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ELECTRIC FIELD-INDUCED TRANSIENT PROCESS OF POLY(p-STYRENESULFONATE) IN AQUEOUS SOLUTIONS AS STUDIED BY REVERSING-PULSE ELECTRIC BIREFRINGENCE TECHNIQUE: EFFECT OF COUNTERIONS AND OTHER ADDITIVES

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By measuring the reverse and decay signals of poly(p-styrenesulfonate) in aqueous solutions which contain either Na^+, Ca^{2+}, or Mg^{2+} as the counterion, usefulness of the title technique was demonstrated. The effect of these ions and other additives like 9-aminoacridinium and glycerol on the transient relaxation times was quite appreciable.

Reversing-pulse electric birefringence (RPEB) is one of the most direct methods for clarifying the polyelectrolyte nature of linear polymers with charged groups.1-6) It provides a means for differentiating the major contributing source for electric field orientation from the permanent dipole moment, the electronic polarizability anisotropy, and the slow and/or fast counterion-induced dipole moment. If the counterions redistribute slowly on the polyion surface under an orienting electric field, the RPEB signal shows an extremum, but if the redistribution time is much faster than the time for the overall molecular rotation, no extremum appears.2) More than two decades have passed since the RPEB technique was introduced,1) but its application has been limited to a few instances because of instrumental difficulties involved. With technical advances, however, the RPEB method has lately been revived and utilized for many diverse macromolecular systems. In this Letter, we present some results newly obtained from the reverse and decay signals of poly(p-styrenesulfonate) (PSS) solutions which contain various counterions and other additives.

The original sample of KPSS, a generous gift from Professor K. Yoshioka of the University of Tokyo, was dialyzed and converted to the sodium, calcium, and magnesium salts. The weight-average degree of polymerization was 1360. The degree of polydispersity was estimated to be 1.3 by the ratio of weight- to number-average molecular weights.7) The residue concentration of PSS (C_p) was kept at 0.66 mmol/dm^3, unless otherwise stated. 9-Aminoacridinium chloride (AA), a strongly binding dye,7,8) was added to the NaPSS solution at a PSS residue-to-AA ratio (P/D) of 6.14. The RPEB signals were measured at 20 °C and at 535 nm on a previously described apparatus.6)

Figure 1 shows typical oscillograms of the transient signals of PSS solutions and applied reversing-pulse electric fields. Each RPEB signal for NaPSS solution (a, b) exhibits no minimum upon a pulse reversal, indicating that the field orientation of the PSS backbone is predominantly due to the fast-induced dipole. Addition of glycerol to the NaPSS solution enhances the bulk viscosity, yielding a much longer field-free relaxation time but no minimum (d). Addition of tight-binding AA cations (e) changes only the magnitude of birefringence (Δn) by about one-tenth that of (a).

It has been shown that the sign of the reduced dichroism ($\Delta A/A$) of the bound AA at 400 nm is positive, while the $\Delta A/A$-value of the phenylsulfonate chromophore of PSS is negative.[7)] Hence, the contributions from the bound dye and the benzene ring to the optical anisotropy factor $\Delta g (= g_3 - g_1)$ of NaPSS-AA at 535 nm must be partially canceled. In fact, a complete reversal of the sign of Δn from negative to positive was observed, when another dye, acridinium chloride, was added to an NaPSS solution. Changes of the Na^+ ion to divalent Mg^{2+} and Ca^{2+} ions (c, f) decrease the magnitude of Δn but do not affect the pattern of the reverse signals. In all cases, ionic additives greatly decrease the field-free relaxation time; thus, they undoubtedly contract the PSS backbone chain. Yet, the mobility of counterions over the PSS surface by an applied electric field is fast enough to create the fast-induced ionic polarization which is responsible for the field orientation of the polyanion.

Figure 2 shows normalized field-free decay curves of RPEB signals. Each NaPSS solution shows a multiexponential decay, indicating that the sample is indeed polydisperse as regards its molecular length, i. e., molecular weight.[7)] This polydispersity of lengths is also substantiated by the fact that the relaxation times decrease with the increase in field strengths (a). The decay process of PSS in the presence of Mg^{2+}, Ca^{2+}, or bound AA is much faster than the case of the Na^+ counterion. For the field-free relaxation time of a polydisperse sample, the birefringence-average relaxation time, $\langle\tau\rangle_{EB}$, is defined (Eq. 16 of Ref. 6) and calculated from the area of the normalized decay curve by the area method.[9)] The results are summarized

