Registry No. Isobutylene–methyl methacrylate–1-naphthylmethyl methacrylate copolymer, 84802-24-4; 1-naphthylmethyl pivalate, 72681-59-5; oxygen, 7782-44-7.

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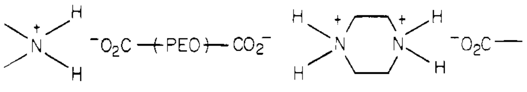
Novel Polycondensations via Poly(oxyethylene) Diglycolic Acid Diamine Salts

Poly(oxyethylene) diglycolic acid[1] ("PEO-acid") (**1**) is a new telechelic derivative of poly(oxyethylene). It is characterized by two terminal carboxyl groups quantitatively introduced by the selective oxidation (Pd–Pt catalyst) of the terminal methylol groups on poly(ethylene glycol) (PEG)[2] and can be prepared with narrow molecular weight distribution with a wide variety of $\bar{M}_n$. We are now studying various chemical syntheses and polymerizations based on PEO-acid.

This first report discloses preparations of novel 1:1 salts of PEO-acids with piperazine (**2a**) and with 1,6-diaminohexane (**2b**) (Scheme I). In the present study, PEO-acids with relatively low molecular weight ($\bar{M}_n$ = 400 (**1a**[3]) and $\bar{M}_n$ = 1000 (**1b**[4])) were utilized. The piperazine salts of **1** were isolated as crystalline solids, while the diaminoxhexane salts were amorphous waxes. These salts are analogues of the well-known "nylon 6,6 salt",[5] formed between adipic acid and **2b**. They, like the "nylon salt", can be converted to high polymer by the removal of water at elevated temperature as shown in Scheme I.

Thus, a mixture of 4.0 mmol each of purified **1a** and **2a** was maintained at 50 °C for 1 h with stirring under a nitrogen atmosphere. A glassy material was produced in quantitative yield and was recrystallized from an 80/20 chloroform–diethyl ether mixture to afford a white crystalline product. After filtration and drying in vacuo **3a-1** was isolated in 45% yield: $\eta_{sp}/C = 0.028$[3] (5.0 g/L in H_2O at 30 °C); ^1H NMR (D_2O) δ 3.53 (s, NCH_2CH_2N, 8 H), 3.72 (s, OCH_2CH_2O, 26.8 H), 3.97 (s, OCH_2CO_2, 4 H); IR (KBr) 3400 (ν_{O-H}), 3250, 3020 (ν_{N^+-H}), 2930 (CH_2), 1600, 1400 ($\nu_{C=O}$ of CO_2^-), 1100 (ν_{C-O}) cm^{-1}. Anal. Calcd for **3a-1**·$[H_2O]_{1.0}$ (n = 6.7): C, 47.89; H, 8.51; N, 5.25. Found (very hygroscopic): C, 47.53; H, 8.34; N, 5.50. This product melted at 53–56 °C to a liquid that still transmitted polarized light weakly. This finding suggests the existence of a molecular orientation (somewhat liquid crystalline) that may result from intermolecular salt formation (structure **5**). The light transmission sharply disappeared at 80 °C and could be recovered quite reversibly at this temperature unless the samples were heated over 100 °C, around which irreversible polymerization occurred. These results were supported by the DTA analysis shown in Figure 1a. The broad endothermic peak at 55 °C and the complicated exothermic ones over 100 °C correspond, respectively, to the melting point and to the initiation of the condensation reaction (vide infra). The sharp shoulder observed at 80 °C corresponds to the disappearance of the mesomorphic phase.



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The salt **3a-2** was also obtained as a crystalline solid:[6] mp 40 °C; $\eta_{sp}/C = 0.032$[4] (5.0 g/L in H_2O). Anal. Calcd for **3a-2**·$[H_2O]_{2.0}$ (n = 20.3): C, 50.74; H, 8.87; N, 2.43. Found (very hygroscopic): C, 50.85; H, 9.16; N, 2.38. However, the isolated yield was as low as 20% because of difficulty in recrystallization. This compound melted at 40 °C to a liquid that allowed little transmission of polarized light and began to decompose around 150 °C. The mesomorphic state found in **3a-1** was not observed in **3a-2** by DTA (Figure 1b). As for the uncrystallized parts of both **3a-1** and **3a-2**, they were also obtained as solid materials on drying and found to be structurally identical with the crystalline products by spectroscopy.[7]

The reactions of **2b** with **1a** and with **1b** were carried out in a similar manner. In these cases, the products obtained were washed twice with diethyl ether and dried in vacuo and were isolated in 95% yield as an amorphous waxy solid[8] that did not transmit polarized light.

