1983, *16*, 753) that with blends involving copolymers specific group interactions need not be required to achieve miscibility. This is due to the fact that unfavorable energetic interactions between the comonomers in a copolymer are relieved by dilution, leading to the exothermicity of mixing. Shiomi et al. (Shiomi, T.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1986**, *19*, 2274, 2644) have listed a number of systems in which compatibility was due to this principle.

(4) (a) Dobry, A.; Boyer-Kawenoki, F. *J. Polym. Sci.* **1947**, *2*, 90. (b) Kern, R. J. *J. Polym. Sci.* **1956**, *21*, 19. Albertsson, P. A. *Partition of Cell Particles and Macromolecules*, 3rd ed.; Wiley: New York, 1986. (d) Baskir, J. N.; Hutton, T. A.; Suter, U. W. *Macromolecules* **1987**, *20*, 1300.

(5) Djadoun, S.; Goldenberg, R. N.; Morawetz, H. *Macromolecules* **1977**, *10*, 1015.

(6) (a) Eisenberg, A.; Smith, P.; Zhou, Z.-L. *Polym. Eng. Sci.* **1982**, *22*, 1117. (b) Zhou, Z.-L.; Eisenberg, A. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 595. (c) Rutkowska, M.; Eisenberg, A.; *Macromolecules* **1984**, *17*, 821.

(7) Hara, M.; Eisenberg, A. *Macromolecules* **1984**, *17*, 1335; **1987**, *20*, 2160.

(8) (a) Pearce, E. M.; Kwei, T. K.; Min, B. Y. *J. Macromol. Sci., Chem.* **1984**, *A21*, 1181. (b) Moskala, E. J.; Howe, S. E.; Painter, P. C.; Coleman, M. M. *Macromolecules* **1984**, *17*, 1671. (c) Shah, K. R. *Polymer* **1987**, *28*, 1212.

(9) Ohno, N.; Kumanotani, J. *Polym. J.* **1979**, *11*, 947.

(10) Albert, A.; Jérôme, R.; Teyssié, P.; Smyth, G.; Boyle, N. G.; Mc Brierty, V. J. *Macromolecules* **1985**, *18*, 388.

(11) Schurer, J. W.; de Boer, A.; Challa, G. *Polymer* **1975**, *16*, 201.

(12) Förster, T *Discuss. Faraday Soc.* **1959**, *27*, 7.

(13) Amrani, F.; Hung, J. M.; Morawetz, H. *Macromolecules* **1980**, *13*, 649.

(14) Gelles, R.; Frank, C. W. *Macromolecules* **1982**, *15*, 741, 747.

(15) Arshady, R.; Kenner, J. W.; Ledwith, A. *J. Polym. Sci. Polym. Chem. Ed.* **1974**, *12*, 2017.

(16) Bank, M.; Leffingwell, J.; Thies, C. *Macromolecules* **1971**, *4*, 43. Gelles, R.; Frank, C. W. *Ibid.* **1982**, *15*, 747. Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed* **1987**, *25*, 1459. Caravatti, P.; Neuenschwander, P.; Ernst, R. R. *Macromolecules* 1985, *18*, 119; **1986**, *19*, 1889.

(17) Robard, A.; Patterson, D. A. *Macromolecules* **1977**, *10*, 1021.

(18) Hildebrand, J. H.; Scott, R. L. *The Solubility of Nonelectrolytes*, 3rd ed.; ACS Monograph 17; American Chemical Society: Washington, DC, 1950, pp 129, 437, 439.

(19) Frank, C. W.; Gashgari, M. A. *Macromolecules* **1979**, *12*, 163.

(20) By analogy to *N*-acetylglycine, which has a pK = 3.60 (Zind, M.; Edsall, J. T. *J. Am. Chem. Soc.* **1937**, *59*, 2247), lower by 1.24 units than that of acetic acid.

(21) de Meftahi, M. V.; Fréchet, J. M. J. *Polymer* **1988**, *29*, 477.

(22) Gelles, R.; Frank, C. W. *Macromolecules* **1982**, *15*, 1486; *Ibid.* **1983**, *16*, 1448.

(23) Middleton, W. J.; Lindsey, P. V. *J. Am. Chem. Soc.* **1964**, *86*, 4948.

