BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47 (3), 783—784 (1974)

The Use of Hydroxybenzoic Acids to Polymers. II. Polyether-amides Obtained from the Interfacial Polycondensation of *p*-Carboxyphenoxyacetic Acid Dichloride with Aliphatic Diamines

Ichiro HIRAO, Taketoshi KITO, Tsutomu FUJIMOTO, and Hideo YOSHIHARA
Laboratory of Industrial Chemistry, Department of Chemical Engineering, Kyushu Institute of Technology, Tobata-ku, Kitakyushu-shi, 804

(Received September 10, 1973)

Synopsis. Five polyether-amides were prepared from the title reaction. The physical properties ([η], T_m, T_g, and decomp. temp.) and the effects of the reaction conditions were examined. These polymers were superior in some physical properties to the polymers obtained from the melt polycondensation.

We have previously reported[1] on polyether-amides obtained from the condensation of ω-(*p*-carboxyphenoxy)alkanoic acids (CPAA) with aliphatic diamines, in which three types of polymers were included in the variety of diamines; ethylenediamine, hexamethylenediamine, and piperazine. The polymers prepared from CPAA and hexamethylenediamine, Hm, showed higher intrinsic viscosities and moderate melting points (200—240 °C), but the polymer prepared from *p*-carboxyphenoxyacetic acid (CPAC) and hexamethylenediamine, Hl, showed a low intrinsic viscosity (0.38). Similarly, other polymers prepared from CPAC and ethylenediamine, El, or piperazine, Pl, also showed low intrinsic viscosities. In the second polymer, El, it was concluded that the small difference between the decomposition temperature (293 °C) and the melting point (294 °C) may cause a low intrinsic viscosity because the polymerization was carried out in a molten state. However, in the first polymer, Hl, we found that the polymer set to gel or was partially insoluble in *m*-cresol when it was heated at an elevated temperature (higher than 250 °C). This may be caused by the active methylene group placed between the oxygen atom and the carboxyl group of CPAC. A similar reason may be deduced as one of the causes of the intrinsic viscosity of El being low.

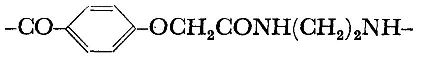
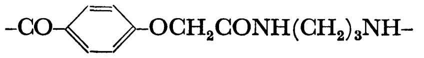
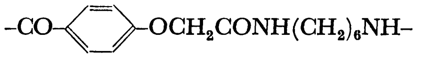
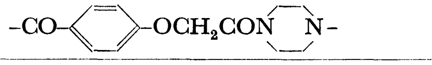
Therefore, we investigated the interfacial polymerization of CPAC dichloride and aliphatic diamines.

Results and Discussion

White polyether-amides were prepared by the interfacial polymerization of CPAC dichloride and such diamines as ethylenediamine, propylenediamine, 1,3-diaminopropane, hexamethylenediamine, or piperazine, whose polymers will be abbrebiated here as Ed, P-2, P-3, Hm, and Pz (the Ed, Hm, and Pz are essentially equal to El, Hl, and Pl respectively, but the latter were obtained by the melt polycondensation). The melting point (T_m), the glass transition temperature (T_g) and the intrinsic viscosity ([η]) of five polyether-amides are summarized in Table 1. These polymers were superior in some physical properties to the polyether-amides obtained by the melt polycondensation. For example, the intrinsic viscosity of Ed was 0.68; this value is 0.56 higher than that of the intrinsic viscosity of El. Ed did not melt on a hot plate below 325 °C. The thermal analysis of Ed showed that the weight loss of Ed began at about 300 °C; no endothermic peak was detected below that temperature. The *T*m of Pz was determined only by observing the temperature at which melting was complete, because Pz showed no endothermic peak in the DTA analysis.

The reaction conditions (the effects of the volume of tetrachloroethylene and of the molar ratio of diamine to CPAC dichloride) were also examined; the results are summarized in Table 2. The relationship between the diamine partition coefficient and the intrinsic

TABLE 1. POLYETHER-AMIDES

Repeating unit		Diamine/Dichloride[a] (mol/mol)	[η]	T_m (°C)	T_{m2}[b] (°C)	T_{m3}[c] (°C)	T_d[d] (°C)	T_g (°C)	Yield (%)
	(Ed)	1.1	0.68	>325	—	294 (El)	324	—	92.3
	(P-2)	1.1	0.56	263.5—264.5	256	—	318	58	52.3
	(P-3)	1.1	0.96	242—246	217	—	—	—	86.9
	(Hm)	1.1	0.90	239—240	242	236 (Hl)	370	50—52	82.7
	(Pz)	1.03	0.39	188—192	—	151 (Pl)	316	—	89.1

a) *p*-Carboxyphenoxyacetic acid dichloride. b) Melting points estimated by DTA. c) Melting points of polyether-amides obtained by the melt polycondensation (see Ref. 1). d) Temperature at which 10% weight loss occurs. T_d of nylon 66: 404 °C.

