The Transition Polymerization of Acrylamide. I. On the Polymerization Condition and the Property of Polymer[*]

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Generally, amino acid tends to cause an intermolecular condensation reaction between two molecules to form a ring compound and almost never makes linear polyamide by heating. It was reported by Breslow[1)] that acrylamide was polymerized into poly-β-alanine (Nylon 3) of high degree of polymerization in the presence of an alkali catalyst and an inhibitor of the vinyl polymerization. The polymerization proceeds through the transition of an amide hydrogen to a double bond of acrylamide and can be designated as the transition polymerization.

$$n\mathrm{CH_2{=}CHCONH_2} \rightarrow [\mathrm{-CH_2CH_2CONH-}]_n$$

The condition of polymerization and the property of the polymer have been investigated in this study.

Experimental

The Effect of Solvent.—Acrylamide was dissolved in various solvents at the concentration of 10% and the solution was heated at 115°C for 2 hr. in the presence of 1/32 mol./mol. of sodium-*tert*-butyrate and 0.02% of phenyl-β-naphthylamine. Polymer precipitated gradually from the solution after the addition of catalyst and adhered massively to the wall of a reaction vessel or a stirrer. Polymer was extracted with water for an hour and the weight of water-soluble and water-insoluble polymer was determined. The relative viscosity of the polymer was determined for 1% solution in 98% sulfuric acid. Polymer was hydrolyzed by sulfuric acid and the qualitative and quantitative analyses of β-alanine were carried out by paperchromatography, using a mixed solvent of *n*-butanol/ammonia =80/20 as a developer. These results are shown in Table I.

The yields of polymer are larger in the solvents of lower dielectric constant and in aromatic solvents than in aliphatic solvents. The polymerization hardly ever occurs in the solvents with active hydrogen, such as alcohol, amine or amide.

In the case of a *N*-substituted amide such as dimethylformamide or dimethylacetamide, the polymer was obtained in the form of suspension in spherical particles of about 100 μ diameters.

The Concentration of Monomer and Inhibitor.—Acrylamide was dissolved in pyridine at various concentrations and the solution was heated in the presence of sodium-*tert*-butyrate. The yield and the relative viscosity of polymer was largest at 10% monomer concentrations, as shown in Table II.

The quantity of an inhibitor of the vinyl polymerization, such as hydroquinone or phenyl-β-naphthylamine, does not necessarily affect the yield of the polymer, and poly-β-alanine is obtained without such inhibitors. These results are shown in Table III.

Contamination of water in the solvents decreases the yield of polymer and the vinyl polymerization occurs in the presence of more than 1% of water in the solvents, as shown in Table IV.

The Effect of Catalyst.—The catalytic effect of several alkali compounds was investigated in chlorobenzene at 10% monomer concentrations, which is shown in Table V. The yield of polymer is largest for tertiary alkoxide and the catalytic effect of alkali metals is in the order of K>Na>Li.

The yield of the polymer is approximately in proportion to the square root of the concentration of the catalyst, while the relative viscosity of the polymer does not change markedly, as shown in Table VI and Fig. 1.

The Rate of Polymerization.—The rates of polymerization of acrylamide were determined in various solvents at 10% monomer concentrations in the presence of 1/32 mol./mol. of sodium-*tert*-butyrate and 0.02% of phenyl-β-naphthylamine. These

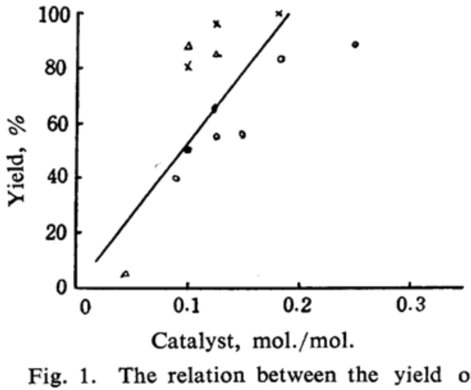

Fig. 1. The relation between the yield of the polymer and the concentration of catalyst.

○ Pyridine
× Monochlorobenzene
△ *N*, *N*-Dimethylaniline
● *N*, *N*-Dimethylformamide

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1) D. S. Breslow, G. E. Hulse and A. S. Matlack, *J. Am. Chem. Soc.*, 79, 3760 (1957).