(24) Painter, P. C.; Park, Y.; Coleman, M. M. *Macromolecules* **1988**, *21*, 66.

(25) Su, C. W.; Watson, J. W. *J. Am. Chem. Soc.* **1974**, *96*, 1854.

(26) Moskala, E. J.; Howe, S. E.; Painter, P. C.; Coleman, M. M., *Macromolecules* **1984**, *17*, 1671.

(27) Helfand, E.; Tagami, Y. *J. Polym. Sci., Part B* **1971**, *9*, 741.

(28) We have recently demonstrated (Horsky; Morawetz, H. *Macromolecules*, submitted for publication) that some of the energy transfer observed in blends of donor and acceptor labeled polymers is radiative, i.e., independent of the spacial distribution of the fluorescent labels. Thus, energy transfer data cannot be interpreted in terms of the dimensions of phase domains as suggested by Albert et al. in ref 10.

Fluorescence Study of the Complexation of Poly(acrylic acid) with Poly(*N*,*N*-dimethylacrylamide-*co*-acrylamide)

Yongcai Wang and Herbert Morawetz*

Department of Chemistry, Polytechnic University, Brooklyn, New York 11201.
Received December 28, 1987

ABSTRACT: Complex formation of poly(acrylic acid) (PAA) with the *N*,*N*-dimethylacrylamide (DAAm) homopolymer and its copolymers with acrylamide (AAm) in water solution was characterized by the enhancement of fluorescence of dansyl labels attached to the PAA. The complexation was more pronounced at pH 3 where the acrylamide residues seemed to contribute to complex stability, while at pH 4 no complex was formed with a copolymer containing 55 mol % AAm. The ratio of monomer residues in PAA and the copolymer in the complexes was independent of the copolymer composition. A number of arguments contradict the concept that polymer complexation in water solution by cooperative hydrogen bonding requires the interaction of long sequences of contiguous monomer residues.

Introduction

Many investigations have been reported on polymer complexation by cooperative hydrogen bonding.[1] If such complexation takes place in aqueous solution, there is only a small difference between the strength of the interpolymer hydrogen bond and the hydrogen bonds of the two polymers with water. It is then not surprising that a large number of interpolymer bonds must be formed to yield a stable complex. It has been claimed[1a] that such complexation involves "noninterrupted linear sequences of bonds" between monomer residues of the hydrogen bond donor and the hydrogen bond acceptor polymer, but it was pointed out that this would involve prohibitive steric strain.[2] It has also been shown that alternating copolymers of carboxylic acids with maleic anhydride form stable complexes with poly(*N*-vinylpyrrolidone) (PVP) in aqueous solution.[3]

Whereas the results obtained with alternating copolymers demonstrate that hydrogen-bonded polymer complexes may form in water solution even if the interacting groups are not attached to neighboring monomer residues, a study of the complexation of a homopolymer with a series of random copolymers containing varying concentrations of inert monomer residues should shed additional light on factors determining complex stability. Bimendina et al.[4] studied complexation of poly(methacrylic acid-*co*-methyl methacrylate) containing 63.6–76.8 mol % of the acid monomer residues with PVP, but this system could only be investigated in water containing 30% ethanol. Iliopoulos et al.[5] considered partially ionized poly(acrylic acid) (PAA) as a random copolymer of hydrogen-bonding and inert monomer residues and studied the complexation of PAA at varying degrees of ionization with poly(oxyethylene) or PVP.

Unfortunately, the introduction of a comonomer into one of the partners of complex forming polymers can never be considered a "structure defect"[5] only, since it will affect the complex stability in various other ways: This may involve hydrophobic interactions stabilizing the complex,[6,12] or in the case of partially ionized PAA, a strong interaction of the anionic acrylate residues with water, which would be expected to weaken the cohesion of the interacting polymer chains. To minimize this difficulty, we chose for our study the complex formation of PAA with

