Communications to the Editor

Synthesis and Intrinsic Viscosity in Salt-Free Solution of a Stiff-Chain Cationic Poly(*p*-phenylene) Polyelectrolyte

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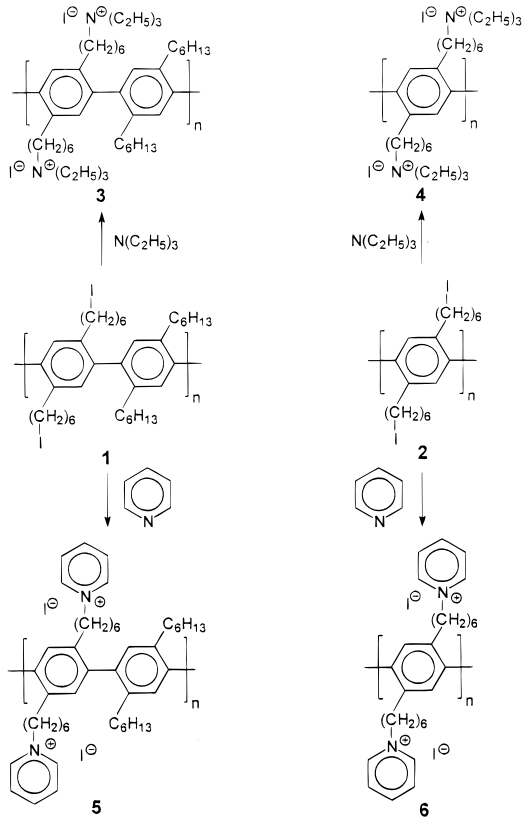
The understanding of flexible polyelectrolytes in dilute aqueous solutions still presents a considerable challenge despite of many decades of research.[1−3] This is due to the long-range nature of the coulombic forces between the charged polymers. In case of flexible polyelectrolytes, a decrease of the ionic strength therefore may lead to an expansion of the coils and an increase of solution viscosity which is due to strong intramolecular forces as well as to marked intermolecular interactions. Both effects are difficult to separate and render the comparison of experimental data with theoretical models a difficult task. Only recently, considerable progress in the understanding of the single-chain behavior of flexible polyelectrolytes has been achieved by Monte Carlo (MC) simulations.[4]

Stiff-chain polyelectrolytes, on the other hand, remain in their extended conformation regardless of the ionic strength of the system. All effects seen upon lowering the ionic strength must be solely due to intermolecular forces. Therefore, these systems represent interesting models for studying the screened coulombic interaction in polymeric systems. These systems may also be of interest for various applications, e.g. in membrane manufacturing.[5]

Reports of the first synthetic rodlike polyelectrolytes were published in the early eighties.[6,7] These polymers were based on poly(1,4-phenylenebenzobisoxazole) and poly(1,4-phenylenebenzobisthiazole). Here we report poly(*p*-phenylene) (PPP) polyelectrolytes which are certainly the most promising candidates among the different chemical structures providing a stiff-chain backbone. The main chain is expected to exhibit a high stiffness together with an excellent stability against chemical and thermal degradation. Consequently, much effort has been spent to overcome the fundamental problems in PPP syntheses.[8] In the late eighties efficient nickel- and palladium-catalyzed polycondensation reactions were developed. These routes allowed, in the first instance, the preparation of high molecular weight PPP derivatives with uncharged side groups.[9−13] Soon after this, carboxylated[14−16] and sulfonated[17] PPP polyelectrolytes were prepared using the above methods. Recently, it has been shown[18] that stiff-chain polyelectrolytes based on the PPP backbone can form lyotropic mesophases.

This rapid progress in PPP research during the recent years was rendered possible mainly by (i) the high tolerance of the Pd-catalyzed polycondensation reactions toward functional groups in the starting materials[12] and (ii) the outstanding thermal and chemical stability of the PPP backbone,[19−21] which allows transformation of the uncharged precursor PPPs into polyelectrolytes with a variety of organic reactions. We recently took advantage of these two features in our efforts for the development of efficient precursor strategies leading to constitutionally well-defined carboxylated PPP polyelectrolytes.[22−24] However, the polymers thus obtained dissolved only in polar organic solvents or mixtures thereof with water, but not in aqueous bases.

