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# Poly-β-Amino Acids. I. The Preparation of Phenyl Substituted β-Amino Acid Polymers

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α-Phenyl-, β-phenyl-, and α,β-diphenyl-β-aminopropionic acid were synthesized. Their polymers were obtained in good yields when the *p*-nitrophenyl esters of β-amino acids were polymerized at 60°C. The ethyl esters gave low-molecular-weight polymers in poor yields at 150°C *in vacuo*. By the thermal polycondensation of β-amino acids themselves at 250°C, polymers were not obtained, but the corresponding cinnamic acid derivatives were obtained by the intramolecular β-elimination reaction. Poly(α-phenyl-β-amino acid), and poly(β-phenyl-β-amino acid) were soluble in trifluoroacetic acid, and chloroform containing a small amount of dichloroacetic acid. On the other hand, poly(α,β-diphenyl-β-amino acid) was soluble only in conc. sulfuric acid, while it was insoluble in usual organic solvents. The DP of poly(β-phenyl-β-amino acid) was about 18. None of the polymers showed any melting point below 300°C.

Many reports and discussions have been published on the syntheses and the properties of poly-α-amino acids. On the other hand, only a few investigations have been reported on poly-β-amino acids, which have only one additional methylene group per residue compared with poly-α-amino acids and which may be expected to have properties as interesting as those of the α-isomers.

Poly(β-alanine) was obtained by Noguchi and Hayakawa[1] *via* the *N*-carbothiophenyl derivative of the amino acid. Breslow and his co-workers[2] prepared the polymer by the polymerization of acrylamide with base catalysts, a process which is called a proton transfer polymerization. Birkofer and Modic[3] also polymerized β-methyl-β-alanine through its *N*-carboxyanhydride. Poly(α,α-dimethyl-β-alanine) was obtained by the thermal polycondensation of β-amino pivalic acid.[4] These polymers seem not to have large molecular weights. Recently, Bestian[5] has obtained high-molecular-weight polymers by the ring-opening polymerization of some substituted β-lactams.

In order to investigate the properties of the polymer, it is necessary that the polymer have a high molecular weight and good solubilities in suitable organic solvents, the solubilities of which may be expected to be brought by a proper substituent in the monomeric unit. In this work, the syntheses of the polymers of α-, β-phenyl-, and α,β-diphenyl-β-aminopropionic acid were investigated. Thermal polycondensations were attempted on the amino acids themselves and their ethyl esters, the latter of which gave only small amounts of the polymers. The *p*-nitrophenyl esters gave the poly-β-amino acids in good yields. The ester is known as an active ester reagent in peptide syntheses. Poly(α-phenyl-β-amino acid) and poly(β-phenyl-β-amino acid) were soluble in trifluoroacetic acid, dichloroacetic acid, and chloroform containing a small amount of dichloroacetic acid. Poly(α,β-diphenyl-β-amino acid) was soluble only in conc. sulfuric acid, while it was insoluble in usual organic solvents. None of the polymers showed any melting point below 300°C.

## Experimental and Results

**Syntheses of β-Amino Acids.** The amino acids were prepared according to the methods of Rodinow and his co-workers[6] and of Steiger.[7] All are racemic forms.

**α-Phenyl-β-aminopropionic Acid (α-PA).** A hot solution of hydroxylamine hydrochloride (11.0 g) in 100 m*l* of water was added, in one portion, to a solution of sodium ethoxide prepared from 3.5 g of sodium

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[1] J. Noguchi and T. Hayakawa, *J. Amer. Chem. Soc.*, **76**, 2846 (1954).

[2] D. S. Breslow, G. E. Hulse and A. S. Matlack, *ibid.*, **79**, 3760 (1957).

[3] L. Birkofer and R. Modic, *Ann. Chem.*, **628**, 162 (1959).

[4] J. Linkoln, U.S. 2500317 (1946).

[5] H. Bestian, *Angew. Chem.*, **80**, 304 (1968).

[6] W. M. Rodinow and W. E. Th. Malewinskaja, *Ber.*, **59**, 2952 (1926).