0024-9297/89/2222-0164$01.50/0

Table I
N,N-Dimethylacrylamide Polymer and Copolymers

designatn	[η] (dL/g, water at 25.5 °C)	AAm (mol %) monomers	polymer (found)	polymer (calcd)
PDAAm	0.94	0	0	0
COP 1	1.12	9.1	6.0	4.8
COP 2	1.15	17.5	11.4	9.9
COP 3	1.08	25.8	15.5	15.3
COP 4	1.19	48.1	34	33
COP 5	1.95	67.6	55	54

copolymers of *N,N*-dimethylacrylamide and acrylamide. The dimethylamide group is known to be a powerful hydrogen bond acceptor.[7] As for the unsubstituted amide, its role as a hydrogen bond donor has been demonstrated by the complexation of PAA with polyacrylamide at relatively high polymer concentrations[8] and the claim that polyacrylamide forms a complex with poly(methacrylic acid)[9] suggests that it is also a hydrogen bond acceptor. Still, we started with the assumption that acrylamide residues are much weaker hydrogen bond acceptors than dimethylacrylamide residues.

To characterize complex formation, we used the increase in the emission intensity of dansyl labels attached to PAA when polymer association reduces the exposure of the dansyl groups to water molecules. This method was employed in previous investigations in this laboratory.[2,10]

Experimental Section

Monomers. Acrylic acid and *N,N*-dimethylacrylamide were distilled before use. Acrylamide was used as received. *N*-dansyl(aminoethyl)methacrylamide (DAM) (mp 136–137 °C) was prepared as described before.[10]

Polymers. Dansyl-labeled poly(acrylic acid) (PAA*) and poly(*N,N*-dimethylacrylamide) (PDAAm) were prepared in methanol solution. Acrylamide and mixtures of acrylamide and *N,N*-dimethylacrylamide were polymerized in a 3:2 mixture of methanol and water. Azobis(isobutyronitrile) was used as polymerization initiator. All polymers were purified by dialysis and freeze-dried. The dansyl content of PAA* (1.3 mol %) was determined by absorption at pH 7 using the extinction coefficient 4700 M^{-1} cm^{-1} at 328 nm.[10a] The intrinsic viscosity was 0.45 dL/g in dioxane at 45 °C. The composition of the copolymers was determined on 5% solutions at 40 °C in 1:1 D_2O/H_2O by ^{13}C NMR using 6000–10000 scans on a JEOL JNM-FX 90Q NMR spectrometer operating in the Fourier transform mode and linked to a Texas Instruments 980 B computer. Dioxane-d_8 served as an external standard. A pulse repetition of 6 s was used, about five times the spin–lattice relaxation time for carbonyl groups.[11] The carbonyl peaks were at 180.3 ppm for polyacrylamide (PAAm) and at 176.6 ppm for PDAAm; these peak positions were little shifted for the corresponding monomer residues in the copolymers, and the areas under these peaks were used to obtain the copolymer composition. Table I lists the monomer compositions, the polymer compositions found and calculated by using the reactivity ratios $r_{AAm} = 0.59$ and $r_{DAAm} = 1.92$, and the intrinsic viscosities of PDAAm and the copolymers.

Fluorescence Measurements. Emission spectra of the dansyl label were recorded on a Perkin-Elmer BPF-44 B fluorescence spectrophotometer using excitation at 304 nm, the isosbestic point of the protonated and unprotonated chromophore. Experimental results were expressed as I/I_0, where I and I_0 are peak emission intensities of the label in the presence and absence of the hydrogen bond acceptor polymer, respectively, as a function of the ratio of the monomer residues in the components of the complex COP/PAA.

Results and Discussion

Both acrylamide and dimethylacrylamide form hydrophilic homopolymers[13] so that the complexation of their copolymers with PAA should not be complicated by effects of hydrophobic bonding. Since PAAm has been reported to form complexes with hydrogen bond acceptor[8] and hydrogen bond donor polymers[9] only at low pH, our experiments were carried out both at pH 3, in 10^{-3} M HCl, where the acrylamide residues may make some contribution to the stability of the complex and in a pH 4 buffer (ionic strength 0.02), where no such contribution is expected.

