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Copolymerization of 4-(Diallylamino)pyridine and Acid–Base Behavior of the Copolymers

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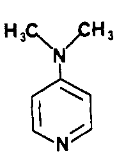
ABSTRACT: 4-(Diallylamino)pyridine (DAAP) cyclopolymerizes with free radical initiators yielding a polymer whose monomer units are identical with 4-pyrrolidinopyridine (PPY), a very active nucleophilic catalyst. It has been found that the catalytic activity of this polymer is higher than that of PPY in all reactions studied to date. We have synthesized copolymers of DAAP with neutral (*N,N*-dimethylacrylamide), cationic (dimethyldiallylammonium chloride), and anionic (acrylic acid) monomers. The reactivity ratios were obtained at 60 °C and show that DAAP active chain ends react with the comonomer faster than with DAAP monomer. All comonomers displayed the opposite behavior. ^{13}C NMR spectra show evidence of both cis and trans isomers in the five-membered ring of the DAAP repeat units. The acid–base properties of the copolymers were investigated with UV spectroscopy and show increasing basicity of the pyridine groups (higher pK_a) with increasing comonomer content in the copolymers of DAAP with *N,N*-dimethylacrylamide and acrylic acid. No apparent dependence of pK_a on composition was observed for the copolymers with dimethyldiallylammonium chloride.

Introduction

It is well-known that nucleophilic reactions catalyzed by pyridine are even more effectively catalyzed by 4-(dimethylamino)pyridine (DMAP, 1) and analogous 4-aminopyridines.[1,2] Among these, 4-pyrrolidinopyridine (PPY, 2) has shown the greatest rate enhancement in at least one study.[2]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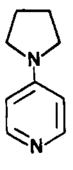
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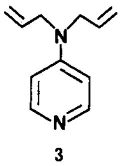
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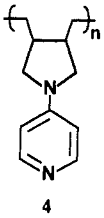
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In many cases, recycle capability and catalytic activity can be modified by attaching the active moiety to a macromolecule.[3,4] Many attempts have been made to bind pyridine and its more reactive derivatives to polymeric chains, leading in some cases to high catalytic activity.[5,6] We have developed a new approach to the synthesis of PPY-containing polymers. Radical homopolymerization of 4-(diallylamino)pyridine (DAAP, 3) in aqueous acid solution yields polymer 4 containing PPY groups on every repeating unit.[7]

This polymer was found to be more effective than monomeric PPY in the catalyzed hydrolysis of *p*-nitrophenyl esters.[8] The reaction followed Michaelis–Menten kinetics similar to that observed for enzymatic reactions. Several literature reports dealing with enhanced catalytic activity due to cooperative effects between different units of the macromolecular catalyst, whether in natural enzymes[9] or synthetic catalysts,[10] led us to the consideration that the activity and selectivity of poly(DAAP) could be modified or even increased further by copolymerization with suitable monomers.

For this initial investigation we chose three comonomers. *N,N*-Dimethylacrylamide (DMAM) yields neutral repeat units, dimethyldiallylammonium chloride (DMDAACl) positively charged ones, and acrylic acid (AA) can lead to carboxylate anions in its copolymers. We report here the synthesis, NMR spectra, and acid–base properties of these copolymers. Their catalytic activity will be discussed in a subsequent paper.

Experimental Section

The synthesis of DAAP was reported previously.[7] Acrylic acid (Aldrich) was freed from inhibitor by distillation under vacuum (bp 48 °C at 2 KPa). DMDAACl (Polysciences) was purchased as a 65% aqueous solution and used without further purification. DMAM (Polysciences) was distilled under vacuum (bp 75 °C at 2 KPa). The free radical initiator V-50 [2,2′-azobis(2-amidino-

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propane hydrochloride), Wako Chemicals] was used as purchased.

All polymerizations were carried out in Schlenk flasks at 60 °C. A 1.4 M excess of HCl with respect to DAAP monomer was necessary to ensure polymerizability of the amine.[7] Monomer solutions were submitted to three freeze–thaw cycles for degassing. After polymerization in a heated water bath, the flasks were chilled, the contents poured into dialysis bags (MW cutoff 3000–6000) and dialyzed against water for 4–5 days. The contents were then freeze-dried to give solid products for determination of conversion and characterization.

NMR spectra were recorded with a Bruker MSL-200 spectrometer. UV spectra were recorded with a Perkin-Elmer 320 spectrophotometer. The pH of the buffers used for pK_a determinations was checked with an Orion pH-meter, Model 701-A, using an Orion combination pH probe 91–55. The calibration was performed with standard buffers (pH 7 and 10, Curtin Matheson Scientific, Inc.).

