The Solubility of Polyelectrolyte Complexes. Calcium Polyacrylate and the Poly(4-vinyl-*N*-pentylpyridinium) Salt of Poly(styrenesulfonic acid)

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ABSTRACT: The solubilities of sparingly water-soluble polyelectrolyte complexes, i.e., calcium polyacrylate (CaPAA) and the complex of poly(styrenesulfonic acid) and poly(4-vinyl-*N*-pentylpyridinium base) (C5PVP·PSS), are measured in the presence of foreign salts, such as NaCl, $CaCl_2$, sodium poly(ethylenesulfonate), the copolymer of dimethyldiallylammonium chloride and sulfur dioxide, and Polybrene. Mean activity coefficients and solubilities of the polyelectrolyte complexes are given theoretically from Manning's theory for polyelectrolyte solutions. An excellent agreement is obtained between the experimental and theoretical results for the solubility of CaPAA. For C5PVP·PSS, Manning's theory predicts the solubilities satisfactorily, when counterion valencies smaller than the real values are taken. The influence of the counterion valency, charge density of macroions, and valency of foreign salt on the solubilities is discussed systematically.

Introduction

Polyelectrolyte complexes are groups of the complexation products of two highly but oppositely charged polymers in aqueous media and are helpful for understanding biological systems. Intensive studies of their preparation, stability, and other basic properties have been reported.[1-20] However, thermodynamic understanding of the electrostatic interactions between macrocations and their counterions in polyelectrolyte complex systems is not always satisfactory. Especially, thermodynamic parameters such as mean activity coefficients and solubilities have seldom been measured or discussed.

Recently, many examples of successful predictions of Manning's limiting law[21,22] lean toward thermodynamic parameters of polyelectrolyte solutions, i.e., osmotic coefficient,[21,23-26] mean activity coefficient,[21,27,28] diffusion coefficient,[29-31] partial molal volume,[32,33] heat of dilution,[34-36] catalytic influences on interionic reactions,[37,38] heat of conformational transition of DNA,[39] etc.

In this work, we measured the solubilities of sparingly water-soluble polyelectrolyte complexes in the presence of foreign salts. The experimental results were compared with Manning's theory satisfactorily.

Experimental Section

Materials. Sodium polyacrylate (NaPAA, degree of polymerization (DP) = 640) was a gift from Toa Gosei Chemical Co., Nagoya. An aqueous solution of NaPAA was passed through columns of a mixed bed of cation- and anion-exchange resins repeatedly in acid form. The calcium salt was obtained by neutralization of the acid with calcium hydroxide, which was purchased from Merck (G.R. grade). Sodium poly(styrenesulfonate) (NaPSS, DP = 3000) was purchased from Polyscience, Inc., Warrington, PA. Poly(4-vinyl-*N*-pentylpyridinium bromide) (C5PVP) was prepared by heating 150 mL of *n*-pentyl bromide and 10.4 g of poly(4-vinylpyridine) (Polyscience, DP = 3000) in 150 mL of nitromethane at 45 °C for 5 days. The solvent and the excess of *n*-pentyl bromide was eliminated by vacuum evaporation. The product was dissolved in ethanol and precipitated in dioxane. A granular hygroscopic white powder was obtained by drying the precipitate in a vacuum (75% in yield). Further purification of the sample was carried out by dialysis against pure water. The degree of quaternization was 0.97 from elemental analysis and conductometric titration of Br^- with $AgNO_3$. Anal. Calcd for $n\text{-}C_{12}H_{18}NBr$ (256.2): C, 56.3; H, 7.1; N, 5.5; Br, 31.2. Found: C, 55.7; H, 7.0; N, 5.2; Br, 30.6. Polyelectrolyte complex C5PVP·PSS was obtained by adding C5PVP solution in NaPSS solution (200 mL, 5×10^{-4} M) drop by drop for 5 h. The precipitate obtained was washed thoroughly with pure water and then dialyzed with pure water for 7 days. The wet precipitate thus obtained was used for solubility measurements. NaCl, $CaCl_2$, KCl, and LiCl were used as guaranteed reagents. Sodium poly(ethylenesulfonate) (NaPES, DP = 770) was kindly donated by the Hercules Powder Co., Wilmington, DE. Polybrene (1,5-dimethyl-1,5-diazaundecamethylene polymethobromide) is an ionen-type cationic polymer purchased from the Aldrich Chemical Co., Milwaukee, WI. Copolymer of dimethyldiallylammonium chloride and sulfur dioxide (DMCS) was a gift from Nitto Spinning Co., Tokyo.[40,41]

