Solid State NMR Investigation of the Structures and Dynamics of Poly(silylenemethylene)s

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ABSTRACT: Poly(silylenemethylene)s with the repeating Si–C backbone units are well-examined carbosilane polymers. We synthesized two poly(silylenemethylene)s, poly(diphenyl-silylenemethylene) (PDPhSM) and poly(methyl phenyl-silylenemethylene) (PMPhSM). These two polymers have different physical, thermal and mechanical properties. This work discusses the structures and dynamics of the Si–C backbone and phenyl side groups of these two polymers by ^{13}C and ^{29}Si solid-state NMR and reveals relationships between the thermal and mechanical properties and between structures and dynamics of the Si–C backbone and the side chains.

KEY WORDS ^{13}C and ^{29}Si Solid-State Nuclear Magnetic Resonance / Poly(silylenemethylene)s / Si–C Backbone Units / Phenyl Side Groups / Structure and Dynamics /

Silicon-based polymers have been extensively studied over the past 30 years due to their high thermal stability as well as unique optoelectrical properties.^{1,2} Poly(silylenemethylene)s with the repeating Si–C backbone units are well-examined carbosilane polymers, and research can be found in the literature.^{3–17} The largest interest in the study of poly(silylenemethylene)s seems to be pyrolytic profiles of these polymers to Si–C ceramics.¹⁸ Few reports have been published dealing with the material properties, such as thermal or mechanical properties rather than pyrolytic properties, of poly(silylenemethylene)s. Several reports dealing with the synthesis and pyrolytic behavior of poly(silylenemethylene)s have been published,^{19–26} and our recent articles report the synthesis and basic physical properties and thermal and mechanical properties of poly(diphenyl-silylenemethylene) (PDPhSM) and poly(methyl phenyl-silylenemethylene) (PMPhSM).^{27–29} PDPhSM is a crystalline polymer with poor solubility in common organic solvents.²⁷ The melting temperature of PDPhSM is about 350°C, and the glass transition temperature is *ca.* 140°C.²⁷ The weight of PDPhSM remains almost unchanged by heating up to *ca.* 400°C in air and in nitrogen.²⁸ PMPhSM is an amorphous polymer with good solubility in common organic solvents.²⁹ The glass transition temperature of PMPhSM is around 20°C and it depends on molecular weight and the tacticity.²⁹ The weight of PMPhSM remained almost unchanged by heating up to *ca.* 400°C in air and in nitrogen.²⁹ Thus the thermal and mechanical properties of these two polymers are very different despite containing the same Si–C backbone. Differences of these properties come from differences of structures and the dynamics of the Si–C backbone and side-chains in the solid-state. But there are no studies on molecular structures or molecular motion of PDPhSM and PMPhSM in the solid-state.

Solid-state high-resolution nuclear magnetic resonance (NMR) spectroscopy has become an enormously fruitful technique in the study of molecular structure and motion

of polymers in the solid-state.^{30,31} In particular, it is useful for structural and molecular motion studies of polymers³² with poor solubility in solvents such as PDPhSM.

This paper reports the ^{13}C and ^{29}Si solid-state NMR spectra of PDPhSM and PMPhSM and discusses the main-chain and side-chain structures and molecular-motion of PDPhSM and PMPhSM.

EXPERIMENTAL

Preparation of Polymers

PMPhSM and PDPhSM were prepared as previously reported.^{27–29} The structure of the polymer is as follows.

The tacticity of PMPhSM (0.31(*rr*):0.46(*mr*):0.23(*mm*)) was determined from the solution state ^{13}C NMR spectrum.

