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Acrolein 과 Amine 류의 중합

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Polymerization of Acrolein with Amines

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Abstract

The polymerization of acrolein with aniline and also with butylamine (BA) was studied in neutral, acidic and basic solution of varying *pH* at various temperatures and reaction times. The yields of the polymers and their molecular weights were determined, and the reaction mechanisms were discussed from analytical results. The polymerization of acrolein with benzidine (BD) and with 4,4'-methylene dianiline (MDA) was also studied by varying mole ratios of acrolein to diamines to prepare polymers of thermoplastic or thermosetting property.

Introduction

It has been reported that Gray and Wright⁽¹⁾ synthesized a stable colored polymer from acrolein with o-, m-, and p-, N, N'-dimethyl p-phenylene diamine in acetic acid solution, and later Kalle⁽²⁾ prepared the photoconductive printing plate with acrolein-aniline condensate. There have not been any reports on the reaction mechanisms of acrolein-amines except a few patents^{(3), (4), (5), (6)}.

In this paper, in order to investigate the reaction mechanisms, the reactions of acrolein with aniline and with BA were carried out in acidic or basic solution at various temperatures and reaction times, and on the basis of the reaction of acrolein with aniline, the reactions of acrolein with BD and with MDA were studied too. The molecular weights and yields of the polymers were determined and their structures were confirmed by infrared absorption

spectra, bromine solution tests, elementary analyses and fusion tests. From the analytical results, the mechanisms of the polymerizations were proposed.

Also, the thermal stabilities and electrical insulating properties of the polymers were measured.

Experimental

Materials

Aniline, BA, BD, and MDA were reagent grades and were used without further purification. Acrolein was purified by the method described by the authors.⁽⁷⁾

Reaction of Acrolein with Amines

Acrolein-Aniline. In a 4-necked round bottom flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser was charged 50% aqueous solution of 1/2 mole of aniline, and after the *pH* of the solution was controlled by addition of 1N hydrochloric acid solution or 1N sodium hydroxide solution respectively, 50% aqueous solution of 1/2 mole of acrolein was added to it dropwise at room temperature. After they were reacted for a given reaction

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time, they gave yellow viscous resinous material as precipitate. The precipitate was washed with distilled water and was purified by dissolving it in benzene and precipitating it from hexane.

As the resin purified by reprecipitation was dried at 50°C in vacuo, reddish brown transparent solid resin was obtained. The results of Run No. 8 through 11 were obtained from the reactions which were carried out again at given *pH* and for 8 hours after 40ml of benzene was added to the intermediate product. The result of Run No. 12 was obtained from being heated for 8 hours after direct reaction with equimoles of acrolein and aniline at room temperature.

Acrolein-BA. The experimental runs from No. 13 to No. 16 were carried out in the same procedure as in the reaction of acrolein with aniline.

Acrolein-BD and Acrolein-MDA

After 1 mole of acrolein was added slowly to 30% solution of 1 mole of BD in methyl ethyl ketone (M-

temperature for 30 minutes and at 80°C for 20 minutes. The reddish yellow opaque lump was precipitated and it was washed with MEK and was dried at 50°C for 72 hours.

The polymerization of acrolein with MDA was carried out to give a red transparent lump in the same experimental procedure as in the polymerization of acrolein with BD except that the mixture was reacted at 0–5°C for 60 minutes and at 80°C for 30 minutes.

Analytical Methods

Molecular Weight Determinations. Molecular weights of acrolein-aniline and acrolein-BA polymers were determined with Hewlett-Packard 302B Vapor Pressure Osmometer, by using benzene as solvent.

Infrared Spectra. The spectra of the acrolein-aniline and acrolein-BA polymers were recorded through film on KBr plate and those of acrolein-BD and acrolein-MDA polymers were recorded through KBr tablet by Beckman IR-12.

Elementary analyses. Polymers were analyzed by Coleman Carbon and Hydrogen Analyzer, and Coleman Nitrogen Analyzer.

Results and Discussion

Reactions of acrolein with Aniline and with BA.