Viscometric measurements employed Cannon–Ubbelohde viscometers at 25 °C. The solvent was a 0.1 M aqueous NaCl solution in order to reduce polyelectrolyte effects at high polymer dilutions.

Calculation of the Reactivity Ratios. Reactivity ratios in copolymerizations are usually evaluated with samples obtained at low conversions (<5%). Calculations are done both by iterative[11,12] or linearization methods.[13,14] If the conversion is known accurately, the Kelen–Tudos method[15] can be modified so that samples obtained at high conversion can also be used.[16]

Copolymer compositions were determined by UV spectroscopy. The protonated DAAP unit shows an absorption maximum at 280 nm. The molar absorptivity for poly(DAAP) in 10% aqueous HCl was determined to be 1.36 × 10^4 L/(mol cm). The copolymers with acrylic acid were only soluble in aqueous formic acid. Solutions were obtained by dissolution in concentrated formic acid followed by dilution with water. The molar absorptivity in 10% formic acid was determined to be 1.43 × 10^4 L/(mol cm).

Determination of pK_a of the Copolymers. The pK_a of organic acids and bases is usually calculated by titration of a solution of the electrolyte with strong base or acid while recording pH as a function of the amount of titrant. This procedure was not feasible in our case due to the weakness of the polybase and, in some cases, to the low solubility of the polymers. Instead, the titrations were carried out spectroscopically.[17,18] Protonated DAAP units absorb at 280 nm while unprotonated groups show an absorbance maximum at 260 nm. The molar fraction of protonated and free base may therefore be calculated by means of the following expression:

$$x(\mathrm{B}) = \frac{\mathrm{Abs}(280)/\mathrm{Abs}(260)_{\mathrm{pH}\,1} - \mathrm{Abs}(280)/\mathrm{Abs}(260)_{\mathrm{pH}\,p}}{\mathrm{Abs}(280)/\mathrm{Abs}(260)_{\mathrm{pH}\,1} - \mathrm{Abs}(280)/\mathrm{Abs}(260)_{\mathrm{pH}\,13}} \quad (1)$$

where x(B) is the molar fraction of free DAAP units at the pH (pH p) under investigation. The absorbances at pH 1 and pH 13 at 260 and 280 nm were obtained from spectra of the corresponding polymer in 0.1 N HCl and 0.1 N NaOH, respectively. Several buffers were prepared with 0.1 M salt solutions[19] and the necessary amount of polymer solution was injected into the spectrometer cell containing the buffer. The amount added was small in comparison to the cell contents to preclude significant changes in pH.

Results and Discussion

Poly(DAAP-*co*-DMAM). DAAP and DMAM were copolymerized in aqueous acid solution at 60 °C. The dry materials were brittle and yellow colored, especially those with high DAAP content. They were very soluble in methanol and aqueous HCl and less soluble in water and DMSO. They swelled in $CHCl_3$ and were insoluble in acetone. Polymer compositions were determined by UV spectroscopy. Table I gives the data necessary for the calculation of the reactivity ratios. In all reactivity ratio symbols, monomer 1 (M_1) is DAAP, while M_2, M_3, and M_4 are DMAM, DMDAACl, and AA, respectively.

Figure 1 gives the corresponding copolymerization diagram, clearly showing the overall behavior and the high degree of scatter for several of the points. Three points were not used for the Kelen–Tudos calculation which gave reactivity ratio values of r_{12} = 0.03 and r_{21} = 3.68 (subscript 1 stands for DAAP and 2 for DMAM).

The ^{1}H NMR spectrum of polymer A_8 is shown in Figure 2. The peaks at 7.9 and 6.7 ppm are assigned to protons in positions 2,6 and 3,5 of the pyridine ring, respectively. Typical line broadening and peak overlap observed in ^{1}H NMR spectra of polymers are seen for additional hydrogens of the copolymer in the region 0–5 ppm. More in-

Table I
Free Radical Copolymerization of DAAP with DMAM at 60 °C in Water

sample	X_{DAAP}[a]	x_{DAAP}[b]	initiator concn, mol/L	polymerizatn time, min	wt conv
A1	0.099	0.029	4.7 × 10^{-3}	20	0.05[c]
A2	0.531	0.121	1.0 × 10^{-2}	240	0.1[c]
A3	0.698	0.24	1.5 × 10^{-2}	1350	0.1[c]
A4	0.753	0.362	2.2 × 10^{-2}	825	0.25
A5	0.798	0.398	2.3 × 10^{-2}	825	0.23
A6	0.815	0.647	2.5 × 10^{-2}	1350	0.1[c]
A7	0.850	0.458	2.4 × 10^{-2}	825	0.17
A8	0.902	0.554	2.5 × 10^{-2}	825	0.15
A9	0.947	0.799	2.6 × 10^{-2}	825	0.11

[a] X_{DAAP}, molar fraction of DAAP in the feed. [b] x_{DAAP}, molar fraction of DAAP in the copolymer. [c] Approximate values.

