Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Conformational Characterization of A Maleic Acid Copolymer with An Inflexible Side Chain

Nobumichi Ohno; Shintaro Sugai

To cite this Article Ohno, Nobumichi and Sugai, Shintaro(1990) 'Conformational Characterization of A Maleic Acid Copolymer with An Inflexible Side Chain', Journal of Macromolecular Science, Part A, 27: 7, 861 — 873

To link to this Article: DOI: 10.1080/10601329008544810

URL: http://dx.doi.org/10.1080/10601329008544810

J. MACROMOL. SCI.—CHEM., A27(7), pp. 861–873 (1990)

CONFORMATIONAL CHARACTERIZATION OF A MALEIC ACID COPOLYMER WITH AN INFLEXIBLE SIDE CHAIN

NOBUMICHI OHNO

Department of Industrial Chemistry
Akita National College of Technology
Akita, Japan

SHINTARO SUGAI*,†

Department of Polymer Science
Faculty of Science
Hokkaido University
Sapporo, Hokkaido, Japan

ABSTRACT

Viscometric, pH, optical, and calorimetric titration studies of an alternating copolymer of maleic acid and indene in aqueous NaCl of 0.01 to 0.27 *M* at 15 to 35°C showed the conformational transition of a compact to an expanded coil upon ionization of the primary carboxyl groups. The thermodynamic parameters of the transition were calculated. The results indicate that the bulky and inflexible side chain in indene sterically interferes with the formation of the compact form of the copolymer, but stabilizes the low entropic hydrophobic region.

†Present address: Institute of Life Sciences, Soka University, Tangi-m chi 1-236, Hachioji, Tokyo 192, Japan.

INTRODUCTION

Poly(carboxylic acid) with a hydrophobic side chain assumes compact conformation in uncharged states and changes the conformation to an expanded coil upon ionization of the carboxyl groups [1]. Such a conformational transition resembles the globular to coil process of proteins, corresponding to tertiary structure melting. The hydrophobic polyacids studied previously are maleic acid copolymers of hydrophobic vinyl compounds. Strauss et al. [2–10] studied the transition of copolymers with longer alkyl vinyl ethers than propyl, and our group [11–18] has studied aromatic vinyl compounds such as styrene. The side chains in the alkyl vinyl ether copolymers are flexible in the coiled form, and even the side chains of our aromatic copolymers were found to be flexible according to NMR measurements [17]. However, conformational characterization of the hydrophobic polyacids in the compact form has not been satisfactorily performed in regard to the bulkiness and flexibility of the side chains.

In this paper we report the conformational characteristics of an alternating copolymer of maleic acid and indene containing a hydrophobic, inflexible side chain. The experimental results of various physicochemical techniques are compared with those of maleic acid copolymers with a flexible side chain studied previously.

EXPERIMENTAL

Materials

Special grade maleic anhydride, indene, and benzene from Wako Chemical Co. (Osaka) were used after purification by ordinary methods. The maleic anhydride–indene copolymer was prepared with α,α'-azobisisobutyronitrile in benzene at 50–60°C and purified by a method similar to that used previously for maleic acid copolymers; it was dissolved in acetone, poured into a large excess of benzene, and precipitated twice. The copolymer probably resulted from the formation of a charge-transfer complex [19] similar to that found in the polymerization of an alternating copolymer of maleic anhydride and styrene. It was then hydrolyzed to obtain the copolymer of maleic acid and indene, $(\text{MA-Ind})_n$. A special grade of the initiator from Wako was used without further purification. Elemental analysis and optical absorption spectra at 250–280 nm showed that the polymer is a 1 : 1 copolymer of maleic acid and indene; the characteristic absorption peaks of indene were found at 260, 267, and 273 nm. The degree of polymerization was estimated to be ~640 by use of the intrinsic viscosity of the anhydride copolymer in tetrahydrofuran at 30°C and the MW–[η] relationship for the maleic anhydride–styrene copolymer [20]. Aqueous NaCl solutions of (MA-Ind)$_n$ were prepared by the method described previously [11–18].

Methods

Potentiometric, viscometric, and optical titration data were obtained by using the same methods as in our previous studies on maleic acid copolymers [11–18]. The concentrations of (MA-Ind)$_n$ used were approximately 1.0×10^{-2}, 1.8×10^{-2}, and 1.6×10^{-3} monomol/dm^3 for pH, viscometric, and optical measurements, respectively.

