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REACTIONS ON POLYMERS WITH AMINE GROUPS. II. REACTIONS OF POLY(*N*-VINYLIMIDAZOLE) AND ITS MODEL COMPOUND WITH UNSATURATED CARBOXYLIC ACIDS

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Key Words: Poly(*N*-vinylimidazole); *N*-Methylimidazole; Addition reaction; Betaine polymers; ¹H-NMR characterization

ABSTRACT

The reactions of poly(*N*-vinylimidazole) and its low molecular weight model, *N*-methylimidazole, with α,β -unsaturated acids such as acrylic, crotonic, itaconic, fumaric, and maleic were studied. It was found that the reactions with monocarboxylic acids lead to betaine products, while reactions with dicarboxylic acids lead to betaine as well as the corresponding salt structures. The rate of addition increases with solvent polarity. Its value is greater for the polymer than for the model. The ¹H-NMR methodology was generally applied for elucidating the chemical structure obtained. It was found that chain configuration is not modified by addition reactions, but the tacticity splitting of chain-methine proton signal shows a significant decrease. The polymers derived from monocarboxylic acids were more water soluble than those from dicarboxylic acids.

INTRODUCTION

As described in a previous paper [1], the reactions of poly(2-vinylpyridine) and poly(4-vinylpyridine) with various α,β -unsaturated carboxylic acids, such as acrylic, itaconic, fumaric, and maleic acids, give macromolecular betaine products. An alternative method to obtain similar macromolecular carboxybetaines is alkylation of the pyridine group with halogenated acetic acid or its esters [2, 3].

The present article presents the chemistry of modification of poly(*N*-vinylimidazole) (PNVI) by reaction of the imidazole group with acrylic (AA), crotonic (CA), itaconic (IA), fumaric (FA), and maleic (MA) acids. Similar reactions were also studied with *N*-methylimidazole (NMI). Macromolecular imidazole betaine compounds were previously obtained by polymerization of vinylimidazole monomers containing betaine groups derived from alkenylsulfonfylchlorides [4], bromoacetic, bromopropionic, and acrylic acids, and bromobutyrate [5].

EXPERIMENTAL

Materials

PNVI was obtained from freshly vacuum-distilled monomer by radical polymerization in methanol at 50°C with AIBN initiator under nitrogen for 72 hours. A low monomer concentration [5% (w/v)] was used in order to avoid gel formation [6]. The chain was found to be of nearly atactic configuration. The weight-average molecular weight was determined from light scattering and found to be 46,000. Before use, NMI and AA were vacuum distilled, and CA, IA, FA, and MA were purified by recrystallization.

Preparation

The compounds described in the present paper were obtained in reactions carried out in glass vessels under controlled conditions with stirring and heating.

The following conditions were mostly used in the model studies: 1/1 molar ratio of reactants at a total reactant concentration of 2 mol/L, conducted in methanol at 50°C for 24 hours. The reaction products from NMI with AA, CA, and IA were dissolved in the reaction mixture so they were separated by precipitation with ethyl ether. The products resulting from AA and CA were crystalline substances of betaine structure. The precipitate from IA was a viscous liquid which contained the corresponding betaine and salt compounds in a ratio of about 1/1.4. The betaine compound from NMI and FA precipitated during reaction, and precipitation with ethyl ether of the remained reaction mixture gave the pure salt compound. The reaction between NMI and MA generated a crystalline precipitate which is a mixture of the corresponding betaine and salt compounds in a ratio of about 7/3. The precipitation with ethyl ether of the remained reaction mixture gave a similar mixture but with a betaine/salt ratio of about 6/4. All the reaction products derived from NMI are given in Table 1.

