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Polyether-amides from the Condensation of ω-(*p*-Carboxyphenoxy)-alkanoic Acids with Aliphatic Diamines

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Polyether-amides were prepared by the polycondensation of ω-(*p*-carboxyphenoxy)alkanoic acids (CPAA) and such aliphatic diamines as ethylenediamine, hexamethylenediamine, and piperazine. The polymers with higher intrinsic viscosities and moderate melting temperatures (200—240°C) were obtained from CPAA and hexamethylenediamine. The polymers from both CPAA and ethylenediamine or piperazine generally have low intrinsic viscosities; the former melted at higher temperatures than did the polyether-amides with hexamethylenediamine, while the latter melted at lower ones.

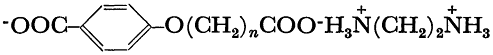
There are various types of polymers on the market in which polyamide, polyester, polyacrylonitrile, *etc.* are included. In addition, poly *p*-(2-hydroxyethoxy)benzoate, which can be classified as a type of polyether-ester, has been found to have some excellent characteristics as a fiber. Other polymers with an ether linkage in the main chain have been prepared from ω-(*p*-carboxyphenoxy)alkanoic acids by many authors. Izard[2] has prepared polyether-esters from ω-(*p*-carboxyphenoxy)alkanoic acids. Kawai and his co-worker[3] have prepared a polyether-ester from *p*-carboxyphenoxyacetic acid and ethylene glycol, and a polyanhydride from *p*-carboxyphenoxyacetic acid. The former melts at 90—93°C and has an intrinsic viscosity of 0.26 (in *m*-cresol at 30°C). Sofue and his co-worker[4] have reported resins prepared from ω,ω-bis(2-methoxy-4-carboxyphenoxy)alkanes and aliphatic diamines. They have inherent viscosities of more than 0.5 (0.5 g/100 ml of *m*-cresol, at 30°C) and melt at 160—230°C.

In connection with the synthesis of ω-(*p*-carboxyphenoxy)alkanoic acids, which we have already reported,[5] we attempted to prepare some polyether-amides by polycondensation from ω-(*p*-carboxyphenoxy)alkanoic acids and aliphatic diamines. They also have a phenyl nucleus and a phenyl-alkyl ether linkage and, in addition, have an amide linkage in the main chain in a repeating unit.

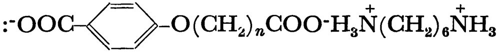
Results and Discussion

Nylon Salt. Nylon salts were prepared from ω-(*p*-carboxyphenoxy)alkanoic acids and aliphatic diamines, and the melting point of each salt was deter-

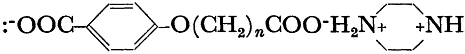
TABLE 1. MELTING POINT OF NYLON SALT

Type SEn:


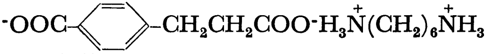
	SE1	SE2	SE3	SE4	SE5	SE6
Mp(°C)	173	—	169.5	154.5	—	139

Type SHn:


	SH1	SH2	SH3	SH4	SH5	SH6
Mp(°C)	228	181	189	189	197	190

Type SPn:


	SP1	SP2	SP3	SP4	SP5	SP6
Mp(°C)	258.5	188	—	174	—	181

SK1:


Mp (°C), 199

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[1] This paper was presented at the 24th (1971) and 26th (1972) Annual Meeting of the Chemical Society of Japan.

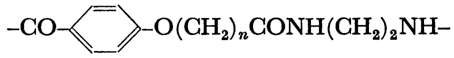
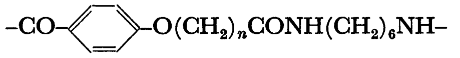
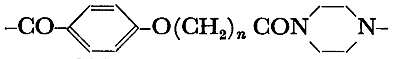
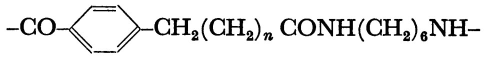
[2] E. F. Izard, *J. Polym. Sci.*, **8**, 503 (1952).