TABLE I. THE TRANSITION POLYMERIZATION OF ACRYLAMIDE IN VARIOUS SOLVENTS
(○ : colored deeply by ninhydrin)

Solvent	Dielectric constant of solvent	Water-insoluble polymer %	Water-soluble polymer %	Total polymer %	η_{rel} of water-insoluble polymer	Confirmation of β-alanine
Toluene	2.38(25°C)	22	62	84	—	○
Dowtherm-A	—	74	22	96	—	○
Tetraline	2.66(20°C)	12	81	93	1.406	○
Diphenyl	2.53(73°C)	84	16	100	1.813	○
Tricresol	5.0 (24°C)	0	0	0	—	—
Aniline	7.2 (20°C)	18	25	43	1.483	○
Monomethylaniline	5.97(22°C)	37	30	67	1.719	○
Dimethylaniline	4.91(20°C)	60	23	83	1.835	○
Chlorobenzene	5.62(25°C)	80	20	100	1.903	○
o-Dichlorobenzene	7.47(25°C)	86	12	98	1.736	○
p-Dichlorobenzene	2.86(53°C)	74	26	100	1.837	○
Nitrobenzene	35.8 (20°C)	2	98	100	—	○
Acetophenone	18.3 (20°C)	0	5	5	—	○
Pyridine	12.3 (25°C)	43	40	83	1.923	○
Quinoline	9.0 (25°C)	36	40	76	1.555	○
Dioxiane	2.21(25°C)	0	69	69	—	○
Methylcellosolve	16 (30°C)	0	0	0	—	—
Methanol	—	0	0	0	—	—
tert-Butanol	—	0	40	40	—	○
Formamide	84 (20°C)	0	0	0	—	—
Dimethylformamide	26.6 (25°C)	46	42	88	1.714	○
Dimethylacetamide	—	84	16	100	1.670	○
Adiponitrile	—	0	16	16	—	—
Mareic Anhydride	—	0	0	0	—	—

TABLE II. THE EFFECT OF MONOMER CONCENTRATION
(Polymerized in the presence of 1/32 mol./mol. of sodium-*tert*-butyrate and 0.02% of phenyl-β-naphthylamine at 115°C for 2 hr.)

Monomer concentration %	Water-insoluble polymer %	Water-soluble polymer %	Total polymer %	η_{rel} of water-insoluble polymer
3.5	32	24	56	1.938
5.0	42	30	72	2.043
6.6	39	28	67	2.037
10.0	43	40	83	2.010
13.4	41	37	78	1.962
20.0	43	32	75	1.975
40.0	44	32	76	1.882

TABLE III. THE EFFECT OF AN INHIBITOR OF THE VINYL POLYMERIZATION
(Polymerized in pyridine at 10% monomer concentrations at 115°C for 2 hr. in the presence 1/32 mol./mol. of sodium-*tert*-butyrate.)

Kind of inhibitor	Inhibitor %/monomer	Water-insoluble polymer %	Water-soluble polymer %	Total polymer %	η_{rel} of water-insoluble polymer
Phenyl-β-naphthylamine	0	32	34	66	2.048
	0.05	34	27	61	2.062
	0.1	37	24	61	1.941
	0.2	43	40	83	2.010
	0.5	34	26	60	1.980
	1.0	37	31	68	1.955
Hydroquinone	0.1	40	—	—	—
Diphenylamine	0.2	40	—	—	—

TABLE IV. THE EFFECT OF WATER

(Monomer concentration=10%)
(Phenyl-β-naphthylamine=0.02%/monomer)
(Sodium-*tert*-butyrate=1/32 mol.)
(Temperature=115°C)

Solvent	Water content %	Time hr.	Water-insoluble polymer %	Water-soluble polymer %	Total polymer %	η_{rel} of water-insoluble polymer	η_{rel} of water-soluble polymer	Confirmation of β-alanine
Dimethyl-formamide	0.13	1	82	16	98	1.624	1.067	○
	0.61	1	70	18	88	1.544	1.087	○
	0.85	1	65	20	85	1.569	1.087	○
Monochloro-benzene	0.02	2	84	16	100	2.063	1.488	○
	1.0	3	9	89	98	—	—	×
	10.0	1	—	90	90	—	—	×

TABLE V. THE CATALYTIC EFFCT OF ALKALI COMPOUNDS

(Polymerized at the catalyst concentration of 1/32 mol./mol., with 0.02% phenyl-β-naphthylamine, at 115°C for 3 hr.)