Here we present an extension of this work[22−24] to the synthesis of the strong cationic polyelectrolytes **3**−**6** according to eq 1. Cationic ammonium and pyridinium



groups were selected for this purpose, the introduction of which into the PPP backbone was expected to be conveniently possible via quaternization of the 6-iodohexyl-substituted precursor PPPs[24] **1** and **2** with tertiary amines such as triethylamine or pyridine. All polymers were characterized with high-resolution NMR spectroscopy to prove their homogeneous molecular constitution. In addition to this, the intrinsic viscosity of polyelectrolyte **4** was studied at different salt concentrations.

Experimental Section. Reagents and Analyses. All reagents and solvents were purchased from Fluka or Aldrich Chemical Co. in pa quality, and used without further purification. Water was distilled twice in a quartz apparatus before use. Precursor PPPs **1** and **2** were prepared as described previously.[24] Nuclear mag-

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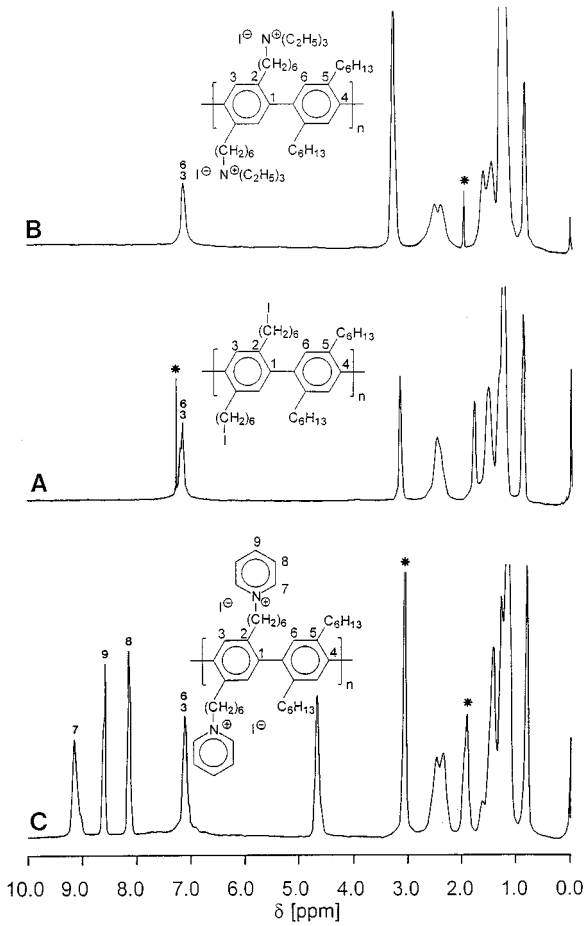

Figure 1. ^{1}H NMR spectra of precursor PPP **1** (A, recorded in chloroform-d_1, 25 °C), of polyelectrolyte **3** (B, recorded in acetonitrile-d_3, 25 °C) and of polyelectrolyte **5** (C, recorded in a 1:1 mixture of dimethyl sulfoxide-d_6 and acetonitrile-d_3, 25 °C). Absorptions of the solvents are indicated by asterisks.