The calorimetric data were measured with a twin-batch microcalorimeter (Tokyo Riko Co., MMC-5111) at 25±0.01°C. In one part of the sample vessel, 3 mL of (MA-Ind)$_n$ of 8×10^{-2} monomol/kg in 0.01 *M* NaCl was placed, and 3 mL of 0.01 *M* NaCl was placed in the other side. The latter side contained NaOH, which induced a change of 0.1 in the degree of ionization of the primary carboxyl groups of the (MA-Ind)$_n$ solution. One side of the reference vessel was filled with the same solution of (MA-Ind)$_n$, while the other was filled with solvent. The (apparent) heat of the reaction, ΔH, at a degree of ionization of the carboxyl groups, was calculated by the method described previously [13]. The standard enthalpy change of the transition, $\Delta H_t°$, was determined by using a plot of ΔH vs α_1 according to a well-known method [21, 22].

RESULTS

1. Potentiometric Titration

(MA-Ind)$_n$ precipitated in aqueous NaCl at high I and low α_1. Figure 1 shows the modified pH–titration curves at four I's in terms of α, the degree of ionization of whole carboxyl groups. We previously expressed the pH–titration results of maleic acid copolymers with α_1 [11–18], because almost all the maleic acid copolymers studied have showed the transition within the ionization ranges of primary carboxyl groups. However, Minakata et al. analyzed the pH–titration curves of maleic acid copolymers, including (MA-Ind)$_n$, in terms of α [23–26]. In order to compare our results with those of Minakata, our curves are shown in the same style. Our curves are very similar to theirs, and they are anomalous in the ionization ranges of primary carboxyl groups. In Fig. 2 the anomalous curves have been replotted in terms of pK_1 vs α_1, and the effects of the ionization of secondary carboxyl groups have been revised, as shown

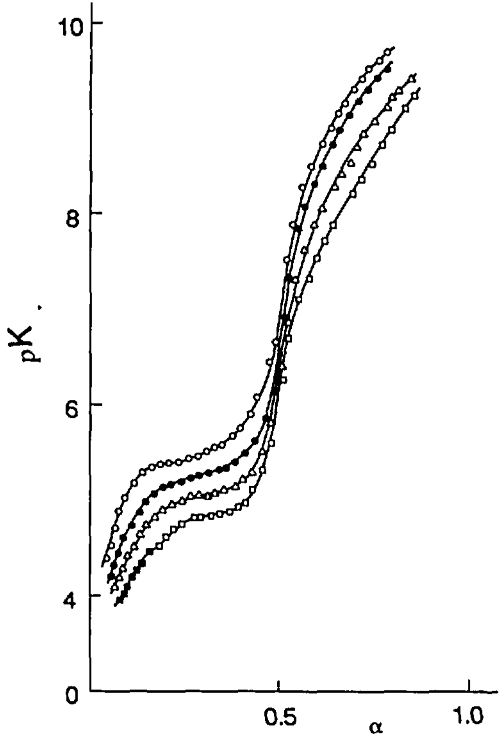

FIG. 1. The modified pH-titration curves of $(\text{MA-Ind})_{640}$, expressed in terms of α, in aqueous NaCl at 25°C and I = 0.01 (○), 0.03 (●), 0.10 (△), and 0.27 (□). ■ shows the pK_1 value for the solution including the precipitation.

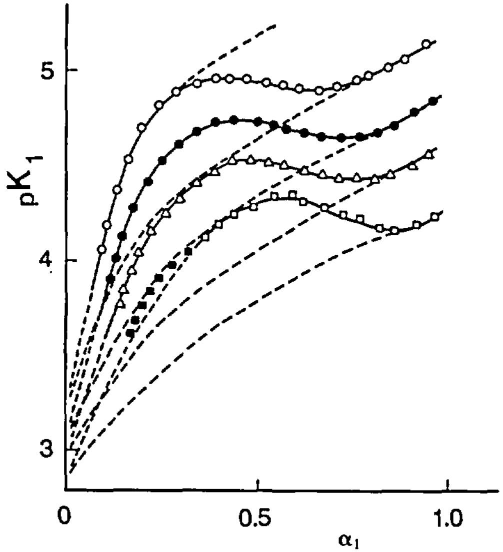

FIG. 2. The titration curves shown in Fig. 1 are replotted in terms of pK_1 vs α_1 in the ionization range of primary carboxyl groups. The symbols have the same meanings as in Fig. 1. The dashed lines show the hypothetical coil curves at four I's and the compact curve at I = 0.01, which were assumed by the method described in the text.