Solubility Measurements. The solubility of CaPAA was determined as follows; 50 mL of salt solution and an excess amount of CaPAA powder were put into an ampule (capacity, 100 mL). Freezing followed by deairing, and resolution was repeated 4-5 times before sealing. The ampules were heated at 80-90 °C in a water bath for 3 h and then placed in a water bath regulated at 25 ± 0.05 °C for at least 14 days. During these periods, the ampules were moved back and forth with a lateral displacement of 1 cm at a frequency of 100 cycles·min^{-1}. This motion was ascertained to be sufficient to attain equilibrium within 10 days. The equilibrium concentrations of calcium ions were determined by using a multichannel atomic absorption flame spectrophotometer (Shimadzu, Kyoto, Model MAF-1). The absorption peak of Ca^{2+} was 422.7 nm. Concentrations of PAA component were determined conductometrically by using an autobalance precision bridge (Wayne Kerr, Bognor Regis, Sussex, Model B331, Mark II). The procedures for determining the solubility of C5PVP·PSS were similar to those for CaPAA; test tubes having a stopper were used instead of the ampules, and the deairing process was omitted. The equilibrium concentrations were determined with a precision spectrophotometer (Union Engineering, Hirakata, Model SM301). Samples were withdrawn through a polyethylene tubing (20 mm in length and 3 mm in diameter) plugged with cotton gauze to filter out coexisting precipitate. A wavelength of 258 nm (molecular extinction coefficient = 3000) was used. Solubilities of CaPAA and C5PVP·PSS in pure water were 2.0×10^{-4} M (base molality) and 3.5×10^{-5} M (base molality), respectively, at 25 °C.

Results

Figure 1 shows the solubility of CaPAA in the presence of NaCl, KCl, or LiCl. The filled circles show the solubilities determined from the atomic absorption of Ca cations, and the other symbols show the solubilities from the conductometric titration of PAA anions. The polyelectrolyte complex sample was solubilized with 1-1 type salts; the solubility increased 7-8 times in the presence of ca. 7×10^{-3} M salt. The counterion specificity of the salts was not observed when we take into account the relatively large experimental error in the experiments. Qualitatively speaking, the solubilization of CaPAA with 1-1 type salts supports the fact that the mean activity coefficient (γ) of CaPAA decreased in the presence of the salt. The solid curve shows the theoretical evaluation of the solubility, which will be described later in detail.

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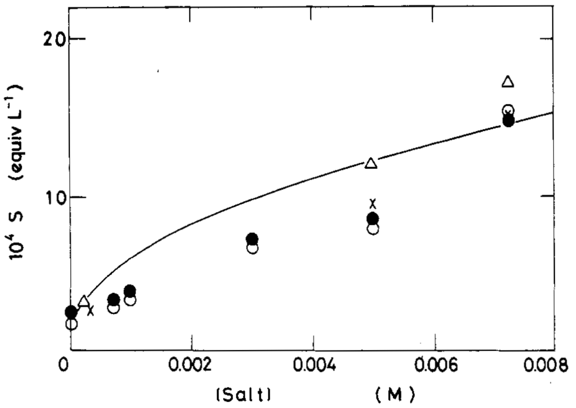

Figure 1. Plots of solubility of CaPAA against the concentration of 1–1 type salts at 25 °C. (○) NaCl (from titration of PAA); (●) NaCl (from atomic absorption of Ca^{2+}); (—) theory; $Z_{2g} = 2$; $Z_{2p} = 640$; $Z_{3c} = Z_{3a} = 1$; $\xi = 2.85$.

