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Thermal analysis of polyacrylic acid modified by some glucosamine derivatives

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Polymerization of acrylic acid in the presence of N-acetylglucosamine and glucosamine hydrochloride was carried out and the products were characterized using IR spectroscopy. A mechanism for the formation of the modified polymers was suggested. Thermal analyses of the polymers formed were studied. It was found that the polymers containing free amino groups are more stable than other polymers. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

The surface activities, biodegradability and antimicrobial properties of glucosamine derivatives containing alkyl chains have been of major interest in the last few years (Matsumura *et al.*, 1993). It has been found that carbohydrates represent the most abundant regenerable resource of these materials.

The hydroxyl groups of the sugar represent different basicities (Muzzarelli, 1977). The ring hydroxyl groups have pK_as of the order 10 to 12 while the methylene "off-ring" hydroxyls have pK_as similar to typical aliphatic hydroxyls with values of about 14. The existence of an amino group in the glucose derivatives increases the basicity. It is well known that in aqueous solution the majority of ring hydroxyls will exist in the deprotonated state, whereas the off-ring hydroxyls will be largely protonated (Naoshima *et al.*, 1985).

In this paper polymerization of acrylic acid (AA) in the presence of N-acetylglucoseamine (AGA) and glucosamine hydrochloride (GA–HCl) was carried out. The polymers formed were characterized and their thermal analyses were studied.

EXPERIMENTAL

AGA and GA–HCl (BDH Chemical Co. Ltd) were used without purification.

AA (Aldrich Chemical Co. Inc.) was purified by degassing in a vacuum line and kept below −18°C.

2,2-Azobisisobutyronitrile (AIBN) (BDH Chemical Co. Ltd) was purified by dissolving in hot ethanol and filtering (Grant & Grassie, 1960).

Preparation of the polymers

Polyacrylic acid (PAA) was prepared by free radical initiation using 0.1% (w/v) AIBN as initiator and 50/50 (v/v) methanol–water as solvent. The polymerization was carried out in a thermostat at 60±0.1°C. PAA was precipitated by pouring into diethyl ether. The polymer was filtered, washed several times with ether and dried in a vacuum oven at 40°C.

Modified AA–AGA and AA–GA–HCl polymers were prepared by refluxing equimolecular amounts of AA and AGA or GA–HCl using 0.1% (w/v) AIBN, dissolved in methanol, and 50/50 (v/v) water as solvent. After refluxing for 4 h the polymers were precipitated in a large excess of diethyl ether, filtered and dried for several days.

Characterization of the polymers

Infrared spectroscopy
Infrared (IR) spectra were recorded in film form using a Pye Unicam SP 2000 spectrophotometer.

Thermogravimetry
Thermogravimetry (TG) measurements were made with a Mettler 3000 thermobalance. Samples (~10 mg) were heated at 10°/min in a dynamic nitrogen atmosphere (70 ml/min); the sample holder was boat-shaped, 10×5×2.5 mm deep, and the temperature measuring thermocouple was placed within 1 mm of the holder.

Differential scanning calorimetry

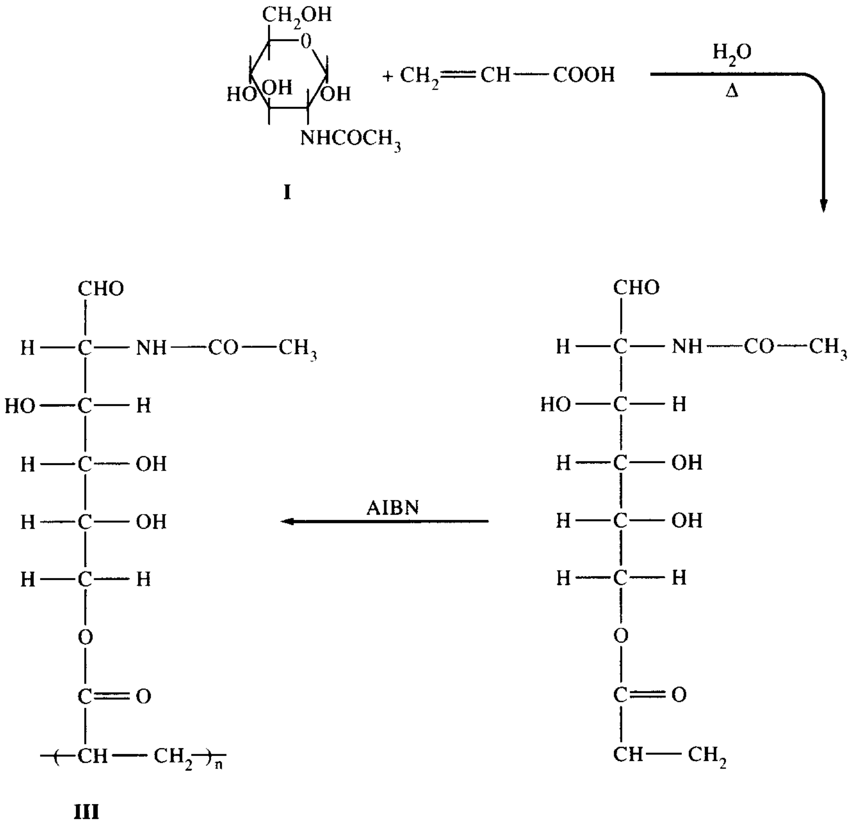
Differential scanning calorimetry (DSC) curves were obtained using the Mettler TA 3000 DSC apparatus. The samples were heated at 10°/min from ambient temperature to 500°C.