All the above salts were allowed to polymerize by thermal condensation. Typically, the salt **3a-1** (1.0 g) was placed in a glass tube, heated under a stream of nitrogen as the temperature was raised slowly to 200 °C in 3 h, and then maintained at 200 °C for another 3 h in vacuo to complete the elimination of water. A white waxy polymer was obtained in quantitative yield and was used without further purification. The structure **4a-1** was confirmed by the following data: ^1H NMR ($CDCl_3$) δ 3.60 (s, NCH_2CH_2N, 8 H), 3.65 (s, OCH_2CH_2O, 18.8 H), 3.70 (s, $C(O)CH_2OC\mathit{H}_2C\mathit{H}_2O$, 8 H), 4.24 (s, $C(O)CH_2O$, 4 H); IR (KBr) 2880 (CH_2), 1640 ($\nu_{C=O}$ of amide), 1450, 1105 (ν_{C-O}) cm^{-1}, etc. Anal. Calcd for **4a-1** (n = 6.7): C, 53.60; H, 8.16; N, 5.85. Found (very hygroscopic): C, 53.21; H, 8.09; N, 5.66. Polymerizations of the other salts were carried out similarly. The results are summarized in Table I. When the mixture of **1** and **2** was directly heated without isolating the salt, the molecular weight of the product was much lower.

The salt **3** is conveniently utilized for the copolycondensation with "nylon 6,6 salt". For example, a 1:1 mixture of **3b-1** with the latter (1.0 g each) was allowed to react[5] at 270 °C for 5 h in vacuo with a gentle stream of nitrogen introduced through a capillary. A pale yellowish copolymer was obtained in quantitative yield: mp 246 °C; η_{sp}/C = 1.81 (5.0 g/L in *m*-cresol at 30 °C); ^1H NMR (HCO_2H) δ 0.8 (m, $C(CH_2)C$), 1.9 (m, CH_2CO_2), 2.7 (m, $NC\mathit{H}_2$), 3.18 (s, OCH_2), 3.53 (s, OCH_2CO_2). In the polymer was detected no fraction soluble in either H_2O, methanol, or $CHCl_3$ (good solvents for poly(oxyethylene)). These data indicate that the product is a block copoly(amide–ether) consisting of the hard polyamide block and the soft poly(oxyethylene) block. A filament of this copolyamide was prepared by a melt-spinning technique and was drawn to four times its length at 50 °C. The filament obtained (diameter $\simeq 80 \times 10^{-6}$ m) showed an elastic flexibility. The following mechanical properties were found: maximum strength = 10 kg/mm^2, elongation at

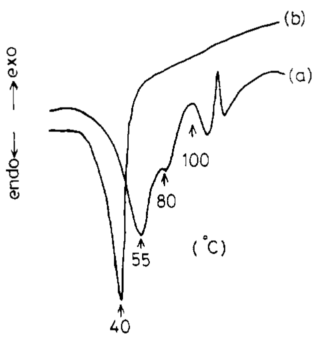

Figure 1. Observed DTA curves for (a) **3a-1** and (b) **3a-2** (20 °C/min).

Scheme I

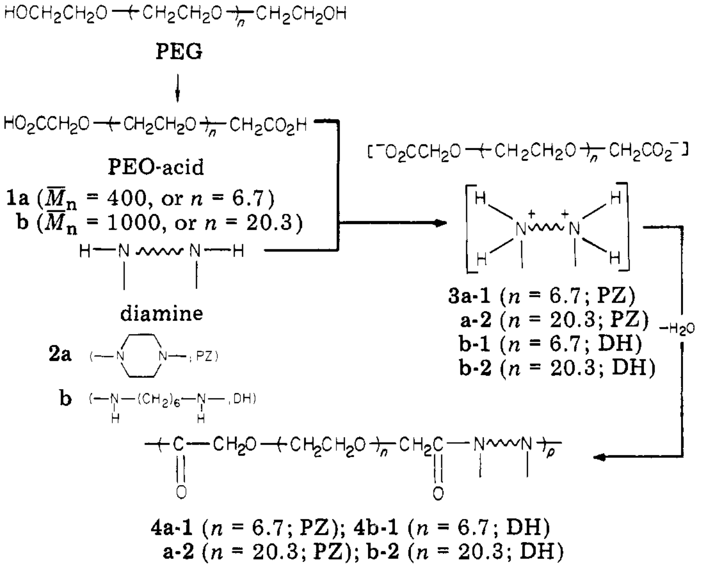

Table I
Thermal Polymerization[a] of the Salts of PEO-acid

salt	product polymer	η_{sp}/C[b]	N anal.	
			calcd	found
3a-1	**4a-1** (white wax)	0.141[c]	5.85	5.66
3a-2	**4a-2** (white solids, mp 32 °C)	0.259	2.59	2.18
3b-1	**4b-1** (pale yellow wax)	0.124	5.85	6.16
3b-2	**4b-2** (white solids, mp 29 °C)	0.310[d]	2.63	2.64

