Polycondensation of β-Amino Acid Derivatives

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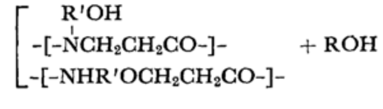
It was previously shown[1-3] that acrylate adds to amino alcohol and then, polycondensation follows at room temperature in the presence of an alkoxide to form polyamide as described below:

$$CH_2{=}CHCOOR + NH_2R'OH \rightarrow$$

$$HOR'NHCH_2CH_2COOR \rightarrow$$



$$\left[\begin{array}{l} \text{-[-}\overset{R'OH}{N}CH_2CH_2CO\text{-]-} \\ \text{-[-}NHR'OCH_2CH_2CO\text{-]-} \end{array}\right. + ROH$$

The reaction medium has an influence on the course of the polycondensation and *N*-(hydroxyalkyl) poly-β-alanine is mainly formed in alcohol solution and polyamide ether is obtained in other polar solvent such as tetrahydrofuran. However,

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[1] N. Ogata and T. Asahara, This Bulletin, **39**, 1486 (1966).

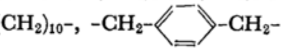
[2] N. Ogata and T. Asahara, *J. Polymer Sci.*, **B-4**, 273 (1966).

[3] N. Ogata and K. Sanui, This Bulletin, in press.

when diamines were used in place of amino alcohol, polycondensation did not occur at room temperature in tetrahydrofuran solution and only a low molecular weight polymer was obtained in methanol solution.

In this paper, several *N*-(amino alkyl)β-alanine esters were synthesized from diamines and ethyl acrylate and their thermal polycondensation has been carried out in the presence of various catalysts. Following diamines were used for the synthesis:

$$NH_2R'NH_2 + CH_2{=}CHCOOR \rightarrow$$
$$NH_2R'NHCH_2CH_2COOR \rightarrow$$
$$-[-NHR'NHCH_2CH_2CO-]- + ROH$$

R': $-(CH_2)_2-$, $-(CH_2)_4-$, $-(CH_2)_6-$, $-(CH_2)_8-$, $-(CH_2)_{10}-$, 

Commercially available ethylenediamine and hexamethylenediamine were used and, tetramethylenediamine and octamethylenediamine were synthesized from adipamide and sebacamide through the Hoffmann's reaction. Decamethylenediamine and *p*-xylylenediamine were synthesized from dehydration of sebacamide and terephthalamide followed by hydrogenation of the nitriles.

When equal moles of diamine and acrylate were mixed together in a solvent, an addition reaction took place immediately at the vinyl group of acrylate at room temperature. Infrared spectrum of the product showed absorptions owing to amino and ester carbonyl groups as can be seen in Fig. 1. The acid titration curve exhibited two inflection points which corresponded with one amino and one imino groups. Color reactions of primary and secondary amine groups were also observed. Therefore, it is presumed that the addition product has a structure of *N*-(amino alkyl)β-alanine ester.

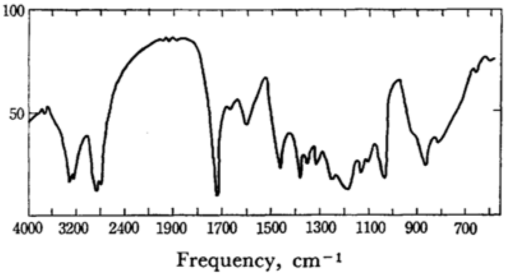


Fig. 1. Infrared spectrum of the reaction product of ethylene diamine and ethyl acrylate.