[7] R. E. Steiger, "Organic Syntheses," Coll. Vol. III, p. 91 (1955).

and 105 m*l* of ethanol. The sodium chloride thus precipitated was filtered out; ethyl atropate (11.5 g) was added to the resulting solution, and the resulting mixture was boiled under reflux for 1 day. White precipitates were filtered out, washed with absolute ethanol, and recrystallized from water and ethanol.

**β-Phenyl-β-aminopropionic Acid (β-PA).** Benzaldehyde (36.9 g) and malonic acid (40.7 g) were added to 120 m*l* of absolute ethanol saturated with dry ammonia, after which the mixture was boiled on a steam bath for 8 hr. After cooling, white precipitates were collected by filtration and recrystallized from water and ethanol.

***α,β*-Diphenyl-*β*-aminopropionic Acid (*α,β*-DPA).** α-Phenylcinnamic acid (78.4 g) was added to a solution of hydroxylamine prepared from its hydrochloride (49.0 g) in 35 m*l* of water and sodium ethoxide (0.7 mol) in 350 m*l* of absolute alcohol, and the mixture was boiled under reflux for 8 hr. White precipitates were collected and recrystallized from water and ethanol.

The yields and the analytical data of the amino acids are listed in Table 1.

TABLE 1. β-AMINO ACIDS $H_2NCHR_1CHR_2COOH$

| $R_1$ | $R_2$ | Mp (dec) °C | Yield % | Found (Calcd) | | |
|---|---|---|---|---|---|---|
| | | | | C% | H% | N% |
| H | $C_6H_5$ | 228 | 31.6 | 65.20 | 6.67 | 8.28 |
| | | | | (65.44 | 6.71 | 8.48) |
| $C_6H_5$ | H | 215 | 67.8 | 65.39 | 6.68 | 8.67 |
| | | | | (65.44 | 6.71 | 8.48) |
| $C_6H_5$ | $C_6H_5$ | 205 | 30.0 | 74.43 | 6.29 | 5.69 |
| | | | | (74.65 | 6.28 | 5.81) |

**Ethyl Esters of β-Amino Acids.** β-Amino acid was suspended in 300 m*l* of dry ethanol, after which dry hydrogen chloride was passed through the mixture until it became homogeneous. The solution was evaporated *in vacuo* at 60°C. Dry ethanol (100 m*l*) was added to the residue and evaporated *in vacuo*. This operation was repeated twice, and then the residue was allowed to stand in a refrigerator overnight. The crude product was recrystallized from ethanol and ether. The results are shown in Table 2.

Into the ethyl ester hydrochloride covered with ether, a 150 m*l* portion of a saturated aqueous solution of sodium carbonate was stirred. The ether layer was separated and the aqueous layer was extracted with ether. The ether solutions were combined and the solvent was distilled off. The vacuum distillation of the residue gave the ethyl esters of amino acid, except for the ester of α,β-DPA which was crystalline and was purified by recrystallization from ethanol and water to give colorless needles. The results are listed in Table 3.

***N*-Carbobenzyloxy-β-amino Acids.** β-Amino acid (30 mmol) was dissolved in 33 m*l* of a 1 N aqueous sodium hydroxide solution. The solution was cooled to −3—0°C, and then 33 m*l* of 2 N aqueous sodium hydroxide solution and carbobenzoxy chloride (6.1 g) was vigorously stirred into it alternately, portion by portion. After the addition, stirring was continued for 2 hr at 0°C. Then, the solution was acidified to pH 3 with 15 m*l* of 6 N hydrochloric acid. The precipitates thus formed were extracted with ether. The extract was dried with anhydrous sodium sulfate, and the ether was evaporated. The residual carbobenzyloxyamino acid was recrystallized from ethanol and water. The results are shown in Table 4.