[3] W. Kawai and S. Tsutsumi, *Nippon Kagaku Zasshi*, **81**, 1167 (1960).

[4] H. Sofue, K. Kaneshige, and K. Murakami, Japan 22613 (1964).

[5] T. Kito, H. Minami, and I. Hirao, *Kygo Kagaku Zasshi*, **74**, 2313 (1971).

TABLE 2. POLYETHER-AMIDE

n	Polymer[a)]	T_m(°C)	T_g(°C)	T_d(°C)	[η][b)]	Appearance
		Type En: Repeating unit				
1	E1	294	—	293	0.12	yellow, opaque
3	E3	319	76	295	0.16	white, opaque
4	E4	235	53	268	0.15	white, opaque
5	E5	273	44	279	0.49	white, opaque
6	E6	219	48	319	0.29	yellow, translucent
		Type Hn: Repeating unit				
1	H1	236	55	364	0.38	yellow, opaque
2	H2	—	—	—	—	rubberlike polymer, transparent
3	H3	193	53	365	0.12	white, opaque
4	H4-1	201	60	368	0.72	white, opaque
4	H4-2[c)]	—	—	—	0.52	white, opaque
5	H5-1	217	58	409	0.70	pale yellow, opaque
5	H5-2[c)]	—	—	—	0.98 1.05	white, opaque
6	H6-1	199	54	403	0.88	white, opaque
6	H6-2[c)]	—	—	—	1.27	white, opaque
		Type Pn: Repeating unit				
1	P1	151	—	234	0.34	yellow, transparent
2	P2	—	—	—	—	yellow, viscous
3	P3	140	36	248	0.33	yellow, transparent
4	P4	130	40	296	0.31	yellow, transparent
5	P5	132	50	375	0.64	yellow, transparent
6	P6	113	41	328	0.46	yellow, transparent
		Type Kn: Repeating unit				
1	K1	263	—	393	0.49	white, opaque

a) Conditions of polymerization and of T_m, T_g, and T_d were described in the experimental.
b) In *m*-cresol at 25°C.
c) Polymerization was run in the absence of H_3PO_4.
d) Intrinsic viscosity of prepolymer.

mined by differential thermal analysis (DTA). The results are listed in Table 1. The melting point of 66-salt was determined by this method to be 198°C (lit,[6)] 196—197°C). Of these salts, however, all attempts to prepare the nylon salts of SE2, SE5, SP3, and SP5 (for the symbols of SEn, SHn, and SPn, see Table 1) were unsuccessful because their analytical values of nitrogen deviated largely from the calculated values. SHn and SPn melted at higher temperatures than did SEn, and SEn and SPn melted with a loss of water, while the two endothermic peaks, that is, the melting and dehydration peaks, of SHn and 66-salt were distinguishable.

Polymerization. Seventeen polyether-amides were prepared by polycondensation. The physical properties and other characteristics are summarized in Tables 2 and 3. The polymerization consists of two steps. From the first step, the prepolymer is obtained by heating nylon salt in an autoclave for several hours, while raising the temperature gradually. From the second-step, a higher polymer is obtained by heating the prepolymer while stirring it under reduced pressure (0.1—0.5 mmHg). By this method, such ploymers as E6, H1, H3, H4, H5, H6, P4, and P6 (for the symbols of En, Hn, and Pn, see Table 2) were prepared, but E1, E3, E4, H2, P1, and P2 were prepared only by the first-step polymerization because H2 was a rubber-like polymer and we failed to raise the viscosities of E1, E3, E4, P1, and P2 by the second step polymerization. The prepolymers of E5, P3, and P5 were prepared by mixing equivalent amounts of diacid and diamine in a sealed glass-tube and by then heating it according to the procedure described in the first step polymerization.

