Polymer Bulletin 22, 155–161 (1989)

Polymer Bulletin

Step-growth polymerization of guanamines with unsaturated aldehydes

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Summary

In acid medium and at temperatures from 50 to 100°C the resins from three different guanamines and three different unsaturated aldehydes were synthesized. The products were red coloured resins, which were soluble in organic solvents and were able to cure with hexamethylenetetramine to form hard and almost insoluble products. Using a combination of NMR and GPC methods it was possible to predict the course and the mechanism of the reactions. The rates of the reactions depend on the reaction conditions and on the type of the monomer.

Introduction

In a series of works we have reported on the reactions of unsaturated aldehydes with different monomers (1-7). A special case was the reaction of melamine with unsaturated aldehydes. Melamine is namely almost insoluble in organic solvents and only when proper conditions were used to dissolve melamine, its conversion was very high (8-9).

In this work the reactions between guanamines and unsaturated aldehydes were investigated. The guanamines are well soluble in organic solvents and with unsaturated aldehydes react intensively to form high viscous red coloured resins. As guanamines (G) caprinoguanamine (CG), benzoguanamine (BG) and acetoguanamine (AG) and as unsaturated aldehydes (A), acrolein (AC), crotonaldehyde (CR) and cinnamaldehyde (CA) in organic solvents and acid media were used. For characterization of the reaction products ^{1}H and ^{13}C NMR spectroscopy and GPC chromatography were used.

Experimental

Materials: CG (2,6-diamino-4-nonyl-1,3,5-triazine), BG (2,6-diamino-4-phenyl-1,3,5-triazine) and AG (2,6-diamino-4-methyl-1,3,5-triazine)were products of SKW, while the unsaturated aldehydes were products of Merck. The guanamines were used as received, while the aldehydes were destilled before use.

Syntheses: The syntheses were performed in a glass vessel equipped with a magnetic stirrer. The guanamines were first dissolved in the selected solvent, then aldehydes and catalyst were added, the mixture mixed and heated to the temperature of reaction. The reaction time varied according to the type of the monomers and to the quantity of phosphoric acid used as catalyst. The molar ratio between guanamines and unsaturated aldehydes was in all cases 1:2, while the molar ratios of the phosphoric acid to monomer varied from 0.01 to 0.1. The detailed experimental data are given in Table 1.

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Table 1
Synthesis data of guanamine - unsaturated aldehyde resins

Synth.	Monomers (molar ratio 1:2)	Molar ratio of catalyst	Solvent	Reaction temp. °C	Reaction time min	Yield %	Unreacted, mol %	
							guanamine	aldehyde
1	Caprinoguanamine - acrolein	0.02	Methanol	55	720	97.3	0.7	1.0
2	Caprinoguanamine-crotonaldehyde	0.05	Toluene	98	320	96.0	1.2	1.8
3	Caprinoguanamine - cinnamaldehyde	0.05	Toluene	100	430	94.6	1.4	2.0
4	Benzoguanamine - acrolein	0.02	DMF	50	280	97.8	0.9	1.2
5	Benzoguanamine - crotonaldehyde	0.05	DMF	85	345	95.6	1.2	1.5
6	Benzoguanamine - cinnamaldehyde	0.05	DMF	70	490	95.9	1.0	2.1
7	Acetoguanamine - acrolein	0.02	DMSO	55	450	93.9	1.2	1.4
8	Acetoguanamine - crotonaldehyde	0.05	DMF	85	440	94.0	1.8	2.0
9	Acetoguanamine - cinnamaldehyde	0.05	DMF	90	450	93.5	1.9	2.5

The spectra for ^1H and ^{13}C NMR spectroscopy were taken on a VARIAN VXR 300 supraconducting spectrometer, using 90° pulse width for both proton and carbon spectra. The pulse delay was 2 s. The 2D COSY spectra were recorded at the same conditions. Attached proton test (APT) was recorded at $\tau = 7.5$ ms. All spectra were quoted on TMS as internal standard, while chloroform d_1 was used as solvent. The molecular weights of the resins were measured by GPC using a UV detector at wavelength $2.54.10^{-7}$ m. The pore sizes of the Ultra-Styragel columns were 1 and 5.10^{-8} m. THF was used as solvent. The columns were calibrated by polystyrene standards and by the guanamines and unsaturated aldehydes used in the work.