Solid-State NMR Measurements

NMR spectra were recorded on a Bruker DSX-300 NMR spectrometer. The observed frequencies of ^{13}C and ^{29}Si are 75.6 MHz and 59.6 MHz, respectively. The 90-degree pulse of ^1H was 4.7 μs , and contact times of the cross polarization experiment were 2 ms for ^{13}C and 5 ms for ^{29}Si , respectively. The repetition time is 300 s

Figure 1. Temperature dependence of the storage modulus G' and loss modulus G'' of PDPHSM (a) and PMPHSM (b) at a constant frequency of 6.28 rad s^{-1} and constant strain of 1%.

and pulse length is $1 \mu\text{s}$ for ^{29}Si DD/MAS experiments. The dipolar dephasing delay time was $400 \mu\text{s}$ for the ^{13}C CP+DDph (dipolar dephasing) experiment. ^{13}C chemical shifts were calibrated indirectly through the adamantane peak observed to low frequency (29.5 ppm relative to tetramethylsilane), and ^{29}Si chemical shifts were calibrated indirectly through the polydimethylsilane peak (-33.8 ppm relative to tetramethylsilane).

WAXD Analysis

Wide angle X-ray diffraction (WAXD) was performed with a JEOL JDX-3530 diffractometer using Ni-filtered $\text{Cu-K}\alpha$ radiation. Intensity distributions ($5^{\circ} < 2\theta < 35^{\circ}$) were recorded in the reflection mode by a goniometer equipped with a monochromator.

Dynamic Mechanical Properties Measurements

Dynamic mechanical properties were examined using a Rheometrics RDA II dynamic analyzer in torsion mode. Each specimen ($10 \times 30 \times 1 \text{ mm}$) was prepared by compression molding.

Figure 2. ^{29}Si CP/MAS (a) and ^{29}Si DD/MAS (b) spectrum of PDPHSM at room temperature. The signal of the non-crystalline region is indicated with an asterisk.

RESULTS AND DISCUSSION

Dynamic Mechanical Properties of PDPHSM and PMPHSM

Figure 1 shows the temperature dependence of storage moduli (G') and loss moduli (G'') for PDPHSM (a) and PMPHSM (b), respectively. The obvious transition at 140°C observed for storage moduli (G') and loss moduli (G'') is assigned to the glass transition, and other transitions at around 60°C and 210°C are observed for G'' in the case of PDPHSM. An ambiguous transition at around -120°C , in addition to clear transition caused by the glass transition at 20°C , was observed for the storage moduli (G') and loss moduli (G'') in the case of PMPHSM. The storage moduli (G') of PDPHSM decrease by only one order of magnitude at the glass transition, but those of PMPHSM decrease by over three orders of magnitude at the glass transition.

Solid-State NMR Studies of PDPHSM at Room Temperature

Figure 2(a) shows the ^{29}Si CP/MAS NMR spectrum of PDPHSM at room temperature. The ^{29}Si CP/MAS NMR spectrum contains two sharp signals at -7.6 ppm and -9.3 ppm and the intensity ratio of these two signals is about 1 : 1. T_1 of the signal at -7.6 ppm is 273 s, and that of the signal at -9.3 ppm is 306 s, so that these signals observed in the ^{29}Si CP/MAS experiment come from the crystalline region of PDPHSM. Figure 2(b) shows the ^{29}Si DD/MAS NMR spectrum of PDPHSM at room temperature. Compared with the ^{29}Si CP/MAS NMR spectrum, a shoulder signal at -8.5 ppm was observed in the ^{29}Si DD/MAS NMR spectrum, which

Figure 3. ^{13}C CP/MAS NMR spectra of PDPhSM at room temperature. SSB means a spinning sideband.

Figure 4. ^{29}Si and ^{13}C CP/MAS NMR spectra of PMPhSM at room temperature. SSB means spinning sideband.

was assigned to the noncrystalline region of PDPhSM. From these results, there exist two conformational isomers in the crystalline region of PDPhSM and the peaks at -7.6 ppm and -9.3 ppm were assigned to these two conformational isomers in the crystalline region.

The phenyl region (from 120 to 150 ppm) of the ^{13}C

Figure 5. ^{13}C CP+DDph NMR spectra in the phenyl region for PMPhSM (a) at room temperature and PDPhSM at room temperature (b), 113°C (c), and 226°C (d).