TABLE 3. SOLUBILITY OF POLYMER IN ORGANIC SOLVENTS

Solvent	Solubility[a)]	
	(±)	(−)
Acetic acid[b)]	E1, E4, E6, H1, H4, P4—P6	E3, E5, H3, H5, H6, P1
Benzyl alcohol	E4, E6, H1, H3—H6, P3—P6	E1, E3, E5, P1
Dimethyl-formamide	E6, P3, P5	E1, E3—E5, P1, P4, P6

a) (±); soluble at 100°C. (−); insoluble even at 100°C
b) P3 was soluble in acetic acid at room temperature.

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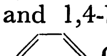
6) W. R. Sorenson and T. W. Campbell, "Kobunshi Gosei Zikkenho," Tokyo Kagakudozin, Tokyo (1963). p. 54.

(a) Melting Point (T_m): Although the Tm of Pn and Hn were evaluated by DTA as endothermic peaks, Pn showed no remarkable endothermic peak. Therefore, the Tm of Pn was determined as the point at which a sample reached a completely molten state.

The alternating character of the melting point associated with the methylene number was also observed in these polyether-amides, and it was found that the polymer containing an odd-numbered methylene group shows a higher melting point than that containing an even-numbered one. As is shown in Table 1, the melting points of nylon salt decreased in the order of SHn≒SPn>SEn, while, on the contrary, the melting points of polyether-amide decreased in the order of En>Hn>Pn. Especially, Pn melted at an appreciably lower temperature than did En and Hn, this being probably due to the structure of *N*-alkyl polyamide.

It is well known that the introduction of a phenyl nucleus into the main chain raises the melting point of the polymer, while the introduction of an ether linkage decreases it. For example, it has been reported that the polyamides from hexamethylenediamine and azelaic acid or sebacic acid melt at 205 and 209°C[7] respectively, while the polyamide from hexamethylenediamine and 1,4-bis(2-carboxyethyl)benzene, HOOC-CH_2CH_2--CH_2CH_2COOH, melts at 295°C,[7] the difference being about 85°C. On the other hand, the polyamide from hexamethylenediamine and 3-(*p*-carboxymethoxyphenyl)propionic acid softens at 218°C (vicat penetrometer).[8] For the sake of comparison, a nylon salt (SK1) and polyamide (K1) analogous to SH1 and H1 respectively were prepared by us from hexamethylenediamine and 3-(*p*-carboxyphenyl)propionic acid, the latter being a diacid with an ether linkage of *p*-carboxyphenoxyacetic acid replaced by a methylene group. As a result, it was proved that K1 melted 27°C higher than H1 in spite of the fact that SK1 melted 29°C lower than SH1. The melting points of SK1 and K1 are also listed in Tables 1 and 2. The lower melting point of K1 compared with that of polyamide from 1,4-bis(2-carboxyethyl)benzene may be due to the fact that 3-(*p*-carboxyphenyl)propionic acid is an unsymmetrical diacid.

(b) Glass Transition Temperature (T_g): The glass transition temperatures of En and Hn were generally higher than that of nylon 66 or 6, but there was no such remarkable regularity between the Tg and the methylene number as was seen in Tm.

(c) Decomposition Temperature (T_d): The Td of Hn lay in the range from 360 to 410°C, while those of En and Pn were below 360°C except for P5. Under similar conditions, the weight loss of nylon 66 occurred at 361°C, which is nearly comparable to the value of H1—H4. The difference between Td and Tm was large for Hn and Pn, but small for En. The small difference for En may cause a lower intrinsic viscosity, because the polymerization was carried out in a molten state.

(d) Intrinsic Viscosity: The intrinsic viscosities of most polymers were less than 0.5; only H4, H5, H6, and P5 showed high values. In addition, it was proved that phosphoric acid was not an effective catalyst for these polymerizations. Thus, high polymers which have intrinsic viscosities of more than 1.0 were prepared in the absence of phosphoric acid.