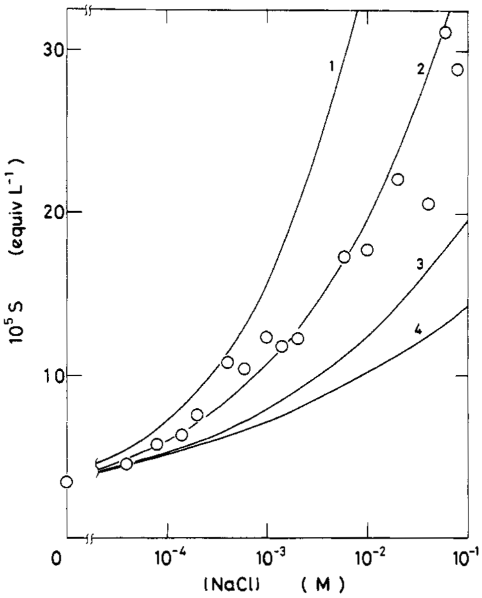

Figure 2. Plots of solubility of C5PVP·PSS against NaCl concentration at 25 °C. (○) Observed; (—) theory; $Z_{2g} = 20$ (curve 1), 30 (2), 40 (3), 50 (4); $Z_{2p} = 3000$; $Z_{3c} = Z_{3a} = 1$; $\xi = 2.85$.

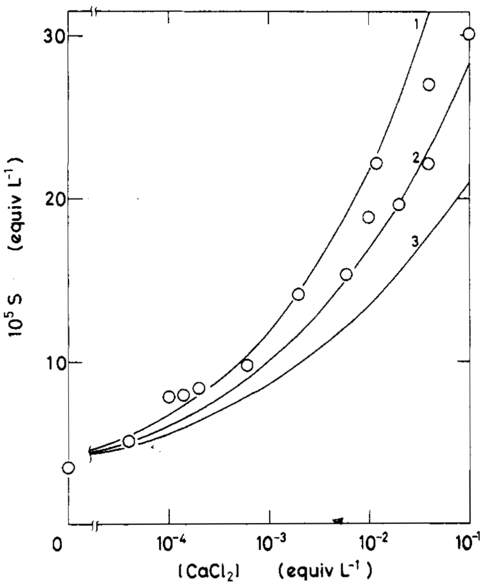

Figure 3. Plots of solubility of C5PVP·PSS against $CaCl_2$ at 25 °C. (○) Observed; (—) theory; $Z_{2g} = 30$ (curve 1), 35 (2), 40 (3); $Z_{2p} = 3000$; $Z_{3c} = 2$, $Z_{3a} = 1$; $\xi = 2.85$.

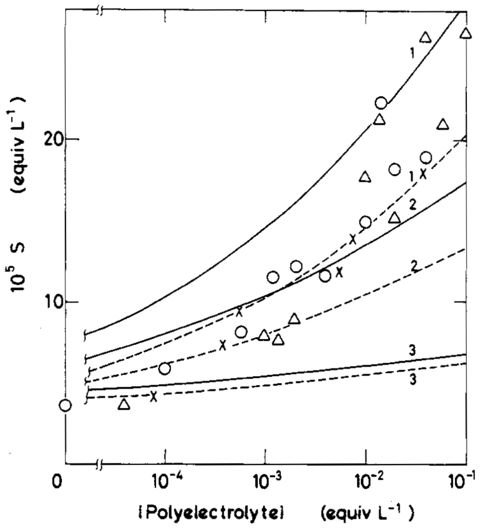

Figure 4. Plots of solubility of C5PVP·PSS against the concentrations of NaPES (○) DMCS (×), and Polybrene (△) at 25 °C. Theory: $Z_{2g} = 50$ (curve 1), 60 (2), 100 (3); $Z_{2p} = 3000$, $Z_{3c} = 1$; $Z_{3a} = 500$ (—), 50 (- - -).