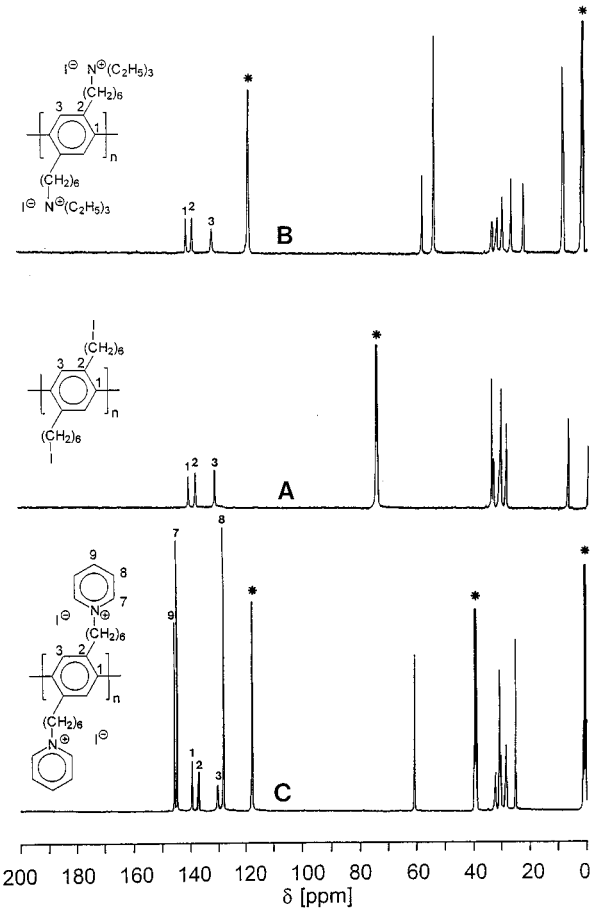

Figure 2. ^{13}C NMR spectra of precursor PPP **2** (A, recorded in 1,1,2,2-tetrachloroethane at 90 °C), polyelectrolyte **4** (B, recorded in acetonitrile-d_3), and polyelectrolyte **6** (C, recorded in a 1:1 mixture of dimethyl sulfoxide-d_6 and acetonitrile-d_3, 25 °C). Absorptions of the solvents are indicated by asterisks.

netic resonance spectra were recorded on a Bruker AM 400 (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR). The signal assignment of the absorptions in the ^{1}H and ^{13}C NMR spectra was done according to the numbering of the protons and carbons given in Figures 1 and 2.

Synthesis of Copolymers 3 and 5; General Procedure. Poly(2,5-dihexyl-1,4-phenylene-*alt*-2,5-bis(6-iodohexyl)-1,4-phenylene) (**1**) (500 mg, 1 equiv) was dissolved in chloroform (50 mL). Acetonitrile (10 mL) and triethylamine (4.7 mL, 33.75 mmol, 25 equiv; for polymer **3**) or pyridine (5.25 mL, 67.5 mmol, 50 equiv; for polymer **5**) were added. The mixture was stirred and refluxed for 24 h. When a brown precipitate appeared (after 1−2 h), another portion of acetonitrile (5 mL) was added to redissolve the solid. Solvents and the excess of amine were then removed by distillation. A slightly brownish, glassy polymer was obtained in quantitative yield which was dried in vacuo (P_4O_{10}). The raw product still contained a certain amount of free amine, even after drying it for several days. To remove this impurity, the material was redissolved in acetonitrile (10 mL) together with water (50 mL), and the resulting homogeneous solution was dialyzed several times against water (doubly distilled prior to use; pore diameter of the tube used for dialysis ≅ 2.4 nm). When a constant conductivity was achieved in the aqueous phase (about 0.7 μS/cm), the polymer solution was concentrated down to about 20 mL, and the remaining aqueous polyelectrolyte solution was freeze-dried.

Synthesis of Homopolymers 4 and 6. The procedure was the same as that described above for polymers **3** and **5**; starting materials: poly(2,5-bis(6-iodohexyl)-1,4-phenylene)[24] (**2**) (1.4 g, 2.82 mmol, 1 equiv) in chloroform (160 mL), acetonitrile (40 mL + 15 mL), and triethylamine (23.58 mL, 169.2 mmol, 30 equiv; for polymer **4**) or pyridine (13.68 mL, 169.2 mmol, 30 equiv; for polymer **6**).

Poly(2,5-dihexyl-1,4-phenylene-*alt*-2,5-bis(6-triethylammonium iodide)hexyl-1,4-phenylene) (3). Yield: 0.637 g (100%). ^{1}H NMR (CD_3CN): δ = 0.86 (m; 6H $(CH_2)_5CH_3$), 1.15, 1.24, 1.30, 1.31, 1.33, 1.35, 1.37, 1.48, 1.62 (9 m; 50H, CH_2, CH_3), 2.40, 2.52 (2 m; 8H, α-CH_2), 3.28 (m; 16H, $N(CH_2)_4$), 7.15 (s; 4H, aromatic-H^3, H^6). ^{13}C NMR (CD_3CN): δ = 7.97 (q; $N(CH_2CH_3)_3$), 14.25 (q; $(CH_2)_5CH_3$), 22.19, 22.93, 23.08, 26.65, 29.37, 29.47, 29.66, 29.77, 31.56, 31.83, 32.10, 33.29 (12 t; CH_2), 53.57 (t, $N(CH_2CH_3)_3$), 57.56 (t, $NCH_2(CH_2)_5$), 131.12 (d; aromatic-C^3, C^6), 138.05, 138.24 (2s, aromatic-C^2, C^5), 140.38 (s; aromatic-C^1, C^4).