Catalyst	Water-insoluble polymer %	Water-soluble polymer %	Total polymer %	η_{rel} of water-insoluble polymer	η_{rel} of water-soluble polymer
CH_3ONa	25	63	88	1.447	1.286
n-BuONa	66	20	86	1.780	1.147
tert-BuOLi	67	32	99	1.841	1.308
tert-BuONa	84	16	100	2.085	1.244
tert-BuOK	86	14	100	2.118	1.170
Na	9	89	98	—	1.357
NaOH	3	89	92	—	1.283
Na_2CO_3	0	0	0	—	—

TABLE VI. THE CONCENTRATION OF CATALYST

(Polymerized at 10% monomer concentration in the presence of 0.02% phenyl-β-naphthylamine for 2 hr.)

Solvent	Temp. °C	Concentration of catalyst (mol./mol.)	Water-insoluble polymer %	Water-soluble polymer %	Total polymer %	η_{rel} of water-insoluble polymer	η_{rel} of water-soluble polymer
Pyridine	115	0	0	0	0	—	—
		1/30	20	20	40	2.118	—
		1/65	32	23	55	2.033	—
		1/43	33	23	56	2.075	—
		1/32	43	40	83	2.010	—
		1/15	59	27	86	1.967	—
Monochloro-benzene	115	1/200	0	0	0	—	—
		1/100	13	67	80	1.820	1.601
		1/64	71	25	96	1.920	1.339
		1/32	84	16	100	2.082	1.287
N,*N*-dimethyl-aniline	130	1/200	0	5	5	—	—
		1/100	45	43	88	1.734	1.351
		1/64	62	23	85	1.833	1.305
N,*N*-dimethyl-formamide	130	1/200	0	0	0	—	—
		1/100	15	35	50	1.296	1.171
		1/64	35	31	66	1.462	1.173
		1/32	89	11	100	1.614	1.063

TABLE VII. THE RATE OF POLYMERIZATION IN PYRIDINE AT 115°C

Time hr.	Water-insoluble polymer %	Water-soluble polymer %	Total polymer %	η_{rel} of water-insoluble polymer
0.5	17	42	59	1.820
1	36	34	70	1.912
2	43	40	83	2.010
3	43	40	83	1.923
5	46	22	68	1.946
7.5	54	27	81	1.826

TABLE VIII. THE RATE OF POLYMERIZATION IN CHLOROBENZENE

Temp. °C	Time hr.	Water-insoluble polymer %	Water-soluble polymer %	Total polymer %	η_{rel} of water-insoluble polymer	η_{rel} of water-soluble polymer
80	1	0	86	86	—	1.256
	1.5	0	95	95	—	1.251
	2	0	97	97	—	1.306
	4	0	95	95	—	1.314
	7	0	100	100	—	1.314
100	0.5	0	96	96	—	1.337
	1	0	97	97	—	1.451
	1.5	0	97	97	—	1.472
	2	4	85	89	—	1.500
	4	48	44	92	1.929	1.373
	7	74	24	98	2.035	1.318
115	0.5	15	76	91	1.905	1.488
	1	75	21	96	2.063	1.336
	1.5	82	18	100	2.095	1.283
	2	84	16	100	2.085	1.244
	4	91	9	100	2.123	1.244
	7	92	8	100	2.133	1.243

TABLE IX. THE RATE OF POLYMERIZATION IN *o*-DICHLOROBENZENE

Temp. °C	Time hr.	Water-insoluble polymer %	Water-soluble polymer %	Total polymer %	η_{rel} of water-insoluble polymer	η_{rel} of water-soluble polymer
100	0.25	0	86	86	—	1.343
	0.5	0	82	82	—	1.390
	0.75	0	86	86	—	1.435
	1	0	86	86	—	1.435
	1.5	0	92	92	—	1.493
	2	3	87	90	—	1.543
	4	43	42	85	2.014	1.493
	7	71	29	100	2.061	1.340
115	0.25	0	91	91	—	1.543
	0.5	9	89	98	—	1.555
	0.75	59	30	89	1.998	1.377
	1	69	23	92	2.082	1.417
	1.5	76	24	100	2.072	1.324
	2	86	12	98	2.205	1.298
	4	93	17	100	2.035	1.309