RESULTS AND DISCUSSION

All the formed polymers are soluble in polar solvents, such as methanol and pyridine, and insoluble in non-polar solvents.

Characterization of the polymers

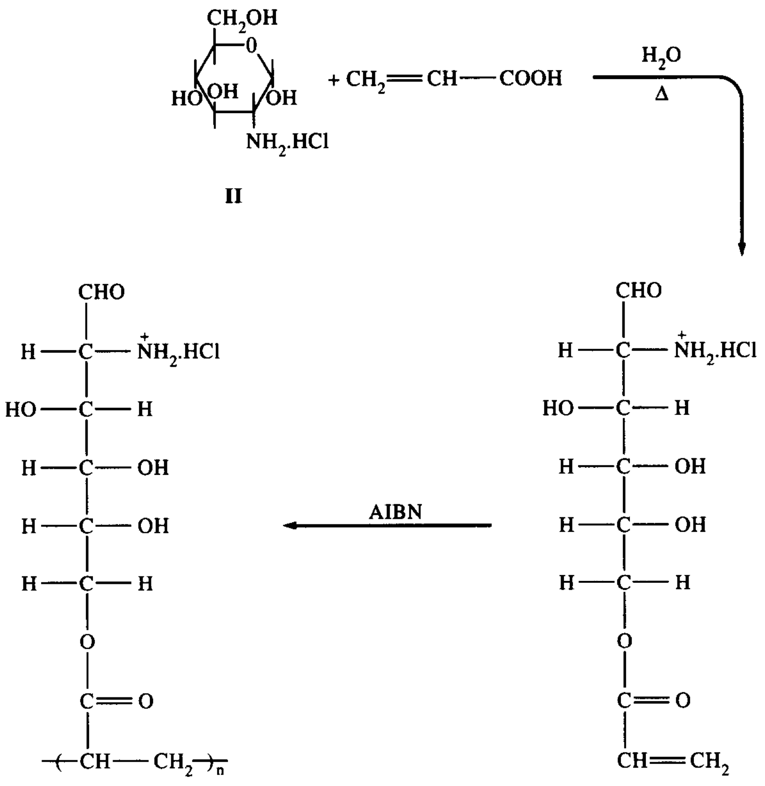
The reaction of AGA (I) with AA using AIBN as initiator afforded poly(N-acetylglucosamine acrylate) (III). Addition of 0.5 ml of concentrated HCl to the reaction mixture catalyzed the reaction. The IR spectrum of III shows absorption bands at 3750–3100, 3000 and 1700 cm^{-1} due to OH, C–H aliphatic and CO groups, respectively. The disappearance of the IR band of the methylene off-ring hydroxyl group suggests that this group is involved in the reaction of AGA with AA. Scheme 1 shows the mechanism of the reaction and Table 1 shows the main characteristic IR bands of the products.



Scheme. 1. Formation of poly(N-acetylgulcosamin acrylate).