Figures 2–4 show the solubilities of C5PVP·PSS in the presence of NaCl, $CaCl_2$, and macroions (NaPES, DMCS, and Polybrene), respectively. The solubility of C5PVP·PSS, which was determined spectrophotometrically, was 3.5×10^{-5} M (in monomer units) in pure water at 25 °C. Clearly, the polyelectrolyte complexes were solubilized greatly in the presence of salts, and the magnitude of the solubilization decreased as the valencies of the salts increased.

Discussion

The activity of a polyelectrolyte complex in saturated solution, a, is given by eq 1 in terms of the single-ion activities of the counterions (a_{2g}) and macroions (a_{2p}).

$$a = a_{2g}^{Z_{2p}} a_{2p}^{Z_{2g}} \qquad (1)$$

Here, Z_{2g} and Z_{2p} are the valencies of counterions and macroions, respectively. The a values must be equal in the presence of the foreign salts and in their absence when there is saturation equilibrium. Then, eq 2 holds

$$\begin{aligned} a &= (S^*\gamma_2^*/Z_{2p})^{Z_{2g}+Z_{2p}} Z_{2g}^{Z_{2p}} Z_{2p}^{Z_{2g}} \\ &= (S\gamma_2/Z_{2p})^{Z_{2g}+Z_{2p}} Z_{2g}^{Z_{2p}} Z_{2p}^{Z_{2g}} \qquad (2) \end{aligned}$$

where S and γ_2 denote the solubility of the polyelectrolyte complex (equivalent per 1 kg of water) and its mean activity coefficient. The asterisk means the reference state in the absence of foreign salt. Equation 2 is simplified to eq 3.

$$S/S^* = \gamma_2^*/\gamma_2 \qquad (3)$$

According to Manning's theory,[21,22] a real polyelectrolyte chain is replaced by an infinite linear charge. When the charge density of a macroion is high, counterions condense on a macroion and lower its charge density. ξ is the charge density parameter given by

$$\xi = e^2/DkTb \qquad (4)$$

where D and e are the dielectric constant and the electronic charge. b is the distance between neighbouring charges on a macroion. When the valency of counterion is Z_{2g}, counterions condense on a macroion to lower ξ to Z_{2g}^{-1}. For $\xi < Z_{2g}^{-1}$, no condensation of counterions occurs.

For $\xi \geq Z_{2g}^{-1}$, the mean activity coefficient of a polyelectrolyte complex, γ_2 [$\gamma_2^{Z_{2g}+Z_{2p}} = \gamma_{2g}^{Z_{2p}}\gamma_{2p}^{Z_{2g}}$], is given as

$$\ln \gamma_2 = -[Z_{2p}\xi^{-1}/2Z_{2g}(Z_{2g} + Z_{2p})] \ln [\xi^{-1}m_2 + (Z_{3c} + Z_{3a})m_3] + [Z_{2p}\xi^{-1}/Z_{2g}(Z_{2g} + Z_{2p})] \ln m_2 - Z_{2p}m_2/2(Z_{2g} + Z_{2p})\xi^2 Z_{2g}[\xi^{-1}m_2 + (Z_{3c} + Z_{3a})m_3] - [Z_{2p}/(Z_{2g} + Z_{2p})] \ln m_2 + \text{constant} \quad (5)$$

Here, Z_{3c} and Z_{3a} denote the valencies of cation and anion of the foreign salt. m_2 and m_3 are the equivalent concentrations of polyelectrolyte complex and foreign salt, respectively.

For $\xi < Z_{2g}^{-1}$, γ_2 is given by

$$\ln \gamma_2 = -[Z_{2g}Z_{2p}\xi/2(Z_{2g} + Z_{2p})]\{\ln [Z_{2g}m_2 + (Z_{3c} + Z_{3a})m_3] + Z_{2g}m_2/[Z_{2g}m_2 + (Z_{3c} + Z_{3a})m_3]\} + \text{constant} \quad (6)$$

From eq 3, 5, and 6, the solubilities of polyelectrolyte complex, S ($=m_2$), are given as follows.