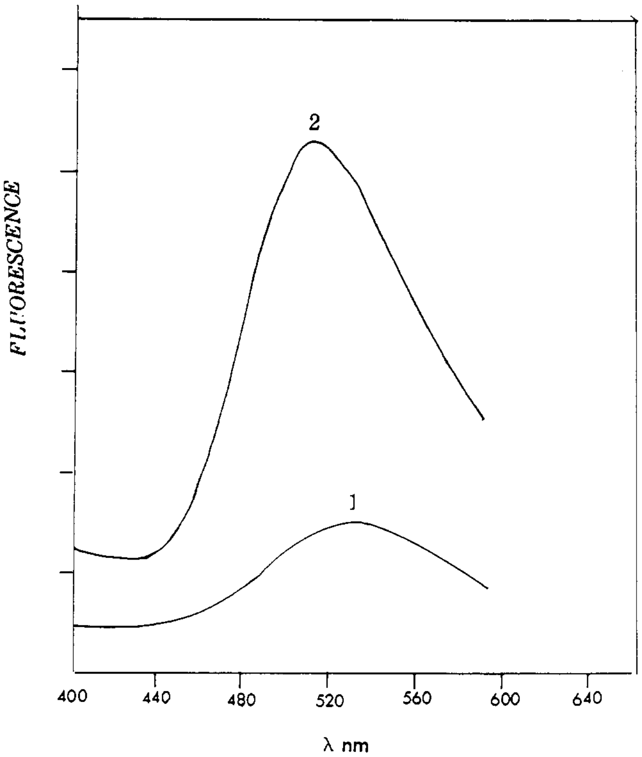


Figure 1. Emission spectra of 1×10^{-4} base molar PAA* in the absence (1) and the presence (2) of 1×10^{-4} base molar PDAAm.

Figure 1 shows emission spectra of 10^{-4} base molar PAA* in the presence and absence of 10^{-4} base molar PDAAm. Complex formation intensified the emission peak by a factor of 3.5 and produced a blue-shift from 525 to 510 nm. Both effects are characteristic for the removal of the dansyl label from the aqueous environment.[10a]

The dependence of I/I_0 on the ratio of monomer residues in the interacting polymers, COP/PAA, is plotted in Figure 2 for pH 3 and in Figure 3 for pH 4 solutions. The following observations can be made: (1) At pH 3, the curves level off at COP/PAA slightly higher than unity but suggest no dependence of the stoichiometry of the complex on the composition of the copolymer. The decreasing emission intensity with an increasing acrylamide content of the copolymer indicates increasing swelling of the PAA* complex. (2) When the pH is raised to 4, the emission intensity of the complex is greatly reduced and there is no indication of complex formation with COP 5, containing 55 mol % acrylamide. A larger polymer excess is required to reach a plateau of I/I_0, but the COP/PAA ratio at which the limiting I/I_0 is attained is again independent of the copolymer composition. The larger swelling of the complex at pH 4 would be expected due to the partial ionization of PAA, and it does not necessarily reflect a change in the hydrogen bond acceptor strength of the copolymer.

Figure 4 shows plots of the limiting values of I/I_0 against the content of acrylamide residues in the DAAm–AAm copolymers. At pH 4 the plot is linear and its extrapolation suggests that copolymers containing more than 45 mol % acrylamide residues would not associate with PAA. At pH 3, I/I_0 seems to level off at higher acrylamide contents in

