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Synthesis of Polyorganosiloxane with N-(4-Pyridyl)amido Group on the Side Chain[1]

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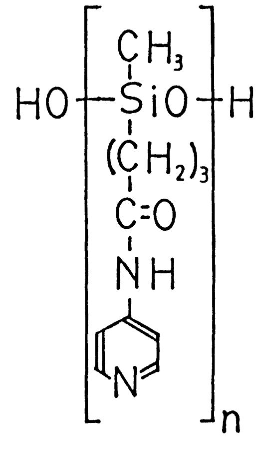
Poly(3-carboxypropylmethylsiloxane) reacts with thionyl chloride and forms acid chloride without significant decomposition. Transparent polyorganosiloxane with N-(4-pyridyl)amido group on the side chain is easily synthesized by polymer reaction of the acid chloride and 4-aminopyridine.

Polyorganosiloxanes with many useful characteristics such as flexibility, heat resistance, water repellent, and biological inertness have interesting possibility as a functional material. These characteristics would be much improved if functional groups were attached to the polymers. From this viewpoint, polyorganosiloxanes with various functional groups have been synthesized and a number of investigators have attempted to apply these polymers to various functional materials, e.g. drug carriers,[2)] liquid crystals,[3)] mould releasing agents,[4)] and fillers for gas chromatography.[5)] However, most of these polymers have been synthesized by hydrosililation with H_2PtCl_6 as a catalyst[2-5)] and it is difficult to remove completely the catalyst residue. This is a serious disadvantage, e.g., for optical materials. Therefore, a synthetic method of the polyorganosiloxane without using such metal catalysts is very valuable. If poly(3-carboxypropylmethylsiloxane)(PCPMS) forms acid chloride derivative without decomposition, the syntheses of functional polyorganosiloxanes become very easy by employing the polymer reaction of the acid chloride and nucleophilic compounds.

This letter describes the synthesis of transparent polyorganosiloxane with N-(4-pyridyl)amido group on the side chain (PPAPMS)[1)] through the miraculous reaction of the acid chlorination of PCPMS.

PCPMS was obtained as described in the previous method.[6)] IR(KBr pellet): 1710 (C=O), and 2500-3300 cm^{-1} (-OH), see Fig. 1. ^{1}H NMR($CDCl_3$): δ = 0.1 (s; Si-$C\underline{H}_3$), 0.6 (t; Si-$C\underline{H}_2$-CH_2), 1.6 (m; Si-CH_2-$C\underline{H}_2$), 2.3 (t; CH_2-$C\underline{H}_2$-CO).

Thionyl chloride (33.3 cm^3; 0.28 mol) was added to PCPMS (2.0 g; 0.014 mol) at 0 to 5 °C. After the reaction for 3 h at 40 °C, excess thionyl chloride was removed i. vac. and crude chlorinated PCPMS was



PPAPMS

obtained. IR(NaCl neat): 1800 cm^{-1} (C=O), see Fig. 1. Stretching vibration of Si-O-Si (1000-1100 cm^{-1}) in Fig. 1 supports none of significant decomposition of PCPMS. However, when the chlorinated PCPMS was hydrolyzed to PCPMS, the molecular weight was partially decreased from $\overline{Mw}$= 20,000 to $\overline{Mw}$= 14,000.

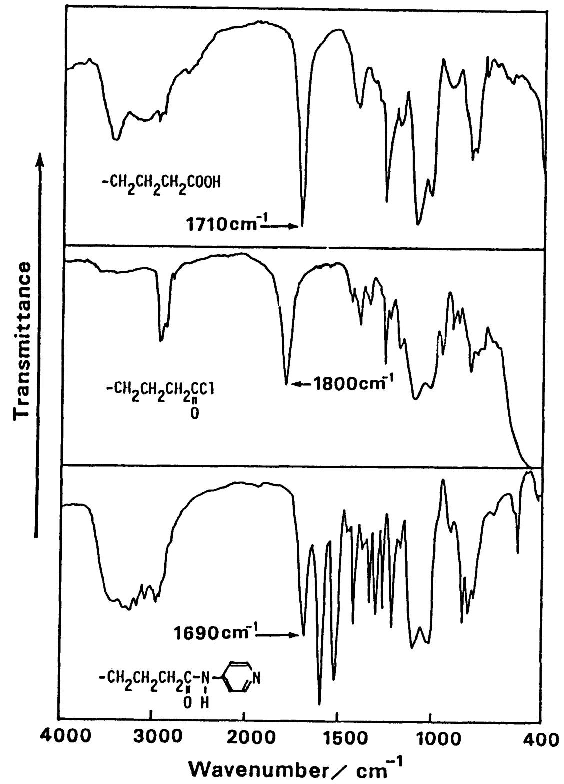


Fig. 1. IR spectra of PCPMS, PCPMS/Cl, and PPAPMS.

4-Aminopyridine (4.0 g; 0.042 mol) dissolved in THF (200 cm^3) was added dropwise to chlorinated PCPMS (2.5 g; 0.014 mol) at 0 to 5 °C and the mixture was refluxed for a day. After removal of the white precipitate of 4-aminopyridine hydrochloride, the filtrate was evaporated. The crude product was dissolved in THF/water solvent, and the solution was dialyzed to remove unreacted 4-aminopyridine using a cellulose tube against water. White precipitates of PPAPMS were gradually produced upon removing free 4-aminopyridine and THF. The dialysis should be repeated until 4-aminopyridine is completely removed. The product was dried at 80 °C i. vac. IR(KBr pellet): 1690 (C=O), 3000-3300 (amido-NH), and 1000-1100 cm^{-1} (Si-O-Si), see Fig. 1. ^{1}H NMR(CD$_3$OD): δ = 0.1 (s; Si-C$\underline{H}_3$), 0.6 (t; Si-C$\underline{H}_2$-CH$_2$), 1.7 (m; Si-CH$_2$-C$\underline{H}_2$), 2.3 (t; CH$_2$-C$\underline{H}_2$-CO), 5.9 (s; amido-N$\underline{H}$), 7.6 and 8.2 (d; pyridyl-4H). The yield of the polymer reaction was 93 % as judged from ^{1}H NMR data.

PPAPMS is soluble in methanol but not in water, acetone, and chloroform. The glass transition temperature, Tg, of PCPMS (-25 °C) is raised to 118 °C by coupling of 4-aminopyridine. A strong inter-segment interaction by hydrogen bonding may lead to such a high Tg. The obtained polymer is not contaminated with metallic components and highly transparent in the visible region.

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