previously [18]. At $I = 0.01$, the effects of the ionization of secondary carboxyl groups are insignificant; however, they become significant as I increases. However, temperature-independent titration results were observed at $I = 0.01$ (Fig. 3), as found previously for $(\text{MA-St})_n$.

2. Viscometric Behaviors

The reduced or intrinsic viscosity of maleic acid copolymers correlates well with the compact to expanded coil transition. The compact to coil transition of $(\text{MA-Ind})_n$ is clearly shown at three I's and 25°C in Fig. 4 in terms of the reduced viscosity in aqueous NaCl. Irrespective of I, the compact molecule at small α_1 expands upon ionization of the primary carboxyl groups and reaches its most expanded state at $\alpha_1 = 1$. At $\alpha_1 > 1$ the viscosity decreases as α_1 increases. Such viscometric behavior has previously been found for other maleic acid copolymers such as those with styrene and isobutylene [11, 26].

3. Optical Titration

Some peaks in the ultraviolet absorption spectrum of the aromatic compounds in maleic acid copolymers were useful for the study of their conformational transition. The transition curves (fraction of monomer in

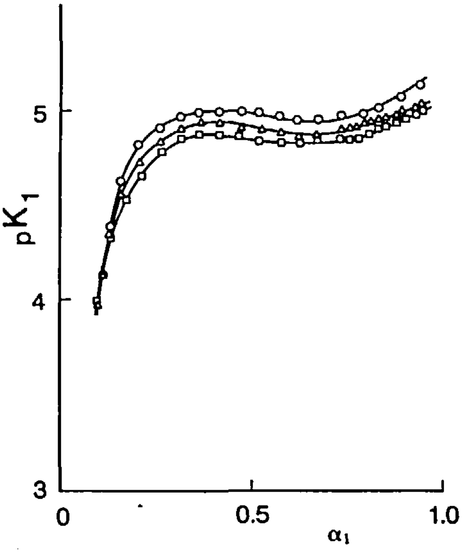

FIG. 3. The pH-titration curves in the ionization range of primary carboxyl groups at $I = 0.01$ (NaCl) and $T = 15$ (○), 25 (△), and 35°C (□).

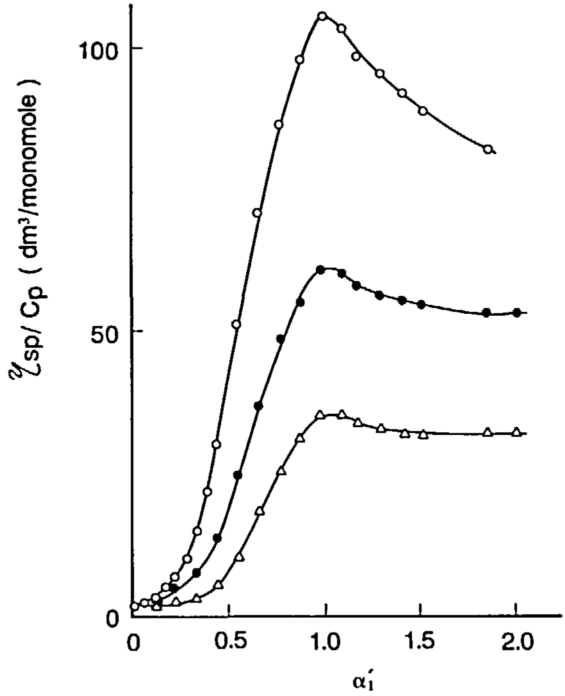

FIG. 4. The reduced viscosity of $(\text{MA-Ind})_{640}$ vs the degree of neutralization of primary carboxyl groups, α_l', in aqueous NaCl at 25°C and $I = 0.01$ (○), 0.03 (●), and 0.10 (△).