The reactions with PNVI were studied at 50°C in methanol, water, and aceto-

TABLE 1. Products Resulting from the Reaction of NMI with α,β -Unsaturated Carboxylic Acids^a

Acid	Structure and proton chemical shifts (D ₂ O/DSS)	Yield, ^b %	
		B	S
AA		35	—
MAA ^c		< 5	—
CA		22	—
IA		41	57
FA		13	42
MA		32	23

^aReaction conditions: 1/1 molar ratio between reactants, 1 mol NMI/L, methanol as solvent, 50°C, and 24 hours.

^bYield relative to the amine reactant. B = betaine structure, S = salt structure.

^cMethacrylic acid.

nitrile. The polymer concentration was 5% (w/v), which means about 0.5 mol imidazole group/L. A 1/1 molar ratio of the reactants and a reaction time of 24 hours were mainly used.

Depending on the solvent and the resulting chemical structure, the polymeric reaction products were dissolved and/or precipitated in the reaction mixture (see Table 2). The soluble polymeric reaction products were isolated by precipitation with ethyl ether or acetone. The precipitated products were separated by filtration and washed well with acetone for removal of all impurities (especially unreacted acids). All products were powdered and vacuum dried before analysis.

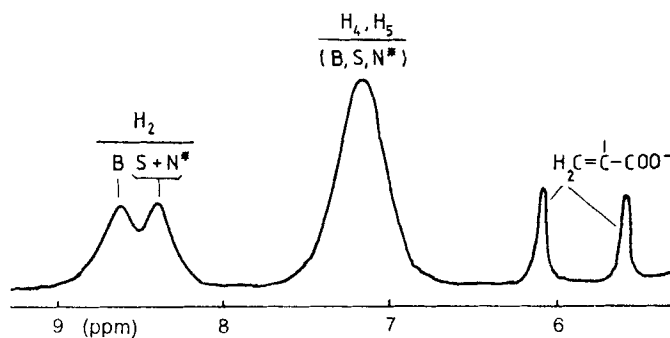


FIG. 1. The 5–9 ppm part of 80 MHz ^1H -NMR spectrum recorded from a PNVI-IA polymer in D_2O acidulated with trifluoroacetic acid at 80°C . The N^* units are initial N units converted into salt units by trifluoroacetic acid.

Characterization

The chemical structure was unequivocally established for all soluble products with ^1H -NMR by which it is even possible to differentiate between betaine (B) and salt (S) structures. The estimation of B and S contents for the polymeric products is rather difficult due to the broadening and overlapping of signals. It was found that this problem may be best solved by using the proton signals of the imidazole ring if the spectra are obtained from acidulated (trifluoroacetic acid) aqueous solution. For example, the signals which allow determination of the fractions of B, S, and N (unmodified) units are given in Fig. 1 for PNVI reacted with IA.

The acidulation shows two effects: unfastening of the interchain hydrogen bonds, which causes the insolubilization of many polymeric products (Table 2), and cancellation of the isotopic exchange between the proton H_2 of the imidazole ring and the deuterium atoms of water (the only solvent for betaine compounds). The H_2 signal is important because it is sensitive to the betaine and salt structures.

The ^1H -NMR method was also used to obtain information on the reaction kinetics for reactions of AA with NMI and PNVI. The majority of NMR spectra were recorded at 80 MHz, but some were obtained at 300 MHz.

The attempt to use the IR spectra for confirming the results of NMR failed because it was not possible to make certain band assignments. The single clear assignment in the IR was the presence of COO^- anion stretching bands at 1590 cm^{-1} ($\text{C}=\text{O}$) and 1400 cm^{-1} ($\text{C}-\text{O}$).

RESULTS AND DISCUSSION

Reactions of NMI

Chemical Structure of the Reaction Products

The chemical structure and the corresponding proton chemical shifts, together with the relative yields of the products resulting from the reaction of NMI with unsaturated carboxylic acids, are given in Table 1.

The betaine compounds are obtained in all cases. The order of addition reactivity corresponding to the measured yields is $IA > AA = MA > CA > FA > MAA$.

Comparison with 4-methylpyridine reacted with the same acids in similar conditions [1] shows that NMI is less active in reactions with AA and FA but more active with IA and MA.