Poly(2,5-dihexyl-1,4-phenylene-*alt*-2,5-bis(6-pyridinium iodide)hexyl-1,4-phenylene) (5). Yield: 0.607 g (100%). ^{1}H NMR (CD_3CN, DMSO-d_6): δ = 0.81 (m; 6H, $(CH_2)_5CH_3$), 1.16, 1.29, 1.44 (3 m; 28H, CH_2), 1.93 (m; 4H, CH_2CH_2N), 2.36, 2.50 (2 m; 8H, α-CH_2), 4.68 (m; 4H, NCH_2), 7.13 (s; 4H, aromatic-H^3, H^6), 8.13 (m; 4H, aromatic-H^8), 8.58 (m; 2H, aromatic-H^9), 9.14 (m; 4H, aromatic-H^7). ^{13}C NMR (CD_3CN, DMSO-d_6): δ = 13.69 (q; $(CH_2)_5CH_3$), 22.16, 22.32, 25.52, 28.67, 28.86, 28.99, 30.72, 31.07, 31.30, 32.54 (10 t; CH_2), 61.20

(t; N(CH_2)), 128.32 (d, aromatic-C^8), 130.36 (d; aromatic-C^3, C^6), 137.45 (s; aromatic-C^2, C^5), 139.59 (s; aromatic-C^1, C^4), 144.79 (d; aromatic-C^7), 145.71 (d; aromatic-C^9).

Poly(2,5-bis(6-triethylammonium iodide)hexyl-1,4-phenylene) (4). Yield: 1.970 g (100%). ^{1}H NMR (CD_3CN): δ = 1.29, 1.48, 1.67 (3 m; 30H, CH_2, CH_3), 2.38, 2.53 (2 m; 4H, α-CH_2), 3.32 (m; 16H, N(CH_2)$_4$), 7.18 (s; 2H, aromatic-H^3). ^{13}C NMR (CD_3CN): δ = 8.05 (q; N(CH_2CH_3)$_3$), 22.13, 22.59, 26.30, 29.52, 31.41, 32.93, 33.44 (7 t; CH_2), 53.79 (t; N(CH_2CH_3)$_3$), 57.89 (t; NCH_2-(CH_2)$_5$), 131.14 (d; aromatic-C^3), 137.85 (s; aromatic-C^2), 140.45 (s; aromatic-C^1).

Poly(2,5-bis(6-pyridiniumium iodide)hexyl-1,4-phenylene) (6). Yield: 1.846 g (100%). ^{1}H NMR (CD_3-CN, DMSO-d_6): δ = 1.20, 1.26, 1.38 (3 m; 12H, CH_2), 1.92 (m; 4H, RCH_2CH_2N), 2.29, 2.50 (2 m; 4H, α-CH_2), 4.72 (m; 4H, NCH_2), 7.09 (s; 2H, aromatic-H^3), 8.16 (m; 4H, aromatic-H^8), 8.63 (m; 2H, aromatic-H^9), 9.29 (m; 4H, aromatic-H^7). ^{13}C NMR (CD_3CN, DMSO-d_6): δ = 25.06, 25.31, 28.14, 28.21, 28.40, 28.58, 30.30, 30.74, 30.89, 30.96, 32.17, 32.43 (12 t; CH_2), 60.90 (t; N-CH_2), 128.20 (d; aromatic-C^8), 130.27 (d; aromatic-C^3), 137.17 (s; aromatic-C^2), 139.40 (s; aromatic-C^1), 144.77 (d; aromatic-C^7), 145.63 (d; aromatic-C^9).

