Step-Growth Polymerization of Unsaturated Aldehydes with Aliphatic Amines

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SYNOPSIS

The step-growth polymerization of unsaturated aldehydes (acrolein, crotonaldehyde, cinnamaldehyde) and aliphatic amines (butylamine, ethylenediamine, triethylenetetramine, diethylenetriamine, hexamethylenediamine) took place intensively in the temperature range between 50 and 90°C. The rates of individual reactions depended on the type of individual aldehydes and amines. The quantity of individual unreacted monomers was mostly under 1%. The average molecular weights of oligomers were between 290 and 710. The individual resins consisted of oligomers with free $-OH$, $-NH$, $-CH=N-$, and $-CH=CH-$ groups, which are further able to cross-link the resins with three blocked isocyanate to insoluble, elastic film with high adhesion to glass and metal substratum. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

In our previous works, we investigated the step-growth polymerization of unsaturated aldehydes with urea, guanamines, and aniline.[1–5] The products were resins, appropriate for cross-linking due to the manifold functionality of the used monomers.

The unsaturated aldehydes are resonant hybrids of different structures.[6] They are highly reactive on the positions of the double bond and of the aldehyde group. They can react according to the Michael's addition mechanism, with all compounds having mobile protons to form several different oligomers. The low oligomers still contain some free double bonds, aldehyde groups, or hydroxyl groups, which further react to higher oligomers and eventually cross-link to insoluble resins. Considering all aspects of the synthesis, the best molar ratio between the aldehyde and amino groups was found to be 1 : 1.

The reactivity between aldehydes and amines depends on the resonance stabilization of the double bond and of the aldehyde group and on the number and reactivity of the amino protons. Acrolein is very reactive and with some amines can react even explosively, especially when acid catalysts are used.

Therefore, for practical use, due to its high boiling point and lower toxicity, cinnamaldehyde is more convenient than is acrolein.[1–5]

In this article, the synthesis, characterization, and cross-linking of resins between unsaturated aldehydes and aliphatic amines are presented. For molecular weight measurements, the GPC, and for the study of the structure, the NMR methods were used. As the cross-linking agent, blocked isocyanate was used. Most of the work was done with cinnamaldehyde.

EXPERIMENTAL

Materials

As unsaturated aldehydes, acrolein (A), crotonaldehyde (CR), and cinnamaldehyde (CA) were used. As amines, butylamine (BA), ethylenediamine (EDA), triethylenetetramine (TETA), diethylenetriamine (DETA), and hexamethylenediamine (HMDA) were used. As the cross-linking agent, 1,3,5-tri(isocyanate hexamethylene) isocyanurate, which is three-blocked with methyl ethyl ketoxime, was used. The aldehydes were products of Merck and amines were products of Aldrich. Before use, the monomers were purified and dried.

Synthesis

To obtain high yields and a low content of unreacted monomers, many syntheses at different reaction conditions were tried. The best properties of the resins for further cross-linking were achieved under reaction conditions as described in Table I. The reactions were carried on in methanol, acetone, or toluene (50 wt %) at reflux temperatures. The solvents were chosen considering the solubility of the monomers and reaction products. In one case (sample 8), an acid catalyst was used. The course of the reactions was followed by measuring the concentration of unsaturated aldehyde (decrease of —CHO groups at 9.5 ppm) in the ^{1}H-NMR spectra (Fig. 1).

When the concentration of the unsaturated aldehyde dropped under 1% of the starting concentration, the reaction was quenched by cooling. The molecular weights were determined by GPC using PL-gel columns. The structure of the final dry resins were determined with ^{1}H and ^{13}C one- and two-dimensional NMR spectroscopy. For selected samples, the elemental analysis was also done.

The hydroxyl equivalents were measured by potential titration with KOH. The formed water in the resin was determined by the Karl Fischer method.

The crosslinking of resins was carried out by heating at 130°C for 3 h, using an acid catalyst and a cross-linking agent. Soxhlet acetone extraction was used to determine the degree of cross-linking.

RESULTS AND DISCUSSION

At the selected reaction conditions (Table I), the yields of individual step-growth polymerizations were near 100% with a very small content of unreacted monomers. Exceptions were the two cases when acrolein and crotonaldehyde were used. Due to low boiling temperature, it was supposed that some of the two monomers evaporated during the reaction or drying. In all cases, the products were yellow-to-red, high viscous resins soluble in organic solvents.

The average molecular weights of the resins were between 290 and 720 (Table II). They depended on the reaction conditions, type of monomers, molar ratio, and reaction temperature. The highest molecular weight was achieved in sample 4, when the molar ratio between DETA and CA was 1 : 2.5 and the reaction temperature 92°C. In this case, the highest value of molecular weight corresponded approximately to oligomers formed from four aldehydes and two amines. The lowest polydispersity was found in the resin HMDA–CA (synthesis 8) where the oligomer of type UAU represented 86% of the total.

