Macromolecules **2002,** *35,* 4143−4149

Charge Interaction of Synthetic Polycarboxybetaines in Bulk and Solution

Jörg Bohrisch,*,† Thomas Schimmel,† Heinz Engelhardt,‡ and Werner Jaeger†

Fraunhofer-Institut für Angewandte Polymerforschung, D-14476 Golm, Germany, and Saarland University, Instrumental and Environmental Analysis, Im Stadtwald, D-66123 Saarbrücken, Germany

Received December 18, 2001; Revised Manuscript Received February 21, 2002

ABSTRACT: Various polycarboxybetaines were synthesized using controlled radical polymerization processes followed by polymer analogous transformations. Structural variation of these exclusively aromatic or heteroaromatic systems includes distance between charges, hybridization and substitution of the ammonium moiety, and additional alkyl chains between the charges. For the first time capillary electrophoresis was used for systematic characterization of the solution properties. It was found to be a very sensitive method to detect even small structural differences and the resulting pH-dependent solution behavior. The electrophoretical mobility compared with an internal standard and the amount of its pH dependence are direct measures for the interaction of charges of polycarboxybetaines in solution. This method clearly reveals a gradual and more or less predictable content of “free” cationic charges dependent on structural and solution parameters. Results obtained coincide in a fairly good way with data from FTIR measurement and charge titration.

Introduction

In recent years polybetaines (e.g., sulfo-, phospho-, and carboxybetaines) as highly dipolar polyelectrolytes have attracted increasing academic attention.[1] With their zwitterionic nature they exhibit some unique properties in bulk and solution. Especially sulfo- and carboxybetaines are already used in textile, medical, and other commercial lines.[2−4] Because of the structural similarity of betaines to proteins and living matter[5] as more or less hydrophilic systems, it is obviously necessary to learn more about the complex solution behavior of these structures. Such study is rather difficult because a lot of interactions such as intra- and interchain interactions as well as long-range electrostatic and hydrophobic interactions have to be simultaneously considered. In recent years the majority of publications in this field was dealing with synthesis and properties of homopolymers and block copolymers containing sulfobetaine functionalities.[6,7] Only few groups published on polycarboxybetaines. One major reason could be the additional pH dependence of the weak anionic charge. Besides the conventional acrylate backbone (homopolymer or block copolymer) with acetate,[8,11] propionate,[9] butanoate,[10,11] and hexanoate[12] at the quaternized nitrogen some special structures were investigated. Laschewsky and co-workers dealt with salt-free synthesis of zwitterionic derivatives of the well-known cyclopolymer poly(diallyldimethylammonium chloride).[13,14] The salt-free procedure was successfully introduced in order to prepare and investigate homogeneous mixtures of polyzwitterions with low molecular weight salt and ionic dyes, respectively.[15,16] Minuora et al. reported on a synthesis of a polycarboxybetaine from poly(γ-methyl L-glutamate).[17]

Studies of polycarboxybetaine properties mainly include solubility investigation and viscosity measurement in different environments (additional salt, pH) for solutions, thermal analysis, and X-ray studies for bulk properties. Intermolecular and intramolecular aggregation does not seem to play a significant role with these structures except when longer alkyl spacers are involved.[11,14] Ali et al.[18] performed potentiometric titration of acetate as well as the hexanoate derivative of poly(diallyldimethylammonium chloride) dependent on salt content and found “apparent” basicity constants. A very recent publication using laser light scattering and ζ potential measurement revealed a significant interchain aggregation of a poly(methacrylamido) derivative.[9]

In our research we focused on a series of polycarboxybetaines with 6π systems as part of the regular structure. Except the pioneering work of Ladenheim[19] and the studies by Engberts et al.[20] with derivatives of *N*-vinylimidazole and Barboiu et al.[21] (vinylpyridine derivatives), no detailed investigation of these structures is found in the literature up to date. First studies with different methods such as potentiometric titration, size exclusion chromatography, and capillary electrophoresis revealed a strong relationship between the type of substitution and hybridization at the quaternary nitrogen atom and the very complex pH-dependent charge interaction dominated by intramolecular phenomena.[22−24]

In our recent investigation we aimed at quantification of pH-dependent solution properties and charge interaction effects of a series of different polycarboxybetaines of the pyridiniocarboxylate and some comparative examples of the ammonioacetate type. Varied parameters are an additional alkyl chain at the α carbon, the alkyl spacer length between both charged moieties, and different substitution at and hybridization of the quaternized nitrogen. The materials were obtained by controlled radical polymerization of 4-vinylpyridine and vinylbenzyl chloride and subsequent polymer analogous reactions finally completed by saponification of an ester moiety.

Quantifying the charge interaction mentioned above, capillary electrophoretical measurement and charge titration at different pH were performed. Additionally, the FTIR spectra of the bulk material were measured.

---

† Fraunhofer-Institut für Angewandte Polymerforschung.
‡ Saarland University.

