α-helix form is present in the *B. mori* fibroin in the solid state. Accordingly, it is concluded that the minor conformer seen in the silk II sample, especially in the cocoons, is not the α-helix but silk I type.

Concluding Remarks

We find that the three forms of silk fibroins, silk I and II and the α-helix forms, are easily distinguished by the conformation-dependent ^{13}C chemical shifts as determined by the high-frequency CP-MAS NMR method. This approach is very useful for the conformational characterization of less crystalline samples such as silk I. We note that the present NMR approach is much more powerful in analyzing the local conformations of the amino acid residues under consideration than previous conventional techniques such as X-ray diffraction, infrared spectroscopy, etc. Accordingly, conformational characterization as viewed from minor amino acid residues, such as Tyr, Val, etc., is possible with selectively ^{13}C-enriched samples prepared by a similar procedure to that of [*Gly*-1-^{13}C]fibroin.

Note Added in Proof: In Table V, the alternative and energetically more favorable conformation[39] of silk I, if the local conformations of all residues are the same, has the torsion angles (−168°, −60°), which gives the identical ^{13}C shift of Ala C_β carbon on the basis of the calculated ^{13}C chemical shift contour map[12] to that of (−25°, 134°).

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Communications to the Editor

High Molecular Weight Reactive Poly(diphenylsiloxane)

Silicone resins are normally viscous liquids or gums because of their –Si–O– main-chain structure. It is well-known that the thermal stability of silicone resins is improved by substituting methyl groups with phenyl groups, but the glass transition temperature (T_g) is still below room temperature even with a high phenyl content. For example, silicone resins containing 75% phenyl groups have a T_g of −30 °C. When all methyl groups in poly(dimethylsiloxane) are replaced with phenyl groups, the resulting polymer is expected to have a high T_g, because the oligomeric diphenylsiloxane has a T_g of 150 °C. However, conventional polymerization yields only small amounts of high molecular weight poly(diphenylsiloxane).

We have found that the polymerization reaction as well as the chloromethylation proceeds in the chloromethylation reaction of oligomeric diphenylsiloxane with a Friedel–Crafts catalyst. In this communication the synthesis and the properties of novel high molecular weight poly(diphenylsiloxanes) with a reactive group in the side chain are described.

Oligomeric diphenylsiloxane having a weight-average molecular weight of 1400 (DP = 7) and OH groups at both chain ends was obtained from Petrearch Systems. The chloromethylation was carried out in chloromethyl methyl ether solution with $SnCl_4$ as a catalyst. We used chloromethyl methyl ether as the chloromethylation reagent because of its availability. In the case of the mass prep-

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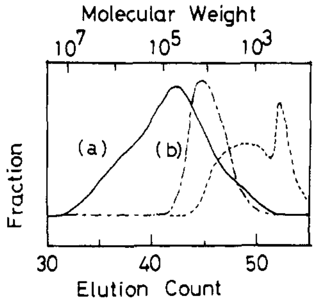

Figure 1. Gel permeation chromatography curves of chloromethylated poly(diphenylsiloxanes): (a) $\bar{M}_w = 5.8 \times 10^5$; (b) $\bar{M}_w = 1.2 \times 10^4$ and starting oligomeric diphenylsiloxane; dotted line, $\bar{M}_w = 1.4 \times 10^3$.

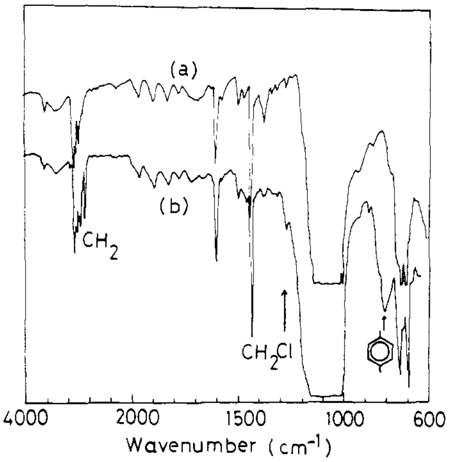

Figure 2. Infrared spectra of oligomeric diphenylsiloxane (a) and chloromethylated poly(diphenylsiloxane), $\bar{M}_w = 1.2 \times 10^4$ (b).