Mixtures of betaine and salt compounds were obtained when NMI was reacted with all dicarboxylic acids, unlike 4-methylpyridine which gives salt only in the case of MA. The values for salt formation yields must be accepted with caution because the salt compound results from equilibrium reactions, and there may be significant differences between the precipitate and the reaction mixture due to the conditions used for precipitation. Of course, such an uncertainty is also present for the polymeric products.

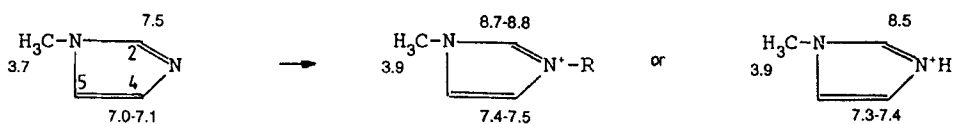
The main NMR arguments supporting a carboxybetaine structure are the following: the absence of double bond proton signals, the presence of signals corresponding to the methine and methylene groups formed by amine addition to the double bond of the acids, and the shift of the reacted imidazole proton signals to a lower field, which agrees with a positive charge on the imidazole ring (see Scheme 1). The insignificant difference between the chemical shifts of the protons H_4 and H_5 indicates a quite uniform distribution of the positive charge on the two nitrogen atoms.

The NMR arguments for a salt structure are the following: the low field positions of the imidazole proton signals, which agree with a positive charge on the imidazole ring, and the presence of double bond proton signals of an acid anion (Scheme 1).

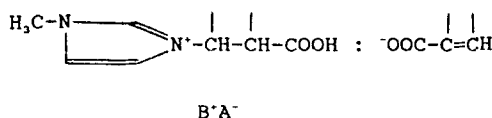
It should be underlined that the imidazole proton H_2 signal distinguishes between the betaine and salt structures. This observation is useful for the analysis of polymeric products where the signal intensities of the methylene and methine groups resulting from addition cannot be measured due to their large broadening and the overlapping with signals of other groups.

Considerations on the Betaine Formation Reaction

The reaction of NMI and AA with $[AA]_0/[NMI]_0 = 2$ and $[NMI]_0 = 1$ mol/L was carried out directly in an NMR tube using CD_3OD as solvent at $50^\circ C$. A kinetic treatment of the yield values as determined from NMR spectra recorded for different reaction times indicated that the process of betaine formation (the salt was not observed for monocarboxylic acids) is not a bimolecular reaction but a reaction with more complex kinetics. Such a deduction is also supported by the fact that the products which are significant at the beginning of reaction are not the betaine compounds but the compounds B^+A^- (Scheme 2).



SCHEME 1.



SCHEME 2.

Such compounds were isolated by fast vacuum removal of the volatile components of the reaction mixture (NMI and solvent) followed by repeated washings with acetone to remove the residual acid. The spectra of the products so obtained (the spectrum of the product derived from NMI and AA is given in Fig. 2) show an equimolarity between the groups which is characteristic of the cation B^+ and anion A^- . On the other hand, it was observed that the molar ratio $[\text{B}^+]/[\text{A}^-]$ apparently increases with acid consumption, growing significant to over 1 at the end of the reaction if the initial molar ratio $[\text{acid}]_0/[\text{amine}]_0$ is about 1 or lower. If $[\text{acid}]_0/[\text{amine}]_0$ is about 2 or higher, then $[\text{B}^+]/[\text{A}^-]$ remains near 1 until the amine is totally consumed.

The observations presented before lead to the supposition that the formation of betaine compounds takes place by the following two coupled reactions:



Equilibrium Reaction (2) explains the cases where the yield of betaine formation was found to be higher than half of $[\text{acid}]_0/[\text{amine}]_0$, which would be the maximum value obtainable if only Reaction (1) were considered.