For $\xi \geq Z_{2g}^{-1}$,

$$f(S) = \ln (S/S^*) + [Z_{2p}/2\xi Z_{2g}(Z_{2g} + Z_{2p})] \ln \{[\xi^{-1}S^* + (Z_{3c} + Z_{3a})m_3^*]/[\xi^{-1}S + (Z_{3c} + Z_{3a})m_3]\} - Z_{2p}(1 - Z_{2g}\xi)/\xi Z_{2g}(Z_{2g} + Z_{2p})] \ln (S^*/S) + [Z_{2p}/2\xi^2 Z_{2g}(Z_{2g} + Z_{2p})]\{S^*/[\xi^{-1}S^* + (Z_{3c} + Z_{3a})m_3^*] - S/[\xi^{-1}S + (Z_{3c} + Z_{3a})m_3]\} = 0 \quad (7)$$

For $\xi < Z_{2g}^{-1}$,

$$f(S) = \ln (S/S^*) + [Z_{2g}Z_{2p}\xi/2(Z_{2g} + Z_{2p})] \ln \{[Z_{2g}S^* + (Z_{3c} + Z_{3a})m_3^*]/[Z_{2g}S + (Z_{3c} + Z_{3a})m_3]\} + [Z_{2g}^2 Z_{2p}\xi/2(Z_{2g} + Z_{2p})]\{S^*/[Z_{2g}S^* + (Z_{3c} + Z_{3a})m_3] - S/[Z_{2g}S + (Z_{3c} + Z_{3a})m_3]\} = 0 \quad (8)$$

where the asterisk denotes again the reference state. Equations 7 and 8 can be solved by the Newton–Raphson method (by computer analysis).[42]

The solid curve in Figure 1 shows the calculated values of S for CaPAA from eq 7. ξ was taken to be 2.85 (b = 0.25 nm). Z_{2g}, Z_{2p}, Z_{3c}, Z_{3a}, S^*, and m_3^* were taken to be 2, 640, 1, 1, 2 × 10^{-4} M, and 0 M, respectively. The agreement between the experiment and the theory is satisfactory.

Theoretical prediction of the solubility of C5PVP·PSS is given by solid curves in Figures 2 and 3 in the presence of NaCl and $CaCl_2$, respectively. ξ was taken to be 2.85 (b = 0.25 nm). S^* and m_3^* were 3.5 × 10^{-5} and 0 M, respectively. Z_{2p} was 3000, which corresponds to the degree of polymerization of PSS anions. The excellent agreement with the observation was obtained when the Z_{2g} value was taken to be 30 (with NaCl) or 35 (with $CaCl_2$) instead of the real valency of C5PVP macrocations, i.e., 3000. This is ascribed to the fact that Manning's theory does not hold for large values of Z_{2g}. However, it should be noted that the solubilization curves obtained experimentally are explained beautifully by the theory.

Figure 4 shows the comparison of the solubilities observed for C5PVP·PSS in the presence of anionic (NaPES) and cationic polyelectrolytes (DMCS and Polybrene) with the theory. The solid and broken curves are the theoretical values for NaPES addition, when the Z_{3a} values were taken to be 500 (real valency of PES macroanions) and 50, respectively. Curves 1–3 show the solubilities when Z_{2g} values, i.e., valencies of C5PVP, were taken to be 50, 60, and 100, respectively. As is clear from the comparison of the crosses and broken curve 1 in the figure, satisfactory agreement between the experiment and the theory was obtained when both Z_{2g} and Z_{3a} were taken to be 50. Z_{2g} and Z_{3a} values smaller than the real values must be taken to get the excellent agreement. This is again ascribed to the fact that the Debye screening parameter used in Manning's theory is not adequate for the very large values of Z_{2g} and Z_{3a}.

