 °C using the WLF equation[27]

$$\log \frac{\tau_c(T_a)}{\tau_c(T_g)} = -\frac{17.44(T_a - T_g)}{51.6 + (T_a - T_g)} \tag{1}$$

This value agrees fairly well with the experimental data but in detail the effect of inner motions should be definitely considered. In a similar manner, the difference $T_{min} - T_g$ was estimated to be 74 °C.

B. Segmental Motions of Polyesters. As shown in Table II, each carbon of the aliphatic polyesters has the same T_a and T_{min}. Also, no significant difference in T_{min} is reported for each backbone carbon of natural *cis*-1,4-polyisoprene.[24] Therefore, these polymers are not greatly different in inner motions of backbone carbons, even though ester groups or double bonds are included in their main chains.

On the other hand, in terephthalic acid polyesters the inner motions have been found to be markedly different among aromatic CH, terminal CH_2, and central CH_2 at T_a and T_{min}, which are associated with the onset of isotropic segmental motions with the orders of $\tau_c = 10^{-4}$–10^{-5} and 5.0×10^{-9} s, respectively. This difference will be produced by the bulky terephthaloyl residues, which are almost planar owing to conjugated double bonds between the benzene ring and ester groups.[28,29] In C_2T these bulky residues restrict greatly the inner motions of CH_2 groups so that each CH_2 will be immobile until the terephthaloyl residues become mobile (this is reflected in the higher T_a and T_{min} of the CH_2 groups than those of aromatic CH). Such a strong effect of terephthaloyl residues also exists on the all CH_2's of C_3T. However, in C_4T, C_6T, and $C_{10}T$ only central CH_2 groups will be free from the restriction, because their T_a and T_{min} values are the lowest of the three kinds of carbons (Figures 3 and 7). That is, these CH_2's will initiate independent inner motions, whereas terminal CH_2's are still highly restricted. Although so-called three-bond motion,[30,31] four-bond motion,[30,31] and crankshaft motion[32] have been proposed as models of inner motions for the CH_2 sequence, three-bond motion must be possible for the 4-CH_2 sequence in C_4T, in which the central two CH_2's change positions even though the terminal CH_2's are fixed on a tetrahedral lattice. This suggests that the 4-CH_2 sequence is the smallest unit for independent inner motions of the CH_2 sequence.

The low mobility of the terminal CH_2 compared to the central CH_2 has been also observed in the glassy state below T_g and in the dissolved state. Jelinski[33] has found by cross-polarization/dipolar-decoupling ^{13}C NMR spectroscopy, using slow magic-angle sample spinning (0.88 kHz), that the central CH_2 of C_4T undergoes motion at a

Table III
Parameters of 3-τ Model Used for the Calculation of the NT_1 Values for Protonated Carbons of C_6T^a

	rotation		libration			isotropic motion	
carbon	θ_R/deg	τ_R/s	θ_L/deg	τ_{L0}/s	ΔE_L/ kJ·mol^{-1}	τ_{I0}/s	ΔE_I/ kJ·mol^{-1}
C-3	29	1.0×10^{-11}	62	3.7×10^{-16}	49	1.1×10^{-15}	50
C-4	86	2.0×10^{-12}	39	9.7×10^{-15}	44		
C-5	80	2.0×10^{-12}	56	1.1×10^{-15}	43		
C-6	77	2.0×10^{-12}	58	1.1×10^{-15}	43		

^{a} It has been assumed that the correlation times τ_L and τ_I change with temperature according to the equations $\tau_L = \tau_{L0} \exp(\Delta E_L/RT)$ and $\tau_I = \tau_{I0} \exp(\Delta E_I/RT)$, respectively, whereas τ_R, θ_R, and θ_L are independent of temperature. Too short values of τ_{L0} and τ_{I0} will indicate that such temperature dependences of τ_L and τ_I fail at much higher temperatures ($T \sim \infty$). Therefore, their values seem to be only parameters to give the values of τ_L and τ_I in the experimental range of temperature. For the case of somewhat higher values of ΔE_L and ΔE_I, see ref 47.