10.1021/ma0122019 CCC: \$22.00

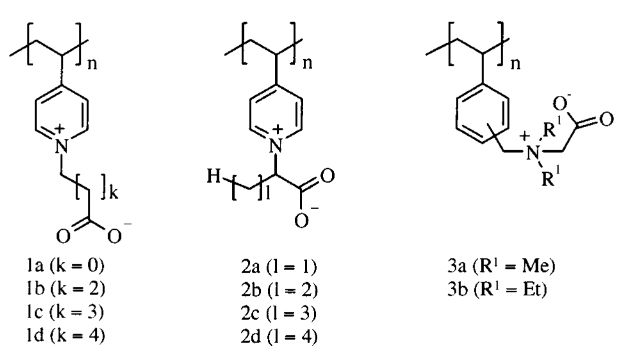

Figure 1. Structures of synthesized polycarboxybetaines **1**, **2**, and **3**.

Table 1. Molecular Weight Determination of 1, 2, and 3

compd	deg of substitution (^{1}H NMR)/%	M_n (10^4 g/mol)^a	M_w/M_n
1a	>95	1.8	1.5
1b	91	1.7	1.3
1c	>95	1.9	1.3
1d	>95	2.0	1.3
2a	>95	1.3	1.3
2b	81	1.3	1.3
2c	72	1.3	1.3
2d	79	1.8	1.3
3a	>95	1.9	1.3
3b	>95	4.3	1.2

[a] Calculated from molecular weight of precursors and degree of substitution.

Results and Discussion

Synthesis of Polymers. Investigation of the structure–property relationship of polybetaines requires well-defined products with a wide structural variety. Therefore, a series of pyridiniocarboxylates differing in the spacer length between both charges (**1a**–**1d)** and in the length of an additional alkyl chain at the α carbon (**2a**–**2d)** were synthesized. Two ammonioacetates (**3a**, **3b)** complete these materials in order to compare sp^2 with a differently substituted sp^3 nitrogen (Figure 1).

The synthesis was performed using controlled radical polymerization with subsequent polymer analogous reactions which has two main advantages:

(i) Differently substituted polymers with *equal* degree of polymerization and molecular weight distribution are obtained.

(ii) The SEC measurement of the precursor polymers is well established compared to direct molecular weight determination of polycarboxybetaines. Hence, effects attributed to strongly varying or low molecular weights are excluded.

The reactive precursor polymers poly(4-vinylpyridine) (p4VP) and poly(vinylbenzyl chloride) (pVBC) were characterized by SEC and then reacted with esters of corresponding bromocarboxylic acids (p4VP) and diethylamine/bromo ethyl acetate or *N*,*N*-dimethyl ethylglycinate (pVBC), respectively. After saponification of the ester moieties, the polymer samples were purified by dialysis and freeze-dried. In most of the cases the derivatization occurred with more than 95% as revealed by ^{1}H NMR (see Table 1). The significantly lower substitution degree of polymers **2b**–**2d** is most likely caused by the sterically demanding bromocarboxylic acids used in the quaternization of p4VP. The molecular data of samples **1**, **2**, and **3** are given in Table 1.

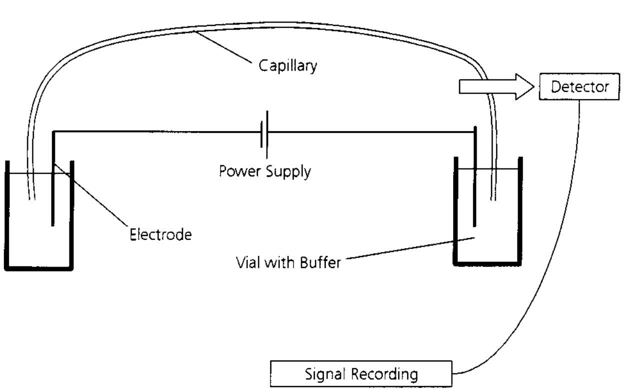

Figure 2. Scheme of the CE instrument basic setup.

Capillary Electrophoresis Measurement. The capillary electrophoresis (CE) measurement has been successfully applied to a variety of polyelectrolytes including biopolymers.[24] It is based on mobility differences of the solutes in an electric field. The system resembles elution chromatography, in that zones migrate at different velocities through the system and in the optimum case are separated from each other by buffer electrolyte. In the CE instrument, a fine fused silica capillary (25–100 μm i.d.) of 20–100 cm length bridges two buffer containers between which a potential of up to 30 000 V is applied (Figure 2).

A short sample plug (a few nanoliters) is introduced at one end of the capillary by pressure or voltage. Detection (UV absorption, fluorescence emission) takes place at the opposite end of the capillary. Because of dissociated silanol functions of the fused silica capillary surface, an electroosmotic flow (EOF) is generated. It transports the buffer and even uncharged compounds in a pluglike stream profile to the cathodic end of the capillary. In polymer analysis, surface-modified capillaries, for example poly(vinyl alcohol) coatings, are used to prevent adsorption of the polymers on the capillary as well as to diminish the EOF. The mobility of the compounds depends on their volume-to-charge ratio as well as on solvent effects of the buffer (pH, solvatation, viscosity, etc.).