Results and discussion

The guanamines are four-functional and compared to melamine differ in the substituent on position 4. The resins from guanamines are more flexible compared to resins from melamine. Due to good solubility of the guanamines the reactions with aldehydes are easy to control.

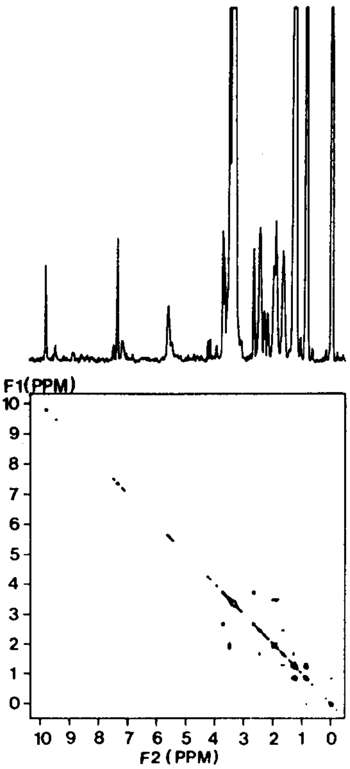
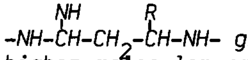


Figure 1. COSY proton-proton spectrum of the product of caprinoguanamine and acrolein

The APT of the resins shows that the signals between 14 and 24 ppm belong to $-CH_3$ groups of bonded or unbonded CG, BG or AG. All the $-CH_3$ signals are oriented to the negative side. To the negative side as well are oriented the signals of the $-\overset{|}{C}H-$ groups of the bonded aldehydes, while the signals of the $-CH_2-$ groups of the substituted guanamines are oriented to the positive side.

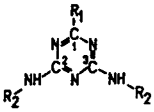
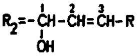
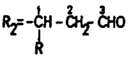
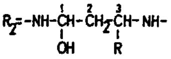
In the COSY proton-proton spectra the interactions between neighbouring protons can be seen as out of diagonal signals (Fig.1). With reaction time some signals disappear and new are formed. First disappear the signals for monomers, later the signals for -CHO and $-\overset{|}{C}HOH$ groups and the signals for the double bonds of oligomers. Finally the signals for



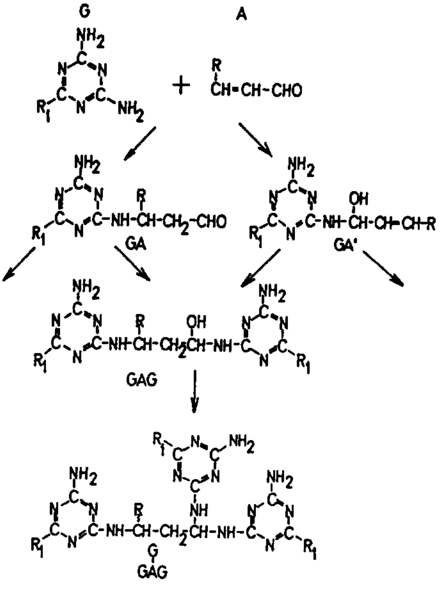
$-NH-\overset{NH}{\overset{|}{C}}H-CH_2-\overset{R}{\overset{|}{C}}H-NH-$

groups belonging to higher molecular products are formed. On the basis of these and literature data, chemical shifts for different oligomers appearing in the reactions between guanamines and unsaturated aldehydes were predicted (6,10-12). The observed chemical shifts for different oligomers are given in Table 2. All similar oligomers, regardless of the used monomers, have chemical shifts in the same regions. The type of the substituent in the guanamine influences only the precise location of the signals in the given region. Thus, the region between 177 and 180 ppm is characteristic for the triazine ring in which the carbon is