TABLE 2. β-AMINO ACID ETHYL ESTER HYDROCHLORIDES
$HCl \cdot H_2NCHR_1CHR_2COOC_2H_5$

| $R_1$ | $R_2$ | Mp °C | Yield % | Found (Calcd) | | | |
|---|---|---|---|---|---|---|---|
| | | | | C% | H% | N% | Cl% |
| H | $C_6H_5$ | 162 —163 | 90.2 | 57.50 | 6.97 | 5.87 | 15.68 |
| | | | | (57.51 | 7.02 | 6.10 | 15.43) |
| $C_6H_5$ | H | 138.5—139.5 | 92.0 | 57.91 | 7.06 | 6.16 | 15.63 |
| | | | | (57.51 | 7.02 | 6.10 | 15.43) |
| $C_6H_5$ | $C_6H_5$ | 194 —197 | 81.5 | 66.89 | 6.67 | 4.45 | 11.59 |
| | | | | (66.79 | 6.60 | 4.58 | 11.59) |

TABLE 3. β-AMINO ACID ETHYL ESTERS
$H_2NCHR_1CHR_2COOC_2H_5$

| $R_1$ | $R_2$ | Bp (°C/mmHg) [Mp (°C)] | Yield[a] % | Found (Calcd) | | |
|---|---|---|---|---|---|---|
| | | | | C% | H% | N% |
| H | $C_6H_5$ | 96— 96.5/0.5 | 56.8 | 68.35 | 7.87 | 7.23 |
| | | | | (68.37 | 7.92 | 7.25) |
| $C_6H_5$ | H | 100—101.5/1.0 | 60.0 | 68.32 | 7.82 | 7.22 |
| | | | | (68.37 | 7.92 | 7.25) |
| $C_6H_5$ | $C_6H_5$ | [65—67.5] | 73.4 | 76.16 | 7.10 | 5.06 |
| | | | | (75.79 | 7.12 | 5.24) |

a) Based on amino acid.

Table 4. *N*-Carbobenzyloxyamino acids
$C_6H_5CH_2OCONHCHR_1CHR_2COOH$

| $R_1$ | $R_2$ | Mp °C | Yield % | Found (Calcd) C% | H% | N% |
|---|---|---|---|---|---|---|
| H | $C_6H_5$ | 122—123 | 92.9 | 68.10 | 5.68 | 4.71 |
| | | | | (68.21 | 5.72 | 4.68) |
| $C_6H_5$ | H | 124 | 84.9 | 68.17 | 5.85 | 4.71 |
| | | | | (68.21 | 5.72 | 4.68) |
| $C_6H_5$ | $C_6H_5$ | 184—186 | 60.2 | 73.38 | 5.68 | 3.75 |
| | | | | (73.58 | 5.64 | 3.73) |

***p*-Nitrophenyl Esters of *N*-Carbobenzyloxyamino Acids.** *N*-Carbobenzyloxy-β-amino acid (20 mmol) and *p*-nitrophenol (2.8 g) were dissolved in 90 m*l* of anhydrous ethyl acetate. Into the solution, dicyclohexylcarbodiimide (6.0 g) was stirred at room temperature. After stirring for 20 hr, the precipitated dicyclohexyl urea (4.4 g) was filtered and the filtrate concentrated at reduced pressure. The residue was recrystallized from ethyl acetate and *n*-hexane to give the *p*-nitrophenyl ester of *N*-carbobenzyloxyamino acid. The results are shown in Table 5.

***p*-Nitrophenyl Ester Hydrobromides of β-Amino Acids.** The *p*-nitrophenyl ester of *N*-carbobenzyloxyamino acid (27 mmol) was dissolved in a saturated solution of hydrogen bromide in 33 m*l* of acetic acid at room temperature. After the solution had stood for 1 hr, 200 m*l* of ether were added; the solution was then kept overnight in a refrigerator. The precipitates thus formed were filtered and recrystallized from ethanol and ether. The results are listed in Table 6.

**Thermal Polymerization of β-Amino Acids.** β-Amino acid (*ca.* 1 g) was placed in a glass ampoule and the ampoule was sealed *in vacuo*. After the ampoule had been heated at 250°C for 24 hr, 10 m*l* of ethanol was added and an insoluble solid was filtered out. The filtrate was then concentrated under reduced pressure, and the residue was recrystallized from ethanol and water. Table 7 shows the results of the thermal polycondensations of the β-amino acids. From α-PA and β-PA, polymeric materials were obtained as solid materials insoluble in ethanol, but the yields were too low for the characteristics to be investigated. The amino acid, α,β-DPA, gave no products insoluble in ethanol. The ethanol-soluble materials were found to be phenyl-substituted acrylic acids, *i. e.*, cinnamic acid from β-PA, and α-phenyl cinnamic acid from α,β-DPA. The material obtained from α-PA was found from the IR spectrum to contain the polymer of atropic acid.