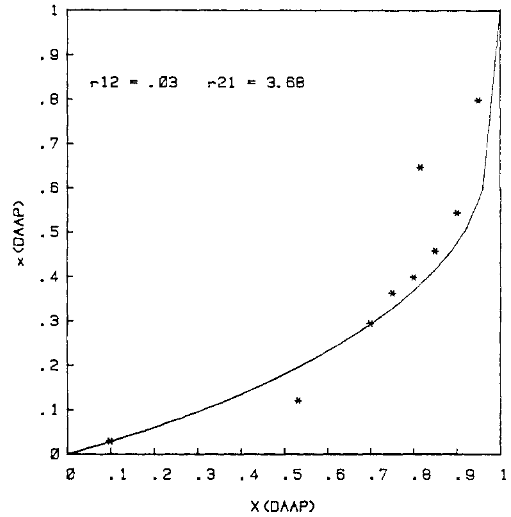

Figure 1. Copolymerization results for DAAP (M_1) with DMAM (M_2) at 60 °C in aqueous HCl with V50.

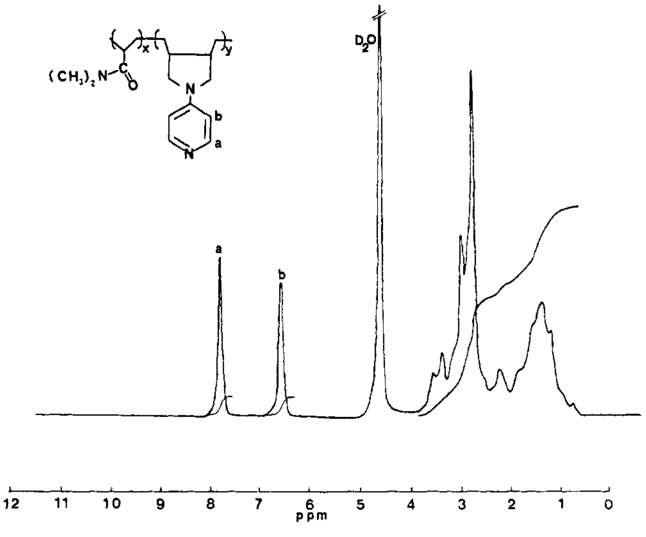

Figure 2. ^{1}H NMR spectrum of copolymer A_8 of DAAP with DMAM in D_2O.

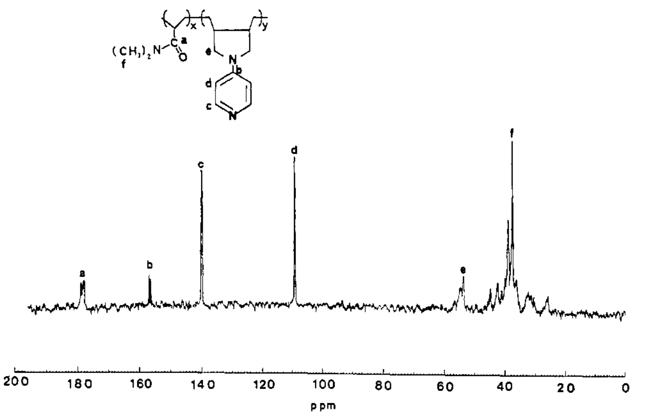

Figure 3. ^{13}C NMR spectrum of copolymer A_8 of DAAP with DMAM in D_2O/DCl.

formation is available from the ^{13}C NMR spectrum (Figure 3). The peak for the carbonyl carbon is observed at 179 ppm, while pyridine carbons 2–4 appear at 140, 109, and 157 ppm, respectively. By comparison with the spectra of the homopolymers of DAAP and DMAM, the peak at 55 ppm is assigned to the pyrrolidine ring carbon bonded to the nitrogen and that at 38 ppm to the methyl groups of the DMAM units. The multiplicity of the peak at 179 ppm is probably the result of different copolymer sequence distributions or backbone tacticity. The pair of peaks seen at 157 ppm (carbon 4 of the pyridine ring) corresponds to cis and trans substitution on the pyrrolidine rings (vide infra).