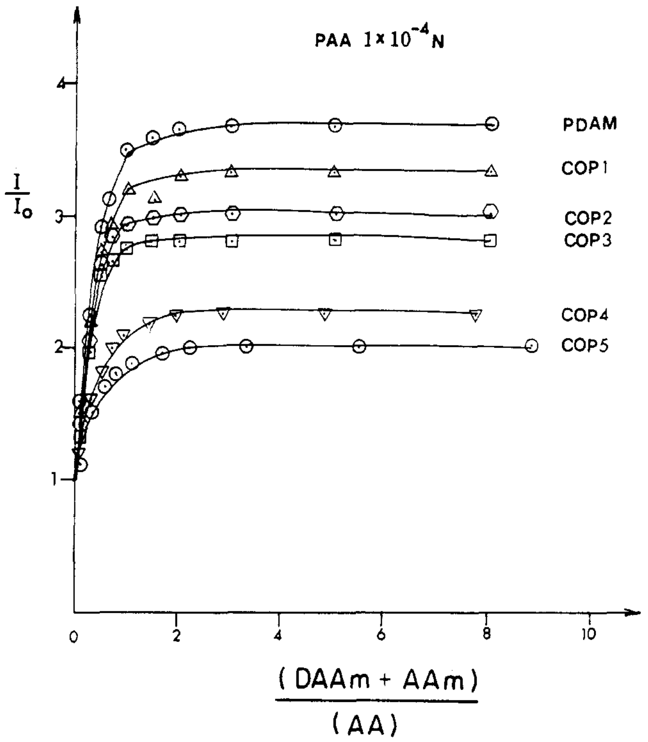


Figure 2. Peak emission intensity of 1 × 10^{-4} base molar PAA* as a function of the ratio of monomer residues in PDAAm or DAAm copolymers and PAA* at pH 3.

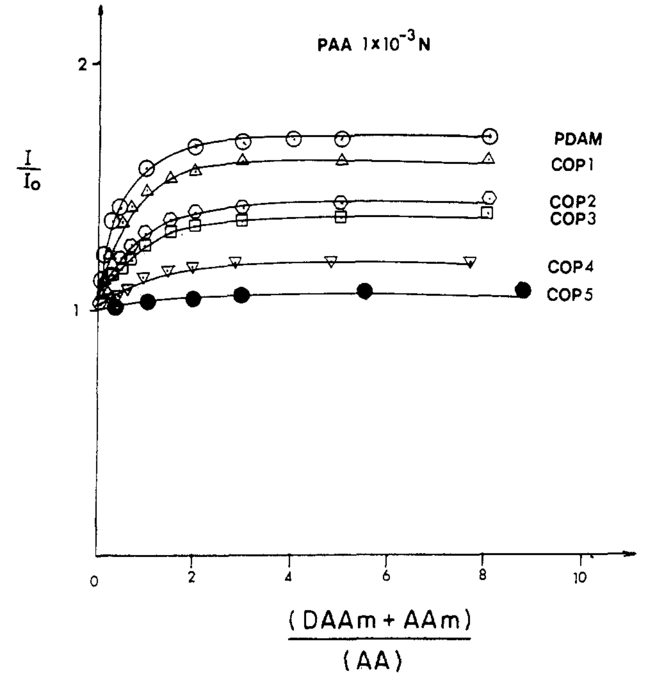


Figure 3. Peak emission intensity of 1 × 10^{-4} base molar PAA* as a function of the ratio of monomer residues in PDAAm or DAAm copolymers and PAA* at pH 4.

the copolymer, suggesting that acrylamide residues contribute significantly to the complex stability.

The weight fraction $W(x)$ of DAAm residues contained in a sequence of length x is given by

$$W(x) = x(P_{\mathrm{DAAm}})^{x-1}(1 - P_{\mathrm{DAAm}})^2 \qquad (1)$$

where P_{DAAm}, the probability that a DAAm residue is followed by a similar residue, is

$$P_{\mathrm{DAAm}} = \left(1 + \frac{1 - f_{\mathrm{DAAm}}}{r_{\mathrm{DAAm}} f_{\mathrm{DAAm}}}\right)^{-1} \qquad (2)$$

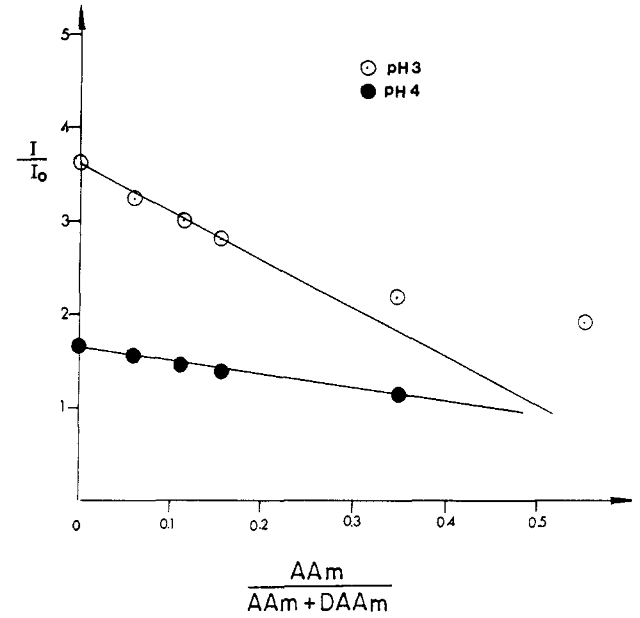


Figure 4. Limiting I/I_0 values as a function of the acrylamide content in the copolymer.