The course of individual step-growth polymerizations was followed by ^{1}H- and ^{13}C-NMR spectroscopy in one- and two-dimensional methods. Beside signals of unreacted monomers, signals of products appeared. In the proton spectra of the individual resins, the signals for $—\overset{|}{C}H—NH—$ were between 3 and 4 ppm, whereas the signals for $—\overset{|}{C}H—OH$ groups were between 4.5 and 5.5 ppm. The signals of unreacted aldehydes were doublets of the —CHO group at 9.5 ppm. In the ^{13}C-NMR spectra, the characteristic signals of the formed compounds were between 40 and 60 ppm for $—\overset{|}{C}H—NH—$, between 60 and 80 ppm for $—\overset{|}{C}H—OH$, and between 160 and 163 ppm for —CH=N— groups (Fig. 1). The observed chemical shifts of individual groups are given in Table III.[1-5,7]

Table I Reaction Conditions of Step-growth Polymerization of Unsaturated Aldehydes and Aliphatic Amines

Synthesis	Monomers	Solvent	Molar Ratio	Reaction Temp (°C)	Reaction Time (min)	Yield (%)	Hydroxyl Equivalent (mmol OH)
1	DETA : CR	Acetone	1 : 2	55	250	69.8	—
2	DETA : CA	Acetone	1 : 1	56	180	98.8	3.1
3	DETA : CA	Acetone	1 : 1.5	58	180	99.2	—
4	DETA : CA	Toluene	1 : 2.5	92	300	100.0	2.4
5	EDA : CA	Toluene	1 : 2	75	310	100.0	4.7
6	TETA : CA	Toluene	1 : 3	81	310	98.2	4.0
7	BA : A	Acetone	1 : 1	56	340	70.0	—
8[a]	HMDA : CA	Methanol	1 : 2	65	500	100.0	2.3

[a] 0.05 mol of HCOOH.

F1 (PPM)

F2 (PPM)
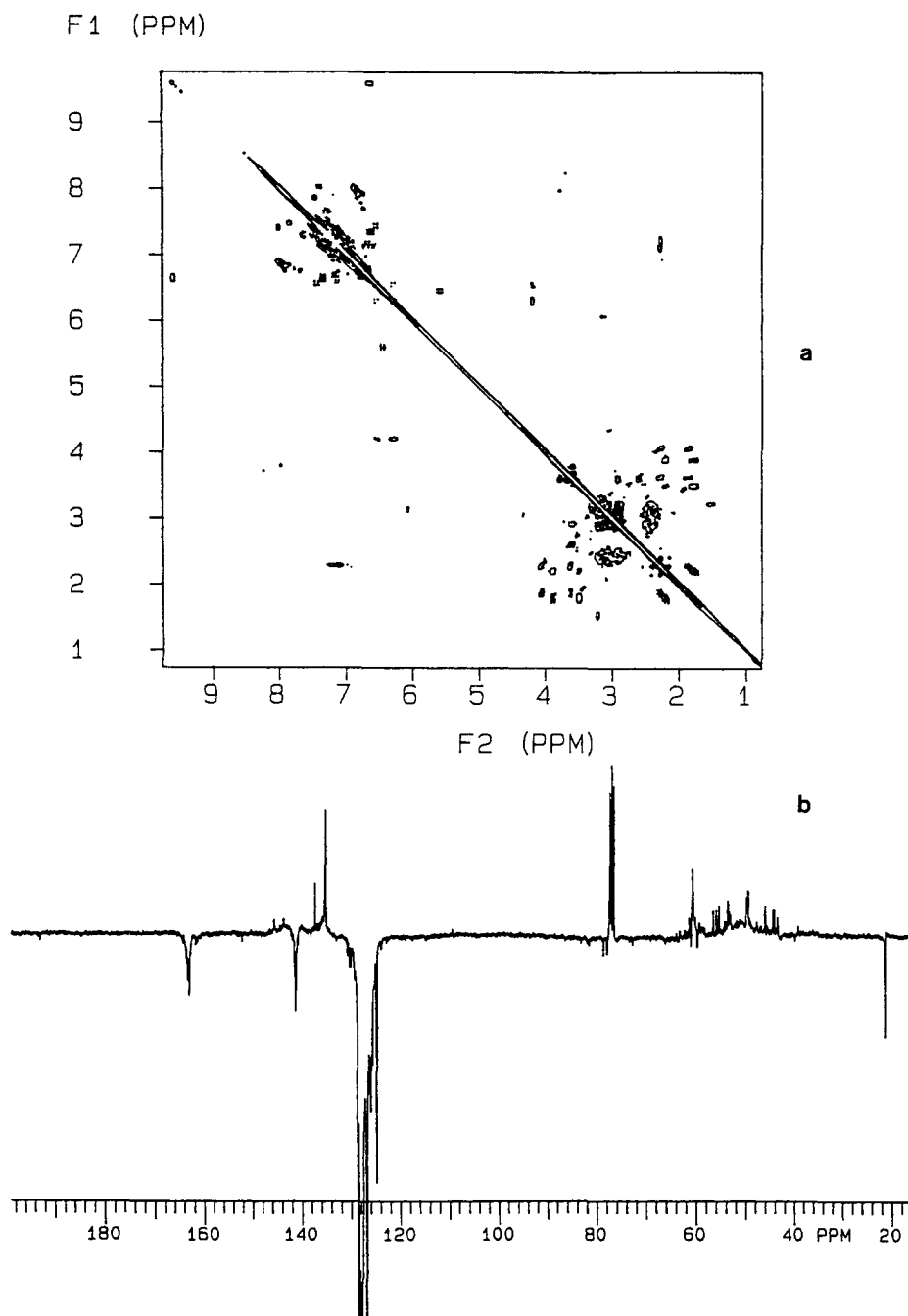
Figure 1 (a) 2D H—H COSY and (b) ^{13}C-APT spectra of the reaction products between CA:DETA 2.5:1.