Acid–Base Behavior of Poly(DAAP-*co*-DMAM). The Henderson–Hasselbalch equation, which describes the dependence of pH on the degree of dissociation, was modified by Katchalsky et al.[20] in order to describe the titration of polyelectrolytes (eq 2).

$$\mathrm{pH} = \mathrm{p}K_a(\mathrm{app}) + n \log [\mathrm{B}]/[\mathrm{BH}^+] \qquad (2)$$

This expression is an approximation in which pK_a(app) (the apparent pK_a) is a function of the degree of ionization of the polyelectrolyte. The change of pK_a with the increasing degree of ionization is a consequence of the fact that further protonation becomes more and more difficult as charge density builds up along the polymer chain. The pK_a(app) is also dependent on the ionic strength of the solution; i.e., with enough low molecular weight ions present, the electrostatic interaction betwen ionized groups along the polymer chain becomes negligible.[21] At high ionic strength, the pK_a becomes a constant and is independent of the degree of ionization. Our results are evaluated according to eq 2 in order to obtain pK_a values that are valid at degrees of ionization close to 0.5 (pK_a = pH) at the ionic strength of the buffers. These conditions are also present in the experiments for measuring catalytic behavior. A more detailed discussion of the copolymer acid–base properties is given in the last Discussion section.

The value of log ([B]/[BH$^+$]) in eq 2 is calculated spectroscopically from eq 1. Then pK_a(app) is obtained by plotting log ([B]/[BH$^+$)] versus pH and extrapolating to 0. Figure 4 shows a typical titration curve (copolymer A_2) and Figure 5 the corresponding plot according to eq 2. Comparison of these two figures illustrates the importance of determining pK_a values by using only data near the half-ionization point. The dashed lines in Figures 4 and 5 correspond to calculations taking into account all data points shown (pK_a 8.71, n = 1.1) while the solid line excludes the point at pH 9.8 (pK_a 8.57, n = 0.8). The relative error in pK_a can be estimated from these two values as approximately 2%. Several repeat determinations were made in order to check the precision of these measurements (values in parentheses in Table II). In all cases, the relative error in pK_a was less than 2%.

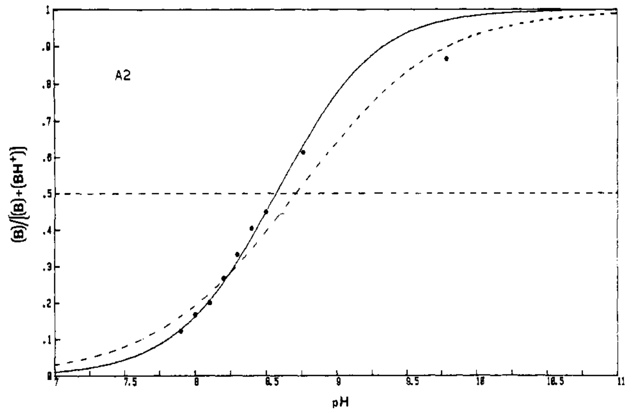

Figure 4. Dependence of the degree of ionization on the pH of copolymer A_2 of DAAP with DMAM; solid line neglects point at pH 9.8, dashed line includes all points.

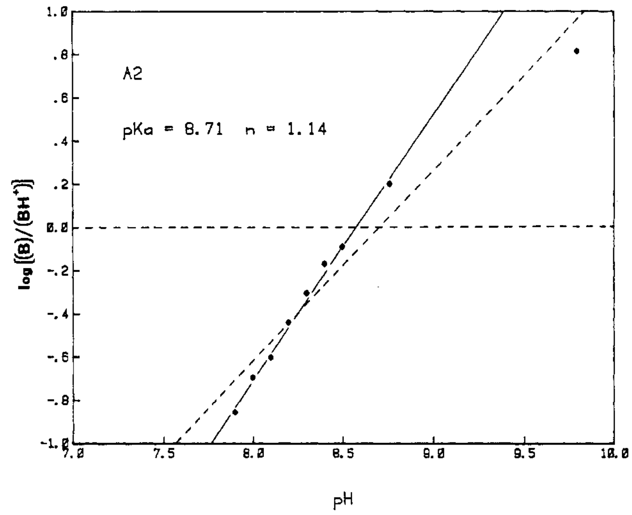

Figure 5. Plot according to the modified Henderson–Hasselbalch equation for the titration of A_2; the solid line neglects the point at pH 9.8.

Table II
Dependence of pK_a on the Composition of Poly(DAAP-*co*-DMAM)

	sample					
	A_0	A_9	A_8	A_6	A_3	A_2
x_{DAAP}	1.00	0.80	0.55	0.65	0.29	0.12
pK_a	7.72 (7.81)	7.98 (7.95)	8.01	7.99	8.52 (8.58)	8.72

The observed dependence of pK_a on copolymer composition may be rationalized in the following way. In DAAP-rich copolymers, adjacent protonated monomer units repel each other leading to easier deprotonation. These copolymers are more acidic than DAAP-poor copolymers where adjacent DAAP units are less common. In fact, with decreasing DAAP content, pK_a values become closer to that of 4-pyrrolidinopyridine 2 (p$K_{a_{\mathrm{PPY}}}$ = 10.5[18]) whose structure is similar to that of the repeating units in poly(DAAP).