TABLE X. THE RATE OF POLYMERIZATION IN *p*-DICHLOROBENZENE

Temp. °C	Time hr.	Water-insoluble polymer %	Water-soluble polymer %	Total polymer %	η_{rel} of water-insoluble polymer	η_{rel} of water-soluble polymer
100	0.25	0.4	85	85	—	1.326
	0.50	—	94	94	—	1.390
	0.75	0.5	93	93	—	1.397
	1	0.7	93	94	—	1.433
	1.5	0.8	81	82	—	1.454
	2	17	78	95	1.946	1.452
	4	41	57	98	2.021	1.403
	7	59	41	100	2.071	1.343
115	0.25	2	96	98	—	1.428
	0.50	14	80	94	2.003	1.444
	0.75	43	49	92	1.976	1.404
	1	70	27	97	2.072	1.336
	1.5	82	18	100	2.120	1.316
	2	80	20	100	2.086	1.310
	4	91	9	100	2.163	1.315

TABLE XI. THE RATE OF POLYMERIZATION IN *N,N*-DIMETHYLFORMAMIDE

Temp. °C	Time min.	Water-insoluble polymer %	Water-soluble polymer %	Total polymer %	η_{rel} of water-insoluble polymer	η_{rel} of water-soluble polymer
115	30	0	37	37	—	1.223
	60	0	52	52	—	1.250
	90	41	37	78	1.525	1.200
	120	37	40	77	1.475	1.221
	240	59	21	80	1.500	1.100
	420	45	34	79	1.505	1.176
130	5	7	61	68	—	1.226
	10	75	17	92	1.485	1.087
	20	79	16	95	1.521	1.067
	30	83	14	97	1.605	1.061
	60	82	16	98	1.624	1.061
	120	82	18	100	1.614	1.063
144	5	55	22	77	1.386	1.084
	10	80	14	94	1.600	1.059
	20	81	16	97	1.616	1.058
	30	82	14	96	1.589	1.058
	60	81	16	97	1.569	1.057
	120	82	14	96	1.575	1.046

results are shown in Tables VII—XII.

The Property of Polymer. — *i) Melting Point.*— The melting point of water-soluble and water-insoluble polymer was determined in the nitrogen atomosphere in an electric heater, which was 330°～335°C.

ii) Infrared Spectrum.—The infrared spectrum of water-soluble and water-insoluble polymer was determined with KBr disc. by Hitachi spectrophotometer IR II. The characteristic absorption band (Amide II band) of a monosubstituted amide appears at 6.5 μ and no absorptions due to ethylenic double bond appear in comparison with the spectrum of polyacrylamide, which is shown in Figs. 2—5.

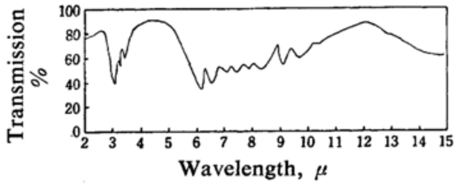

Fig. 2. The infrared spectrum of water-insoluble poly-β-alanine, which is obtained in chlorobenzene at 115°C for 30 min. (KBr disc).

TABLE XII. THE RATE OF POLYMERIZATION IN ANILINE AND ITS DERIVATIVES

Solvent	Temp. °C	Time hr.	Water-insoluble polymer %	Water-soluble polymer %	Total polymer %	η_{rel} of water-insoluble polymer	η_{rel} of water-soluble polymer
Aniline	115	0.5	16	21	37	1.541	1.229
		1	17	11	28	1.508	1.224
		1.5	22	15	37	1.497	1.234
		2	23	15	38	1.410	1.206
		4	26	15	41	1.435	1.176
		7	23	19	42	1.405	1.185
Monomethylaniline	115	0.5	8	50	58	—	1.388
		1	40	34	74	1.670	1.243
		1.5	38	37	75	1.709	1.248
		2	37	30	67	1.719	1.239
		4	40	34	74	1.670	1.243
		7	48	32	80	1.625	1.227
Dimethylaniline	115	0.5	3	80	83	—	1.354
		1	40	52	92	1.802	1.322
		1.5	61	37	98	1.810	1.296
		2	60	23	83	1.835	1.256
		4	64	32	96	1.805	1.254
		7	67	18	85	1.705	1.220

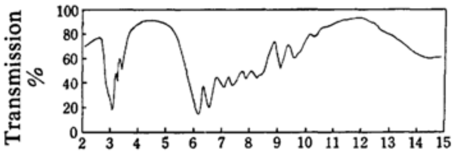

Fig. 3. The infrared spectrum of water-soluble poly-β-alanine, which is obtained in chlorobenzene at 115°C for 30 min. (KBr disc).