**Thermal Polycondensation of Ethyl Esters of β-Amino Acids.** The ethyl ester (1—2 g) was placed in an ampoule and sealed *in vacuo*. After it had then been heated at 150°C for 10 days, 20 m*l* of ethanol was added. An insoluble solid was separated by filtration, and the filtrate was concentrated *in vacuo*. The residue was extracted with 50 m*l* of ether, and an ether-insoluble solid was filtered out. When the ether solution was then concentrated, only a syrupy residue was obtained. The results are shown in Table 8. The thermal polycondensations of the ethyl esters gave the ethanol-insoluble polymers in appreciable yields not only *in vacuo*, but also at an ordinary nitrogen pressure. These polymers were insoluble in water, ethanol, acetone, dimethylformamide, and dimethyl sulfoxide, partially soluble in formic acid and *m*-cresol, and soluble in dichloroacetic acid. From the ethanol-soluble parts, lower-molecular-weight polymers were obtained as frac-

Table 6. β-Amino acid *p*-nitrophenyl ester hydrobromides
$HBr\cdot H_2NCHR_1CHR_2COOC_6H_4NO_2\,(p)$

| $R_1$ | $R_2$ | Mp (dec) °C | Yield % | Found (Calcd) C% | H% | N% | Br% |
|---|---|---|---|---|---|---|---|
| H | $C_6H_5$ | 138 | 96.0 | 49.20 | 4.50 | 7.34 | 21.68 |
| | | | | (49.06 | 4.12 | 7.63 | 21.76) |
| $C_6H_5$ | H | 175.5 | 72.3 | 49.08 | 4.28 | 7.74 | 21.60 |
| | | | | (49.06 | 4.12 | 7.63 | 21.76) |
| $C_6H_5$ | $C_6H_5$ | 199 | 79.6 | 56.47 | 4.38 | 6.25 | 18.17 |
| | | | | (56.89 | 4.32 | 6.30 | 18.03) |

Table 7. Thermal polycondensation of β-amino acids
Temp. 250°C, Time 2 hr, Pressure 7mmHg

| Amino Acid | mg | EtOH Insol. mg | Yield % | EtOH Sol. mg | Yield % |
|---|---|---|---|---|---|
| α-PA | 256 | 3.5 | 1.3 | — | — |
| β-PA | 836 | 6.0 | 0.8 | 664 | 86.8$^{a)}$ |
| α,β-DPA | 1020 | 0 | 0 | 260 | 25.0$^{b)}$ |

a) Cinnamic acid
b) α-Phenyl cinnamic acid

Table 5. *N*-Carbobenzyloxyamino acid *p*-nitrophenyl esters
$C_6H_5CH_2OCO\text{-}NHCHR_1CHR_2\text{-}COOC_6H_4NO_2(p)$

| $R_1$ | $R_2$ | Mp °C | Yield % | Found (Calcd) C% | H% | N% |
|---|---|---|---|---|---|---|
| H | $C_6H_5$ | 74 — 76 | 72.8 | 65.65 | 4.82 | 6.65 |
| | | | | (65.70 | 4.80 | 6.66) |
| $C_6H_5$ | H | 116.5—117.5 | 77.6 | 65.98 | 4.84 | 6.62 |
| | | | | (65.70 | 4.80 | 6.66) |
| $C_6H_5$ | $C_6H_5$ | 144 —146 | 55.0 | 69.73 | 4.93 | 5.56 |
| | | | | (70.15 | 4.87 | 5.64) |

