

Room-Temperature Polycondensation of β -Amino Acid Derivatives. IV.*¹ Solvent Effect on the Michael Reaction of Acrylates

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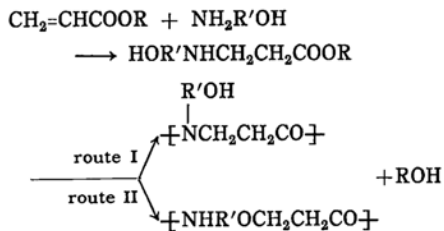
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It was previously shown^{1,2)} that acrylates add with amino alcohols, followed by polycondensation at room temperature to form polyamide in alcohol solution in the presence of basic catalysts. When ethanolamine and acrylate are mixed in a solvent, an addition reaction of ethanolamine with acrylate takes place at the amino group and *N*-(hydroxyethyl) β -alanine ester is formed.

In this addition reaction, it was found that amino alcohol has a much higher reaction rate than amine itself and the addition of amine to acrylate is accelerated to a large extent in

the presence of alcohol.³⁾ Also, it was found⁴⁾ that solvent has a great influence on the course of the polycondensation in the presence of basic catalysts, and polyamide is formed in methanol solution *via* route I, while polyamide ether is mainly formed in tetrahydrofuran *via* route II through rearrangement.



*1 Part III: K. Sanui and N. Ogata, This Bulletin, **40**, 1727 (1967).

1) N. Ogata and T. Asahara, *J. Polymer Sci.*, Part B, **4**, 273 (1966).

2) N. Ogata and T. Asahara, This Bulletin, **39**, 1359 (1966).

3) K. Sanui and N. Ogata, *ibid.*, **40**, 1727 (1967).

4) N. Ogata, T. Asahara and K. Sanui, *J. Polymer Sci.*, Part A-1, **6**, 1195 (1968).

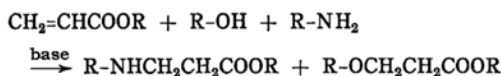
TABLE 1. SOLVENT EFFECT OF THE COMPETITIVE ADDITION REACTION OF ACRYLATES
(Concn., 1 mol/l., Catalyst, ROK=5 mol%, * at 30°C., ** at 25°C)

Acrylate	Solvent	ϵ (20°C)	Amount of acrylate A (%)	$n\text{-BuNHCH}_2\text{CH}_2\text{COOR}$ [I]		$\text{ROCH}_2\text{CH}_2\text{COOR}$ [II]		[II]/[I]
R				B (%)	C (%)	D (%)	E (%)	
Ethyl*	Cyclohexanone	18.3	39	61	99	1	1	0.01
	Ethanol	24.3	2	81	81	17	19	0.23
	Acetone	21.4	69	17	36	14	14	0.39
	Dioxane	2.21	27	46	71	27	29	0.41
	Ethanol/THF =50/50		5	55	55	40	45	0.82
	<i>n</i> -Heptane	1.92	3	42	42	55	58	1.4
	DMF	36.6	6	40	40	54	60	1.5
	THF		6	32	38	62	62	1.6
	Acetonitrile	37.5	0	20	20	80	80	4.0
Methyl**	Dioxane	2.21	25	70	95	5	5	0.05
	Methanol	32.6	0	91	91	9	9	0.10
	THF		0	30	30	70	70	2.3

A, B, D: after 3 hr, C, E: final yield, ϵ : Dielectric constant

These results suggest that the nucleophilicity of amino and hydroxyl groups may depend on solvent, hence the variation of the solvent results in the change in the course of the polycondensation.

Therefore, the solvent effect on the course of the competitive addition reaction of acrylate with aliphatic amine and alcohol was investigated in the presence of alkali metal alkoxide.



The reaction was carried out as follows: methyl or ethyl acrylate, *n*-butylamine and methanol or ethanol were dissolved in various solvents each in the concentration of 1 mol/l in the presence of 5 mol% of potassium methoxide or ethoxide, and the amount of each reactants and also products in the solution were determined by gas chromatographic analysis using a dioctyl phthalate column.