Poly(DAAP-*co*-DMDAACl). Copolymers of DAAP and DMDAACl were obtained as soft, yellow, and hygroscopic products, especially those containing larger ratios of DMDAACl units. Water solubility was very good, although the copolymers containing more DAAP units were more readily soluble in aqueous HCl. These copolymers were also soluble in methanol but insoluble in acetone,

Table III
Free Radical Copolymerization of DAAP with DMDAACl at 60 °C

sample	X_{DAAP}[a]	x_{DAAP}[b]	initiator concn, mol/L	polymerizatn time, min	wt conv	limiting viscosity no., dL/g
B_1	0.116	0.071	2.2×10^{-2}	120	0.24	0.553
B_2	0.209	0.124	2.2×10^{-2}	130	0.15	
B_3	0.402	0.254	2.3×10^{-2}	130	0.07	0.168
B_4	0.502	0.422	1.9×10^{-2}	280	0.08	
B_5	0.601	0.388	2.2×10^{-2}	410	0.11	
B_6	0.697	0.477	2.4×10^{-2}	280	0.06	
B_7	0.797	0.602	2.1×10^{-2}	410	0.05	0.074
B_8	0.902	0.756	2.2×10^{-2}	280	0.03	
B_9	0.947	0.802	2.1×10^{-2}	410	0.03	0.045

[a] X_{DAAP}, molar fraction of DAAP in the feed. [b] x_{DAAP}, molar fraction of DAAP in the copolymer.

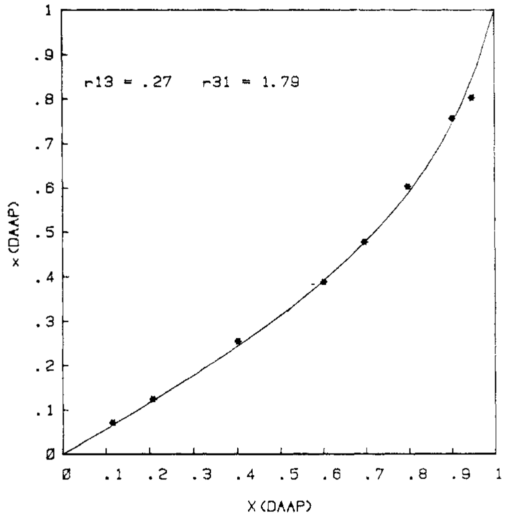

Figure 6. Copolymerization results for DAAP (M_1) with DMDAACl (M_3) at 60 °C in aqueous HCl with V50.

DMSO, and $CHCl_3$. The calculation of reactivity ratios was performed in the same way as for the DAAP–DMAM system. Table III summarizes the results.

Figure 6 clearly shows reduced scatter in the data and the much more random nature of the copolymerization of DAAP with DMDAACl compared to DMAM. The reactivity ratios computed with the modified Kelen–Tudos procedure are $r_{13} = 0.27$ and $r_{31} = 1.79$ (subscript 1 stands for DAAP and 3 for DMDAACl).

Table III also includes the intrinsic viscosity values for several of the copolymers. A systematic decrease in molecular weight with increasing DAAP composition is observed. However, we do not believe that this variation has a very strong effect on the pK_a of the copolymers. Overberger and Okamoto showed that molecular weight differences have a very weak influence on the pK_a of poly(4-vinylimidazole).[22] The differences in pK_a(app) observed in these copolymers are probably due mainly to differences in copolymer composition.

Figure 7 gives the ^{13}C NMR spectrum of copolymer B_5. Peaks d, e, and f are assigned to the pyridine carbons, while the peak at 73 ppm corresponds to the ring methylene carbons bonded to the pyrrolidine nitrogen of the DMDAACl units. This peak became a triplet in the off-resonance experiment. The peaks at higher field are assigned to the methyl and backbone pyrrolidine carbons. The fine structure of the peaks is due to cis–trans ring isomers and perhaps also to backbone tacticity. The former was studied by Johns et al. for poly(methyldiallylamine).[23] They based their peak assignments on comparison with spectra of monomeric pyrrolidines. The similarity of the spectrum of their polymer with that of B_5 led to the assignment of peaks at 28 and 32 ppm to the methylene backbone carbons and the peaks at 40 and 44 ppm to the methine carbons of the cis and trans isomers, respectively. Peaks at these positions were also observed in the spectrum of poly(DMDAACl) in D_2O–DCl. The peak at 42 ppm was also observed in poly(DAAP). The methyl carbons attached to the nitrogen of the pyrrolidine ring appeared between 52 and 57 ppm. The fine structure observed in this spectrum contrasts with that observed for poly(methyldiallylamine) but was also seen in spectra of poly(DAAP) and poly(DMDAACl).