TABLE 8. THERMAL POLYMERIZATION OF $\beta$-AMINO ACID ETHYL ESTERS
Temp. 150°C, Time 10 days, pressure 7mmHg

| Et Ester | | Polymer | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | EtOH Insol. | Anal.[a] | | | Ether Insol. | | | |
| | g | % | C% | H% | N% | % | C% | H% | N% |
| $\alpha$-PA-Et | 1.345 | 1.6 | — | — | — | 3.2 | — | — | — |
| $\beta$-PA-Et | 1.137[b] | 3.1 | 73.1 | 6.4 | 7.8 | 17.3 | 71.4 | 6.5 | 7.3 |
| | 1.166 | 8.2 | 73.1 | 6.3 | 8.0 | 22.3 | 72.4 | 6.5 | 7.4 |
| $\alpha,\beta$-DPA-Et | 2.000 | 1.4 | 78.9 | 5.2 | 9.1 | 7.4 | — | — | — |

a) Calcd for $C_6H_5CH{=}CHCO[NHCH(C_6H_5)CH_2CO]OC_2H_5$
$n=6$ C, 73.7; H, 6.3; N, 7.9%
$n=4$ C, 73.8; H, 6.3; N, 7.3%
Calcd for $H[NHCH(C_6H_5)CH(C_6H_5)CO]_3NH_2$
C, 78.7; H, 6.1; N, 8.2%
b) Pressure 760 mmHg

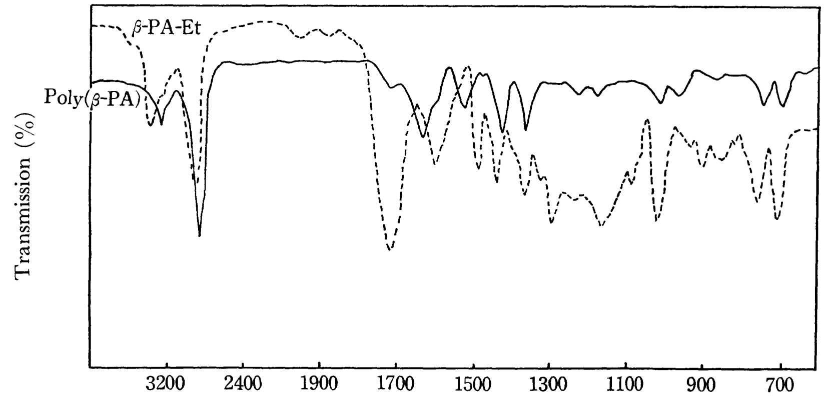
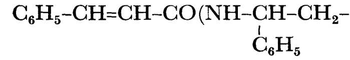


Fig. 1. Infrared spectra of ethyl $\beta$-phenyl-$\beta$-aminopropionate and polymer. The spectra were taken with JASCO IR-S spectrophotometer with nujol mulls method.

tions insoluble in ether. Figure 1 shows the IR spectra of the monomeric ethyl ester of $\beta$-PA and the polymer which was insoluble in ethanol. In the spectrum of the polymer, there are absorptions of polyamide (3240, 1650 and 1530 cm$^{-1}$), the free ester (1730 cm$^{-1}$), and $\alpha,\beta$-disubstituted C=C double bond (1620 and 960 cm$^{-1}$). From these absorptions, the probable structure of the polymer may be presented as follows:



$$C_6H_5\text{-}CH{=}CH\text{-}CO(NH\text{-}\underset{\displaystyle C_6H_5}{CH}\text{-}CH_2\text{-}CO)_n\text{-}OC_2H_5$$

**Polycondensation of *p*-Nitrophenyl Esters of $\beta$-Amino Acids.** The *p*-nitrophenyl ester (PNP) hydrobromide (2 g) was suspended in 15 m*l* of a purified solvent in an ampoule, which was then flushed with dry nitrogen. In all the solvents used except dimethylformamide, the ester hydrobromides were insoluble. A slight excess of triethylamine was then added to the suspension by means of a hypodermic syringe. Triethylamine hydrobromide was thus separated, and the reaction mixture turned pale yellow. In dimethylformamide the monomer hydrobromides were dissolved completely, but massive precipitates soon appeared when triethylamine was added. The ampoule was left to stand for 72 hr at 60°C with occasional shaking. The reaction proceeded in a heterogeneous state, and the precipitates solidified after 30 minutes. The solid was crushed, filtered, and washed three times with ethanol by applying centrifugration. The resultant pale yellow powder was washed with ether and dried *in vacuo*. No insoluble material was obtained by adding ethanol.