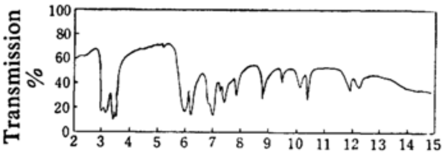

Fig. 4. The infrared spectrum of acrylamide. (KBr disc).

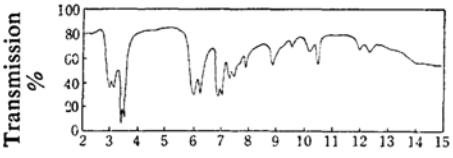

Fig. 5. The infrared spectrum of polyacrylamide. (Film).

TABLE XIII. SOLUBILITY OF POLY-β-ALANINE

Solvent	Concentration of polymer %	Solubility
1,1-Dichloroethanol-1	10	Insoluble
1,1-Dichloroethanol-2	10	〃
1,1-Dichloropropanol-2	10	〃
Trichloroethanol	10	〃
α-Dichlorohydrin	10	〃
1,1,1-Trichloroisopropanol	10	〃
m-Cresol	10	〃
Resorcinol	30	〃
52% Aqueous $SnCl_2$ solution	30	〃
50% Aqueous $CaCl_2$ solution	30	〃
Alkaline cupro-glycerol solution	30	〃
Cupro-ethylenediamine solution	30	〃
Cupro-ammonium solution	30	〃
Phosphoric acid	30	〃
ε-Caprolactam	10	〃
α-Pyrrolidone	10	〃
α-Pyperidone	10	〃
Acetamide	10	〃
Dimethylformamide	10	〃
Urea	10	Swelling
70% Aqueous $CaCl_2$ solution	30	〃
Anhydrous formic acid	30	〃
Phenol	30	〃
98% Sulfuric acid	10	Soluble
Aqua regia	30	〃
60% Nitric acid	30	〃
Anhydrous formic acid (containing 5% $CaCl_2$)	30	〃
Methanol saturated with $ZnBr_2$	10	〃
Methanol saturated with $CaCl_2$	10	〃

iii) Moisture Absorption. — The moisture content of the polymer ($\eta_{rel}=1.9-2.1$) at various relative humidities is shown in Fig. 6.

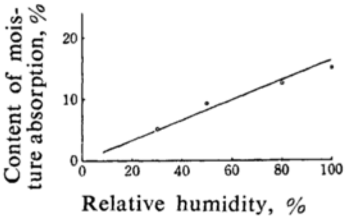

Fig. 6. The moisture content of poly-β-alanine.

iv) Solubility of polymer.—The solubility of the polymer in various solvents at 25°C is shown in Table XIII. Anhydrous formic acid containing 5% of calcium chloride is a good solvent for poly-β-alanine.

Discussion

The conversion curve of acrylamide to water-soluble poly-β-alanine shows a maximum, while the yield of water-insoluble polymer increases with time after a short induction period. The total yield of water-soluble and insoluble polymer is not affected so much with time. The final yield of water-insoluble polymer increases as the reaction temperature becomes higher. Therefore, it is expected that the transition reaction of acrylamide to poly-β-alanine occurs very rapidly as soon as a catalyst is added and then the growth of polymer follows slowly.

It is assumed that the transition of an amide hydrogen may be hindered in the solvents with active hydrogen, as the yield of polymer decreases with the amount of active hydrogen of the solvents. The alkoxide ion may decompose in the solvents with active hydrogen, as follows:

$$\mathrm{RO{-}Na + H{-}X \rightleftarrows ROH + Na{-}X}$$

It is expected that the transition polymerization may proceed at first through the addition of alkoxide ion to acrylamide, because no absorptions due to double bond appear in the infrared spectrum of water-soluble polymer which is obtainded at the initial stage of the reaction.

The reaction mechanism will be proposed in a later paper, and the further investigation on the property of polymer and the application to fiber or plastics is now being carried out.

Summary

The polymerization condition for the transition polymerization of acrylamide to poly-β-alanine has been investigated in the presence of alkali catalyst. The catalytic effect of alkali catalysts is largest for tertiary alkoxide and that of alkali metals is in the order as K>Na >Li. The yield of polymer is larger in the solvents of lower dielectric constant and in aromatic solvents than in aliphatic solvents. The polymerization seldom occurs in the solvents with active hydrogen. The property of the polymer has also been investigated.

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