(e) Fiber-forming Property: En did not have a fiber-forming property. Hn and Pn formed fibers when a glass rod was inserted into the molten polymer and then drawn up at a moderate rate, but only weak fibers were formed from En. H2 and P2 were rubber like and viscous materials respectively, both incapable of being formed into fibers.

Experimental

*ω-(*p*-Carboxyphenoxy)alkanoic Acid.* It was prepared according to a procedure described before.[5]

*3-(*p*-Carboxyphenyl)propionic Acid.* *(a) 4-Carboxycinnamic Acid (I)*: A mixture of 104 g of pyridine, 2 g of piperidine, 25 g of malonic acid, and 19 g of methyl *p*-formylbenzoate was heated while being stirred for 2 hr on a water bath and was then refluxed for 30 min after 200 ml of water had been added. The reaction mixture was acidified with hydrochloric acid, and the resulting precipitate was collected on a filter and washed with water. Yield, 95%. Mp 207—208°C. Found: C, 63.90; H, 4.80%. Calcd for $C_{11}H_{11}O_4$: C, 64.06; H, 4.90%.

(b) Dimethyl Ester of (I): Twenty-six grams of (I) were esterified by refluxing for 8 hr with 200 ml of methanol and 4 ml of sulfuric acid. Yield 82%. Mp 124—124.5°C (AcOMe); lit,[9] 125.5—126.5°C. Found: C, 65.20; H, 5.48%. Calcd for $C_{12}H_{12}O_4$: C, 65.44; H, 5.50%.

*(c) Methyl 3-(*p*-Methoxycarbonylphenyl)propionate (II)*: In 150 ml of methyl acetate, a 2.5 g portion of the methyl ester of (I) was dissolved. Palladium charcoal (containing 5% of palladium, 0.15 g) was added, and the mixture was hydrogenated between 50—60°C for 4 hr (the initial pressure of hydrogen was 20 kg/cm^2). Yield 87%. Mp 27—28°C (aq. EtOH); lit,[10] 29—31°C (hexane). Found: C, 64.55; H, 6.21%. Calcd for $C_{12}H_{14}O_4$: C, 64.84; H, 6.36%. The IR absorption at 1644 cm^{-1} which was observed in the methyl ester of (I) disappered.

*(d) 3-(*p*-Carboxyphenyl)propionic Acid*: A mixture of 15 g of (II) and 540 ml of 5% aq. sodium hydroxide was refluxed for 2 hr. The mixture was then acidified with hydrochloric acid, and the precipitate was collected and washed with water. Yield 90%. Sublimes at about 280°C (water); lit,[10] melts at 286—289°C (AcOH). Found: C, 61.62; H, 5.16%. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19%.

Nylon Salt. *(a) SE1, SH1, and SP1*: Nylon salt was precipitated from an aqueous solution containing *p*-carboxyphenoxyacetic acid and an equivalent amount of diamine by dilution with methanol, and was then collected. Then, the salt was washed with ether and dried in a vacuum.

(b) SE3, SE4, SE6, SH2, SH3, SH4, SH6, SP2, SP6, and SK1: A solution of diamine in ethyl alcohol was added, drop by drop, to a boiling solution of an equivalent amount of diacid in ethyl alcohol. The salt was then filtered and recrystallized from aqueous methanol.

(c) SH5: This was prepared by the method (b), but the ethyl alcohol was replaced with *n*-propyl alcohol.

Polymerization. *(a) First-step Polymerization*: A mixture

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[7] Y. Iwakura, *Kobunshi*, **11**, 963 (1962).

[8] P. R. Thomas and G. J. Tyler, Brit. 804225 (1956).

[9] R. F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968).