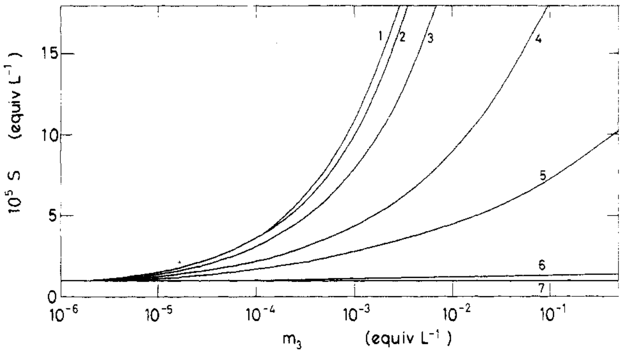

Figure 5. Plots of solubility of polyelectrolyte complex estimated theoretically against the concentration of 1–1 type foreign salt. Influence of counterion valencies. Z_{2g} = 2 (curve 1), 5 (2), 10 (3), 20 (4), 30 (5), 100 (6), 1000 (7); Z_{2p} = 1000; Z_{3c} = Z_{3a} = 1; ξ = 1.5; S^* = 1 × 10^{-5} M.

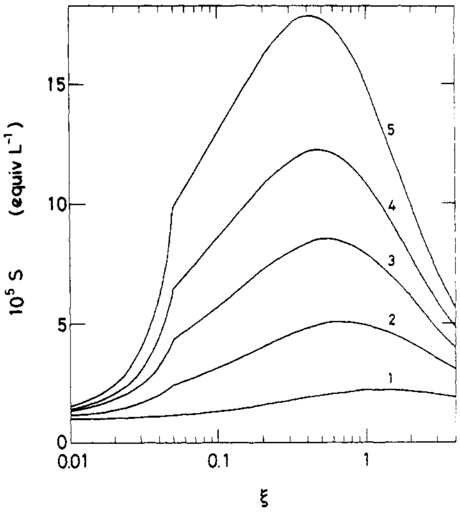

Figure 6. Plots of solubility of 20–1000 type polyelectrolyte complex estimated theoretically against ξ. Influence of charge density (ξ) of polyelectrolyte complex. Z_{2g} = 20; Z_{2p} = 1000; Z_{3c} = Z_{3a} = 1; m_3 = 1.01 × 10^{-4} M (curve 1), 1.18 × 10^{-3} (2), 4.48 × 10^{-3} (3), 1.09 × 10^{-2} (4), 2.67 × 10^{-2} (5); S^* = 1 × 10^{-5} M.

Next, we discuss the general features of the solubilities of polyelectrolyte complexes using the theoretical equations derived in this work. Influence of the valencies of the counterions of the polyelectrolyte complex on the solubility in the presence of 1–1 type foreign salt (NaCl, for example) is shown in Figure 5. m_3 is the equivalent concentration of the foreign salt. Clearly, solubilization of the polyelectrolyte complex is depressed significantly for the large Z_{2g} values. This means that the electrostatic shielding effect of the 1–1 type foreign salt is not effective for the typical polyelectrolyte complexes, where both Z_{2g} and Z_{2p} are large.

Figure 6 shows the solubility of the 20–1000 type polyelectrolyte complex in the presence of various amounts of 1–1 type foreign salt and the influence of the charge density parameter, ξ. Discontinuity in the S–ξ curve corresponds to the ξ values where the relation of $\xi = Z_{2g}^{-1}$ holds. This graph shows clearly that the solubilization effect by 1–1 type foreign salt becomes more significant as ξ increases in the regions of ξ smaller than 0.4–0.6. However, the solubilization effect begins to be less significant as ξ increases for ξ values larger than ca. 1. Thus, the theory predicts that the polyelectrolyte complex having ξ values around 0.4–0.6 will be substantially solubilized by