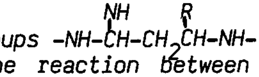
Table 2
Chemical shifts of carbons in the compounds appearing in the reaction between substituted guanamines and unsaturated aldehydes

		Chemical shifts (ppm)	
		carbon	proton
	1	170-172	
	2,3	166-168	
$R_1=-C_9H_{19}$		14-39	0.9-2.0
$R_1=-C_6H_5$		128-137	6.8-7.7
$R_1=-CH_3$		24-25	0.7-0.9
 $R_2=-\underset{OH}{\overset{1}{C}H}-\overset{2}{C}H=\overset{3}{C}H-R$	1	65-72	5.3-5.6
	2	130-135	5.5-6.5
	3	145-155	5.5-6.5
 $R_2=-\underset{R}{\overset{1}{C}H}-\overset{2}{C}H_2-\overset{3}{C}HO$	1	40-50	3.0-3.6
	2	32-36	
	3	200-205	9.4-9.8
 $R_2=-NH-\underset{OH}{\overset{1}{C}H}-\overset{2}{C}H_2-\underset{R}{\overset{3}{C}H}-NH-$	1	65-70	5.3-5.6
	2	25-35	1.2
	3	30-40	

$R=-H,-CH_3,-C_6H_5$



$R_1=-CH_3,-C_9H_{19},-C_6H_5$
$R=-H,-CH_3,-C_6H_5$

substituted by different -R groups and the region between 164 and 167 for the triazine in which the carbon is substituted by $-NH_2$ or -NH-groups. Chemical shifts for groups  $-NH-\overset{NH}{C}H-CH_2\overset{R}{C}H-NH-$ formed in the reaction between $-NH_2$ groups of the guanamines and the double bonds or the aldehyde groups of the aldehydes, are in the region between 30 and 50 ppm. Actually, this is the first step of the reaction between the two monomers. The quantity of the particular oligomers is influenced by the type of the monomers used in the reaction. In the scheme the formation of the oligomers is shown.

In Table 3 the molecular weights of the reaction products are given. The molecular weights depend on the type of solvent, on the quantity of catalyst and on the reaction conditions. The increasing quantity of catalyst, higher temperature and longer time of reaction increase the molecular weights. In the GPC

Table 3

The molecular weight distribution of the reaction products between guanamines and unsaturated aldehydes

Synth.	Monomers	Molecular weight					
		<300	300-600	600-800	8000-1500	1500-2500	2500<
1	Caprinoguanamine - acrolein	0.01	0.33	0.38	0.18	0.10	-
2	Caprinoguanamine - crotonaldehyde	0.02	0.07	0.05	0.06	0.20	0.60
3	Caprinoguanamine - cinnamaldehyde	0.03	0.08	0.07	0.09	0.28	0.45
4	Benzoguanamine - acrolein	0.01	0.22	0.30	0.27	0.13	0.07
5	Benzoguanamine - crotonaldehyde	0.02	0.20	0.25	0.33	0.15	0.05
6	Benzoguanamine - cinnamaldehyde	0.02	0.25	0.27	0.36	0.09	0.03
7	Acetoguanamine - acrolein	0.01	0.24	0.31	0.23	0.15	0.06
8	Acetoguanamine - crotonaldehyde	0.02	0.34	0.20	0.18	0.16	0.1
9	Acetoguanamine - cinnamaldehyde	0.03	0.20	0.30	0.24	0.14	0.09

chromatograms several areas of molecular weights can be seen: the area of monomers and the area of molecular weights from 200 to 600, belonging to products of the type GA, AGA or GAG. From the low content of free -CHO and -CH=CH-groups observed in the spectra it can be concluded that the GAG type is prevailing. The area of molecular weights from 600 to 800
A A G
belongs to products of the type GAGA, AGA or GAG. The type GAG must be prevailing since the signal for the structure $-NH-\overset{NH}{C}H-CH_2-\overset{R}{C}H-NH-$ *in the spectra is the most intensive. The area of 800 to 1500 belongs to products of five to ten monomer units and the last area to products of higher molecular weights.*

The kinetics of the reactions was followed by measuring the molecular weights in dependence of reaction time. The samples were taken from the reaction vessel in regular time intervals, then cooled and dissolved in THF. In Fig. 2 an example of this dependence for the reaction between caprinoguanamine and crotonaldehyde is given.