[10] W. S. Emerson and R. A. Heimsch, *ibid.*, **72**, 5152 (1950).

of 10 g of nylon salt, 0.25 g of phosphoric acid, and 1.0 g of water was charged in a glass tube open at the top, and then the glass tube was placed in an autoclave. After the air had been replaced by nitrogen, the salt was heated to afford the prepolymer. The heating conditions were as follows: PE3; 150—200°C (8 hr), 200(12). PE4; ∼150(3), ∼180(3), ∼200(2), 200(10), ∼230(3). PE6; ∼160(3), 160(3), ∼250(2), 250(1). PH1; 150—200(2.5), ∼250(5). PH2; ∼150(2), ∼180(1.5), ∼200(2), 200(2). PH3; 150—180(2.5), ∼200(4.5). PH4—1; 150—200(5), ∼230(5). PH4—2(heated in the absence of phosphoric acid); ∼180 (3), ∼200(1.5), ∼230(2), ∼250(1), 250(2). PH5—1, PH5—2(see PH4—2) and PH6—1; 150—180(3), ∼200(2), ∼230(3.5). PH6—2(see PH4—2); 150—180(2.5), ∼200 (1.5), ∼250(1), 250(2). PP1; 180—200(4), ∼230(6). PP2; 150—180(5). PP4; 150—180(2.5), ∼200(5), PP6; 150—180(2), ∼200(5.5). PK1; ∼150(1), ∼180(1.5), ∼200(1.5), 200(1.5), ∼230(3), ∼250(1), 250(2). The first letter, P, in PEn, PHn, PPn, or PK1 indicates the "Prepolymer" of En, Hn, Pn, or K1.

(b) First-step Polymerization in a Sealed Tube: When nylon salt could not be prepared, a diamine and an equivalent amount of a diacid were sealed in a glass tube, and the polymerization was run according to the procedure described in (a). The heating conditions were as follows: PE5; 150—250°C (9hr), 250(10). PP3; 150—180(3.5), ∼200(4.5). PP5; 150—180(2.5), ∼200(3), ∼250(5). However, the prepolymer of E1 was obtained by heating SE1 in a sealed tube as follows: 150—200(6), ∼250(5), 250(12).

(c) Second-step Polymerization: The prepolymer was placed in a round-bottomed flask equipped with a side arm, which connected to a vacuum pump; the flask was then equipped with a mechanical air-tight stirrer and gradually brought to a high vacuum (0.5—0.1 mmHg) with heating and stirring. The heating conditions were as follows: E6; 250—265°C(6 hr). H1; 190—240(5.5). H3; 220—230(1.5). H4-1(prepared from PH4-1); 210—260(7). H4-2(from PH4-2); 220—250(5). H5-1(from PH5-1); 240—250(6). H5-2(from PH 5-2); 250—260(1). H6-1(from PH6-1); 220—270(2). H6-2 (from PH6-2); 220—270(2). P3; 200—240(5). P4; 200—230(6). P5; 210—280(6). P6; 200—260(6.5).

Melting Point (T_m) and Decomposition Temperature (T_d). The Tm was determined by observing the point at which the sample reached a completely molten state (for Pn) or by DTA (for En and Hn) (Rigaku Denki, cat. No. 8001MS; heating rate, 10°C/min). In the latter method, the Tm was defined as the intersecting point of a base line and a tangent line of the peak on the lower-temperature side. The Td was measured by TGA (Cho Keiryoki, $TRDA_1$-L; heating rate, 2.8°C/min in N_2) and was defined as the temperature at which the weight loss began to occur.

Glass Transition Temperature (T_g). The Tg was measured by means of a dilatometer.

Intrinsic Viscosity. The specific viscosity was measured in *m*-cresol at 25°C with an Ubbelohde viscometer, plotted *versus* the concentration, and extrapolated to zero.

Solubility in a Solvent. A mixture of 0.1 g of a sample and 3 ml of a solvent was allowed to stand for 24 hr at room temperature, with occasional shaking. If a clear solution was obtained by this treatment, the plus sign (+) was given. When some solid mass remained insoluble in a solution, the mixture was kept at about 100°C for 10 min with shaking; the plus-minus sign (±) was given when the solution became clear, and the minus sign (−), when some solid mass still remained insoluble.