TABLE 2. EFFECTS OF THE CONCENTRATION OF CPAC DICHLORIDE AND THE MOLAR RATIO[a)]

Aqueous layer		Organic layer		HMDA	
HMDA[c)] (mol)	NaOH (mol)	Dichloride[d)] (mol)	TCE[e)] (ml)	Dichloride (mol/mol)	[η]
0.02	0.04	0.018	20	1.11	0.58
0.02	0.04	0.018	50	1.11	0.68
0.02	0.04	0.018	100	1.11	0.78
0.02	0.04	0.018	150	1.11	0.80
0.02	0.04	0.018	200	1.11	0.82
0.02	0.004	0.002	150	10	0.80
0.02	0.008	0.004	150	5	0.92
0.02	0.020	0.010	150	2	0.87
0.02	0.040	0.020	150	1	0.84
0.02	0.080	0.040	150	0.5	0.25
0.02	0.200	0.100	150	0.2	0.06

a) A series of polymerization (the first five and the last six) was carried out using the same reagents. b) Total volume is 300 ml, containing ice. c) Hexamethylenediamine. d) See Table 1. e) Tetrachloroethylene.

TABLE 3. EFFECT OF THE DIAMINE PARTITION COEFFICIENT ON THE INTRINSIC VISCOSITY OF H_m[a)]

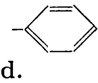
Organic solvent	Diamine partition coefficient K[b)]	[η]
Carbon tetrachloride	66.0	1.07
Tetrachloroethylene	43.7	0.91
1,2-Dichloroethane	13.1	0.85
Chloroform	1.03	0.54

a) H_m: See Table 1. b) K is the equilibrium partition coefficient at 25 °C for hexamethylenediamine ($C_{H_2O}/C_{solvent}$).

viscosity is shown in Table 3.

Morgan and Kwolek[2)] said that the polyamidation takes place near the interface in the organic phase. The results listed in Tables 2 and 3 can best be explained on the basis of their idea. When the polymer terminates at the chlorocarbonyl group, it reacts with the diamine or it is hydrolyzed by water; the latter case leads to the termination of the polymerization. Therefore, the amino group is desirable as the polymer-end; that is, a higher diamine/CPAC dichloride ratio may be favorable so long as the transfer rate of the diamine from the aqueous layer to the organic layer is not as fast as the reaction rate of diamine and CPAC dichloride. The low concentration of CPAC dichloride is also favorable.

The following results were obtained by Morgan and Kwolek;[2,3)] In the unstirred polymerization, a solvent which extracts diamine strongly, such as chloroform, gives a polymer with a higher intrinsic viscosity, and the optimum reactant diamine/dichloride ratio at which the highest polymer is obtained shifts to a lower value. On the contrary, in the stirred polymerization, the intrinsic viscosities in the optimum reactant ratio are nearly equal when the solvent is changed. In this paper, the polymerization was carried out in four solvents, with the ratio of diamine/dichloride kept at a constant value (1.11). As a result, the intrinsic viscosity increased with an increase in the diamine partition coefficient.

CPAA, unlike CPAC, was not chlorinated by a similar method, so other polyether-amides with a repeating unit of --O(CH$_2$)$_n$CONHRNH-(n≧2) were not obtained.

Experimental

p-Carboxyphenoxyacetic Acid Dichloride. A mixture of 58.9 g (0.3 mol) of *p*-carboxyphenoxyacetic acid (CPAC) and 107 g of (0.9 mol) thionyl chloride was refluxed for 5 hr. After an excess amount of thionyl chloride had been distilled off, the CPAC dichloride was distilled under a vacuum. Distillation was then repeated two times. bp 164—165 °C /0.9 mmHg (lit,[4)] bp 107—108 °C/0.08 mmHg) Yield, 95.0%.

Interfacial Polycondensation. A typical example will be shown as follows. A mixture of 0.02 mol of diamine, 0.04 mol of sodium hydroxide, and 60 g of ice was diluted with water to 300 ml. The aqueous solution was placed in a home-mixer (Matsushita Electric, type MX-83). While the solution was being stirred vigorously, a solution of 0.02 mol of CPAC dichloride in 150 ml of tetrachloroethylene was prepared and then poured rapidly into the aqueous solution. After 10 min, the resulting polymer was collected on a glass filter, washed with a sufficient amount of hot water, and dried in a vacuum.

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.

Melting Point. The melting point was determined by observing the temperature at which the sample on a hot plate reached a completely molten state (T_m) or by DTA (T_{m2}).

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

Decomposition Temperature (T_d). The T_d was measured by TGA (Cho Keiryoki, TRDA$_1$-L; heating rate, 2.8 °C/min in N$_2$).

Diamine Partition Coefficient. Conditions: hexamethylenediamine, 0.002 mol; sodium hydroxide, 0.004 mol; water, 60 ml; organic solvent, 30 ml; temperature, 25 °C.

References

1) Part I of this series: T. Kito, T. Fujimoto, R. Mikami, and I. Hirao, This Bulletin, **46**, 209 (1973).

2) P. W. Morgan and S. L. Kwolek, *J. Polym. Sci.*, **62**, 33 (1962).

3) P. W. Morgan and S. L. Kwolek, *ibid.*, **40**, 299 (1959).

4) V. Rosnati, *Chem. Abstr.*, **52**, 7216g (1958).