Measurement of the samples **1** bearing different numbers of methylene groups between the charges reveals a strong pH- and structure-dependent shift in electrophoretical mobilities. In all cases increasing pH leads to more efficient charge interaction along the polymer chains and therefore to lower electrophoretical mobilities. In coincidence with studies of Ali et al.,[18] who proposed an apparent basicity of carboxylic goup comparing ammonioacetate and ammoniohexanoate, we found increasing protonation of carboxylic units with increasing charge distance at each pH within the range investigated. This leads to a growing net charge of the molecule and therefore to enhanced mobility. The objected run times lowered from 7 to 18 min (**1a**) to 4–5 min (**1d**) at pH 1.8–2.6. As expected, there exists a “mobility gap” between **1a** with one methylene group separating charges and **1b**–**1d** with more than two methylene units (Figures 3–5). The mobility differences among the latter derivatives are comparatively low. For low molecular weight zwitterionic compounds as for ammoniocarboxybetaines,[25,26] the influence of the tether length on pK_a values is well documented and quantified. Moreover, the important problem of zwitterion conformation defining the effective charge distance as a function of the tether length is discussed for these model species.[26–28] In general, the low molecular weight zwitterions adopt a slightly curled instead of “ion pair” or

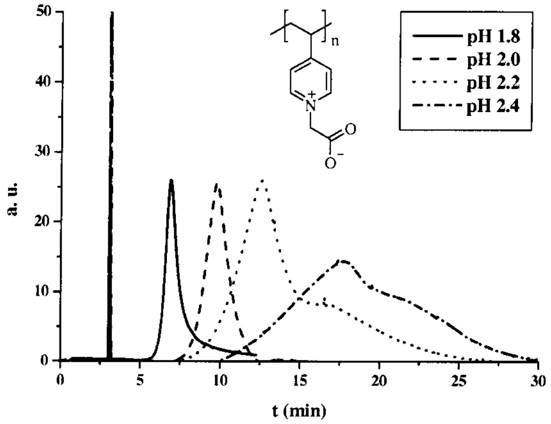

Figure 3. pH-dependent mobility of compound **1a**.

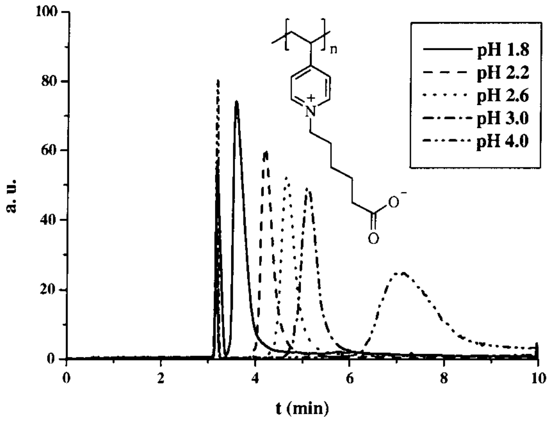

Figure 4. pH-dependent mobility of compound **1d**.

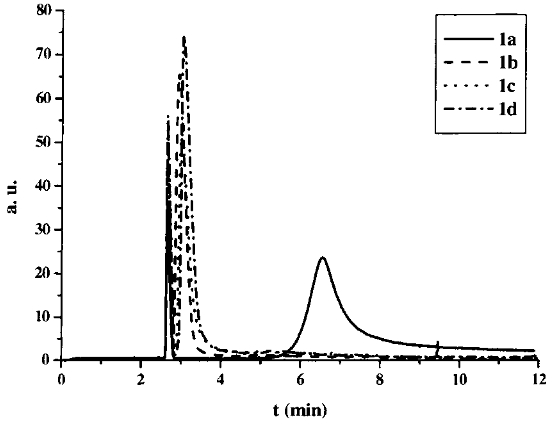

Figure 5. Electrophoretical mobility of compounds **1a**–**d** at pH 1.8.

completely stretched conformation. Nevertheless, an additional sterical demand of the architecture of pyridiniopolycarboxybetaines obviously leads to a less pronounced dependence of mobility on charge distance due to packing constraints and electrical interactions between the side chains.

The efficiency of the intramolecular charge interaction is decreased by additional alkyl chains at the α carbon, too. However, this effect is not as drastic as in the case of different spacer length as can be seen in Figures 6 and 7 (for compound **1a** see Figure 3). The corresponding run times are lowering from **1a** (7–18 min) without additional alkyl chain to **2d** (5–8 min) with an butyl group at the α carbon at pH 1.8–2.4.

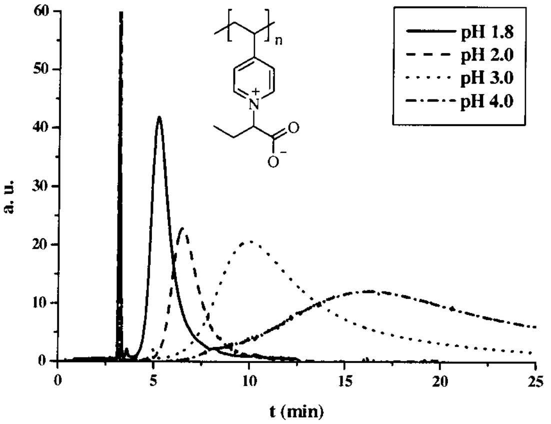

Figure 6. pH-dependent mobility of compound **2b**.