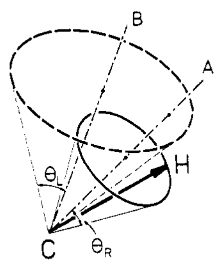

Figure 9. Schematic diagram of 3-τ model for the motion of a C–H internuclear vector.

rate that is fast relative to the CH_2 chemical shift interaction ($\tau_c < 10^{-3}$ s), whereas the terminal CH_2 is less mobile. The low mobility of the terminal CH_2 of the polymer was also confirmed by solid-state high-resolution ^{13}C T_1 measurements at room temperature.[34] In addition, Komoroski[35] and we[36] observed that the terminal CH_2's of C_4T, C_6T, and $C_{10}T$ have significantly shorter ^{13}C T_1's than the corresponding central CH_2's in solution. Since the barrier to rotation around the CH_2–O bond (ca. 1 kcal/mol[37,38]) is lower than that around the CH_2–CH_2 bond (ca. 3 kcal/mol[39]), the rotation around the CH_2–O bond does not relate to the reduction of the mobility of terminal CH_2. A possible cause will be the low mobility of the CH_2–O bond itself, which must move cooperatively with the bulky terephthaloyl residue.

In order to know in more detail the effect of terephthaloyl residues on the segmental motions of the polyesters, it is necessary to analyze the temperature dependences of T_1 (shown in Figures 4–6), using appropriate models. Since $(NT_1)_{min}$ values are easily obtainable from measurements in the bulk state compared to measurements in the solution state,[35,36] the analysis is highly reliable. As already pointed out, the $(NT_1)_{min}$'s are not only different among the individual carbons but also much higher than those expected from the single-correlation-time model. Such high $(NT_1)_{min}$ values have not been explained[25] by means of models of distribution of correlation times[9,40,41] or a defect diffusion model.[31,42] Woessner's 2-τ model[43] has been also unsuccessful,[25] because polymeric chain motions are not well represented by only two kinds of correlation times.

On the other hand, the 3-τ model, proposed by Howarth,[24,44] seems suitable for the analysis of segmental motions of the polyesters. In this model, schematically depicted in Figure 9, three correlation times, τ_R, τ_L, and τ_I, are considered, which represent a stochastic rotation of C–H internuclear vectors around axis A, the librational motion of axis A around another axis B, and the isotropic spherical motion of axis B, respectively. Here, the librational motion indicates that axis A moves at random to all directions within a cone, whose axis is axis B. We assumed in this work that τ_I and τ_L change with temper-

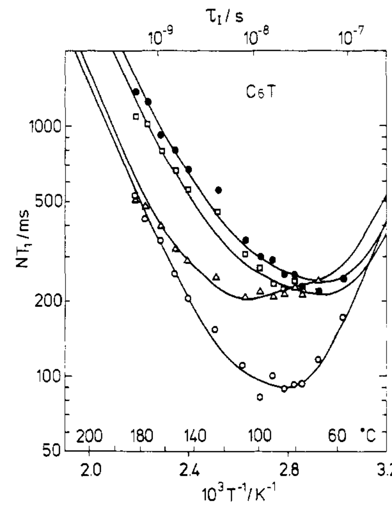

Figure 10. Comparison between experimental NT_1's (symbols) and calculated NT_1's (solid curves). The experimental values are the same as shown in Figure 5 and the calculated ones are obtained by using the parameters given in Table III.

ature according to the Arrhenius equation, i.e., $\tau_I = \tau_{I0} \exp(\Delta E_I/RT)$ and $\tau_L = \tau_{L0} \exp(\Delta E_L/RT)$, whereas τ_R is independent of temperature. $\tau_R < \tau_L < \tau_I$ and $\Delta E_L < \Delta E_I$ are also assumed. These assumptions are reasonable to describe the motions of polymeric chains. In addition, the vertical angles θ_R and θ_L for the rotation and the libration are also assumed to be independent of temperature, though θ_L may somewhat increase with increasing temperature.[47]