CP/MAS NMR spectrum of PDPhSM shown in Figure 3 is very complicated in structure and contains several lines so that motion of the phenyl rings of PDPhSM is restricted at room temperature. There are two peaks at 0.0 ppm and -3.1 ppm assigned to the methylene carbons of the main chain in a similar manner with the ^{29}Si result. There thus exist two conformational isomers in the crystalline region of PDPhSM.

Solid-State NMR Studies of PMPhSM at Room Temperature

Figure 4 shows ^{29}Si and ^{13}C CP/MAS NMR spectra of PMPhSM at room temperature. From the ^{29}Si CP/MAS NMR spectrum, only one broad line is observed, compared with PDPhSM, at -4.5 ppm. This polymer is an amorphous polymer so that this broad signal means a conformational distribution along the Si-C backbone.

Peaks at 141.7 ppm (C1), 134.0 ppm (C2), 128.5 ppm (C3 and C4), 7.0 ppm (the methylene carbons) and 0.5 ppm (the methyl carbons) are observed in the ^{13}C CP/MAS NMR spectrum. The broad signal assigned to the methylene carbons of the main-chain implies conformational distribution along the Si-C backbone in a similar manner for ^{29}Si .

Motion of Phenyl Rings of PDPhSM and PMPhSM

Figure 5 shows the ^{13}C CP+DDph NMR spectra in the phenyl region for PMPhSM, and PDPhSM at room temperature, 113°C and 226°C , respectively. Dipolar/

Figure 6. ^{29}Si CP/MAS NMR spectra of PDPhSM at various temperatures. Each spectrum was recorded for 56 scans and repetition time of 20 s.

dephasing spectra are obtained by inserting a dephasing period between the CP period and detection. During the dephasing period, the carbons with directly attached hydrogens undergo rapid dephasing (on a time scale of tens of μs); and hence their ^{13}C magnetizations are dramatically depressed before ^{13}C detection. Since sometimes rapid rotation of a methyl group or a phenyl group dramatically attenuates ^1H – ^{13}C magnetic dipolar interactions, dipolar-dephasing spectra of the phenyl region are very useful to evaluate the motion of the phenyl group.³²

The three signals at 141.7 ppm, 134.0 ppm, and 128.5 ppm observed in the ^{13}C CP + DDph NMR spectrum of PMPhSM (Figure 5(a)), are assigned to the C1, C2, and C3 carbons, respectively. This shows that the dipole–dipole interaction with ^1H vanishes due to the flip–flop motion of the phenyl ring of PMPhSM at room temperature.

Three or more sharp signals assigned to the C1 carbons with directly attached no hydrogen and very small signals assigned to the C2 and C3 are observed in PDPhSM at room temperature (Figure 5(b)). This indicates that the flip–flop motion of the phenyl rings of PDPhSM is restricted at room temperature, and more than three magnetically unequal phenyl rings exist at room temperature. In the ^{13}C CP + DDph NMR spectrum of PDPhSM at 113°C, signals corresponding to C2 and C3 are observed, but the signal intensities are smaller than those at room temperature. This suggests that the flip–flop motion of the phenyl rings of PDPhSM starts at this temperature but motion is not rapid enough to

Figure 7. Change of ^{29}Si chemical shifts and relative intensities of two signals of PDPhSM at various temperatures from 27°C to 226°C. (○, chemical shift of lower frequency signal; ●, chemical shift of higher frequency signal; □, intensity of lower frequency signal; ■, intensity of higher frequency signal.)

remove ^1H – ^{13}C dipole–dipole interactions completely. Signals corresponding to C2 and C3 are obviously observed in the ^{13}C CP + DDph NMR spectrum of PDPhSM at 226°C, so that the motion of phenyl rings is enough to remove ^1H – ^{13}C dipole–dipole interactions.