Figure 1 shows the rate of the addition reaction of acrylate in methanol and tetrahydrofuran solutions, where it is seen that the addition of alcohol to acrylate takes place mainly in tetrahydrofuran and the ratio of the addition products of alcohol and amine is 7/3, while acrylate adds almost exclusively with amine in methanol without the addition of methanol.

Table 1 shows results of the competitive addition reaction in various solvents. Solvents in which the addition takes place almost exclusively with amine were cyclohexanone, methanol and dioxane. Methyl acrylate is more reactive than ethyl acrylate. Ethyl acrylate adds with both amine and ethanol in the

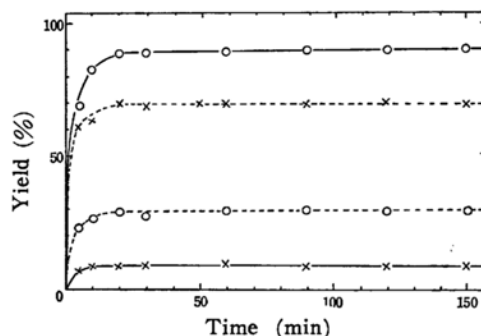


Fig. 1. The competition reaction of methyl acrylate with *n*-butylamine and methanol in methanol (—) and tetrahydrofuran (----). (Concn., 1 mol/l, at 25°C., Catalyst, CH_3OK =5 mol %)

○ : $n\text{-BuNHCH}_2\text{CH}_2\text{COOCH}_3$
× : $\text{CH}_3\text{OCH}_2\text{CH}_2\text{COOCH}_3$

ethanol solution, although the addition with amine still predominated. In a mixed solvent of ethanol and tetrahydrofuran, the addition reaction with both amine and alcohol took place as can be seen in Table 1. In all other solvents except acetone the addition reaction of acrylate proceeded almost quantitatively, leaving very small amount of unchanged acrylate in the solution. In the acetone solution, almost half amount of ethyl acrylate remained unchanged and the addition reaction did not further proceed even after several days. Several unidentified peaks were detected in the gas chromatographic analysis of the acetone solution after the reaction occurred. When only *n*-butylamine was dissolved in acetone, the amount of *n*-butylamine in the

solution decreased very rapidly to a trace after 30 min, and a new peak appeared in the gas chromatograph which coincided with one of the unidentified peaks.

The dielectric constant of solvent does not necessarily affect the course of the competitive addition reaction as can be seen in Table 1, whereas the rate of the addition reaction increased generally in a solvent with a higher dielectric constant.

The observed solvent effect on the Michael-type reaction of acrylate might be due to the change of the nucleophilicity of amine and alcohol in different solvents.

In the tetrahydrofuran solution, the rate of the simple addition of acrylate with alcohol alone in the presence of potassium alkoxide is much faster than that with amine alone.²⁾ However, when an acrylate and an amine are dissolved in an alcohol, the addition reaction of the acrylate takes place almost exclusively with the amine, and the alcohol does not react at all. Dioxane and cyclohexanone had the same solvent effect on the addition reaction of acrylates. Therefore, amines are more nucleophilic than alkoxide ions in such solvents as alcohol, dioxane and cyclohexanone.

Thus, the formation of polyamide through the polycondensation between amino and ester groups in an alcohol solution is explained from the increase in the nucleophilicity of the amino group in alcohol, while the formation of polyamide ether in tetrahydrofuran is attributed to the increase in the nucleophilicity of the hydroxyl group in this solvent.

It is known that the interfacial polycondensation of aromatic amine and dicarboxylic acid chloride in ordinary organic solvents resulted in a low molecular weight polyamide, because of low basicity of aromatic diamine. However, a very high molecular weight polyamide is formed⁵⁾ when cyclohexanone is used as the solvent for the aromatic amine. This might be correlated with the present results that the nucleophilicity of amine is greater in cyclohexanone solution.

The above-mentioned results on the course of the addition reaction of acrylates offer a cue to obtain a high molecular weight polymer by the room-temperature polycondensation of the β -alanine derivatives.

5) H. F. Mark, S. M. Atlas and N. Ogata, *ibid.*, **61**, s 49 (1962).