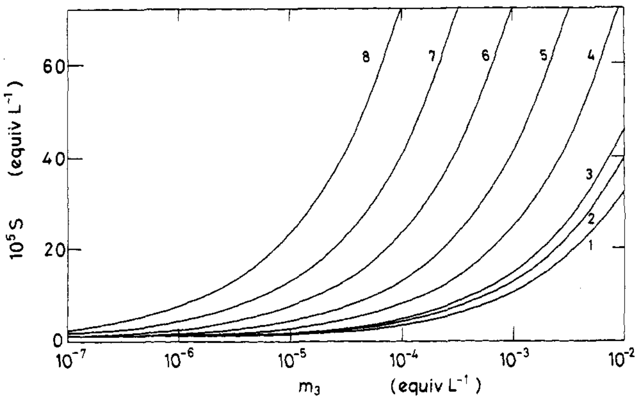

Figure 7. Plots of solubility of 2–1000 type polyelectrolyte complex estimated theoretically against the concentration of foreign salt. Influence of valencies of anionic components of foreign salt. $Z_{2g} = 2$; $Z_{2p} = 1000$; $Z_{3c} = 1$; $Z_{3a} = 1$ (curve 1), 2 (2), 3 (3), 10 (4), 30 (5), 100 (6), 300 (7), 1000 (8); $\xi = 1.5$, $S^* = 1 \times 10^{-5}$ M.

the foreign salt compared with the complex of $\xi = 2.85$ (for typical vinyl-type macroions).

The influence of the valency of the anionic component of the foreign salt on the solubility of 2–1000 type polyelectrolyte complex is shown in Figure 7. Clearly, the foreign salts solubilize more effectively as the valency (Z_{3a}) increases. This is explained reasonably by the fact that the electrostatic shielding effect of foreign salts of high valencies is substantial against the macrocation–macroanion attraction. It should be mentioned here that the use of Manning's theory will not be justified in the strict sense for the polyelectrolyte complex systems with high valencies of counterions because their conformations may deviate from an infinite line charge.

Registry No. NaPES, 25053-27-4; DMCS, 27577-32-8; NaPSS·C5PVP, 114943-71-4; NaCl, 7647-14-5; KCl, 7447-40-7; LiCl, 7447-41-8; polybrene, 28728-55-4.