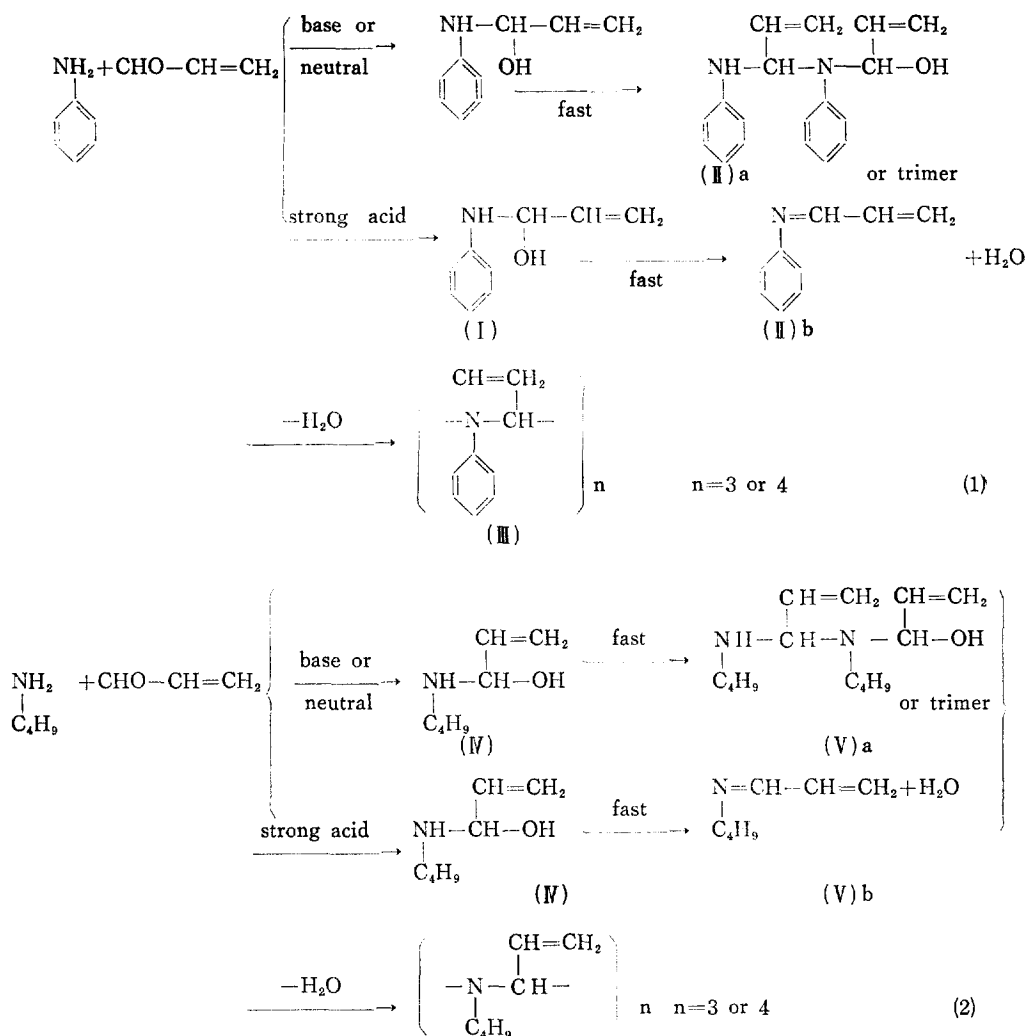
Table I shows that acrolein-aniline, and acrolein-BA are reacted into condensates easily at room temperature, and that the molecular weights of intermediate condensates are about 260 (dimer) for acrolein-aniline and about 236 (dimer) for acrolein-BA under basic condition, and about 140 for the former and about 118 for the latter under acidic condition. The molecular weights of the final polymers are not increased over about 460–680 (trimer or tetramer) for acrolein-aniline and 341–362 (trimer) for acrolein-BA by even further reaction at 80–110°C. As considered from the functionality and polarity of the aldehyde group of acrolein and the amino group of aniline, it can be suggested that it is a kind of Schiff's base reaction.⁹⁾ But the reaction of acrolein with aniline is carried out through Schiff's base reaction to form polymers like resinous material as follows.

Table 1. Equimolar reactions of Acrolein with Aniline and with Butylamine

Run No.	Conditions			Products	
	Temp. °C	Time hr.	pH	Mol. wt.	Yield ^a %
1	22–24	0.5	2.0	142	42
2	21–23	0.5	4.0	—	32
3	20–25	0.5	7.2	—	28
4	20–23	0.5	11.5	264	60
5	22–25	0.5	17.5	—	62
6	19–23	1.5	12.0	246	43
7	22–24	3.0	12.5	—	62
8	90–95	8.0	2.0	495	71
9	110–114	8.0	4.0	463	59
10	60–65	8.0	11.5	492	66
11	90–95	8.0	12.0	580	70
12	90–95	8.0	—	406	61
13	19–22	0.5	2.0	118	41
14	20–25	0.5	11.5	236	62
15	90–95	5.0	2.0	341	65
16	90–95	5.0	11.5	362	75

a. Percentage of the amount of the obtained polymer to the total amount of acrolein and aniline or butylamine after a reprecipitation.