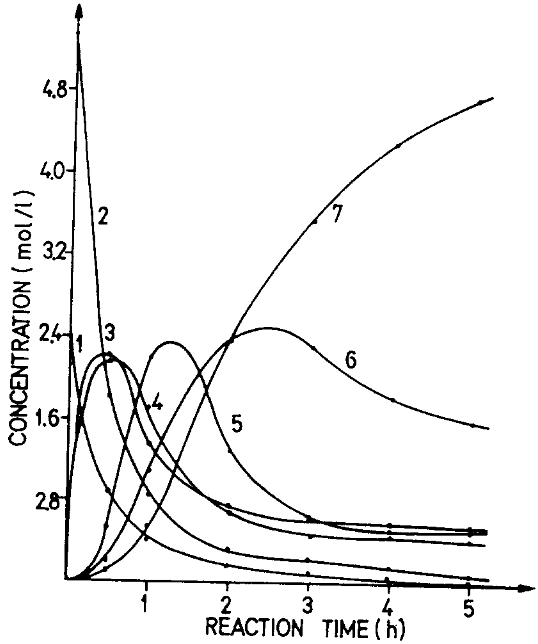


Figure 2. The dependence of MWD on reaction time: 1=caprinoguanamine, 2=crotonaldehyde, 3=MW 400, 4=MW 700, 5=MW 1000, 6=MW 2200, 7=MW 6500

The kinetic equation for the first step of the reaction is the following:

$$\frac{d[A]}{dt} = k_1[A][G] \qquad (1)$$

$$\frac{d[GA]}{dt} = k_1 [A][G] \quad -k_2 [GA][A] \; .k'_2 \; [GA][G] \qquad (2)$$

where A and G are the corresponding aldehyde and guanamine respectively. In the first approximation it can be assumed that for the early stage of the reaction $k_2 = k'_2$ and [GA] > [GAG]. By time differentiation of experimental values for A , G and GA the values for k_1 and k_2 were calculated. In Table 4 the rate constants for the reaction between different guanamines and unsaturated aldehydes are given.

Table 4

The rate constants of the reaction between guanamines and unsaturated aldehydes

	Molar ratio	**Rate constant /l/mol.sek/**	
		k_1	k_2
Caprinoguanamine:acrolein: H_3PO_4	1:2:0.02	$3.2 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$
Caprinoguanamine:crotonaldehyde: H_3PO_4	1:2:0.05	$4.9 \cdot 10^{-4}$	$4.0 \cdot 10^{-4}$
Benzoguanamine:crotonaldehyde: H_3PO_4	1:2:0.05	$3.0 \cdot 10^{-4}$	$2.2 \cdot 10^{-4}$
Acetoguanamine:crotonaldehyde: H_3PO_4	1:2:0.05	$3.5 \cdot 10^{-4}$	$3.1 \cdot 10^{-4}$

By comparing the rate constants with reaction conditions it can be concluded that the rate of resins formation depends on the type of the monomers, on the reaction conditions, and on the type of solvent. The best solvents are toluene and DMF, which both are good solvents for the resins as well. Between the unsaturated aldehydes acrolein is the most and cinnamaldehyde the less reactive.

The resins were crosslinked by heating them for three hours at 135°C and by the addition of hexamethylenetetramine. In both cases the crosslinked resins were more than 85 % unsoluble in organic solvents. The behaviour at crosslinking indicates that the products of reaction between guanamines and unsaturated aldehydes belong to termosetting resins.

Acknowledgements

The authors are grateful to the Research Community of Slovenia for supporting the work.

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Accepted July 8, 1989 C