The trimolecular Reaction (1) is predominant when $[\text{B}^+\text{A}^-] < 0.5[\text{acid}]_0$. When $[\text{acid}]_0/[\text{amine}]_0 = 2$, the kinetic equation of this reaction has the following integral form:

$$(1 - x)^{-2} - 1 = 8k_1[\text{amine}]_0^2 t \quad (3)$$

where $x = [\text{B}^+\text{A}^-]/[\text{amine}]_0$ at time t .

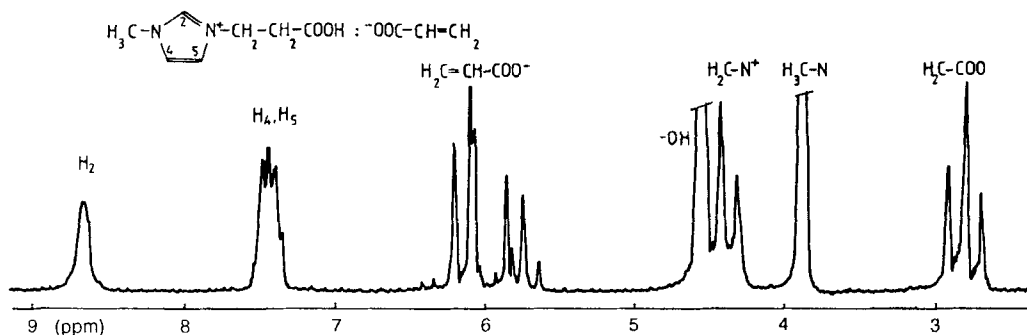


FIG. 2. The ^1H -NMR spectrum in D_2O from the product of a B^+A^- type which appears predominantly at the beginning of the reaction between NMI and AA.

It was found that the values of $x(t)$ determined for the reaction as observed by NMR agree well with Relation (3) if $x < 0.5$.

The reaction rate constant was found to be $k_{1(\text{NMI-AA})} = 0.8 \times 10^{-3} \text{ mol}^{-2} \cdot \text{L}^2 \cdot \text{min}^{-1}$.

Addition of acetone to an alcoholic or aqueous solution of B^+A^- causes precipitation of the pure betaine compound. This means that the added solvent, which is a nonsolvent for B^+A^- compounds and a good solvent for free acid, makes the equilibrium of Reaction (2) shift strongly to the right.

The presumed mechanism for B^+A^- formation involves an initial nucleophilic attack of the nitrogen atom at the β -carbon atom of the acid double bond, with dipolar ion formation [7]. Protonation of this carbanion is probably an intermolecular process involving a new acid molecule rather than a solvent molecule because the B^+A^- and B compounds were obtained in both protic and aprotic solvents (see Ref. 1 and Table 2). The reactions which promote the formation of a B^+A^- compound in protic deuterated solvent are given in Scheme 3. α -Carbon atom deuteration was indeed observed.

Reactions of PNVI

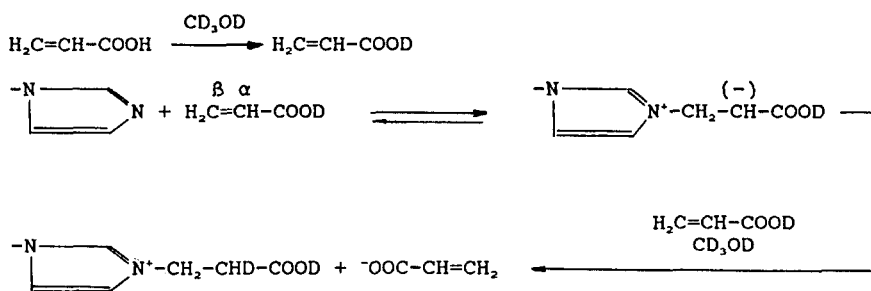
Chemical Structure of the Polymeric Products

The general chemical structures of the polymers resulting from the reactions of PNVI with AA, CA, IA, FA, and MA are given in Scheme 4. The reaction with methacrylic acid was not tried due to the insignificant yield observed in the model compound case.