the coil form vs α_l) were more easily obtained by the optical method than by pH measurements for $(\text{MA-St})_n$ [12]. The differences in the optical absorption spectra of $(\text{MA-Ind})_n$ in aqueous NaCl are shown at $I = 0.01$, 25°C, and various α_l in Fig. 5(a) where the copolymer at $\alpha_l = 0.94$ is used as a reference. The intensities of the three positive and one negative peaks between 250 and 280 nm decrease in the same manner as α_l increases, and three isosbestic points are found. Figure 5(a) shows a two-state transition of $(\text{MA-Ind})_n$ between the compact and coil forms [16]. The intensity at the most significant peak (at 276 nm) in the difference spectrum proves there is a cooperative transition (Fig. 5b). The copolymer is almost in the compact form at $\alpha_l < 0.25$ and in the coil form at $\alpha_l > 0.80$ at $I = 0.01$ and 25°C (Fig. 6). The optical method suggests that indene, which is buried in the interior of the polymer coil in its compact form, is exposed after the transition.

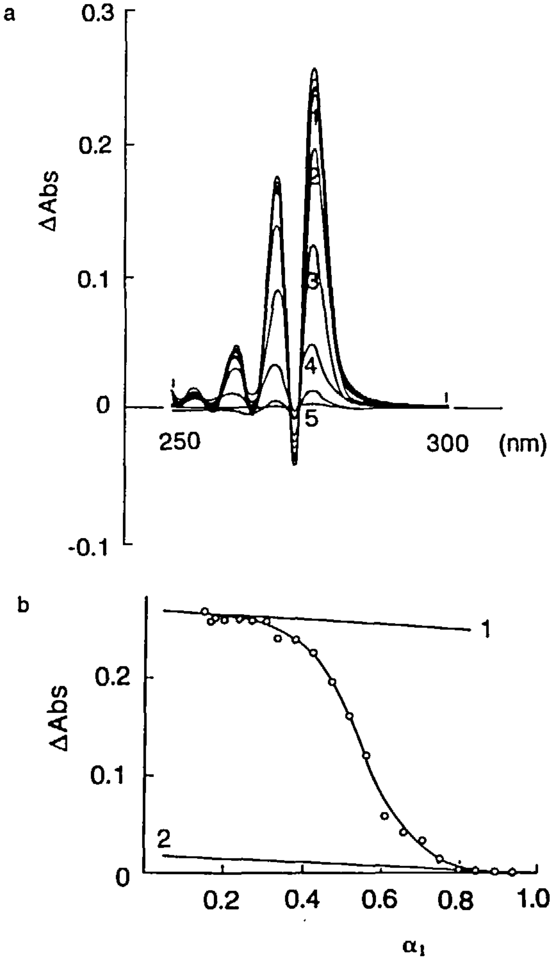

FIG. 5. (a) The difference optical absorption spectra of $(\text{MA-Ind})_{640}$ in aqueous NaCl at $I = 0.01$ and 25°C with the reference at $\alpha_I = 0.94$. The values of α_I are 0.38 (1), 0.52 (2), 0.61 (3), 0.71 (4), and 0.80 (5). (b) Difference in absorbance at 276 nm vs α_I. Temperature, I, and the α_I value of the reference are the same as in (a). The assumed differences for the hypothetical compact and coil forms are expressed by straight lines 1 and 2, respectively.

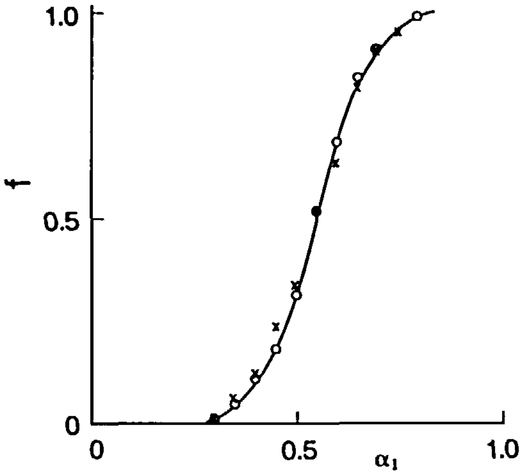

FIG. 6. The normalized transition curve of $(\text{MA-Ind})_{640}$ in aqueous NaCl of 0.01 M at 25°C determined by the optical (O) and pH methods (×).