TABLE 1. THERMAL POLYCONDENSATION OF $NH_2(CH_2)_nNHCH_2CH_2COOC_2H_5$*

n	Catalyst 1 mol%	Yield %	η_{inh}**	M.W.	Degree of crosslinking	Character
2	—	100	0.05[a)]	500	—	yellow grease
	K	95	0.05[a)]		—	yellow grease
	$SnCl_2$	67	0.09[a)]		—	yellow solid
	$SnCl_4$	98	0.09[a)]		—	yellow solid
	$TiCl_4$	93	0.13[a)]	1000	—	yellow solid
	$AlCl_3$	93	0.11[a)]		—	yellow solid
	$ZnCl_2$	90	0.07[a)]		—	yellow solid
	BF_3OEt_2	96	0.08[a)]		—	yellow solid
4	—	100	0.11[a)]		—	white solid
	$SnCl_4$	100	0.21[a)]	1800	—	white solid
	$TiCl_4$	100	0.14[a)]	1400	—	white solid
6	—	100	0.04[b)]	460	—	white grease
	$SnCl_2$	98	—	—	30%	white elastic
	$SnCl_4$	100	—	—	15%	white elastic
	$TiCl_4$	100	—	—	22%	white elastic
	$AlCl_3$	98	0.27[b)]	—	—	white solid
	$ZnCl_2$	95	0.08[b)]		—	white grease
	BF_3OEt_2	100	—	—	28%	white elastic
8	$SnCl_4$	100	—	—	48%	white solid
10	—	100	—	—	19%	white elastic
	Na	100	—	—	51%	white elastic
	$SnCl_4$	100	—	—	67%	white solid
	$TiCl_4$	100	—	—	52%	white solid
	$AlCl_3$	100	—	—	27%	white elastic
	$ZnCl_2$	100	—	—	18%	white elastic

* Polymerization temperature, 153°C; time, 5 hr; vacuum, 2 mmHg.

** Measured a) in water, b) in methanol, at 30°C.

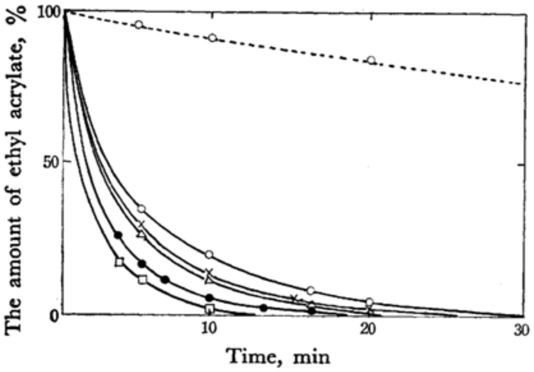
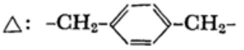
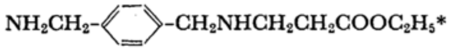


Fig. 2. The rate of reaction of diamines and ethyl acrylate (Concn., 1 mol/*l*, at 20°C).
----: in THF, ——: in methanol
○: $-(CH_2)_2-$, ×: $-(CH_2)_4-$, ●: $-(CH_2)_6-$
□: $-(CH_2)_8-$, $-(CH_2)_{10}-$,

△: $-CH_2-C_6H_4-CH_2-$

These esters were purified by a fractional distillation or recrystallization from alcohol and water.

The rates of the addition of several diamines to acrylate were determined in tetrahydrofuran or methanol solutions at 25°C by gas chromatographic analysis. The results in Fig. 2 show that the rate becomes faster with increasing carbon numbers of diamine and the rate in methanol solution is about 100 times as fast as in tetrahydrofuran solution. The accerelating effect of alcohol on the Michael reaction of acrylate was previously reported.⁴⁾

The boiling or melting points of the esters is as follows; $NH_2(CH_2)_2NHCH_2CH_2COOC_2H_5$: bp 97°C/2 mmHg, $NH_2(CH_2)_4NHCH_2CH_2COOC_2H_5$: bp 140°C/7 mmHg, $NH_2(CH_2)_6NHCH_2CH_2COOC_2H_5$: bp 135°C/3 mmHg, $NH_2(CH_2)_{10}NHCH_2CH_2COOCH_3$: mp 92°C. *N*-(4-Aminomethyl benzyl) β-alanine ethyl ester polycondensated easily during distillation and it was used for polycondensation without distillation.

TABLE 2. THERMAL POLYCONDENSATION OF

$NH_2CH_2-C_6H_4-CH_2NHCH_2CH_2COOC_2H_5$*

Catalyst 1 mol%	Yield %	η_{inh}**	M.W.	Character
—	85	0.03	670	yellow solid
K	88	0.03	—	yellow solid
$SnCl_4$	73	0.07	1800	yellow solid
$TiCl_4$	75	0.06	—	yellow solid
$AlCl_3$	82	0.04	—	yellow solid
BF_3OEt_2	80	0.05	—	yellow solid

* Polymerization temperature, 153°C; time, 5 hr; vacuum, 2 mmHg.
** Measured in methanol at 30°C.