[a] At 200 °C for 6 h. The yields were quantitative. [b] At a concentration of 5.0 g/L in H_2O (30 °C). [c] A GPC analysis of this polymer indicated $\overline{M}_n$ = 13 000 with $\overline{M}_w/\overline{M}_n$ = 1.55. [d] GPC analysis: $\overline{M}_n$ = 20 000; $\overline{M}_w/\overline{M}_n$ = 1.76.

break = 150%, and Young's modulus = 7 kg/mm². We are now studying copolycondensations using other amine salts of PEO-acid.

Acknowledgment. We are indebted to both Nippon Shokubai Kagaku Kogyo Co. Ltd. (Osaka, Japan) and Kawaken Fein Chemicals Corp. (Tokyo, Japan) for the sample of PEO-acid.

References and Notes

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(3) M_n range = 380–420; η_{sp}/C = 0.030 (5.0 g/L in H_2O at 30 °C).
(4) M_n range = 950–1050; η_{sp}/C = 0.053 (5.0 g/L in H_2O at 30 °C).
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(6) The spectroscopic data were very similar to those of **3a-1**.
(7) After recrystallization, generally, the PEO components of the recrystallized parts may become narrower in molecular weight distribution than the parent one. Thus, the uncrystallized parts involve ones with rather wider molecular weight range, which may cause the difficulty in recrystallization.
(8) Spectroscopic and analytical data, being similar to those of **3a-1**, were obtained to support the structures of both **3b-1** and **3b-2**.

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Conformational Characterization of Silk Fibroin in Intact *Bombyx mori* and *Philosamia cynthia ricini* Silkworms by ^{13}C NMR Spectroscopy

We report here that the intact ^{13}C NMR approach has been successfully applied to the conformational characterization of silk protein, mainly silk fibroin, stored in the middle silk gland of silkworms before spinning. It has been confirmed that the conformation of silk fibroin in the solid state from *B. mori* depends strongly on the conditions of sample preparations: silk fibroin mildly dried at room temperature becomes the silk I type (loose helix); the silk II type (antiparallel β-sheet structure) appears as a more stable form in samples dried at higher temperature or under mechanical stress.[1] The intact NMR approach gives unique and novel information about the structure of the native protein in solution because the samples are free from any external forces. Here, the conformation of liquid silk stored in silk glands is characterized by a ^{13}C NMR spectroscopic comparison of intact *B. mori* with *P. c. ricini*,[2] whose amino acid composition is appreciably different.

Experimental Section. The ^{13}C NMR spectra of intact *B. mori* and *P. c. ricini* silkworms were observed with a JEOL FX-200 NMR spectrometer operating at 50 MHz.[3,4] The spectral width was 12000 Hz, and 8K data points were used. It was not necessary to employ sample spinning or magnetic field locking because of the high stability of the superconductive magnet. The ^{1}H nuclei were decoupled only during the sampling time of 0.34 s to avoid an increase of temperature in the sample tube. In the ^{13}C NMR measurements of the liquid silk in urea solution, complete ^{1}H decoupling was used. Chemical shifts are reported in ppm downfield from external Me_4Si.

Results and Discussion. Figure 1 shows the ^{13}C NMR spectra of the silk gland portion of the intact mature larvae of *B. mori* and *P. c. ricini* and of the abdomen of a *P. c. ricini* pupa. The peak assignments have been reported previously;[3] mobile components such as the silk protein, triglyceride, and α,β-trehalose in the silkworms give well-resolved spectra. It has been confirmed that the amino acid peaks are essentially due to the silk protein. This conclusion is based on measurements of the ^{13}C NMR spin–lattice relaxation time, T_1, using 180–τ–90° pulse sequences in intact silkworms. The T_1 values of the amino acid carbons in intact *B. mori* are considerably shorter than those of the corresponding free amino acids. For example, the NT_1 values of the α-carbons of the Gly, Ala, and Ser residues in the spectrum, where N is the number of hydrogen atoms directly attached to specified carbon atoms, are ca. 0.20 s and they are near the corresponding values

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