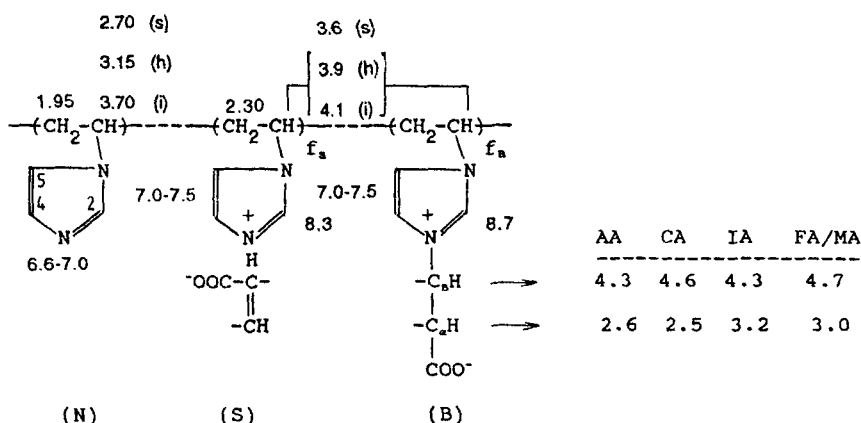
Characterization of these polymeric products together with their codification are given in Table 2.

It can be observed that the addition reaction occurs for all acids, while the neutralization reaction seems to take place only for dicarboxylic acids.

The presence of betaine (B) units is supported, as in the case of products from NMI, by $^1\text{H-NMR}$ signals characteristic of the methylene and methine groups resulting from the addition of the unsubstituted nitrogen atom of imidazole groups to the double bond of acids. The chemical shift values for these groups are also given in Scheme 4. As an example, the 300-MHz NMR spectra of unmodified PNVI and PNVI-AA with a high content of B units are shown in Fig. 3. The methylene



SCHEME 3.



SCHEME 4.

TABLE 2. The Content^a of B and S Units for Polymers Resulting from Reactions of PNVI with Unsaturated Carboxylic Acids Performed in Three Solvents^b

Solvent (ϵ)	Acid, pK_a									
	AA 4.86		CA 4.44		IA ^c 3.82, 5.65		FA ^c 3.02, 4.49		MA 1.84, 6.49	
	f_B	f_S	f_B	f_S	f_B	f_S	f_B	f_S	f_B	f_S
CH ₃ OH (32.6)	0.46	—	0.1	—	0.55	0.25	0.33	0.35	0.33	0.50
	—	—	—	—	Insoluble		0.43	0.32	0.34	0.47
H ₂ O (81.8)	0.75	—	0.2	—	0.60	0.22	0.35	0.30	0.34	0.50
	—	—	—	—	Insoluble		Insoluble		—	—
CH ₃ CN (38.8)	—	—	0.2	—	—	—	—	—	—	—
	0.78	—	0.4	—	0.65	0.20	0.57	0.25	0.37	0.53
Polymer code	PNVI-AA	PNVI-CA	PNVI-IA	PNVI-FA	PNVI-MA					

^aThe upper values are for the polymer dissolved in the reaction mixture, and bottom values are for the polymer precipitates during reaction. A dash means that polymeric products or salt units were not observed in significant quantities.

^bOther reaction conditions: 1/1 molar ratio between reactants, 0.5 mol imidazole groups/L, 50°C, and 24 hours.

^cThe corresponding products were soluble only in acidulated (trifluoroacetic acid) water.