Table 1. Characteristic bands of the IR spectra of AGA, GA–HCl, PAA and modified PAA polymers

Compound	IR (KBr) (cm^{-1})
AGA	3450 (OH), 3280 (NH), 2890 (CH aliphatic), 1630 (CO) and 1550 (C–O–C)
GA–HCl	3800–2600 (OH), 3250 (NH_2Cl), 2890 (C–H aliphatic) and 1530 (C–O–C)
PAA	3850–3000 (OH), 1700 (CO), 1640 (C–O–C) and 1180
III	3750–3100 (NH, OH), 3000 (C–H aliphatic), 1700, 1630 (CO), 1400, 1180, 1100, 1050, 900
IV	3750–2750 (OH, NH_2), 1630–1710 (CO), 1400, 1180, 1100, 1050
V	3250–2500 (OH), 3100–3200 (NH_2), 1700 (CO), 1520 (C–O–C), 1400, 1180, 1050
VI	2500–3300 (NH amidic and OH), 3000 (C–H aliphatic), 1700 (CO), 1580 (C–O–C), 1030, 1180, 1250



II

IV

Scheme. 2. Formation of poly(glucosamine hydrochloride acrylate).

In a similar manner, the polymerization of AA in the presence of GA–HCl afforded poly(glucosamine hydrochloride acrylate) (IV). The IR spectrum of IV shows bands at 3750–2750 cm^{-1} (OH and NH_2 groups) and 1700 cm^{-1} (CO group). Addition of 0.5 ml of concentrated HCl catalyzed the polymerization process, forming the same polymer (IV) (Scheme 2 and Table 1).

Addition of excess $NaHCO_3$ solution to polymer IV afforded poly(glucosamine acrylate) (V). The IR spectrum of polymer V shows absorption bands at 3250–2900 cm^{-1} (OH and NH_2 groups) and 1760 cm^{-1} (CO group) (Scheme 3 and Table 1).

Polymerization of equimolar amounts of AA and V using AIBN as initiator afforded the crosslinked polymer VI. The IR spectrum of polymer VI shows characteristic absorption bands at 3300 cm^{-1} (NH, amide) and 1700 cm^{-1} (CO group) (Scheme 3 and Table 1).

Thermal methods of analysis

DSC

DSC curves of PAA hompolymer and the modified polymers III, IV, V and VI are shown in Figure 1. AGA and GA–HCl show one endothermic peak at 222 and 226°C, respectively, and a second exothermic peak at 408 and 445°C, respectively. This is similar to the result suggested by Bihari-Varga *et al.* (1975). DSC of the PAA homopolymer shows three endothermic peaks at 115, 340 and 434°C, indicating that three degradation steps are involved. PAA modified by AGA and GA–HCl shows different degradation stages and these are listed in Table 2.

TG

The TG curves of PAA homopolymer and the modified PAA polymers III, IV, V and VI are shown in Figure 2. AGA and GA–HCl degrade in two stages. The first stage starts at 199 and 198°C with weight loss percentages of ~49 and 55%, respectively. The second stage starts at 246 and 326°C with weight losses of 36 and 33%, respectively. PAA homopolymer exhibits three TG stages of decomposition. The first stage starts at ~100°C and reaches a maximum at ~145°C with a weight loss of 39%. The second stage starts at 306°C with a weight loss of ~20%, while the third stage starts at ~352°C and reaches a maximum at 434°C with a weight loss of 19%. The modified polymer III has four TG degradation stages starting at ~176, 281, 379 and 425°C with weight loss percentages of ~43, 18, 10 and 6%, respectively. The TG of polymer IV shows two decomposition stages starting at 180 and 326°C with weight losses of 67 and 22%, respectively. Poly(glucosamine acrylate) (V) shows two TG stages, the first at 189°C with a weight loss of 69% and the second at 334°C with a weight loss of ~22%. Three degradation stages were observed for polymer VI, at