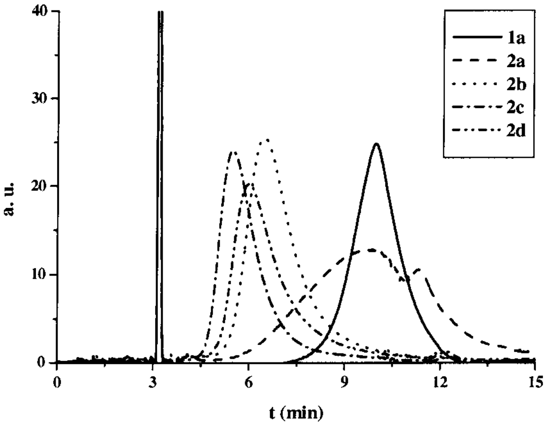

Figure 7. Electrophoretical mobility of compounds **1a**/**2a**–**d** at pH 2.0.

Figure 7 displays two groups of betaine mobilities, one bearing longer alkyl chains (**2b**–**2d**) and the other H or methyl (**1a**, **2a**) at the α carbon. The mobility difference between both should be even smaller considering the lower degree of substitution of compounds **2b**–**2d** (see Table 1). This leads to enhanced mobility caused by protonated pyridine moieties. In general, it is evident that free C–C rotation of the carboxylate group supports an optimized conformation scarcely disturbed by an additional alkyl chain.

Assuming a preference of intramolecular “ion pair” like association, it is interesting to see the influence of the hybridization of and substitution at the nitrogen atom. Therefore, dimethyl- and diethylammonioacetate **3a**/**3b** are compared with some sp^2-nitrogen-containing pyridiniocarboxylates (Figures 8–10). In general, the sample run times considerably increase [6 to about 25 min (**3a**) and 4 to about 12 min (**3b**)] with rising pH, revealing a strong pH dependence of charge interaction.

As expected, the intensity of interaction clearly drops having a sp^3 instead of a sp^2 ammonium ion. Anyway, the remarkable difference in electrophoretical mobility of **3a** and **3b** at any pH displays the importance of accessibility of the cationic charge for efficient interaction. To define the nature of the interaction phenomena observed, a couple of equimolar mixtures of different polycarboxybetaines were measured at pH 2. However, no intermolecular aggregation could be observed. At low pH, capillary electrophoresis is a very suitable method to separate polycarboxybetaines.

Figure 8 displays a plot splitting of **3a** at a pH above 2.4. Obviously, a separation of two differently interact-

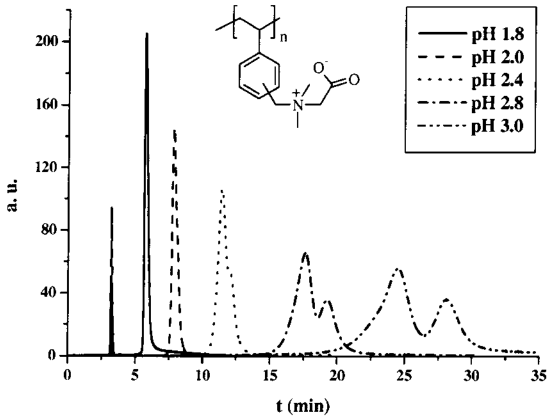

Figure 8. pH-dependent mobility of compound **3a**.

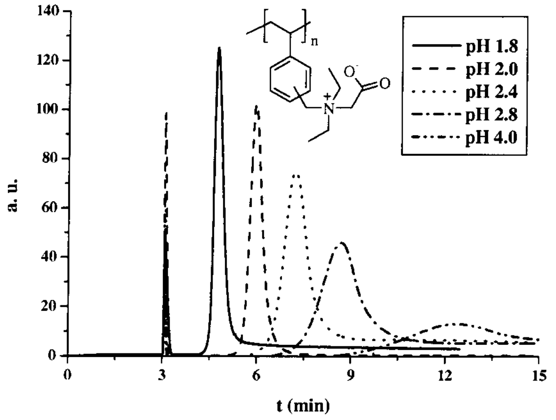

Figure 9. pH-dependent mobility of compound **3b**.

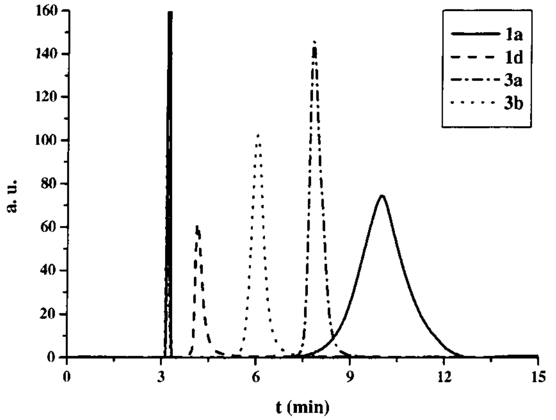

Figure 10. Electrophoretical mobility of compounds **3a**/**3b** and **1a**/**1d** at pH 2.0.

ing groups of macromolecules occurs. One possible explanation could be a change in interaction efficiency, leading to two distinct molecular weights of the associates.