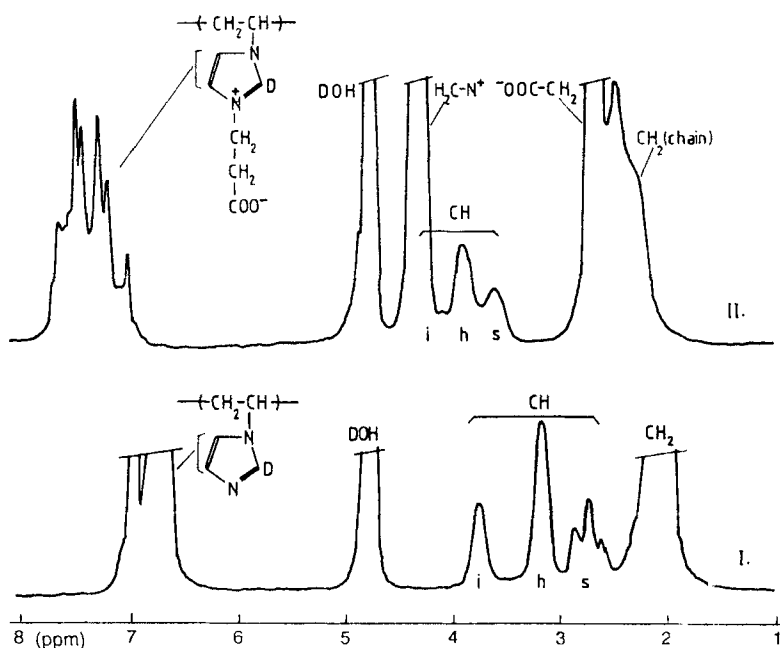


FIG. 3. The 300 MHz ^1H -NMR spectra of normal PNVI (Spectrum I) and a PNVI-AA polymer with $f_B = 0.94$ (Spectrum II) recorded on D_2O solutions at room temperature.

signals for the group $\text{N}^+ - \text{CH}_2 - \text{CH}_2 - \text{COO}^-$ together with a low field shift of about 0.5 ppm for the imidazole protons H_4 and H_5 are clearly observed in the spectrum of the macromolecular betaine compound. The signal of the H_2 proton is absent due to the exchange with deuterium from deuterated water. As stated previously, such an exchange is canceled if the polymer solution is acidulated (see Fig. 1).

The spectra in Fig. 3 show that the methine signal of the main chain is sensitive to polymer chain configuration. The assignment of this signal on the tacticity triads of PNVI is given elsewhere [8].

By using the relation $A_i:A_h:A_s = P_m^2:2P_m(1 - P_m):(1 - P_m)^2$, where A_i , A_h , and A_s are the signal intensities for the isotactic (i), heterotactic (h), and syndiotactic (s) triads, and P_m is the probability for the meso diads, it was found that $P_m = 0.44$ for the unmodified polymers (Spectrum I); therefore, this polymer is almost atactic. Because Spectrum II shows an $A_h:A_s$ ratio with the same value as Spectrum I, chain configuration is not changed by the addition reaction, as expected.

An interesting observation is that splitting of the methine proton signal is smaller for the betaine polymer than for the unmodified polymer. This decrease in splitting may be explained by the reduction of π -electron density in the imidazole rings due to nitrogen quaternization.

The signal of chain-methine groups in PNVI-AA polymers with a medium or low content of B units shows a much more complex pattern. An analysis of such

signals in terms of triads differentiated by composition and configuration (there are 20 different triads, theoretically) to find some eventual microstructure effect on the considered addition reaction is in progress.

As expected from studies on the model, polymers resulting from dicarboxylic acids contain all three types of possible units B, S, and N (Scheme 4 and Table 2). The values of f_S were determined from NMR signals of acid anion double bonds, therefore the values in Table 2 may be somewhat larger than the real ones due to free acid impurities. However, the conclusion that the fraction of salt units increases with the pK_a values of the acids seems to be proper.

About the Addition Reaction of PNVI

If the values of f_B for polymers obtained in the same solvent are compared (Table 2), the order of acids reactivity would be $AA > IA > FA > MA > CA$, which is different from that found in the study of NMI.