^{29}Si Variable Temperature CP/MAS Experiments on PDPhSM

Figure 6 shows the ^{29}Si CP/MAS NMR spectra of PDPhSM at 27°C to 226°C. Each spectrum was recorded at 56 scans and repetition time of 20 s. Plots of the ^{29}Si chemical shifts and relative intensities of the PDPhSM signals are presented in Figure 7. The lower frequency peak (−9.3 ppm at room temperature) moves to high frequency by 1.2 ppm with increase in temperature below 130°C. The chemical shifts are unchanged above 130°C. The higher frequency peak (−7.6 ppm at room temperature) moves to high frequency by 0.6 ppm with increase in temperature below 130°C. The chemical shifts are unchanged above 130°C. Both signals have intensity minima at about 130°C, so this polymer has motion of the several tens of kHz which dramatically attenuates ^1H dipolar interactions at 130°C. From the ^{13}C CP + DDph NMR experiment which shows that the flip–flop motion of the phenyl rings of PDPhSM starts at 113°C, this motion with several tens of kHz corresponds to the flip–flop motion of the phenyl rings. Loss of storage moduli (G') at 140°C comes from the flip–flop motion of the phenyl rings.

Above T_g at 140°C, obtained by the storage moduli (G') and loss moduli (G''), there are still two signals assigned to the two conformational isomers. This shows that this polymer has no micro-Brownian motion of the Si–C backbone and there still exist two conformational isomers above T_g obtained by storage moduli (G') and loss moduli (G'').

Figure 8 shows the intensity distribution for the WAX diffraction of PDPhSM at 25°C, 100°C, 200°C, and 300°C. No significant change in diffraction was found

Figure 8. Wide-angle X-ray diffractograms of PDPHSM at 25°C (a), 100°C (b), 200°C (c), and 300°C (d).

Figure 9. Plots of the ^{29}Si chemical shifts and half widths of the PMPHSM signal at various temperatures from -37°C to 65°C .

from 25°C to 200°C , but every peak position shifted to a smaller 2θ value at 300°C . The strongest maximum of the diffraction patterns between 25°C and 200°C is around $2\theta=8.7$ and spacing is $10.2\text{ \AA}$. The strongest maximum of the diffraction patterns at 300°C was around $2\theta=8.5$, and d spacing was $10.4\text{ \AA}$. This comes from increase in inter-chain distance of the neighbouring polymer at 300°C which is responsible for side-chain phenyl ring motion. The ^{29}Si NMR chemical shift changes with increase in temperature. This seems to arise from the lengthening of the inter-chain distance of

neighbouring polymer which is responsible for side-chain phenyl ring motion.

^{29}Si Variable Temperature CP/MAS Experiments on PMPHSM

Figure 9 shows plots of the chemical shifts and half width of ^{29}Si NMR signals of PMPHSM at various temperatures from -37°C to 65°C . The chemical shift moved low frequency for 0.2 ppm with increase in temperature. The half height width of NMR signal from -37°C to 25°C is about 170 Hz , but above 45°C , 50 Hz . T_g of this polymer is about 20°C obtained by storage moduli and loss moduli. The broad signal below T_g means conformational distribution along the Si-C backbone and a micro-Brownian motion of the Si-C backbone of PMPHSM starts above T_g . This motion causes the half width to decrease.

CONCLUSIONS

Based on the results of ^{29}Si and ^{13}C solid-state NMR, we conclude that PDPHSM has two conformational isomers in the crystalline region and motion of the phenyl rings is restricted at room temperature. Above T_g , at 140°C , motion of the phenyl rings starts and inter-chain distance of the neighboring polymer lengthens, but there is no micro-Brownian motion of the Si-C backbone and there still exists two conformational isomers. PMPHSM has conformational distribution along the Si-C backbone and there is motion of phenyl rings at room temperature. The micro-Brownian motion of the Si-C backbone of PMPHSM starts above T_g .

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