Viscosity measurements were carried out at 25 °C (±0.1 °C) using Ubbelohde viscosimeters (type 0a, Schott). By carefully choosing the width of the capillary, the time (t) needed for the solutions to flow through the capillary was adjusted to be above 200 s. Aqueous solutions of polyelectrolyte **4** were prepared by dissolution of the freeze-dried material in doubly distilled water. Measurements in the presence of added salt were carried out by dissolving the polymer in 0.01 M aqueous KCl solutions. Prior to all measurements, the solutions were carefully freed from dust by repeated filtration through a filter (pore diameter 16−40 μm). Flow times on the order of 200−300 s were measured with an accuracy of ±0.1 s. Every determination of the specific viscosity, η_{sp} [$\eta_{sp} = (t - t_0)/t_0$; t and t_0 are the flow time of solution and solvent, respectively], was repeated at least six times to check the reproducibility. In order to avoid errors in t_0 measurement due to polyelectrolyte adsorption on the capillary wall, the elution time of pure solvent was determined by continued diluting of the polymer solutions until a constant value was reached.

Number-average degrees of polymarization (P_n) of the uncharged precursor polymers **1** and **2** were determined by membrane osmometry in toluene solutions at 50 °C using a Knauer 01.00 membrane osmometer (membrane, cellulose triacetate).

Results and Discussion. Polymer Synthesis. The precursor strategy used here for the preparation of the cationic PPP polyelectrolytes **3**−**6** has the distinct advantage that the uncharged precursors **1** and **2** can be characterized first. Thus, a number-average degree of polymerization (P_n) between 20 and 40 was obtained by membrane osmometry as described previously[25,26] for both precursors. The persistence length of the PPP backbone was estimated[27] by Bohdanecky's method[28] (cf. also the discussion of this method in ref 29) to be 22 nm. This is in good agreement with the result from a recent computer simulation[30] but considerably higher than the value (13 nm) deduced from a similar PPP recently by Vanhee et al.[31] Despite this discrepancy, it seems to be justified to regard the rather short chains under consideration here (contour length between 10 and 20 nm) as rodlike entities.

The reaction conditions for the conversion of precursors **1** and **2** to polymers **3**−**6** were first optimized in order to guarantee the full conversion. For this purpose **1** and **2** were treated with an excess of triethylamine or pyridine in a variety of solvents at different temperatures. Representative samples of the reaction mixtures were analyzed at regular intervals with ^{1}H NMR spectroscopy to monitor the progress of the model reactions. By this method, the disappearance of the reactive iodoalkyl functionalities of precursors **1** and **2** could easily be followed by considering the resonances of the iodomethylene protons (δ = 3.2 ppm). Simultaneously, new characteristic absorptions appear in the spectra (δ = 3.3 ppm for **3** and **4**; δ = 4.7 ppm for **5** and **6**), originating from the CH_2N^+ methylene protons formed. An almost quantitative conversion was achieved in all cases after refluxing the starting materials in a mixture of chloroform and acetonitrile for 24 h.

It turned out that the homogeneity of the reaction mixtures had to be ensured during the whole reaction time. At the beginning of the conversions an excess of chloroform was used in the solvent mixture because acetonitrile proved to be a precipitant for the precursors. When the partially quaternized intermediate precipitated, additional portions of acetonitrile had to be added to redissolve it. No fractionation was admitted during the workup. Therefore, identical P_n values can be assumed for polyelectrolytes **3**−**6** as were determined in advance for their precursors **1** and **2**.

After workup, polymers **3**−**6** obtained proved to be insoluble in chloroform but could be dissolved completely in solvents such as acetonitrile or dimethylacetamide. The ^{1}H and ^{13}C NMR spectra of these polymers (cf. the spectra of **3** and **5** in Figures 1 and 2) show that full conversion was reached under the conditions described above: The quaternization results in the complete disappearance of the iodomethylene absorptions and all new signals in the ^{1}H NMR spectra are in full agreement with the molecular structures of polyelectrolytes **3**−**6**. Side reactions such as elimination or cross-linking processes were thus excluded for sure within the scope of the accuracy of the NMR method. The narrow splitting of some of the absorptions in the ^{1}H as well as in the ^{13}C NMR spectra is due to the occurrence of atropic isomers within the polymer chains, as has been discussed elsewhere in more detail.[22]