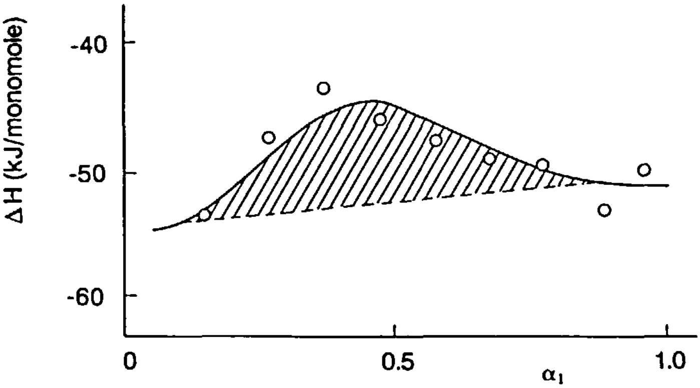

FIG. 7. The (apparent) reaction heat, ΔH, of $(\text{MA-Ind})_{640}$ in aqueous NaCl at $I = 0.01$ and 25°C vs α_I. The broken line is the sum of ΔH_w and ΔH_{dis}, which was assumed by referring to the results in Fig. 6. The solid line was also assumed from the data of ΔH and the results in Fig. 6 (see the text).

4. Calorimetric Measurements

ΔH was calculated at each α_1 at $I = 0.01$ and 25°C by using the calorimetric data and is shown in Fig. 7. The plot is anomalous. The reaction heat includes water formation enthalpy (ΔH_w), dissociation heat of the carboxyl groups (ΔH_{dis}), and enthalpy change in the transition (ΔH_t). The calorimetric anomaly is due to the last factor, as shown previously [13]. The transition of $(\text{MA-Ind})_n$ in aqueous NaCl could also be examined by calorimetry.

DISCUSSION

Sasaki and Minakata [23] showed the transition of $(\text{MA-Ind})_n$ but only with pH-titration data. The four methods used in this study showed the same transition from the compact to the expanded coil. The side chain of indene is bulky and more hydrophobic than the phenyl groups in styrene, and it is not at all flexible. Its steric hindrance interferes with the compact form stabilization in a less-charged region. The stability of the hydrophobic region in the globular protein has been reported to be partially affected by the steric factors of side chains in amino acids [27]. In order to research the causes of destabilization of the compact hydrophobic region by the inflexible bulky side chain, thermodynamic parameters of the transition of $(\text{MA-Ind})_n$ were determined.

The standard free energy change $\Delta G_t°$ of the transition at a noncharged state can be estimated from the modified pH-titration curve by assuming the curves for the hypothetical compact and coil forms at each I. The exact curve for the hypothetical coil could not easily be determined for the maleic acid copolymers. Minakata et al. [24–26] applied Lifson's pH-titration theory of polyacid to the titration of a maleic acid copolymer. Their theory may be applicable to the hypothetical coil of maleic acid copolymers. Kitano et al. [26] developed this theory and applied it to the pH-titration behavior of a maleic acid-isobutyrene copolymer, which does not change conformation with any change in α. Their theory explains the characteristics of maleic acid copolymers in the ionization region of secondary carboxyl groups, but it cannot be used in the ionization region of primary carboxyl groups. In order to compare the results of $(\text{MA-Ind})_n$ with the previous results of maleic acid copolymers, the same method of generating the theoretical curves was used here.

In Fig. 2 the curve in the compact region was extrapolated to $\alpha_1 \rightarrow 0$ at $I = 0.01$, and pK_1 (K_1 is the ionization constant of the primary carboxyl groups) was estimated only within an error of ±0.1. Then the curves for the hypothetical compact and coil forms were drawn by referring to the normalized optical transition curve shown in Fig. 6. The hypothetical curves at other I's were written by consulting the curves at $I = 0.01$. By this method, $\Delta G_t°$ of the transition was calculated within an error of ± 250 J/monomol, and it is shown in Table 1 for each I. Although the side chain of indene is more hydrophobic than the phenyl residues (the contribution of a CH_2 group to stabilization of the compact form is ~1700 J/mol for the hydrophobic polyacids [3, 28, 29]), stabilization of the compact form of $(MA\text{-}Ind)_n$ is almost the same as that for $(MA\text{-}St)_n$. The steric factors of indene compensate for its hydrophobic effects. Such a compensation has previously been shown for an alternating maleic acid copolymer with α-methylstyrene [30]. Also, the values of $\Delta G_t°$ are almost the same at three temperatures between 15 and 35°C at $I = 0.01$. The van't Hoff ΔH of the transition is very small.