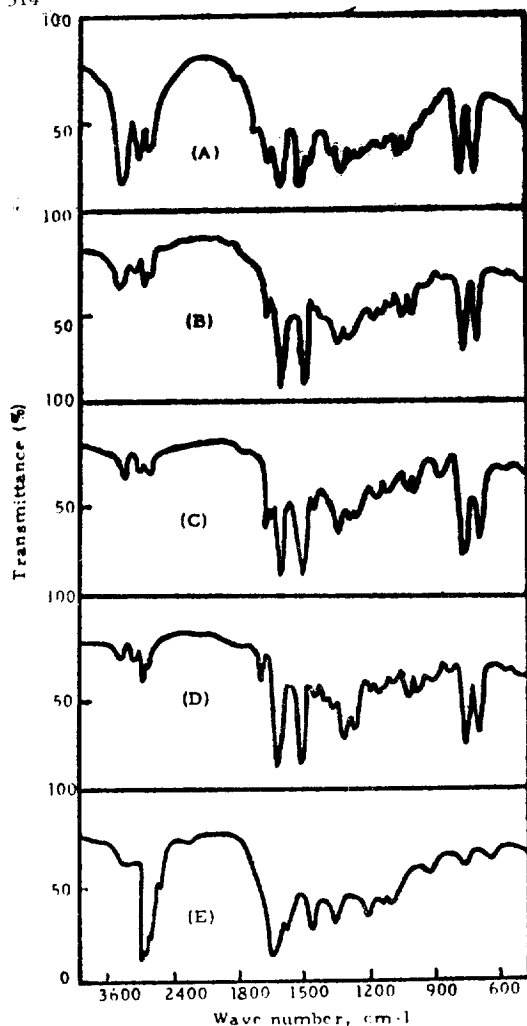
EK) at 0–5°C, the mixture was reacted at the same



While aniline and BA have the weak basicity of $K_b=3.83 \times 10^{-10}$ and $K_b=4.1 \times 10^{-4}$ respectively, the acrolein (3.04D) has greater polarity due to distortion of a pair of electrons of the double bond than other aldehydes or ketones (2.7D). Accordingly, since the aldehyde group of the acrolein has a stronger reactivity for the amino group of aniline and BA, they tend to form condensate at room temperature by reaction directly with equimoles of the acrolein and monoamines.

In basic solution or neutral solution the reaction from (I) to (II)a in eq. (1) took place easily at room temperature, and in strong acid solution the reaction from (I) to (II)b did more vigorously than

in the former experimentally. The molecular weight of intermediate (II) a is greater than that of (II) b due to easy condensation in strong acid condition as shown in Run No. 4 and 1 of Table 1. In further reaction above 70°C, drying or heating process, the unstable forms (II) a and (II) b which make a form (III) of trimer or tetramer as shown in the molecular weights of Run No. 9, 10 and 11 listed in Table I whose degree of polymerization is about 3 or 4. From a generalized theoretical viewpoint, under basic or neutral solution, the imine groups^{9), 10)} resulted from the form (I) by condensation are polymerized to the form (II) a and finally to the form (III) which will be a cyclic polymer form. Similarly, under



(A) Run No. (4) acrolein-aniline
 (B) Run No. (10) "
 (C) Run No. (1) "
 (D) Run No. (8) "
 (E) RunNo. (16) acrolein-BA

Fig. 1 Infrared spectra of intermediate condensates and final polymers of acrolein-monoamines

strongly acidic solution, the imine group of (II) b resulted form (I) by self-condensation will be polymerized to form (III), cyclic polymer product too.

In the spectra of the intermediate condensate (II) a and the final condensate (III), while the absorption bands of sec. OH at 1120cm^{-1} , C=C at 1670cm^{-1} and OH at 3400cm^{-1} appeared in (A) of Fig. 1, the absorption band of C=C remained, that of OH at 3400cm^{-1} and that of sec. OH disappeared in (B) of Fig. 1.