Quantifying these findings, the electrophoretic mobility μ can be calculated from voltage applied, length of the capillary, and run time at the peak maximum (eq 1).

$$\mu = l/Et \quad [\mathrm{cm}^2/(\mathrm{V\ s})] \qquad (1)$$

where l is the capillary length between anode and detector (6 cm), E is the strength of electrical field (170 V/cm), and t is the sample migration time at peak maximum (seconds).

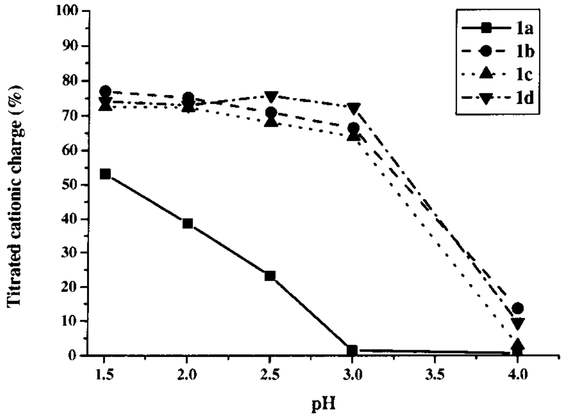

Figure 11. pH-dependent cationic charge content of compounds **1a**–**d**.

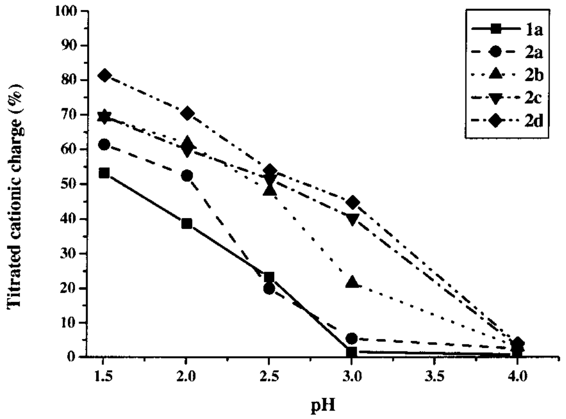

Figure 12. pH-dependent cationic charge content of compounds **1a**/**2a**–**d**.

The data for μ are presented in Table 2. 4-Aminopyridine ($\mu = 18.1 \times 10^{-5}$ cm^2/(V s) at pH 2) was used as internal standard to control the reproducibility of each run.

Table 2 reveals both the pH and the structural dependence of electrophoretic mobilities in the range of pH 1.8–4.0. While rising pH values always lead to decreasing mobilities, the intensity of interaction of the structures investigated strongly differentiates this general tendency. Summarizing all these results, it becomes clear that CE is a very sensitive method to detect differences in highly charged pH-dependent systems such as polycarboxybetaines via electrophoretic mobility. The determining factor of this method is the net charge of the macromolecules. This finally depends on a lot of internal and external parameters. To abstract as far as possible from CE conditions (buffer concentration, capillary properties), we aimed at finding an independent method to confirm our results.

Charge Titration. Providing that intrachain interaction hinders carboxylic groups from being protonated, the same tendencies should be detectable by observing the cationic charges. Dependent on pH and chemical structure of the polycarboxybetaines, different amounts of titrable "free" cations are expected. The results of titration of 10^{-3} M polycarboxybetaine solutions with 10^{-3} M poly(styrenesulfonate sodium salt) leading to a (in some cases insoluble) polyelectrolyte complex are presented in Figures 11–13 and Table 3 [standard 10^{-3} M poly(diallyldimethylammonium chloride)].

The results clearly demonstrate the different influence of structural parameters on titrable charge content.

Table 2. Electrophoretical Mobility of Compounds 1−3

	mobility/10^{-5} cm^2/(V s) at pH							
compd	1.8	2.0	2.2	2.4	2.6	2.8	3.0	4.0
1a	8.7	6.1	4.8	3.4				
1b	17.5	15.2					12.5	7.9
1c	17.1	14.9					12.4	8.1
1d	16.8	14.5	14.3	13.4	12.9	12.1	11.8	8.4
2a	10.0	6.1						4.1
2b	13.5	9.3					6.1	3.6
2c		11.0						
2d	13.7	10.0						4.5
3a[a]	10.5	7.7	6.1	5.2	4.0	3.4	2.4	
3b	12.7	10.1	9.6	8.3	7.4	6.9	6.3	4.9

[a] Peak splitting; maximum of the peak with the shortest run time.

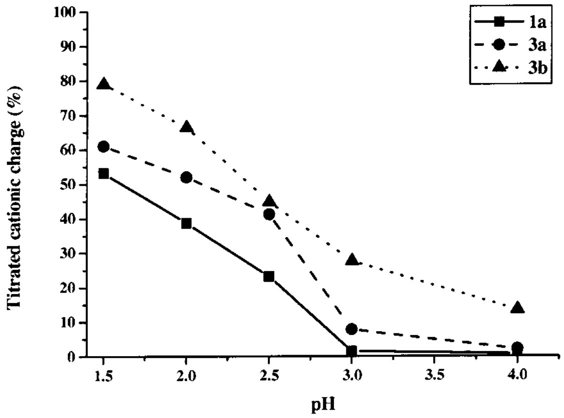

Figure 13. pH-dependent cationic charge content of compounds **1a**/**3a**/**3b**.