The anomalous calorimetric curve in Fig. 7 determines the standard enthalpy change $\Delta H_t°$ at $I = 0.01$ by eliminating two enthalpies, ΔH_w and ΔH_{dis}, from ΔH. By considering the optical (and pH) results shown in Fig. 6, a sum of the above two enthalpies vs α_i was assumed, as shown by the broken line. Estimation of the heat at $\alpha_i = 0\text{–}0.20$ is also important when assuming the sum of both enthalpies. However, the calorimetric data have many errors in this region. The sum is ~ −55 kJ/monomol, which is the same as that of other maleic acid copolymers [23, 24]. The $\Delta H_t°$ of the transition is shown by the shaded area in Fig. 7, and it is ~2600 (±500) J/monomol. Strictly speaking, the transition midpoint estimated from the data points in Fig. 7 does not exactly correspond to that shown in Fig. 6. The difference may be due to errors in the amount of measured ΔH, the degree of ionization of the solution introduced into the small vessel, etc. The solid line was assumed to fit both the calorimetric data and the midpoint shown in Fig. 6. The line corresponding only to the data gives $\Delta H_t°$ similar to that of the shaded area (the difference between the two values is within the degree of error shown above). For $(MA\text{-}St)_n$ at $I = 0.03$, the value of $\Delta H_t°$ (~1500 J/monomol) is less than that for $(MA\text{-}Ind)_n$, so the standard entropy change $\Delta S_t°$ of the transition of $(MA\text{-}Ind)_n$ should be larger than that of $(MA\text{-}St)_n$ (because the $\Delta G_t°$'s of the transition of both copolymers are almost the same). A possible cause for the large $\Delta S_t°C$ of $(MA\text{-}Ind)_n$ is the low entropic compact form, because calorimetry shows a similarity in the coil forms of both maleic acid copolymers; a similar hydration profile of the coil form can be assumed for both copolymers [13], although the maleic acid–butyl vinyl ether copolymer is in a different hydration state in its coil form [22].

TABLE 1. Parameters of the Conformations of the Maleic Acid Copolymers

Copolymer	I, M	pK_1	pK_2	$\Delta G_t°$, J/monomol	$\Delta H_t°$, J/monomol	$\Delta S_t°$, J/monomol · K
$(\text{MA-Ind})_n$	0.01	3.2	7.0	1590 (±250[a])	2600 (±500[a])	3.39
	0.03	3.1	6.7	1500		
	0.09	3.0	6.4	1520		
	0.27[b]	2.9	6.0	1250		
$(\text{MA-St})_n$	0.01	3.3	7.4	1550		
	0.03	3.2	7.3	1460	1500	0.13
$(\text{MA-BVE})_n$	0.04			1300	−1500	−9.40

[a] Errors for $(\text{MA-Ind})_n$.

[b] Precipitation was found at low α_1.

The compact form of the latter copolymer, which has a flexible side chain, is not in the low entropic state. $(MA\text{-}St)_n$ seems to assume a compact form of intermediate entropy. The side chain flexibility of the maleic acid copolymer affects the thermodynamic properties of its compact form.

Molecular expansion upon ionization of the primary carboxyl groups is due to long-range electrostatic interaction. However, the abnormal viscometric behavior of the maleic acid copolymers in the ionization range of the secondary carboxyl groups has yet to be explained. Kitano et al. [26] considered the hydrogen bond between either two COOH's or between COOH and COO^- in a maleic acid in the copolymers in order to analyze their potentiometric and viscometric behaviors. They have not given a satisfactory explanation of the viscometric anomalies, however, in terms of the hydrogen bond. The high local charge density leads to considerable counterion condensation on the copolymers. This may be a possible cause for such anomalies.

