

One- and Two-Dimensional CP/MAS ^{13}C NMR Analyses of Dynamics in Poly(2-hydroxypropyl ether of bisphenol-A)

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The dynamics of amorphous poly(2-hydroxypropyl ether of bisphenol-A) (PHR), quenched from the melt, has been investigated by one- and two-dimensional solid-state ^{13}C NMR spectroscopy. CP/MAS ^{13}C NMR spectra from -150 to 180 °C give two specific features: (1) below 23 °C, resonance lines for C-H carbons of phenylene rings split into two lines; (2) linewidths of resonance lines become broad at 20 - 50 °C above the glass transition temperature. The feature (1) indicates that phenylene C-H carbons exist in chemically different two sites at low temperatures. These two sites are probably associated with OH ... π hydrogen bond formation. The coalescence of the resonance lines at elevated temperatures is caused by π flip motion of phenylene rings, which corresponds to the γ relaxation for PHR. The correlation time of the π flip motion is analyzed by the two-site exchange model, and is found to follow the Arrhenius equation. The apparent activation energy is 51 kJ mol $^{-1}$ by assuming an inhomogeneous correlation time distribution described by a Kohlrausch-Williams-Watts (KWW) function with an exponent of 0.2. The feature (2) is caused by the so-called motional broadening, which is originated by enhanced segmental motions. This dynamics corresponds to the α relaxation for PHR and can be described by William-Landel-Ferry (WLF) equation. Two-dimensional CP/MAS ^{13}C exchange NMR experiments confirm the existence of flip angle distribution as well as the distribution of correlation times of phenylene ring π flip motion with a KWW exponent of 0.2.

Keywords : Phenoxy resin / Amorphous polymer / Dynamics / Relaxation / CPMAS ^{13}C NMR

Poly(2-hydroxypropyl ether of bisphenol-A), known as phenoxy resin (PHR), is an amorphous linear polymer and the structure and dynamics have been studied by X-ray diffraction [1], mechanical relaxation [2], and solid-state NMR [3]. Although three relaxations are observed between -100 and -40 °C, between 20 and 40 °C, and between 70 and 100 °C on mechanical relaxation experiments, the molecular origins have not been well understood. In this article, we investigate the dynamics of PHR by analyzing one- and two-dimensional CP/MAS ^{13}C NMR spectra.

PHR films (Union Carbide, grade PKHJ) were prepared by being hot-pressed at 160 °C under 100 kg cm $^{-2}$, quenched in ice-water, and dried at room temperature under vacuum for three days. Solid-state ^{13}C NMR measurements were conducted on a Chemagnetics CMX-400 spectrometer operating under a static magnetic field of 9.4 T. The glass transition temperature (T_g) determined

by DSC measurements was 80 °C. No other obvious exothermic and endothermic peaks were observed between -100 and 200 °C.

Figure 1 shows CP/MAS ^{13}C NMR spectra of PHR ranging from -150 to 180 °C. We can find two interesting features. One feature is that the resonance lines for C-H carbons of phenylene rings split into two resonance lines at -150 °C. This indicates that the phenylene C-H carbons exist in chemically different two sites at low temperatures, which would be caused by an OH ... π hydrogen bond [4] between the hydroxyl group and the phenylene ring. The coalescence of the resonance lines with increasing temperature is originated from phenylene ring π -flip motion. The correlation time of the π -flip motion, whose temperature range corresponds to the mechanical γ relaxation, is determined by using the two-site exchange model [5]. For the analysis, the correlation time distribution with a Kohlrausch-Williams-Watts (KWW) func-

FUNDAMENTAL MATERIAL PROPERTIES — Molecular Dynamic Characteristics —

Scope of Research

The research activities in this subdivision cover structural studies and molecular motion analyses of polymers and related low molecular weight compounds in the crystalline, glassy, liquid crystalline, solution, and frozen solution states by high-resolution solid-state NMR, dynamic light scattering, electron microscopy, X-ray diffractometry, and so on, in order to obtain basic theories for the development of high-performance polymer materials. The processes of biosynthesis, crystallization, and higher-ordered structure formation are also studied for bacterial cellulose.



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tion with an exponent of $\beta = 0.2$ as well as the flip angle distribution, quantified from the following 2D MAS exchange experiments, are applied. The result, shown by closed squares in Figure 2, indicates that the Arrhenius relation holds with the apparent activation energy, E_a , of 51 kJ mol^{-1} . This value agrees with the previously reported E_a for the π flip motion of phenylene groups for several polymers with bisphenol-A residues, $48 - 56 \text{ kJ mol}^{-1}$ [3,6,7]. In contrast, the value of $\beta = 0.2$ is not consistent with that of $\beta = 0.6$ for ^2H NMR lineshape analyses of π -flip motion in PHR [3]. However, the value of $\beta = 0.2$ seems to be reasonable because mechanical relaxations and NMR line shape analyses of π -flip motion in cured epoxy resins give $\beta = 0.28$ [8], and CSA lineshape analyses of π -flip motion in PC gives $\beta = 0.154$ [6].