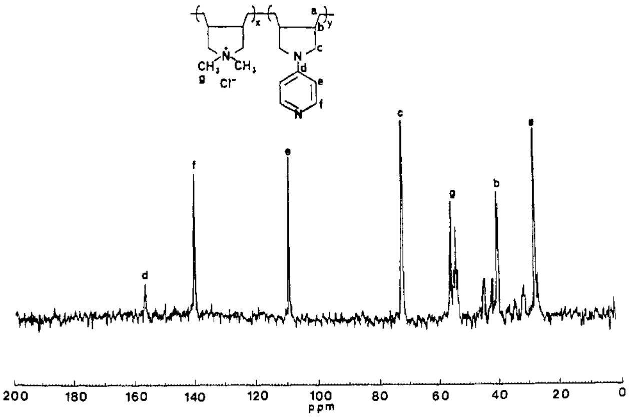

Figure 7. ^{13}C NMR spectrum of copolymer B_5 of DAAP with DMDAACl in D_2O/DCl.

Table IV
Dependence of pK_a on the Composition of Poly(DAAP-*co*-DMDAACl)

	sample					
	B_1	B_2	B_3	B_6	B_7	B_9
x(DAAP)	0.07	0.12	0.25	0.48	0.60	0.80
pK_a	8.15	8.13	8.19	8.13	8.14	7.96

Acid–Base Behavior of Poly(DAAP-*co*-DMDAACl). Several copolymers were titrated spectroscopically as described for the DAAP–DMAM system. The modified Henderson–Hasselbalch calculations only employed data using buffers with pH's close to the pK_a's of the copolymers; i.e., at degrees of dissociation close to 0.5, when pH = pK_a(app). The data in Table IV show that there is no remarkable pK_a change with increasing DAAP content for these copolymers.

Poly(DAAP-*co*-AA). DAAP and acrylic acid were copolymerized under the conditions specified in the experimental section. Table V gives the conditions for the individual copolymerizations. Glassy, hard products were obtained that displayed colors from clear to dark yellow depending on monomer composition. Copolymers with a large proportion of acrylic acid were scarcely soluble in water or aqueous HCl and gave turbid solutions which often precipitated during dialysis. Fortunately, aqueous

Table V
Free Radical Copolymerization of DAAP with Acrylic Acid in Aqueous HCl at 60 °C

sample	X_{DAAP}[a]	x_{DAAP}[b]	initiator concn, mol/L	polymerizatn time, min	wt conversion
C_1	0.200	0.157	0.006	20	0.320
C_2	0.303	0.171	0.013	20	0.374
C_3	0.496	0.234	0.019	45	0.234
C_4	0.597	0.373	0.021	60	0.299
C_5	0.693	0.466	0.022	130	0.280
C_6	0.745	0.554	0.023	190	0.275
C_7	0.800	0.594	0.023	130	0.194
C_8	0.848	0.652	0.025	190	0.147
C_9	0.893	0.863	0.025	190	0.090

[a] X_{DAAP}, molar fraction of DAAP in the feed. [b] x_{DAAP}, molar fraction of DAAP in the copolymer.

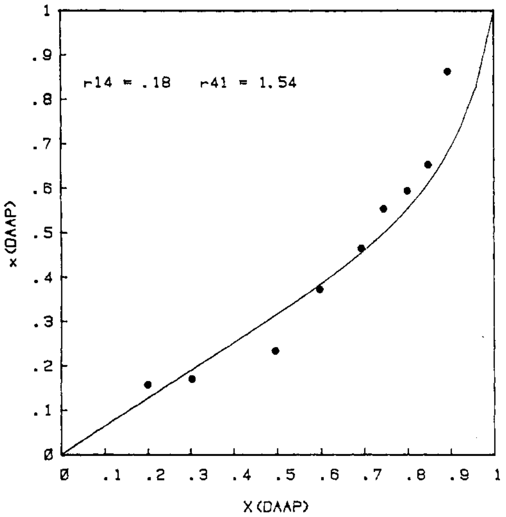

Figure 8. Copolymerization results for DAAP (M_1) with acrylic acid (M_4) at 60 °C in aqueous HCl solution with V50.

formic acid was found to be an excellent solvent for these copolymers. For the UV spectroscopic determination of composition, the polymers were dissolved first in concentrated formic acid and then diluted with water in order to obtain a 10% formic acid solution. No precipitation was observed.