Table 3. Charge Titration of Polycarboxybetaines at Different pH

	titrable cations (related to *p*-DADMAC)/% at pH				
compd	1.5	2.0	2.5	3.0	4.0
1a	53.2	38.7	23.2	1.5	0.7
1b	77.0	75.1	70.9	66.3	13.7
1c	72.6	72.4	68.0	63.9	2.9
1d	74.1	73.0	75.7	72.3	9.6
2a	61.4	52.4	19.9	5.4	2.5
2b	69.4	61.8	48.0	21.5	2.9
2c	69.5	59.9	51.4	40.3	3.3
2d	81.4	70.5	53.9	44.8	3.9
3a	61.0	52.0	41.2	7.8	2.1
3b	79.0	66.4	44.8	27.6	13.5

If there are more than two methylene groups as spacer between the charges, a spacer length independent charge content up to pH 3 is observed (Figure 11). Additional alkyl chains at the α-carbon do not efficiently prevent charge interaction; hence, the decrease of titrable charges takes place at lower pH values (Figure 12). Aromatic ammonium functions interact more efficiently and thus leaving a lower titrable amount of cationic charges as aliphatic ones as seen in Figure 13.

The coincidence of the findings of both methods applied is evident. That is remarkable due to the fact of very different levels of ionic strength caused by different buffer constitution (CE) and varying HCl content (charge titration). This implies the relative independence of the charge interaction of polycarboxybetaines regarding the ionic strength of solutions. Therefore, it should be possible to verify the graduation found in aqueous medium also in bulk. An appropriate method to detect different association strength of the carboxylic groups turned out to be FTIR measurement.

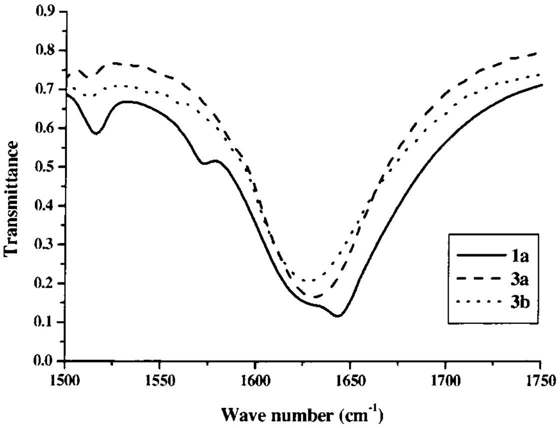

Figure 14. Overlay of FTIR spectra of **1a** and **3a**/**3b** in the COO stretching vibration region.

Table 4. Wavenumbers of the COO Stretching Vibration of All Compounds

compd	wavenumber/cm^{-1}	compd	wavenumber/cm^{-1}
1a	1643.1	**2b**	1638.5
1b	1641.8	**2c**	1638.0
1c	1640.8	**2d**	1637.6
1d	1640.3	**3a**	1629.4
2a	1640.0	**3b**	1627.8

FTIR Measurement. Using the antisymmetric COO stretching vibration as a direct measure for interaction of the carboxylate moiety with the ammonium group, we obtained wavenumber differences up to 16 cm^{-1} (Figure 14).

In general, we found a rather good coincidence with CE results in the graduation of polycarboxybetaine structures of different spacer length, varying additional alkyl chain at the α carbon and alternative hybridization of and substitution at the nitrogen atom. The findings of the FTIR measurement reveal that the association structures of the polybetaines are preformed in bulk (Table 4). Sterically less shielded positive charges as of **1a** (1643.1 cm^{-1}) permit a strong interaction with the carboxylate moiety. This leads to increasing bond strength of the COO moiety and therefore to higher wavenumber values. The opposite happens with highly shielded cationic charges as in **3b** (1627.8 cm^{-1}) or charges separated by spacers (**1d**, 1640.3 cm^{-1}). Here the carboxylate bond strength is weakened by the well-known resonance stabilization of the carboxylic group. It is to note that there is another strong vibration of compounds **1b**−**1d** between 1570.2 and 1564.8 cm^{-1} as expected for a R−COO$^-$ moiety not influenced by cationic charge. It is evident that in bulk association properties the sp^3 hybridization of the nitrogen atom

(**3a**/**3b**) outweighs all the structural differences among the pyridiniocarboxylates. We suggest that the probability of an efficient "ion pair" like association with the delocalized charge of the "flat" pyridinium moiety is remarkably higher than with the sp^3 nitrogen. Analogous measurements on a series of low molecular weight ammoniocarboxybetaines in D_2O solution[26] show a much stronger decrease of the wavenumber when increasing the tether length. The reason for that is the different hydration state of solvated species compared with bulk amorphous polymer.