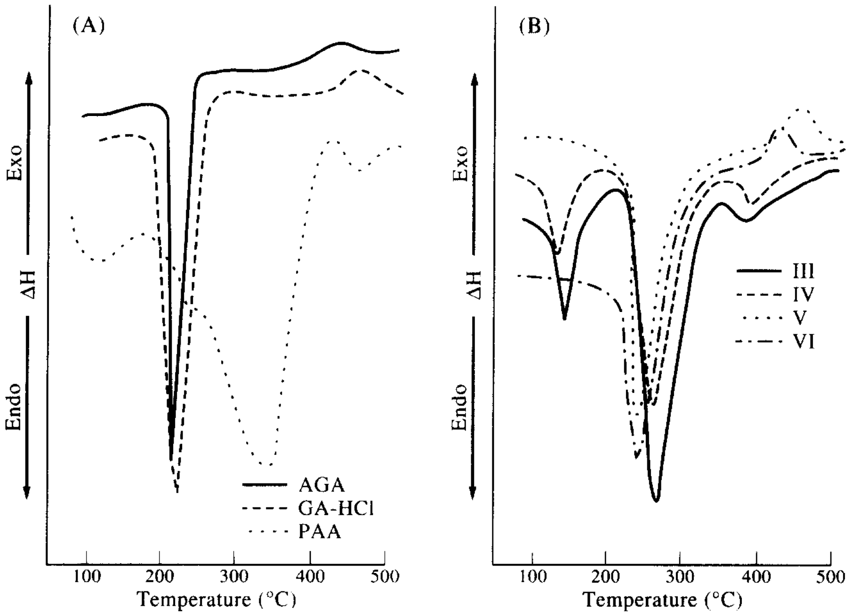


Fig. 1. DSC curves of AGA, GA-Hcl, PAA, III, IV, V and VI.

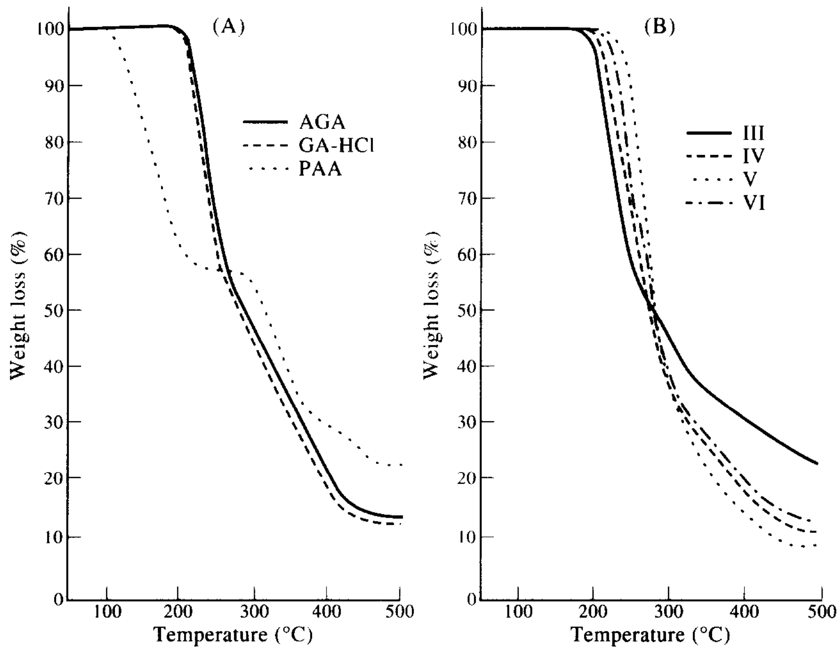
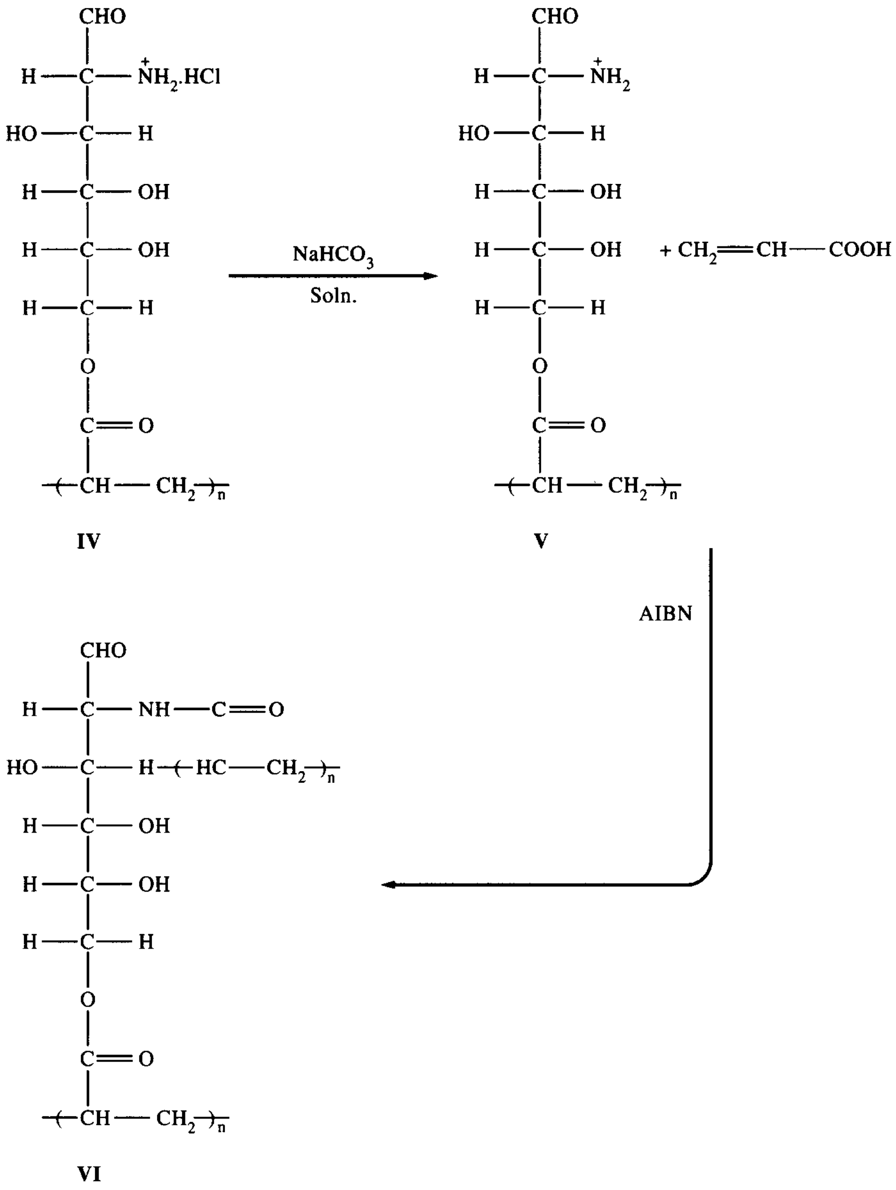