To follow the course of reactions comparing the signals of the aldehyde group at 9.4 ppm in the ^{1}H spectra and the signals at 194 ppm in the ^{13}C spectra and the signals of double bonds between 5 and 6 ppm and 120 and 150 ppm in proton and carbon spectra, respectively, with the signals of the aromatic rings is the most convenient. In Figure 2, the decrease of the quantity of the aldehyde groups and of the double bonds vs. reaction time for syntheses

4 and 8 as representative cases are given. From the spectra, it can be concluded that the decrease of the quantity of aldehyde groups is much faster than is the decrease of double bonds; e.g., in sample 4 (Fig. 2), the decrease of the quantity of the aldehyde groups is three times faster than the decrease of double bonds. It can be concluded that in the first step of polymerization the reaction of aldehyde groups with the formation of hydroxyl groups pre-

Table II   Molecular Weight Distribution (Mol %) of the Products Between Unsaturated Aldehydes and Aliphatic Amines

| Synthesis | Monomers | Molecular Weight | | | | | $\bar{M}_w$ |
		150–200	200–300	300–400	400–500	500–1000	
1	1.2	15.0	46.0	20.7	17.1	0.0	291
2	1.0	10.9	41.6	11.1	21.2	14.2	384
3	0.6	9.2	48.6	20.9	9.5	11.2	366
4	0.4	9.1	5.9	23.3	0.0	61.3	710
5	0.8	2.0	87.5	1.9	4.4	3.4	280
6	0.3	8.9	20.3	0.0	59.4	11.1	496
7	0.3	1.1	20.5	10.4	40.2	27.5	476
8	0.3	0.0	0.0	86.0	0.0	13.7	470

dominates. Later, the hydroxyl groups reacted with the neighboring imino groups to form the —CH=N— group and water. During the reaction (synthesis 4), part of water azeotropically distilled (2.1%) while part of it remained in the reaction products (1.1%).

—CH=N— groups were formed only when the molar ratio between the reactants was higher than 1 : 1.5 and the reaction temperature over 60°C. With the progress of the reaction, the double bonds disappeared and new signals of —CH$_2$— and —CH—NH— appeared. The reactions were quenched when the concentration of the aldehydes was about 1 mol % of the initial values, with the aim to preserve the hydroxyl and the imino groups

for further cross-linking. One of the proposed (representative) schemes of the reaction between CA and DETA is given in Figure 3. The schemes of the reactions for other aldehydes and amines are similar except in the fractions of individual oligomers (Table II).

The hydroxyl equivalents for individual samples were between 2.3 and 4.7 mmol OH/g (Table I). The hydroxyl equivalent for sample 4 was 2.4 mmol/ g, which corresponds to 1.5 of —OH group per molecule with M = 710. The elemental analysis of sample 4 gave 79.445%, C; 7.15%, H; and 11.18%, N. The hydroxyl equivalent calculated from the difference of percentages of C, H, and N content and 100% is 1.5 mmol OH/g, which is close to the observed