Solution Properties. Polymer **4** was chosen for studying the viscosity in dilute solution because of its extraordinary solubility in water, even at room temperature. It bears two charged groups per repeat unit at the ends of the hydrophobic *n*-hexyl side chains. This material was therefore expected to have solution properties almost undisturbed by the hydrophobic moieties of the repeating unit. The P_n of polymer **4** under consideration here was 27 ($M_n \sim$ 16 900g/mol, determined for the precursor). Accordingly, the number average contour length, L_n, of this polymer was ca. 12 nm. Figure 3 shows the reduced specific viscosity as function of concentration (Huggins plot) of PPP **4** in pure water and in 0.01 M KI solution. In presence of added salt the data could be fitted by a straight line. The intrinsic viscosity, [η], was found to be 15.1 mL/g for polyelectrolyte **4** at this concentration of added salt. Because of the high ionic strength, the Coulomb interaction of the different chains is strongly screened. Therefore, the intrinsic viscosity obtained under these conditions is in excellent agreement with a value of the intrinsic viscosity [η] measured for its uncharged pre-

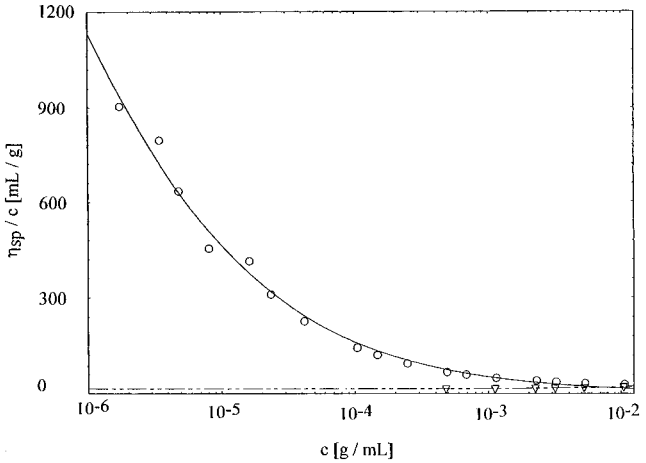

Figure 3. Plot of the reduced specific viscosity η_{sp}/c vs concentration for the polyelectrolyte **4** in salt-free aqueous solution (open circles) and in 0.01 M KI solution (open triangles). The solid line denotes the fit according to Fuoss and Strauss;[32,33] the dashed line corresponds to a linear fit.

cursor PPP ($[\eta]$ = 16.5 mL/g, measured in 1,1,2,2-tetrachloroethane at 35 °C). A polydispersity of $M_w/M_n \approx 2$ is characteristic for polymers prepared by Pd-catalyzed polycondensation.[26,27] Thus, a contour length, L_w, of about 24 nm can be assumed for the PPPs under consideration here. For rodlike chains, furthermore, $[\eta]M_L$ depends mainly on L_w and only weakly on the chain diameter, d (M_L is the mass per unit length, i.e., 1 nm). Therefore, intrinsic viscosities on the order of $[\eta] \approx 15$ mL/g as found here for the PPPs (P_n of ca. 27) are in excellent agreement with the corresponding values of other rodlike polymers like polyimides, reported recently.[26]

Without added salt, i.e., at very low ionic strength, a pronounced polyelectrolyte effect is seen despite the rather small contour length of polymer **4**. The observed increase of the reduced viscosity upon dilution can be described by the Fuoss−Strauss equation:[32,33]

$$\frac{c}{\eta_{sp}} = A + B\sqrt{c}$$

As is evident, no maximum is found in the Huggins plot of the pure aqueous solution of the rodlike polyelectrolyte **4**, at least within the limits of the present measurements. This is in clear contrast to Huggins plots reported for flexible polyelectrolytes in literature[1,34] but also to the rodlike polyelectrolytes reported earlier.[6,7] To ensure the accuracy of the present measurements, additional investigations of the specific viscosity of flexible polyelectrolytes have been performed. The maximum of the specific viscosity found by previous authors[34] could be reproduced. Thus, we are sure that the measurements displayed in Figure 3 are significant.

Certainly the specific viscosity is expected to decrease again at still lower concentrations not accessible by the present experimental technique. Although a conclusive explanation for this lack of a maximum is presently not available, the distinct differences in the Huggins plots of flexible and rodlike polyelectrolytes point toward a significantly longer range of intermolecular interactions in these polyelectrolytes as compared to flexible polyelectrolytes of much higher molecular weights. This effect must be traced back to the elongated conformation of the PPP **4**, which obviously leads to a less effective screening of the charge on the stiff-chain backbone. A more detailed investigation of polyelectrolyte **4** is under way.

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