The calculated NT_1's for C_6T, obtained by trial and error analysis, are shown as solid curves in Figure 10 and the parameters used for the calculation are tabulated in Table III. The calculated curves fit well to the experimental points for all protonated carbons.[48] Similar good agreements between calculated and experimental NT_1's were obtained for the other polyesters and the differences in parameters were not great among the polymers. Therefore, we summarize here the common features of molecular motions of the polyesters, based on the results given in Table III. Since the θ_R values of the CH_2 carbons are nearly equal to the supplementary angle (72°) of the bond angle C–C–H, the C–H vectors of the CH_2 groups rotate around the CH_2–CH_2 or CH_2–O bonds.[49] On the other hand, the aromatic C–H vectors rotate around the axis with the angle of about 30° against the long axis of the terephthaloyl residue,[50] whose rotating axis is almost parallel to the direction of the CH_2 sequence in the trans–trans conformation state.[28] This axis as well as CH_2–CH_2 and CH_2–O bonds further librates within the individual cones and their vertical angles increase in the order of terminal CH_2, central CH_2, and aromatic CH. The value of $(NT_1)_{min}$ has been found to depend primarily on the θ_R and to tend to increase with increasing θ_R.

According to these results, the high T_{min} value of terminal CH_2 cannot be explained by any factor for rotational motion of the CH_2 around the CH_2–CH_2 or CH_2–O bond, but by the low vertical angle, i.e., the low amplitude, of librational motion of the CH_2–O bond. This explanation is highly plausible, because there is no inner freedom in the terephthaloyl residues including the CO–O bond owing to the conjugated system and therefore the librational motion of the CH_2–O bond directly depends on the motion of the bulky terephthaloyl residues. A more detailed discussion of polymeric chain motions will be made after the completion of this series of works.

Registry No. C_2T (repeating unit), 25038-59-9; C_3T (repeating unit), 26546-03-2; C_3T (copolymer), 26590-75-0; C_4T (repeating unit), 24968-12-5; C_4T (copolymer), 26062-94-2; C_6T (repeating unit), 26637-42-3; C_6T (copolymer), 28085-76-9; $C_{10}T$ (repeating unit), 27043-73-8; $C_{10}T$ (copolymer), 27055-32-9; C_2S (repeating unit), 25667-11-2; C_2S (copolymer), 25569-53-3; C_4S (repeating unit), 26247-20-1; C_4S (copolymer), 25777-14-4.

References and Notes

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(26) According to our recent results, the T_a's of the poly(*n*-butyl acrylate) backbone carbons are 46 °C higher than the value reported by Axelson and Mandelkern.[12] Therefore $T_a - T_g$ is 100 °C for poly(*n*-butyl acrylate).

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(47) This assumption will relate to the cause of the high values of ΔE_L and ΔE_I given in Table III. If the temperature dependence of θ_L can be introduced to this analysis, reasonable values will be obtained for ΔE_L and ΔE_I.

(48) The τ_I values of 10^{-9}–10^{-7} s shown in Figure 10 seem somewhat short to be physically sensible. Since this suggests that the Howarth model cannot fully describe the long-range motions of the polyester chains, some appropriate analyses should be tried for detailed discussion of the long-range motions.

(49) If the θ_R value for the CH_2's is changed from 77–86° to 36–39° without any change of other parameters shown in Table III, similar good agreements are obtained between calculated and experimental NT_1's. However, the meaning of such low θ_R values is not clear at present.

(50) Though the axis perpendicular to the long axis of the terephthaloyl residue has also the angle of 30° against all C–H vectors of the same terephthaloyl residue, this axis is not reasonable for the librational motion of the C–H vectors in long-chain molecules. On the other hand, the axis mentioned in the text has angles of 30° and 90° against the C–H vectors. However, this axis has been concluded to be the librational axis because almost equal values of NT_1 are also obtained for θ_R = 90° and $\tau_R = 1.0 \times 10^{-9}$ s without any change of other parameters and the analysis considering these two types of C–H vectors leads to the same conclusion.