Separation of ^{13}C spectra of polyurethane soft and hard segments by ROSY

Product used : Nuclear Magnetic Resonance (NMR)

The ROSY (Relaxation Ordered SpectroscopY) is a method in which the ^{13}C CPMAS spectrum of a mixture is classified by a longitudinal relaxation time of ^{1}H, and the ^{13}C CPMAS spectrum is displayed separately for each substance. In solution NMR, each peak in the ^{1}H spectrum has its own longitudinal relaxation time. In solid-state NMR, however, spin diffusion occurs due to the dipolor interaction between ^{1}H, and all ^{1}H have the same longitudinal relaxation in the domain within a certain distance. The ^{13}C spectrum can be separated for each domain by using this difference in relaxation time of ^{1}H. The longitudinal relaxation time (T_1^H) obtained by the saturation recovery method as shown in Fig.1a is usually used to separate the ^{13}C spectrum of the mixture. The size of the domain that can be separated by this method is about 100 nm. To separate domains smaller than this, a measurement using the relaxation time at rotational flame ($T_{1\rho}^H$) obtained by the spinlock method as shown in Fig.1b is effective. The domain size that can be separated by $T_{1\rho}^H$ is about several nm, and it is possible to determine the phase separation structure of block copolymers and the molecular compatibility.

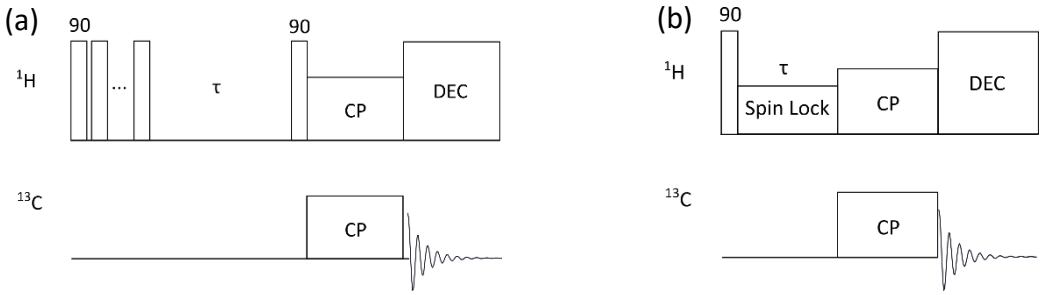

Fig.1 Pulse sequence diagrams of saturation recovery (T_1^H) based ROSY(a) and spinlock ($T_{1\rho}^H$) based ROSY(b).

$T_{1\rho}^H$ based ROSY – Separation of soft segment and hard segments of polyurethane -

As a measurement example of the $T_{1\rho}^H$ based ROSY, we will introduce the separation of soft and hard segments of the ^{13}C spectrum of polyurethane (a smart phone cover case). Polyurethane has soft and hard segments in the molecule, each of which aggregates between the molecules to form their respective domains. A typical method for distinguishing between soft and hard segments is measuring CPMAS which tends to observe hard segments, and the LD (Low power Decoupling) MAS which tends to observe soft segments (Fig.2). Although it is possible to see the difference in segments to some extent in the both measurements, it is often difficult to assign domains because CPMAS observes soft segments as well as hard segments, and LDMAS observes hard segments as well as soft segments in small increments. On the other hand, the ROSY separates the spectrum from spatial differences through ^{1}H spin diffusion, allowing the two segments to be separated more clearly. Fig.3 shows the $T_{1\rho}^H$ based ROSY spectrum. In the T_1^H-ROSY spectrum, both segments cannot be separated (not shown). On the other hand, in the $T_{1\rho}^H$-ROSY spectrum, the soft segment and the hard segment can be clearly separated. In addition, this indicates that the domain size of the segment ranges from a few nm to a few tens of nm.

ECZ500R
3.2mm HXMAS probe
MAS=5kHz

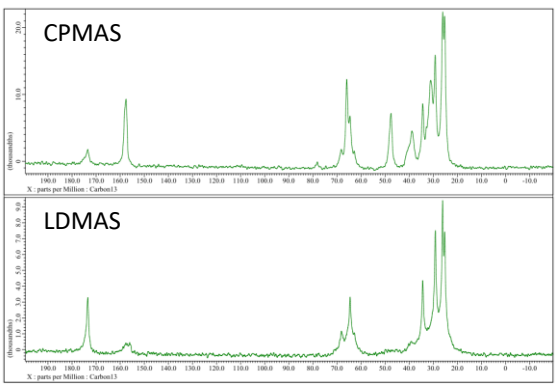

Fig.2 ^{13}C CPMAS and LDMAS spectra of poly urethane.

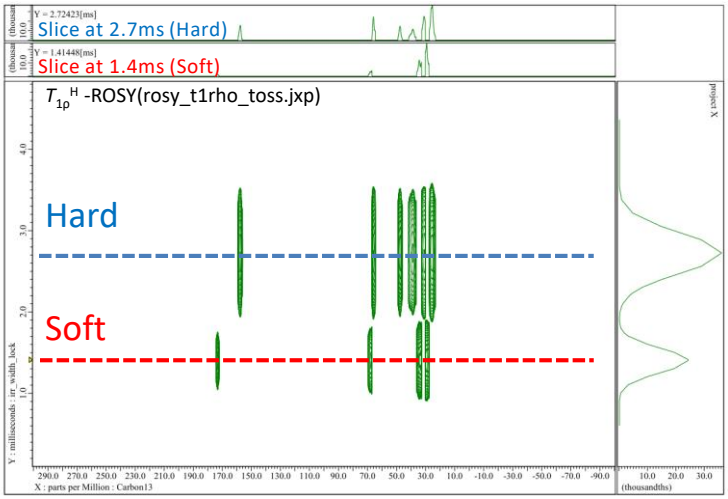

Fig.3 A $T_{1\rho}^H$ -ROSY spectrum of poly urethane.

JEOL Ltd.
3-1-2 Musashino Akishima Tokyo 196-8558 Japan Sales Division Tel. +81-3-6262-3560 Fax. +81-3-6262-3577
www.jeol.com ISO 9001 • ISO 14001 Certified
▼Local office
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