aration of the polymers, other nontoxic chloromethylation reagents can be used. Under suitable reaction conditions, the polymerization reaction occurs without forming a significant amount of gels, and the molecular weight of the polymers can be controlled. A typical reaction was as follows. The oligomeric diphenylsiloxane (30 g) was dissolved in chloromethyl methyl ether (500 mL), and $SnCl_4$ (25 mL) was added to the solution. The reaction mixture was stirred for 17 h at 0 °C, and white polymer powders were isolated by reprecipitation in methanol. An average yield of polymer was about 60% after two reprecipitations. Figure 1 shows the gel permeation chromatography curves of several polymers obtained and the starting oligomer. A longer reaction time tends to provide a higher molecular weight, and so far we have obtained a maximum $\bar{M}_w$ of 1×10^6 before gelation. The chemical structure of the polymers was analyzed by IR and NMR spectroscopy, of which results are shown in Figures 2 and 3, respectively. The IR spectrum of the polymer obtained shows the specific absorption of the siloxane chain at 1000–1200 cm^{-1}, the phenyl group at 1450 and 1600 cm^{-1}, the para-substituted phenyl group[1] at 800 cm^{-1}, and the chloromethyl group at 1260 and 2900 cm^{-1}, indicating the structure of chloromethylated poly(diphenylsiloxane). The NMR spectrum of the polymer shows a broad peak around 3.0 ppm due to methylene of the chloromethyl group and loses a small peak at 1.5 ppm in the spectrum of the starting oligomer, which would be assigned to terminal OH since the OH group in $Ph_2Si(OH)_2$ resonates at 1.9 ppm. The chloromethyl group content determined by elemental analysis was about 20% for almost all polymers and did not show an increase with reaction time. In the absence of either chloromethyl methyl ether or $SnCl_4$, no polymerization reaction occurred. These results clearly indicate that the introduction of chloromethyl groups in the phenyl ring occurs as well as the polymerization. No polymerization reaction was observed in the chloromethylation of the CH_3-terminated copolymer of diphenylsiloxane and methylphenylsiloxane, suggesting the contribution of the OH group to the polymerization reaction. The SiOH group is normally unstable in conventional silicone resins and undergoes self-condensation by a dehydration reaction, resulting in a high molecular weight polymer. However, this type of condensation is prohibited in oligomeric diphenylsiloxane because the terminal OH groups are stabilized by the diphenyl structure. But as chloromethyl groups replace OH groups in the polymer, the electronic stability of the diphenyl structure may change, allowing a high molecular weight polymer to form by condensation. Another consideration is that the combination of $ClCH_2OMe$ and $SnCl_4$ generates an active catalyst, which can initiate condensation as well as chloromethylation. The detailed reaction scheme is now under investigation and will be published later.

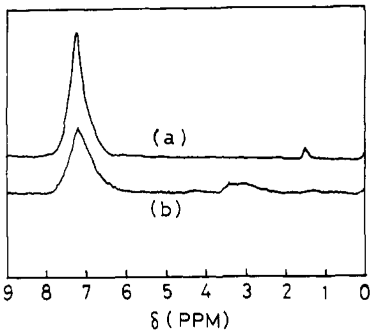

Figure 3. NMR spectra of oligomeric diphenylsiloxane (a) and chloromethylated poly(diphenylsiloxane), $\bar{M}_w = 1.2 \times 10^4$ (b) measured in $CDCl_3$.

The structure of the poly(diphenylsiloxanes) containing the chloromethyl group is quite equivalent to that of chloromethylated polystyrenes (CMPS), which is now an important reactive intermediate to design various functional vinyl polymers.[2] The polymers can be easily cross-linked by irradiating with far-UV light, an electron beam, or X-rays, suggesting the application to resist material without further modification of the polymers. As compared with CMPS, the chloromethylated poly(diphenylsiloxanes) have a higher T_g (150 °C) and show better solubility in various solvents such as ketones, ethers, esters, and aromatic hydrocarbons. Transparent films can be easily formed by either casting or spin-coating. These properties as well as a highly reactive chloromethyl group allow a wide application to synthesizing functional silicone resins.

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Received January 23, 1984