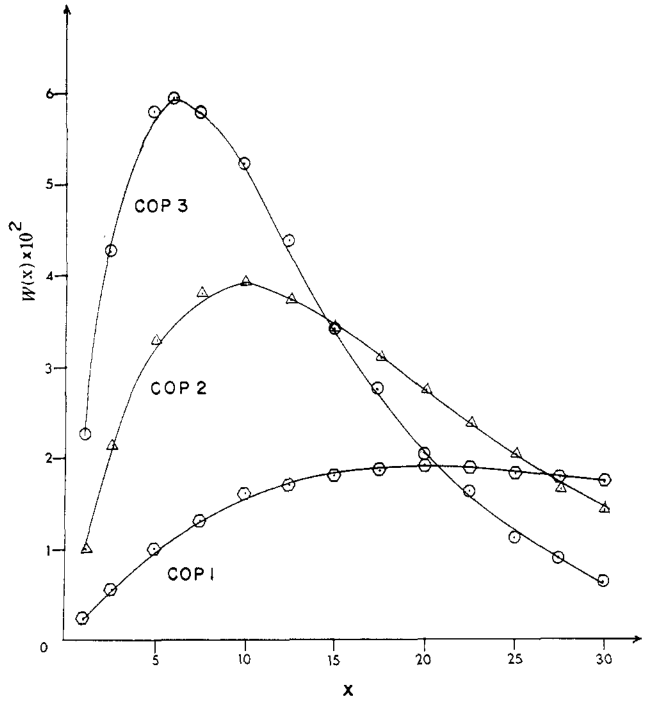
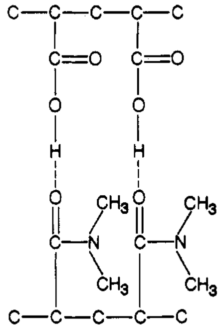


Figure 5. Weight fraction of DAAm in sequences of x monomer residues, $W(x)$, in copolymers COP 1, COP 2, and COP 3.

where f_{DAAm} is the fraction of DAAm in the mixture of monomer from which the copolymer was prepared and r_{DAAm} is the reactivity ratio of the DAAm radical. The $W(x)$ for copolymers COP 1, COP 2, and COP 3 are plotted in Figure 5. From the areas under the curves we obtain the fraction of DAAm residues in sequences shorter than some x value. We find that half the residues are in sequences shorter than $x = 30$ in COP 1 and shorter than $x = 10$ in COP 3. Yet, the stability of the PAA complex is hardly changed in substituting COP 1 for PDAAm and is still substantial with COP 3, although $x = 10$ is much less than the sequence length postulated for stable complexes by Baranowsky et al.[12]

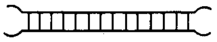
We concede that the emission enhancement of PAA* is only an indirect index of complexation. If we could assume that the dansyl label exists only in two discrete environments, one in which it is fully exposed to water and the other in which polymer complexation protects it from the aqueous medium, then $I/I_0 - 1$ would represent the fraction of the label in the complexed regions. Yet, this view is clearly simplistic, and we cannot conclude from our results whether or not the polymer complex depends on "noninterrupted sequences of bonds" between contiguous monomer residues. Our conclusion that this model is unrealistic rests on the structure, as shown below for two monomer residues, which this would imply two consecutive residues of PAA hydrogen bonded to two consecutive residues of PDAAm:



Even a single 14-membered ring, represented by this structure, is most improbable. To assume a long sequence of such rings, condensed with each other, seems utterly fantastic.