While the absorption bands of C=C at 1660cm^{-1} and C=N at 1680cm^{-1} appeared in (C) of Fig. 1, the absorption band of C=C remained and that of C=N disappeared in (D) of Fig. 1. Similarly, in the spectra of the final prout of acrolein-BA in (E) of Fig. 1, the absorption band of C=C at 1670cm^{-1} remained, that of sec. OH disappeared, and that of -OH at 3400cm^{-1} was decreased. Also C=C group was confirmed in both intermediate condensates and final polymers by spot tests of bromine solution.

In elementary analyses of Table II, the oxygen content of the condensate (II) a formed in basic solution is greater than that of the condensate (II) b formed in acidic solution, which means easy dehydration in acidic solution. By further reaction of the intermediate condensates, (II) a and (II) b, they gave the final polymers of same elemental contents, which are similar to form (III).

Such analytical results as infrared spectra, elementary analyses, and the properties of melting point and solvency of the polymers confirm the assumed mechanisms of the condensation polymerization, eq. (1) and eq. (2)

Table. 2 Characterization of Acrolein-Aniline and Acrolein-BA Polymers

Run No.	Formula	Color	Elementary analyses				Found (%)		
			Calculated (%)				C	N	H
			Mp ^d , °C	C	N	H			
Run No. 4	(II) _a	red ^c	65	77.15	10.00	7.14	76.87	10.08	7.16
1	(II) _b		58	88.47	10.67	6.86	82.16	10.26	7.01
10	(III)	red-brown ^c	86	"	"	"	81.31	10.58	6.98
9	(III)		87	"	"	"	82.12	10.58	7.30
14	(V) _a	red	57	70.00	11.67	11.66	69.57	11.24	11.78
13	(V) _b		51	75.65	12.63	11.72	75.55	12.61	11.84
16	(VI)	red-brown ^c	76	75.65	12.63	11.72	75.90	12.31	11.65
15	(VI)		74				75.55	12.61	11.84

Remarks; solvent; benzene, toluene, xylene, ketones, dimethyl formamide, pyridine, dioxane.

^c transparent, MP $\pm 1^\circ\text{C}$.

It is well known that Skraup^{11),12),13)} synthesized quinoline from acrolein and aniline but in this experiment the formation of quinoline was not found by comparing the infrared absorption spectra of (A) and (B) of Fig. 1 with the standard spectrum of quinoline.¹⁴⁾

Polymerization of Acrolein-BD and Acrolein-MDA.

In case that 1 mole of acrolein is reacted with less than 1 mole of diamines, the polymer obtained is soluble and fusible, however with more than 1 mole of diamines, the polymer is insoluble and infusible.

The reaction of acrolein with diamines takes place

at random at room temperature and becomes explosive in acidic solution to form insoluble random polymers. The reaction is controlled by adding the acrolein stepwise at low temperature with efficient cooling apparatus. Since the polymers of acrolein-diamines have different cured states due to the reaction condition, the crosslinking degree will be related to the severity of the reaction except the ratio of the monomers.

In the spectra of the final polymers of acrolein-BD and acrolein-MDA as shown in Fig. 2, the absorption bands of C-N (tertiary aromatic amine) at