ACKNOWLEDGMENTS

The authors thank Professor A. Minakata of Hamamatsu Medical University and Dr. K. Nitta of our laboratory for their helpful discussions and suggestions.

REFERENCES

[1] S. Sugai and G. Ebert, *Adv. Colloid Interface Sci., 24,* 247–282 (1986).

[2] P. L. Dubin and U. P. Strauss, *J. Phys. Chem., 71,* 2757–2759 (1967).

[3] P. L. Dubin and U. P. Strauss, *Ibid., 74,* 2842–2847 (1970).

[4] P. L. Dubin and U. P. Strauss, *Ibid., 77,* 1427–1431 (1973).

[5] U. P. Strauss and G. Vesnaver, *Ibid., 79,* 1558–1561 (1975).

[6] U. P. Strauss and G. Vesnaver, *Ibid., 79,* 2426–2429 (1975).

[7] U. P. Strauss and M. S. Schlesinger, *Ibid., 82,* 571–574 (1978).

[8] U. P. Strauss and M. S. Schlesinger, *Ibid., 82,* 1627–1632 (1978).

[9] P. J. Martin and U. P. Strauss, *Biophys. Chem., 11,* 397–402 (1980).

[10] U. P. Strauss, in *Microdomains in Polymer Solutions* (P. L. Dubin, ed.), Plenum, New York, 1985, pp. 1–12.

[11] N. Ohno, K. Nitta, S. Makono, and S. Sugai, *J. Polym. Sci., Polym. Phys. Ed., 11,* 413–425 (1973).

[12] S. Sugai, N. Ohno, and K. Nitta, *Macromolecules, 7,* 961–963 (1974).

[13] T. Okuda, N. Ohno, K. Nitta, and S. Sugai, *J. Polym. Sci., Polym. Phys. Ed., 15*, 749–755 (1977).

[14] S. Sugai and N. Ohno, *Biophys. Chem., 11*, 387–395 (1980).

[15] N. Ohno, *Polym. J., 13*, 719–726 (1981).

[16] S. Sugai, K. Nitta, and N. Ohno, *Polymer, 23*, 238–242 (1982).

[17] S. Sugai, K. Nitta, and N. Ohno, in *Microdomains in Polymer Solutions* (P. L. Dubin, ed.), Plenum, New York, 1985, pp. 13–32.

[18] N. Ohno and S. Sugai, *Macromolecules, 18*, 1287–1291 (1985).

[19] L. F. Kim, L. L. Stotskaya, B. A. Krentsel, V. F. Zubov, V. B. Golubev, and L. L. Stoyachenko, *J. Macromol. Sci.—Chem., A12*, 1197–1210 (1978).

[20] R. Endo, T. Hinokuma, and M. Takeda, *J. Polym. Sci., Part A-2, 6*, 665–673 (1968).

[21] V. Crescenzi, F. Quardrifoglio, and F. Delben, *Ibid., 10*, 357–368 (1972).

[22] V. Crescenzi, in *Polyelectrolytes* (E. Selegny, M. Mandel, and U. P. Strauss, eds.), Reidel, Dordrecht, Holland, 1974, pp. 115–133.

[23] S. Sasaki and A. Minakata, *Rep. Prog. Polym. Phys. Jpn., 19*, 65–68 (1976).

[24] S. Sasaki and A. Minakata, *Biophys. Chem., 11*, 199–216 (1980).

[25] A. Minakata, K. Matsumura, S. Sasaki, and H. Ohnuma, *Macromolecules, 13*, 1549–1553 (1980).

[26] T. Kitano, S. Kawaguchi, N. Anazawa, and A. Minakata, *Ibid., 20*, 2498–2506 (1987).

[27] W. A. Lim and R. T. Sauer, *Nature, 339*, 31–36 (1989).

[28] D. E. Joyce and T. Kurucsev, *Polymer., 22*, 415–417 (1981).

[29] S. Sugai, K. Nitta, N. Ohno, and H. Nakano, *Colloid Polym. Sci., 261*, 159–165 (1983).

[30] P. J. Martin, L. R. Morss, and U. P. Strauss, *J. Phys. Chem., 87*, 577–582 (1980).

Received August 9, 1989
Revision received December 18, 1989