Figure 3 shows 2D CP/MAS ^{13}C exchange NMR spectra for the C4 and C5 carbons of PHR at -120°C . While only the diagonal peaks are observed for the mixing time of 10 ms, the exchange signals are clearly observed in the mixing time of 2.0 s. The correlation time of the π -flip motion at -120°C is analyzed by the mixing time dependence of the exchange signal intensities, $I(t_m)$. The experimental data cannot be explained by calculated $I(t_m)$ curves with $\beta = 1$ or 0.6. In contrast, the calculated $I(t_m)$ curve with $\tau = 2.0 \times 10^2 \text{ s}$ and $\beta = 0.2$ agree well with the experimental data. It is therefore found that the 2D CP/MAS ^{13}C exchange NMR experiments offer us quantitative information on average correlation times and the width of the correlation time distributions for respective ^{13}C species.

The other feature in Figure 1 is that the linewidths become broad at $20 - 50^\circ\text{C}$ above T_g . This is caused by the modulation of MAS and ^1H dipolar decoupling efficiency by enhanced segmental motions [9], which correspond to the α relaxation.

The correlation times are analyzed quantitatively from the temperature dependence of the linewidth for each resonance line by assuming the William-Landel-Ferry (WLF) equation. The temperature dependence of correlation times thus obtained is also plotted in Figure 2 as closed circles. It is found that the temperature dependence of the correlation time can be described by WLF equation with typical parameters.

The correlation times at 90 and 120°C analyzed from 2D CP/MAS ^{13}C exchange NMR experiments are also shown in Figure 2. The dynamics of each ^{13}C site can be investigated by these simple 1D and 2D solid-state NMR experiments, which are crucial methodology for the elucidation of the origin of relaxations.

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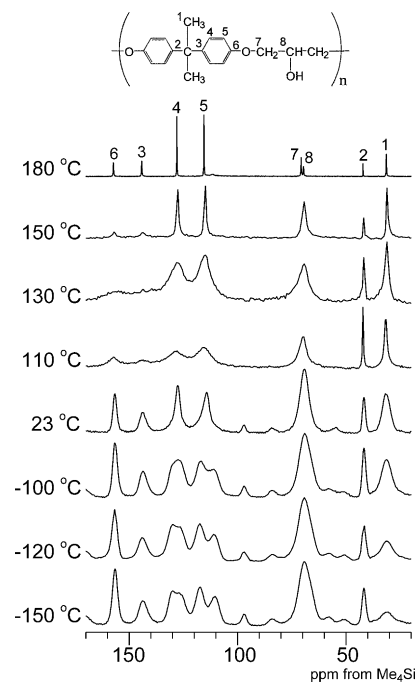


Figure 1. CP/MAS ^{13}C NMR spectra of PHR at different temperatures.

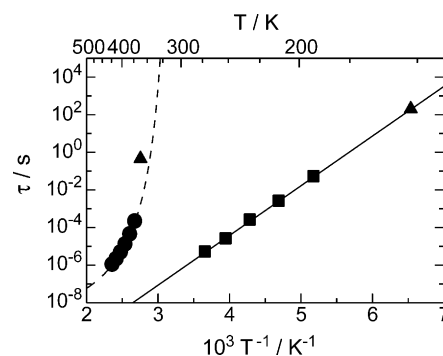


Figure 2. The Arrhenius plot for the correlation time of motion associated with the α and γ relaxations of PHR. \bullet : motional broadening, \blacktriangle : 2D exchange, \blacksquare : two-site exchange with KWW $\beta = 0.2$

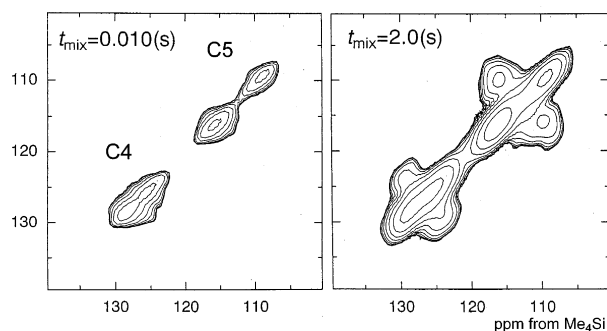


Figure 3. 2D CP/MAS ^{13}C exchange spectra for C4 and C5 carbons of PHR in the glassy state at -120°C .