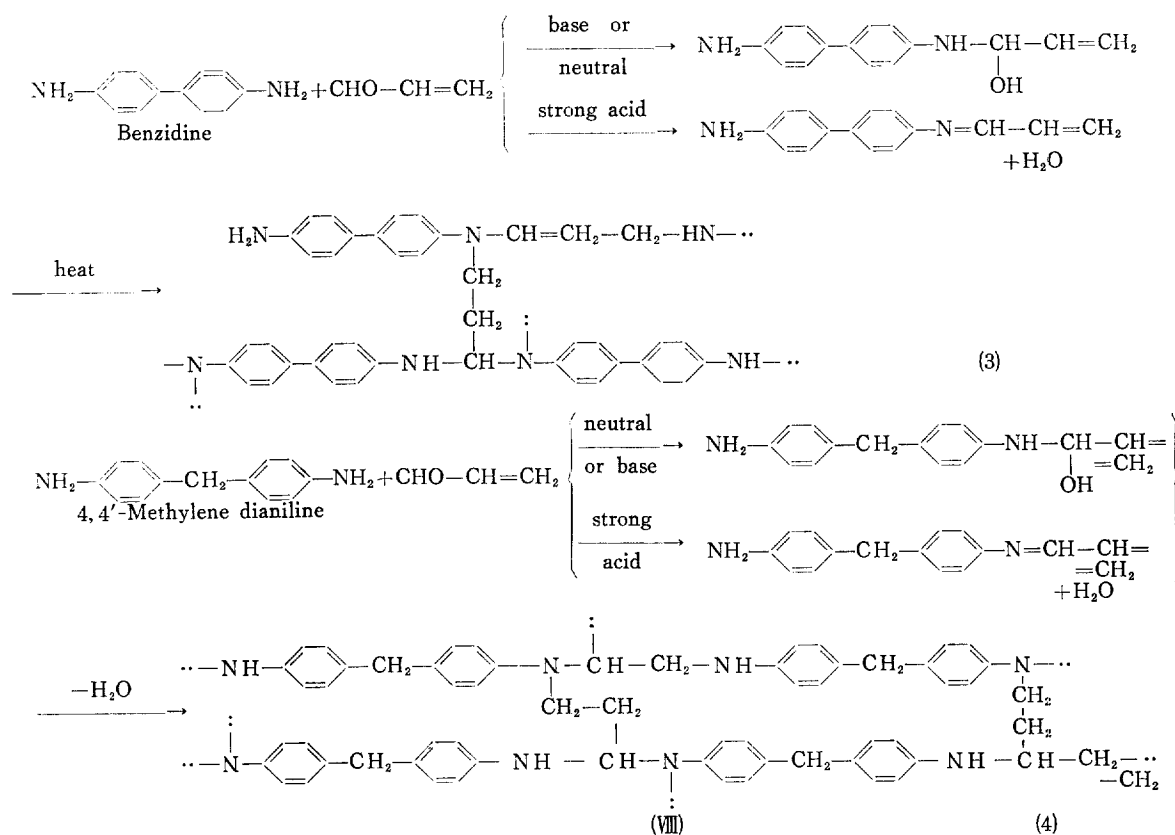
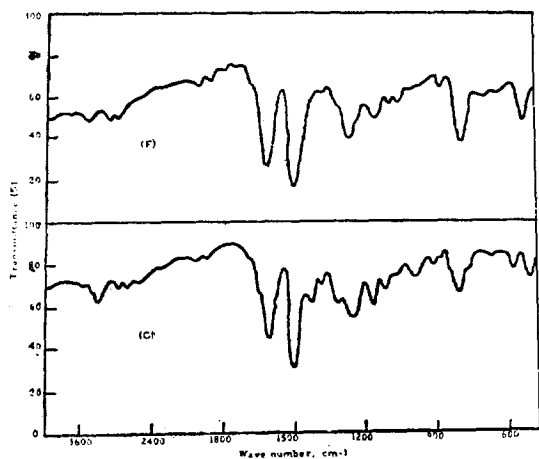


Table. 3 Characterization of Acrolein-BD and Acrolein-MDA Polymers

Polymer	Formula	Color	Mp°C	Elementary analyses					
				Calculated (%)			Found (%)		
				C	N	H	C	N	H
Acrolein-BD	(VII)	red Yel. a	c	81.08	12.61	6.31	80.81	12.51	6.41
Acrolein-MDA	(VIII)	red ^b	c	81.35	11.87	6.78	81.05	11.98	6.97
a. Opaque,	b. Transparent	c Infusible							



(F) acrolein-BD. (G) acrolein-MDA
Fig. 2 Infrared spectra of acrolein-diamines polymers;

1270cm^{-1} and N—H at 3370cm^{-1} appeared, and that of —OH at 3400cm^{-1} disappeared.

In Table 3, the elementary analyses of the final polymers of acrolein-BD, and acrolein-MDA are consistent with the calculated values of the form (VII) and (VIII) of acrolein-BD, and acrolein-MDA respectively. The molecular weight determinations of those polymers are not possible because they are not soluble or fusible.

Also it was confirmed that the polymers of acrolein and other diamines e.g., ethylene diamine, hexamethylene diamine, 4,4'-diamino diphenyl ether, 4,4'-diamino diphenyl sulfone, and etc. were insoluble and infusible in preliminary experiments.

The results of the infrared spectra, the elementary analyses, the insolubilities and infusibilities confirm the above mechanism of the random condensation polymerization, eq. (3) and (4).

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