Figure 8 shows the copolymerization results; sample C_9 (highest DAAP content) was not used for the determination of the reactivity ratios $r_{14} = 0.18$ and $r_{41} = 1.54$ (subscript 4 refers to acrylic acid). The reactivity ratios show that both DAAP and AA terminal radicals react preferably with an AA monomer. In addition, the rate of copolymerization was higher for AA-rich monomer mixtures, indicating that DAAP slows down the polymerization process.

Figure 9 gives the ^{13}C NMR spectrum of copolymer C_7 in formic acid. The peaks at 178–179 ppm correspond to the carbonyls of the AA units. Peaks b–d are pyridine carbons from DAAP. Peak e is assigned to the pyrrolidine ring carbons attached to nitrogen. Peaks at higher fields show complexity due to copolymer sequence distribution and perhaps tacticity. As observed in the copolymers with DMAM, peaks a and d also show fine structure arising from tacticity, sequence distribution and pyrrolidine ring cis–trans isomers.

Acid–Base Properties of Poly(DAAP-*co*-AA). Due to low solubility, we could not directly prepare aqueous solutions of these copolymers for UV measurement of pK_a. The copolymers were first dissolved in formic acid, then diluted with distilled water, and neutralized with *n*-butylamine. No turbidity or precipitation was observed, even after addition of excess aqueous KOH. The same behavior was observed when morpholine or 2-(methylamino)ethanol were used for neutralization. Use of other amines (triethylamine and dimethylamine) as well as inorganic bases resulted in opalescent solutions. Table VI gives the pK_a(app) obtained for these copolymers by using the procedure described previously.

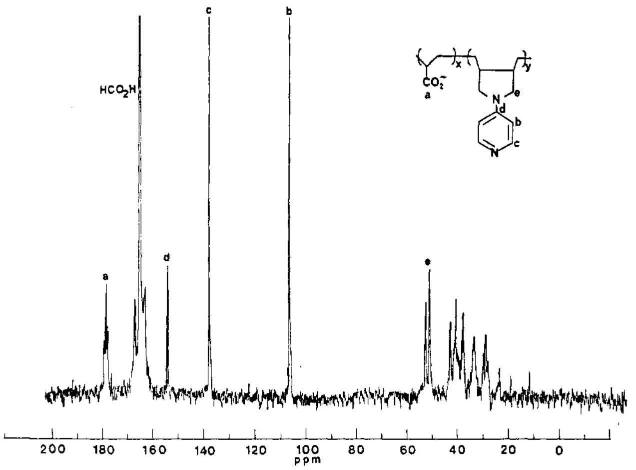

Figure 9. ^{13}C NMR spectrum of copolymer C_7 of DAAP with AA in formic acid.

Table VI
Dependence of pK_a(app) on the Composition of Poly(DAAP-*co*-AA)

	sample			
	C_2	C_5	C_8	C_9
x_{DAAP}	0.171	0.466	0.652	0.863
pK_a	11.02	10.81	10.39	10.06

At pH values close to the pK_a's of these polymers, most of the acrylic acid units are deprotonated (pK_a of polyacrylic acid = 6.17[24]). Increasing electrostatic stabilization of the protonated pyridines in the vicinity of carboxylate anions is probably the reason for the change in pK_a with composition, and for the very different values of pK_a obtained for these copolymers compared to those with DMAM and DMDAACl.

Discussion of the Titration Behavior of the Copolymers. The validity of the modified Henderson–Hasselbalch equation (eq 2) for describing the titration curves was further considered. We observed in many cases a consistent (nonrandom) deviation from eq 2 at pH's that were far from the pK_a(app) of the copolymers. Values of α, the degree of dissociation, obtained at extreme pH's were therefore not taken into account for the calculation of pK_a(app). The consistency of the observed deviations confirms that eq 2 is only an approximation. In other words, both pK_a and the slope of the linear plot (n) are actually variable parameters. This behavior has been reported for several natural[25,26] and synthetic[21,27] polyelectrolytes.