Fig. 2. TG curves of AGA, GA-HCl, PAA, III, IV, V and VI.



Scheme. 3.Effect of $NaHCO_3$ on poly(glucosamine hydrochloride acrylate).

Table 2. DSC data for PAA and modified PAA

Compound	First stage		Second stage		Third stage	
	Peak temperature (°C)	Heat flow	Peak temperature (°C)	Heat flow	Peak temperature (°C)	Heat flow
AGA	222	Endo	408	Exo	—	—
GA-HCl	226	Endo	445	Exo	—	—
PAA	115	Endo	340	Endo	434	Endo
III	149	Endo	288	Endo	340	Endo
IV	130	Endo	270	Endo	348	Endo
V	238	Endo	417	Exo	—	—
VI	230	Endo	403	Exo	—	—

185, 335 and 416°C with weight losses of 67, 12 and 7%, respectively. Table 3 represents the TG data for PAA and modified PAA polymers.

From the TG curves it was found that poly(glucosamine acrylate) (V) is more stable than PAA and modified PAA III, IV and VI. It seems that the free amino group in polymer V has a stabilizing effect. This is similar to the results suggested by

Table 3. TG data for PAA and modified PAA

Compound	First stage			Second stage			Third stage			Fourth stage			Weight remaining after 500°C
	*T_{st}	T_{max}	Weight loss (%)	T_{st}	T_{max}	Weight loss (%)	T_{st}	T_{max}	Weight loss (%)	T_{st}	T_{max}	Weight loss (%)	
AGA	199	243	49	246	250	36	—	—	—	—	—	—	15
GA-HCl	198	241	55	326	249	33	—	—	—	—	—	—	12
PAA	100	145	39	306	309	20	352	434	19	—	—	—	22
III	176	265	43	281	285	18	379	421	10	425	447	6	23
IV	180	247	67	326	422	22	—	—	—	—	—	—	11
V	189	277	69	332	434	22	—	—	—	—	—	—	9
VI	185	272	67	335	402	12	316	424	7	—	—	—	12

*Starting temperature.

Nagasawa *et al.* (1971) who concluded that chitosan is more stable than chitin to depolymerization due to the stabilizing effect of the free amino group in chitosan. Nud'ga *et al.* (1973) have produced a further contribution to this subject. They used a Schiff base derivative in order to protect the amino group to obtain less stable polymers. Therefore polymer V is more stable than polymers III, IV and VI due to the existence of a free amino group.

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