TABLE 9. POLYCONDENSATION OF $\beta$-AMINO ACID *p*-NITROPHENYL ESTERS

Monomer HBr 2 g (5.4 mmol) $Et_3N$ 0.658 g (6.5 mmol) Solvent 15 m*l*, Temp. 60°C, Time 72 hr

| Solv. | $\alpha$-PA-PNP[a] | | $\alpha\beta$-PA-PNP[a] | | $\alpha,\beta$-DPA-PNP[b] | |
|---|---|---|---|---|---|---|
| | Yield % | $\eta_{sp}/c$ (d*l*/g) | Yield % | $\eta_{sp}/c$ (d*l*/g) | Yield % | $\eta_{sp}/c$ (d*l*/g) |
| Tol | 98.5 | 0.10 | 91.3 | 0.12 | 51.8 | 0.05 |
| Cl-Bz | 87.3 | 0.11 | 89.6 | 0.12 | 54.4 | 0.03 |
| THF | 90.0 | 0.09 | 93.6 | 0.11 | 3.2 | — |
| Diox | 86.9 | 0.09 | 84.8 | 0.10 | 21.0 | 0.03 |
| DMF | 56.9 | 0.12 | 72.0 | 0.09 | 0.0 | — |

Viscosity of the polymer was measured a) in trifluoroacetic acid solution ($c$=1.0 g/d*l*) at 30.0°C and b) in conc. sulfuric acid solution ($c$=0.5 g/d*l*) at 30.0°C.

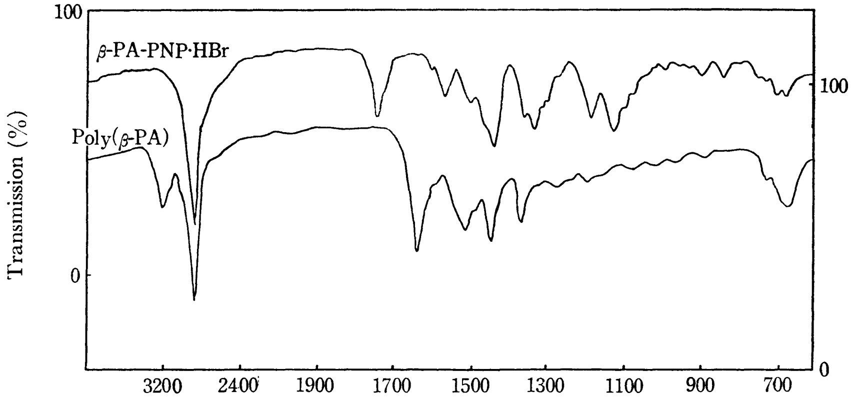


Fig. 2. Infrared spectra of *p*-nitrophenyl β-phenyl-β-aminopropionate hydrobromide and polymer. The spectra were taken with JASCO IR-S spectrophotometer with nujol mulls method.

to supernatant liquid of the reaction mixture. The results of the polymerization reaction are shown in Table 9. The polymers from α-PA-PNP and β-PA-PNP were soluble in dichloroacetic acid and trifluoroacetic acid, partially soluble in *m*-cresol, and insoluble in other usual organic solvents. They were also soluble in the mixture of dichloroacetic acid and chloroform. On the other hand, the polymer from α,β-DPA-PNP was insoluble not only in usual solvents but also in trifluoroacetic acid and dichloroacetic acid. It was soluble only in concentrated sulfuric acid, in which the solution viscosity of the polymer showed no change for a long time. All the polymers were crystalline, and none showed a melting point below 300°C. The IR spectra of β-PA-PNP·HBr and poly(β-PA) are shown in Fig. 2. The degree of polymerization was estimated from the content of the *p*-nitrophenyl group, which was analyzed as the end group by means of UV spectroscopy. The measurements were made on the polymer solution in dichloroacetic acid using the absorption band at 300 mμ and the molar extinction coefficient of the monomeric ester hydrobromide ($\varepsilon=6390$). The degree of polymerization was found to be about 18, with the polymer having a $\eta_{sp}/c$ value of 0.15.