Summarizing the consistent results obtained with CE, charge titration and FTIR measurement leads to some clear statements concerning structure property relationship of polycarboxybetaines. As expected, the unsubstituted pyridinio acetate **1a** represents the overall strongest aggregating system. It exhibits the lowest mobility at all pH values, even at pH 1.5 only 53% of the theoretical cationic charge is titrable, and the COO stretching vibration is found at the highest wavenumber of all structures investigated. An increasing number of methylene groups between the charges (a pyridinio propionate could not be synthesized due to its instability) strongly decreases charge interaction and effects increasing mobilities in CE, up to 77% titrable cations in charge titration and lower COO wavenumbers compared with **1a**.

Surprisingly, the modification of the pyridinio acetate **1a** with additional alkyl chains at the α-carbon leads to a rather inefficient disturbance of intrachain charge interaction in the case of R = methyl to moderately increasing effects with structures **2b**−**2d** as revealed by all three methods.

Comparison of ammonio acetates **3a** and **3b** with pyridinio acetate **1a** shows a decrease in charge interaction and therefore enhanced mobility values especially for the sterically more hindered compound **3b**. The titrable cationic charge at pH 1.5 strongly increases from **1a** (53%) to **3a** (61%) and **3b** (79%). Because of interaction with a sp^3 nitrogen, the COO wavenumbers of **3a**/**3b** are found at distinctly lower values.

Finally, it is to note that all investigated polycarboxybetaines dependent on their structure show differently decreasing electrophoretical mobilities and a lower number of titrable cations with increasing pH values. All structures with one methylene unit between the charges exhibit significant charge interaction effects. The reduction of those is efficiently achieved only by separating the charges with more than two methylene groups.

Conclusion

We systematically investigated solution and bulk properties of a series of 10 polycarboxybetaines. The complex charge interaction behavior of these materials requires a new method combination to detect differences at even small structural changes. Using capillary electrophoresis with properly adapted conditions, we succeeded in correlating electrophoretic mobility in the pH range 1.8−4.0 with structure variations concerning distance and additional alkyl chain between the charges as well as hybridization of the nitrogen. Charge titration with a polyanion in the pH range 1.5−4.0 fully confirmed mobility measurement results. It has been shown that most of polycarboxybetaines with a 6π system in the side chain exhibit remarkable "ion pair" like association behavior. Mixture experiments in CE revealed intrachain charge interaction as dominating type. Increasing sterical demand at the positively charged nitrogen and growing distance between the charges lead to higher mobility values and more "free" cations at any pH investigated. A comparatively strong shift in solution properties is caused by a simple change from a dimethyl to diethylammonium derivative.

FTIR measurement completed these results and revealed the same tendencies in charge interaction as found in aqueous medium.

Further investigations regarding the interesting pH-dependent complex forming properties of these polycarboxybetaines are currently underway.

Experimental Section

Synthesis. Controlled free radical polymerization of 4-vinylpyridine[29] and vinylbenzyl chloride (mixture of meta and para isomers)[30] resulted in reactive polymers with narrow molecular weight distribution, which were further modified. Syntheses of the polycarboxybetaines **3a** and **3b** were performed as described elsewhere (**3a** in ref 30, **3b** in ref 22). The degree of functionalization was >95% as revealed by ^1H NMR. Polycarboxybetaines **1a**−**1d** and **2a**−**2d** were synthesized in a slightly modified way according to the procedure[29] of **1a**. The corresponding bromocarboxylic acid esters were used without further purification. Poly(4-vinylpyridine) was dissolved in DMF and stirred with a 10-fold excess of the ester. After 5 days the solution was dialyzed against distilled water. Saponification of the ester was performed by adding 1 M NaOH dropwise to the aqueous polymer solution, supervised by phenolphthalein as acid−base indicator to avoid side reactions. The polybetaine solution was dialyzed against distilled water and freeze-dried to obtain the polymer. The residual water content was about 5%.

CE Measurement. *Instrumentation.* Measurement was performed on a PACE/MDQ with UV detection (Beckman Instruments, Fullerton, CA). Fused silica capillaries (75 μm i.d.) were purchased from Polymicro Technologies (Phoenix, AZ) and modified with a PVA coating. The PVA coating was performed as described elsewhere.[31] The capillaries were preconditioned rinsing with 1% (w/w) PVA buffer (1 min, 30 psi) and buffer solution (3 min, 20 psi) at the respective pH value. Between the runs the capillary was rinsed in the same way. The buffer was obtained by mixing appropriate quantities of 0.05 M aqueous solutions of phosphoric acid, sodium dihydrogen phosphate, disodium hydrogen phosphate, and acetic acid. The pH was controlled by a glass electrode (Mettler-Toledo).

Sample Preparation. A 4 mg sample of the polymer sample was dissolved with 2 mg of 4-aminopyridine (Sigma-Aldrich) in 4 mL of 0.01 M HCl and left for 24 h.

Measurement. The samples were injected by pressure (3 s, 30 psi) to avoid charge-dependent injection differences when using electrical field. The effective length of the capillary is only 6 cm due to the low mobility of the polymer samples. The strength of the electrical field is 170 V/cm (voltage 5 kV, capillary length 30 cm). The samples were detected at 214 nm.