As for NMI, it was found that Reaction (1) takes place, and B^+A^- -like units are obtained. Several $f_B(t)$ values were determined by carrying out the reaction of PNVI with AA at $[NVI]_0 = 1 \text{ mol/L}$ and $[AA]_0/[NVI]_0 = 2$ in methanol at 50°C . Using Relation (3) with $x = f_B$, it was found that Reaction (1) is characterized by a rate constant of $k_1 = 5.7 \times 10^{-3} \text{ mol}^{-2}\cdot\text{L}^2\cdot\text{min}^{-1}$. This k_1 value is significantly greater than the one for the reaction of NMI with AA. Moreover, all the f_B values corresponding to the polymeric products obtained in methanol (Table 2) are greater than the yield values for the betaine compounds in Table 1.

Such findings are surprising since, for example, the addition reaction between poly(4-vinylpyridine) and AA is much slower than the same reaction performed with 4-methylpyridine and AA [1]. It is difficult to give a solid explanation at the moment, but similar observations have been reported [9].

Regarding the solvent effects on the addition reaction performed on PNVI, a clear systematization was not possible due to the different solubilities of the polymeric products (Table 2). However, it can be observed for the reaction of PNVI with AA that the addition rate increases with the solvent polarity and is higher in aprotic than in protic solvents. Nevertheless, the use of a polar aprotic solvent (like acetonitrile) is not recommended when $f_B \approx 1$ values are involved because the polymer product precipitates during synthesis when the f_B unit fraction exceeds certain values.

PNVI-AA polymers were synthesized in water at 50°C for several molar ratios of reactants. The f_B values obtained after some reaction times are given in Table 3, and they show that it is possible to obtain polymers with f_B values of almost 1.

About the Solubility of Polymeric Products

Some solubility characteristics may be deduced from Table 2. The polymeric products can only be dissolved in protic solvents, generally water. The polymers derived from monocarboxylic acids are water-soluble even with a high content of B units. Except for PNVI-MA polymers obtained in methanol or water, all the polymers derived from dicarboxylic acids are not soluble in pure water. Some of these are soluble in acidulated (trifluoroacetic acid) water but a few of them (see Table 2)

TABLE 3. A Matrix with f_B Values for PNVI-AA Polymers Obtained in Water with 5% PNVI (w/v) at 50°C and Using Three Values for the Initial Molar Ratio between Reactants

[NVI] ₀ /[AA] ₀	<i>t</i> , hours		
	8	24	48
0.5		0.37	0.42
1	0.53	0.75	0.86
2	0.84	0.91	0.94

are insoluble even in water with sulfuric acid at 80–90°C. The interchain hydrogen bonds formed between carboxyl groups belonging to betaine units can cause a decrease in solubility but not total insolubility. In the literature [5], insolubility is associated with low pK_a values of the carboxyl groups on the one hand, and with short and unsubstituted spacers between the opposite charges on the other. Since none of these correlations is applicable to the present study, a credible explanation may be based on accidental crosslinkings and/or high crystallinity.

CONCLUSIONS

With α,β -unsaturated carboxylic acids, the reaction of PNVI leads to betaine units in the case of AA and CA (which can be considered weak acids) and to betaine and salt units in the case of IA, FA, and MA (which are dicarboxylic acids and stronger than the former).

The reactions of the low molecular weight model, NMI, with the same acids are similar to those related to PNVI. The addition rate is generally higher for PNVI than for NMI.

The addition reaction does not directly lead to betaine structures but to cation–anion pairs which generate the betaine structure by an equilibrium reaction.

The fraction of betaine units is dependent on the reaction conditions. Thus, the addition rate increases with solvent polarity and is higher in an aprotic solvent than in a protic solvent.

The chain configuration is not modified by addition reactions. Splitting of the ¹H-NMR signal by the chain-methine group (which is sensitive to tacticity) is smaller for the modified polymer than for the unmodified polymer because of the effect of decreasing the imidazole π -electron density due to nitrogen atom quaternization.

The polymer derived from monocarboxylic acids are more water soluble than those from dicarboxylic acids.

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