References and Notes

(1) Bungenberg de Jong, H. G.; Kruyt, H. R. *Kolloid Z.* **1930**, *50*, 39.
(2) Holleman, L. W. J.; Bungenberg de Jong, H. G.; Tjaden Modderman, R. S. *Kolloid-Beih.* **1934**, *39*, 334.
(3) Fuoss, R. M.; Sadek, H. *Science (Washington, D.C.)* **1949**, *110*, 552.
(4) Voorn, M. J. *Recl. Trav. Chim. (Pays-Bas)* **1956**, *75*, 317, 405, 427, 925.
(5) Michales, A. S.; Miekka, R. G. *J. Phys. Chem.* **1961**, *65*, 1765.
(6) Michaels, A. S. *Ind. Eng. Chem.* **1965**, *57*, 32.
(7) Vogel, M. K.; Cross, R. A.; Bixler, H. J.; Guzman, R. J. *J. Macromol. Sci. Chem.* **1970**, *A4*, 675.
(8) Tsuchida, E.; Osada, Y.; Sanada, K. *J. Polym. Sci., A1* **1972**, *10*, 3397.
(9) Nakajima, A.; Sato, H. *Biopolymers* **1972**, *11*, 1345.
(10) Zezin, A. B.; Rogacheva, V. B.; Kabanov, V. A.; Kargin, V. A. *Vysokomol. Soedin., Ser. A* **1972**, *14*, 772.
(11) Pal, M. K.; Ghosh, A. K. *Makromol. Chem.* **1973**, *169*, 273.
(12) Tsuchida, E.; Osada, Y. *Makromol. Chem.* **1974**, *175*, 593.
(13) Sato, H.; Nakajima, A. *Colloid Polym. Sci.* **1974**, *252*, 294.
(14) Lohman, T. M.; De Haseth, P. L.; Records, M. T., Jr. *Biophys. Chem.* **1978**, *8*, 281.
(15) Cundall, R. B.; Lawton, J. B.; Murray, D. *Makromol. Chem.* **1979**, *180*, 2913.
(16) Kabanov, A.; Papisov, N. M. *Vysokomol. Soedin., Ser. A* **1979**, *21*, 243.
(17) Duszeln, J.; Martin, V.; Klein, J. *Makromol. Chem.* **1979**, *180*, 255.
(18) Domard, A.; Rinaudo, M. *Macromolecules* **1980**, *13*, 898.
(19) Okubo, T.; Hongyo, K.; Enokida, A. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 2087.
(20) Dautzenberg, H.; Dautzenberg, H. *Acta Polym.* **1985**, *36*, 102.
(21) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(22) Manning, G. S. *Polyelectrolytes*; Selegny, E., Ed.; Reidel: Dordrecht, Holland, 1974.
(23) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 924.
(24) Kozak, D.; Kristan, J.; Dolar, D. *Z. Phys. Chem.* **1971**, *76*, 85.
(25) Kozak, D.; Dolar, D. *Z. Phys. Chem.* **1971**, *76*, 93.
(26) Wells, J. D. *Biopolymers* **1973**, *12*, 223.
(27) Oman, S.; Dolar, D. *Z. Phys. Chem.* **1967**, *56*, 1, 13.
(28) Dolar, D.; Leskovsek, H. *Makromol. Chem.* **1968**, *118*, 60.
(29) Manning, G. S. *J. Chem. Phys.* **1969**, *51*, 934.
(30) Dixler, D. S.; Ander, P. *J. Phys. Chem.* **1973**, *77*, 2684.
(31) Kowlansky, A.; Sasso, R.; Spagnuola, V.; Ander, P. *Macromolecules* **1977**, *10*, 78.
(32) Skerjanc, J. *J. Phys. Chem.* **1973**, *77*, 2225.
(33) Ise, N.; Okubo, T. *Macromolecules* **1978**, *11*, 439.
(34) Mita, K.; Okubo, T. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 1546.
(35) Mita, K.; Okubo, T.; Ise, N. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 1932.
(36) Vesnaver, G.; Rudez, M.; Pohar, C.; Skerjanc, J. *J. Phys. Chem.* **1984**, *88*, 2411.
(37) Mita, K.; Kunugi, S.; Okubo, T.; Ise, N. *J. Chem. Soc., Faraday Trans. 1* **1975**, *71*, 936.
(38) Mita, K.; Okubo, T.; Ise, N. *J. Chem. Soc., Faraday Trans. 1* **1976**, *72*, 1033.
(39) Manning, G. S. *Biopolymers* **1972**, *11*, 937, 951.
(40) Harada, S.; Arai, K. *Makromol. Chem.* **1967**, *107*, 78.
(41) Negi, Y.; Harada, S.; Ishizuka, O. *J. Polym. Sci.* **1967**, *5*, 1951.
(42) Hildebrand, F. B. *Introduction to Numerical Analysis*; McGraw-Hill: New York, 1956.

Microdomains in Poly(4-methylpentene-1) Single Crystals

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ABSTRACT: It is shown that in a given single crystal of poly(4-methylpentene-1) (P4MP1) polymorph III there exist narrowly delimited microdomains that give rise to different electron diffraction patterns. These domains have the same crystallographic unit cell but opposite *c* axis (chain axis) orientation. Dark field electron microscope images show that the number, size, and shape of the microdomains vary from one crystal to another. The domain boundaries are usually perpendicular to one crystal edge. These effects are discussed in relation to twinning by merohedry.

The presence of domains having different crystallographic orientation is well-known in twinned polymer crystals.[1,2] However, apart from this special case, polymer single crystals are generally considered to be structurally homogeneous. Here we report that single crystals of poly(4-methylpentene-1) (P4MP1) contain narrowly delimited microdomains that give rise to different electron diffraction patterns. The location and shape of these domains have been precisely defined by diffraction con-

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