According to Tanford,[21] the dependence of the degree of dissociation on pH may be expressed as follows:

$$\mathrm{pH} + \log\,[(1-\alpha)/\alpha] = pK_a(\mathrm{int}) - 0.868wZ \qquad (3)$$

where pK_a(int) is the pK_a observed in the absence of electrostatic interaction between groups on the macromolecule, Z is the average charge of the macromolecule, and w is a parameter that depends on the model chosen to represent the geometry of the macromolecule. This expression is similar to that obtained by Katchalsky et al.:[28]

$$\mathrm{pH} = pK_0 - \log\frac{(1-\alpha)}{\alpha} - \frac{0.434}{kT}\frac{dF_e}{d\nu} \qquad (4)$$

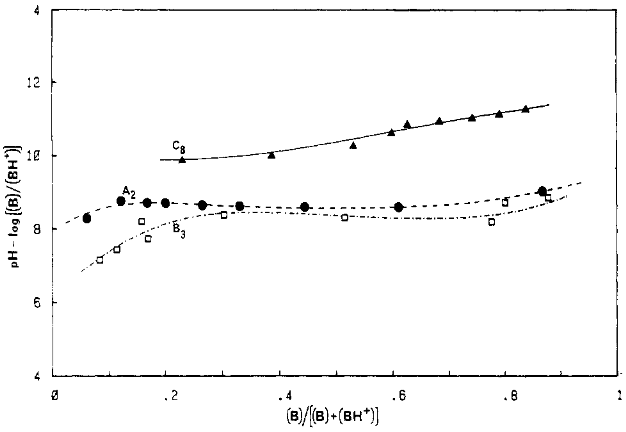

Figure 10. Dependence of pK_a on the degree of dissociation for polymer B_3 (lower plot), A_2 (middle plot), and C_8 (upper plot).

where pK_0, the dissociation constant of the ionizable group, is independent of the ionic strength and F_e is the electrostatic free energy of the ionized macromolecule with v charged groups. Procedures for the evaluation of w and (dF_e/dv) are reported by the authors. According to eq 4, a plot of pH + log $[(1 - \alpha)/\alpha]$ against α gives the value of pK_0 at $\alpha = 1$. At this point the polybase is uncharged, $Z = 0$ and pK_a(int) = pK_0, the intrinsic dissociation constant of the ionizable groups. Any change in the value of pH + log $[(1 - \alpha)/\alpha]$ reflects a variation of the electrostatic interaction between charged groups in the macromolecule.

Figure 10 gives the plots according to this procedure for polymers A_2 (poly[DAAP-*co*-DMAM]), B_3 (poly[DAAP-*co*-DMDAACl]), and C_8 (poly[DAAP-*co*-AA]). The sigmoidal shapes observed for A_2 and B_3 are similar to those displayed by other synthetic macromolecules like poly(methacrylic acid)[29] and various polybases.[27] At $\alpha = 1$ the macromolecule is not charged or highly solvated. The first groups that are protonated experience no electrostatic interaction with each other, and pK_a(app) at α values close to 1 resembles that of the corresponding low MW base (PPY) but in the nonaqueous environment of the tightly coiled polymer chain. With increasing protonation (decreasing α), the polymer coil begins to stretch out. This increases solvation of protonated sites and exposure of the hydrophobic backbone to solvent water. This may cause the system to respond in a nonregular fashion in this regime. At the other end of the scale (as α approaches 0), the drop in pK_a(app) is a consequence of the high degree of protonation of titratable units which makes it extremely difficult to completely react all DAAP units.

The plot in Figure 10 for C_8 (poly[DAAP-*co*-AA]) is slightly different. Instead of a sigmoidal dependence on the degree of ionization of the pyridine units, with a slope close to zero for $\alpha = 0.5$, pK_a(app) changes steadily with α. At $\alpha = 1$, only the pyridine groups are uncharged while the AA units are mostly in the form of carboxylate anions. This negatively charged environment makes pK_a(app) even greater than that of the model monomeric base, PPY. Titration of this polymer now involves simultaneous and opposing ionization of the DAAP units and neutralization of the carboxylate moieties.

Conclusions

1. (Diallylamino)pyridine was cyclocopolymerized by a free radical mechanism with neutral, anionic, and cationic comonomers. Statistical copolymers were obtained, DAAP being the less reactive monomer in all three cases.

2. The change in pK_a(app) of DAAP with composition of the copolymers of dimethylacrylamide and acrylic acid can be explained by the interaction of the protonated DAAP units with carboxylate anions and with each other.

3. Copolymers with acrylic acid, because of their ampholytic character, were only slightly soluble in water but could be dissolved in formic acid. Solutions at pH 7 and even higher could be prepared provided that the interactions between anionic and cationic monomer units were decreased by addition of a low molecular weight base such as *n*-butylamine.

4. Copolymers of DAAP with DMDAACl showed no substantial change of pK_a(app) with DAAP content. This result is rather surprising because Coulombic interactions between charged DMDAACl units and pyridinium groups from DAAP units should facilitate their deprotonation and therefore lower the pK_a(app). Such behavior was not observed.

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