**Viscosity of the Poly(β-Phenyl-β-aminopropionic Acid) *p*-Nitrophenyl Ester in a Chloroform-Dichloroacetic Acid Mixture.** The polymer prepared from β-PA-PNP was dissolved in dichloroacetic acid at a given concentration. The solution was then diluted with chloroform and dichloroacetic acid in such a way that the resulting solution had a constant polymer concentration at 0.5 g/d*l* and a known composition of the solvents, the ratios of chloroform to dichloroacetic acid ranging from 0/100 to 90/10 (vol/vol). The viscosity of the solution was measured at 30°C. The results are shown in Fig. 3. No precipitation of the polymer was observed even in the mixed solvent consisting 90% of chloroform. The viscosity was almost constant over the whole range of solvent compositions measured.

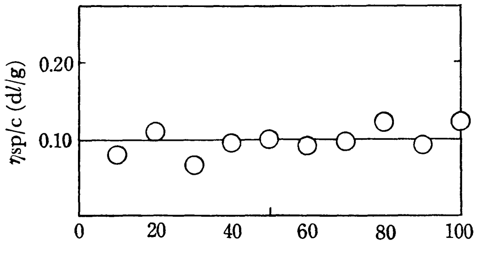
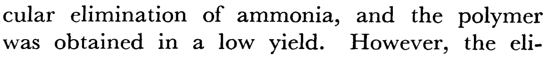


Fig. 3. Viscosity of poly(β-PA) in chloroform-dichloroacetic acid mixture at 30.0°C ($c=0.5$ g/d*l*).

## Discussion

Contrary to the polycondensation of β-amino pivalic acid by Linkoln,[4] the polycondensation of the phenyl-substituted β-amino acids used here was not successful because of the removal of ammonia by β-elimination reaction. The removal of ammonia took place intramolecularly much faster than the intermolecular dehydration of β-amino acid.



$$NH_2\text{-}\underset{R_1}{CH}\text{-}\underset{R_2}{CH}\text{-}COOH \longrightarrow \underset{R_1}{CH}{=}\underset{R_2}{C}\text{-}COOH + NH_3$$

From α-PA, atropic acid would be obtained, but the acid polymerized easily to poly (α-phenylacrylic acid) above 200°C, so it was difficult to isolate it in a monomeric form.

In the thermal reaction of the ethyl ester of β-amino acid, the polycondensation reaction can compete, although only slightly, with the intramolecular elimination of ammonia, and the polymer was obtained in a low yield. However, the elimination reaction also took place in the polymer thus produced and terminated the further growth of the polymer, forming a double bond in its molecule. By the elementary analysis, the degree of polymerization was roughly estimated to be 4—6 for the polymer derived from the β-PA ethyl ester. The large N content in the polymer obtained from the α,β-DPA ethyl ester may be due to the amide group formed by the reaction between the ester group and the ammonia produced during the polymerization.

The polycondensation of the *p*-nitrophenyl ester seemed to proceed very fast, judging from the observation of the polymer deposit in the reaction mixture. The IR spectrum of the polymer showed an absorption due to NH stretching at 3240 cm$^{-1}$ and no absorption band in the region of the C=C double bond, suggesting that no *β*-elimination reaction occurred under the reaction conditions empolyed. However, the degree of polymerization of the obtained polymer did not exceed twenty and was almost constant independently of the solvent used in the reaction, as was shown by the viscosity of the polymer in solution. The low degree of polymerization may be attributed to the precipitation of the polymer during polymerization because of its insolubility in the reaction mixture.

In all the polycondensation reactions, *α*,*β*-diphenyl-*β*-amino acid and its esters gave the polymers in low yields and with a low degree of polymerization compared with the other two amino acids and their esters. This must be caused by the steric hindrance due to the bulky substituents occupying both the *α* and *β* positions.

Contrary to our expectation, none of the polymers exhibited any solubilities in non-polar organic solvents. The poly(*β*-phenyl-*β*-aminopropionic acid) *p*-nitrophenyl ester could be dissolved in chloroform-dichloroacetic acid mixtures, but no distinct changes corresponding to the "helix-coil" transformation such as that found in poly-*α*-amino acid were observed in the polymer viscosity with the variation in the solvent composition.