Concluding Remarks

Our belief that the formation of stable hydrogen-bonded complexes between polymers in water solution does not involve the interaction of long sequences of contiguous monomer residues is supported by several arguments: (1) Such complexes have been described for alternating copolymers in which one of the comonomers cannot participate in hydrogen bonding. (2) The usual representation of such bonded sequences by two lines with evenly spaced connections



may be shown to be unrealistic once the chemical structure of such a complex is taken into account. A complex in which PVP, with its bulky side chains, acts as the acceptor would present even greater steric difficulties in such complexation with PAA than the structure of a pair of PAA and PDAAm residues shown above. (3) The derivation of the fraction of hydrogen-bonded residues from the shift of pH accompanying complex formation[14] may not be reliable since the transfer of a carboxyl group from water to a medium of lower dielectric constant will reduce sharply its dissociation even if it does not participate in a hydrogen bond. Thus, the experimental basis for data with which theoretical analyses are compared may be questioned. (4) The present study shows that stable complexes may be formed with polymers containing relatively few long sequences of monomer residues participating in complex formation.

Acknowledgment. We are grateful for financial support of this investigation by the National Science Foundation through their Grant DMR 8700712, Polymers Program.

Registry No. PAA, 9003-01-4; PDAAm, 26793-34-0; (DAAm)(AAm) (copolymer), 30973-80-9.

References and Notes

(1) (a) Baranovsky, V. Yu.; Litmanovich, A. A.; Papisov, I. M.; Kabanov, V. A. *Eur. Polym. J.* **1979**, *17*, 1981, and papers cited therein. (b) Bekturov, E. A.; Bimendina, L. A. *Adv. Polym. Sci.* **1981**, *41*, 99. (c) Tsuchida, E.; Abe, K. *Adv. Polym. Sci.* **1982**, *45*, 1.

(2) Bednář, B.; Li, Z.; Huang, Y.; Chang, L.-C. P.; Morawetz, H. *Macromolecules* **1985**, *18*, 1829.

(3) Bimendina, L. A.; Tleubaeva, G. S.; Bekturov, E. A. *Vysokomol. Soed., Ser. A* **1977**, *A19*, 71. Bimendina, L. A.; Bekturov, E. A.; Tleubaeva, G. S.; Frolova, V. A. *J. Polym. Sci., Polym. Symp.* **1979**, *66*, 9.

(4) Cited on p 115 of ref 1b.

(5) Iliopoulos, I.; Audebert, R. *Eur. Polym. J.*, in press. Iliopoulos, I.; Halary, J. L.; Audebert, R. *J. Polym. Sci., Polym. Chem. Ed.*, in press.

(6) Papisov, I. M.; Baranovsky, V. Yu.; Sergeieva, E. I.; Antipina, A. D.; Kabanov, V. A. *Vysokomol. Soed., Ser. A* **1974**, *A16*, 1133.

(7) Su, C. W.; Watson, J. W. *J. Am. Chem. Soc.* **1974**, *96*, 1854. Drago, R. S.; O'Bryan, N.; Vogel, G. C. *J. Am. Chem. Soc.* **1970**, *92*, 3924.

(8) Klenina, O. V.; Fain, E. G. *Vysokomol. Soed., Ser. A* **1981**, *A23*, 1298.

(9) Abe, K.; Koide, M.; Tsuchida, E. *Macromolecules* **1977**, *10*, 1259.

(10) (a) Chen, H.-L.; Morawetz, H. *Eur. Polym. J.* **1983**, *19*, 923. (b) Bednar, B.; Morawetz, H.; Shafer, J. A. *Macromolecules*, **1984**, *17*, 1634.

(11) Hutchinson, B. H.; McCormick, C. L. *Polymer* **1986**, *27*, 623.

(12) Litmanovich, A. A.; Papisov, I. M.; Kabanov, V. A. *Eur. Polym. J.* **1981**, *17*, 981.

(13) In the Mark-Houwink equation for the relation of the intrinsic viscosity and the molecular weight, $[\eta] = M^a$, both PAAm and PDAAm are characterized by $a = 0.8$ in water solution, indicating that water is a powerful solvent for both polymers: Scholtan, W. *Makromol. Chem.* **1954**, *19*, 169. Trosarelli, I.; Meirone, M. *J. Polym. Sci.* **1962**, *57*, 445.

(14) Antipina, A. D.; Baranovskii, V. YU.; Papisov, I. M.; Kabanov, V. A. *Vysokomol. Soed. Ser. A* **1972**, *A14*, 1941. Osada, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, 3485. See also ref 5.