Titration of Cationic Charges. Polyelectrolyte titration was carried out at particle charge detector PCD 03 (Mütek), connected to an automatic buret Titrino 716 (Metrohm). Polycarboxybetaine solutions (10^{-3} M) were titrated with 10^{-3} M poly(styrenesulfonate sodium salt) to zero potential. Poly(diallyldimethylammonium chloride) solution (10^{-3} M) (M_w 70 000 g/mol) was used as a standard. The pH value of the solutions was adjusted by adding HCl and controlled by a glass electrode (Mettler-Toledo).

IR Investigation. FTIR measurement was performed at a Nicolet 800 spectrometer with a resolution of 2 cm^{-1}. The samples were prepared by mixing with KBr.

Acknowledgment. The authors thank the German Research Fund (DFG) for financial support (Grant Ja 555/5-3).

References and Notes

(1) Galin, J. C. Polyzwitterions. In *Polymeric Materials Encyclopedia*; Salamone, J. C., Ed.; CRC Press: Boca Raton, FL, 1996; Vol 9, p 7189.
(2) Mizuguchi, R.; Ishikura, S.; Takahashi, A.; Uenaka, A. US Patent No. 4215028, 1980.
(3) Itoh, Y.; Abe, K.; Senoh, S. *Macromol. Chem.* **1986**, *187*, 1691.
(4) Galin, M.; Marchal, E.; Mathis, A.; Galin, J. C. *Polym. Adv. Technol.* **1997**, *8*, 75.
(5) Dautzenberg, H.; Jaeger, W.; Kötz, J.; Philipp, B.; Seidel, Ch.; Stscherbina, D. *Polyelectrolytes-Formation, Characterization, Application*; Carl Hanser Publ.: Munich, Germany, 1994; pp 11−65.
(6) Tuzar, Z.; Pospisil, H.; Plestil, J.; Lowe, A. B.; Baines, F. L.; Billingham, N. C.; Armes, S. P. *Macromolecules* **1997**, *30*, 2509.
(7) Lowe, A. B.; Billingham, N. C.; Armes, S. P. *Macromolecules* **1999**, *32*, 2141.
(8) Kathmann, E. E.; White, L. A.; McCormick, C. L. *Polymer* **1997**, *38*, 879.
(9) Niu, A.; Liaw, D.-J.; Sang, H.-C.; Wu, C. *Macromolecules* **2000**, *33*, 3492.
(10) Kathmann, E. E.; White, L. A.; McCormick, C. L. *Polymer* **1997**, *38*, 871.
(11) Bonte, N.; Laschewsky, A. *Polymer* **1996**, *37*, 2011.
(12) Kathmann, E. E.; McCormick, C. L. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 243.
(13) Favresse, P.; Laschewsky, A. *Macromol. Chem. Phys.* **1999**, *200*, 887.
(14) Favresse, P.; Laschewsky, A. *Polymer* **2001**, *42*, 2755.
(15) Bonte, N.; Laschewsky, A.; Mayer, B.; Vermylen, V. *Macromol. Symp.* **1996**, *102*, 273.
(16) Bonte, N.; Laschewsky, A.; Vermylen, V. *Macromol. Symp.* **1997**, *117*, 195.
(17) Nagaya, J.; Uzawa, H.; Minoura, N. *Macromol. Rapid Commun.* **1999**, *20*, 573.
(18) Ali, S. A.; Aal-e-Ali *Polymer* **2001**, *42*, 7961.
(19) Ladenheim, H.; Morawetz, H. *J. Polym. Sci.* **1957**, *26*, 251.
(20) Wielema, T. A.; Engberts, J. B. F. N. *Eur. Polym. J.* **1990**, *26*, 415.
(21) Barboiu, V.; Streba, E.; Luca, C.; Simionescu, C. I. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 389.
(22) Jaeger, W.; Wendler, U.; Lieske, A.; Bohrisch, J. *Langmuir* **1999**, *15*, 4026.
(23) Bohrisch, J.; Grosche, O.; Wendler, U.; Jaeger, W.; Engelhardt, H. *Macromol. Chem. Phys.* **2000**, *201*, 447.
(24) Grosche, O.; Bohrisch, J.; Wendler, U.; Jaeger, W.; Engelhardt, H. *J. Chromatogr. A* **2000**, *894*, 105 and references cited therein.
(25) Laughlin, R. G. *Langmuir* **1991**, *7*, 842.
(26) Weers, J. G.; Rathman, J. F.; Axe, F. U.; Crichlow, C. A.; Foland, L. D.; Scheuing, D. R.; Wiersema, R. J.; Zielske, A. G. *Langmuir* **1991**, *7*, 854.
(27) Chevalier, Y.; Le Perchec, P. *J. Phys. Chem.* **1990**, *94*, 1768.
(28) Chevalier, Y.; Storet, Y.; Pourchet, S.; Le Perchec, P. *Langmuir* **1991**, *7*, 848.
(29) Bohrisch, J.; Wendler, U.; Jaeger, W. *Macromol. Rapid Commun.* **1997**, *18*, 975.
(30) Wendler, U.; Bohrisch, J.; Jaeger, W.; Rother, G.; Dautzenberg, H. *Macromol. Rapid Commun.* **1998**, *19*, 185.
(31) Engelhardt, H.; Cunat-Walter, M. A. *J. Chromatogr. A* **1995**, *716*, 27.

MA0122019