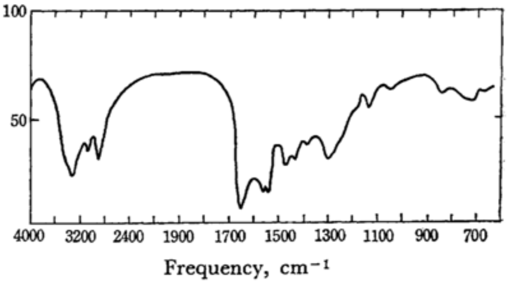


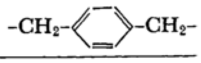
Fig. 3. Infrared spectrum of the polymer of $NH_2(CH_2)_2NHCH_2CH_2COOC_2H_5$.

The thermal polycondensation of the esters was carried out by heating in vacuum in the presence of 1 mol% of basic or acidic catalysts. Results are shown in Tables 1 and 2. It is seen that acidic catalysts such as $SnCl_4$ or $TiCl_4$ are effective for the thermal polycondensation of *N*-(amino alkyl) β-alanine esters and the degree of crosslinking of polymers increases with increasing number of *N*-alkyl group.

Infrared spectrum of the polymers showed absorptions owing to secondary amide group as can be seen in Fig. 3 and it is presumed that the polycondensation takes place between primary amino and ester groups since no amide II band should be appeared at 1550 cm⁻¹ if polycondensation takes place between imino and ester groups.

Solubility of the polymers in various solvents is summarized in Table 3. Solubility decreases in

TABLE 3. SOLUBILITY OF POLYAMIDE IMINE $-[-NHRNHCH_2CH_2CO-]-$* IN VARIOUS SOLVENTS

Solvent	R $-(CH_2)_2-$	$-(CH_2)_4-$	$-(CH_2)_6-$	$-(CH_2)_8-$	$-(CH_2)_{10}-$	 $-CH_2-C_6H_4-CH_2-$
H_2O	○	○	△	△	×	×
CH_3OH	○	○	△	△	△	○
H_2SO_4	○	△	△	—	—	○
HCOOH	○	○	△	—	—	○
DMF	×	×	×	△	△	○
DMSO	○	△	△	—	—	○
$[(CH_3)_2N]_3PO$	×	△	△	—	—	○

○: Soluble ×: Insoluble △: Swelling * Catalyst: $SnCl_4$, 153°C, 5 hr, 2 mmHg

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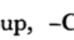
4) N. Ogata and K. Sanui, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, to be submitted.

the following order owing to crosslinking: *N*-amino alkyl group, $-CH_2-$$-CH_2-$, $-(CH_2)_2-$ $>-(CH_2)_4->-(CH_2)_6->-(CH_2)_8-$, $-(CH_2)_{10}-$.

N-(2-Aminoethyl)β-alanine ethyl ester gave a polymer with a molecular weight of 1000, which had a greenish yellow fluorescence and was water-soluble, and *N*-(4-aminobutyl)β-alanine ethyl ester yielded a white solid with a molecular weight of 1800 which was also water-soluble. *N*-(4-Aminomethyl benzyl)β-alanine ethyl ester gave a water-insoluble but alcohol-soluble polymer. It is assumed from their solubility that linear polyamide imines were obtained in these cases. However, thermal polycondensation of higher *N*-alkyl esters resulted in a white, elastic and infusible polymer which had a crosslinked structure. It is assumed that the reactivity of imino group increases with increasing carbon number of *N*-alkyl group, resulting in a crosslinked polymer. The degree of crosslinking, which was determined by acid titration, was about 15 to 30%. The film from *N*-(6-aminohexyl)β-alanine ester could be elongated almost 300%.

In the case of thermal polycondensation of *N*-(6-aminohexyl)β-alanine ester, two-steps polycondensation is possible to obtain an elastic polymer film, that is, pre-polycondensation followed by secondary polycondensation in the presence of acidic catalyst. This method leads to the processing or the film casting. It might be possible to use these polymers as an anion exchange resin since basic imino group is placed in the polymer.