Table III ^{1}H and ^{13}C Chemical Shifts of the Main Groups of Reaction Products Between Unsaturated Aldehydes (U) and Aliphatic Amines (A)

| Type of Oligomers | Type of Group | | Chemical Shifts (ppm) | | |
			^{1}H Observed	^{13}C Observed	^{13}C Calculated
UA	OH | —NH—CH—CH=CH— 1 2 3	1 2 3	4.5–5.5 5.5–6.5 6.0–7.0	63–70 124–132 142–148	— 130.2 145.1
AUA UAUA	OH NH | | —NH—CH—CH$_2$—CH— 1 2 3	1 2 3	4.5–5.5 2.5–3.5 3.0–4.0	63–70 30–40 40–60	— 35.2 57.1
AU, AUA, AUAU	—N=CH—CH=CH— 1 2 3	1 2	7.7–8.2 5.5–6.5	160–163 128–130	163.0 130.2
UA UAU	NH | —CH—CH$_2$—CHO 1 2 3	1 2 3	3.0–4.0 2.5–3.5 9.4–9.6	40–60 30–40 192–194	57.1 35.2 192.4

Figure 2 Decrease of aldehyde groups (1, 3) and double bonds (2, 4) for the reaction between CA:DETA (1, 2) and CA:HMDA (3, 4).

value. On the basis of the NMR spectra, GPC measurements, hydroxyl equivalent, elemental analysis, and ratio between the reacted aldehyde groups and the double bonds, it can be concluded that the main oligomer in sample 4 consisted of two amines and four aldehyde units with 1.5—OH groups and 2.5 conjugated —N=CH—CH=CH— groups. There are also possible other stereoisomers besides the ones named, but due to the similar structures, it was impossible to make a more precise characterization of the individual oligomers.

Cross-linking of Resins

As can be seen from the spectra of individual resins, the dominant reactive groups are —NH—, double bonds, and —OH groups. As mentioned, their quantity depends on the reaction conditions, on the

Figure 3 General course of the reaction between unsaturated aldehydes (U) and aliphatic amines (A).
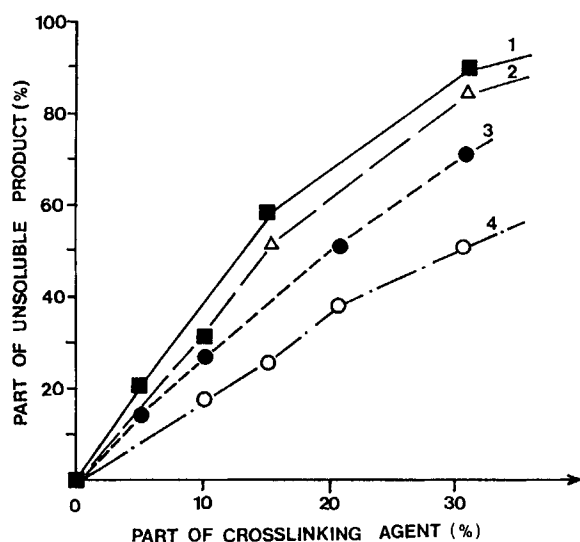
Table IV The Dependence of the Adhesion to the Glass and Metal Substratum and Hardness of the Film

Part of Cross-linking Agent (%)	Adhesion to Glass Substratum (%)		Adhesion to Metal Substratum (%)		Hardness of the Film(s) (%)	
	a	b	a	b	a	b
0	40	50	50	60	60	65
10	60	90	70	95	70	80
15	90	100	100	100	100	100
20	100	100	100	100	110	110
30	100	100	100	100	115	120

Cross-linking time was 3 h at 130°C. Synthesis 4 (a); synthesis 8 (b).

molar ratio, and on the type of monomers used for the synthesis. To obtain insoluble elastic film, we tried various types of cross-linking agents. The best results were achieved with three-blocked isocyanates, which, after deblocking, reacted with the free hydroxyl and imino groups to form urethanes and substituted urea groups. In Figure 4, the degree of cross-linking in terms of the dependence of the insolubility on the concentration of the cross-linking agent is given. For sample 4, the maximum of cross-linking was achieved with 30% of the blocked isocyanate. The films were elastic and highly adhesive on metal or glass substratum. The adhesion to the

glass and metal substrata determined according to DIN 55151 increases with the increasing part of cross-linking agents (Table IV). The hardness of the film determined by Konig pendulum (DIN 53157), where the time of the oscillation of the pendulum depends on the hardness of the film, reaches the highest value with 30% of cross-linking agents.

CONCLUSION

In the step-growth polymerization of unsaturated aldehydes with aliphatic amines, yellow-to-red resins are formed. The resins are capable of further cross-linking, e.g., with a three-blocked isocyanate. The cross-linked films are insoluble and elastic and exhibit a high adhesion to metal or glass substratum.

Figure 4 Dependence of insolubility on the concentration of triblocked isocianate: (1) synthesis 4, cross-linking time 3 h; (2) synthesis 4, cross-linking time 2 h; (3) synthesis 8, cross-linking time 3 h; (4) synthesis 8, cross-linking time 2 h. Cross-linking temperature 130°C.

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