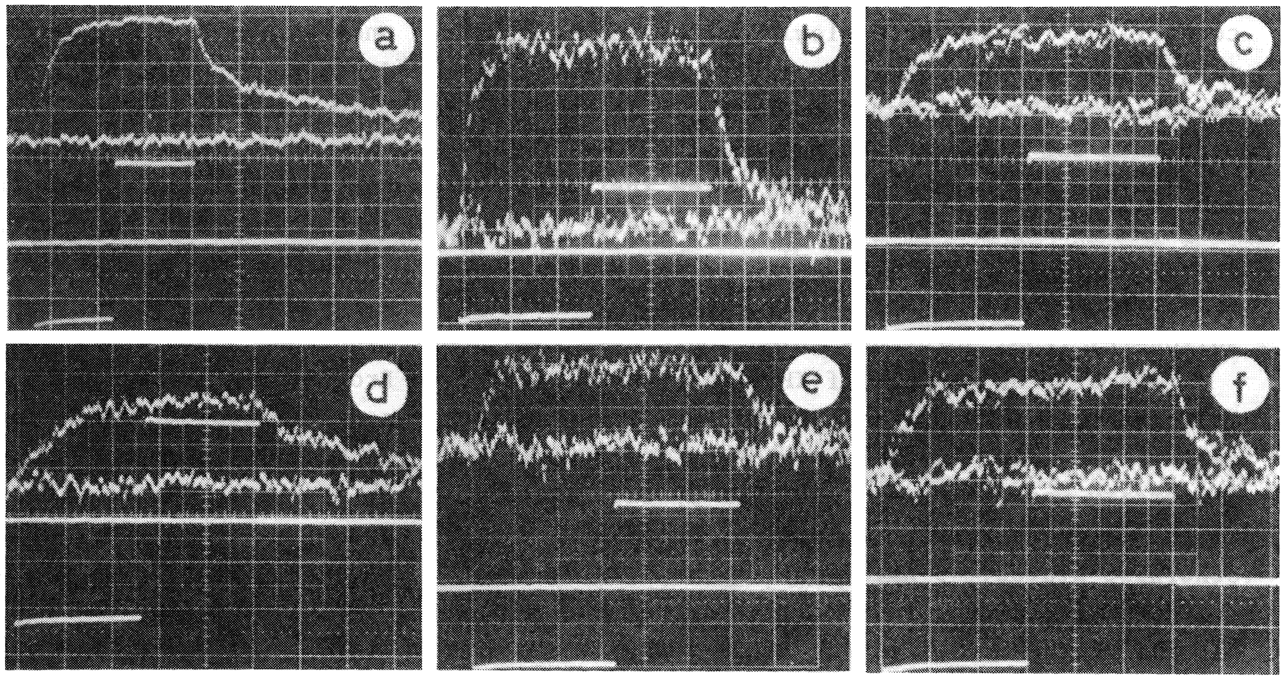

Fig. 1. Some RPEB signals of PSS in aqueous solutions in which counterions are Na^+ (a, b, d, and e), Mg^{2+} (c), and Ca^{2+} (f). Additives are 0.11 mM NaCl (b), 50% (v/v) glycerol (d), and 0.11 mM AA (e). Sweep times in µs/division are 50 (a, b, d, and e) and 20 (c and f). Electric field strengths in kV/cm are 2.8 (a), 5.7 (b), 5.0 (c), 3.7 (d), 3.2 (e), and 4.7 (f). Signals in mV/division are 20 (a) and 10 (b–f). The sign of these RPEB signals is always negative. $C_p = 0.33\ mmol/dm^3$ in (d).

in Table 1. Values of $<\tau>_{EB}$ and $<\tau>_{EB}/\eta_o$ (η_o is the viscosity of solvent) were calculated at low and medium electric field strengths, where the Kerr law nearly holds, and also at high field strengths, where the birefringence tends to saturate. It is clearly seen that $<\tau>_{EB}/\eta_o$ of the PSS chain decreases in the presence of ionic or alcoholic additives and of the divalent counterions. Hence, the high orientability of the salt-free PSS polyanion by an external electric field[10,11] is probably due to the chain extension by the Coulombic repulsion between ionized sulfonate groups. The rigidity of the chain should be reduced considerably by the neutralization or the suppression of these negative charges. It is indeed surprising to see that the neutralization of one out of six sulfonate groups by AA cations (at P/D ≒ 6, nearly all AA cations in solution are bound[8]) is enough to contract the PSS backbone. Quantitative interpretations of values of $<\tau>_{EB}$ for a polydisperse sample in terms of appropriate hydrodynamic models remain to be resolved.[12]

In order to estimate the rigidity of the PSS chain on a semiquantitative basis, the persistence length q was calculated with the aid of Hearst's equation for the wormlike chain model under the assumption of a monodisperse system;[13]

$$\tau = (\eta_o q h^2 M^2/12kTM_o^2)[0.1265(hM/qM_o)^{1/2}+0.159\ \ln(2q/b)-0.387+0.16(b/a)]^{-1}, \quad (1)$$

where M is the molecular weight of the salt of PSS, M_o is the molecular weight of the monomer unit, and h is the length of the monomer unit, for which a value of 2.5 Å is adopted.[12] Both a and b are the frictional parameters, which are assumed to be equal to the diameter of a PSS molecule (a value of 16 Å is assigned[12]).[14] τ is the rotational relaxation time of the whole molecule, to which the values of $<\tau>_{EB}$ obtained from the decay curves were used (Table 1). The values of persistence length calculated from Eq. 1 are given in Table 1. Since the maximal contour length is about 3400 Å, the values of q in the salt-free NaPSS solution indicate that the PSS backbone is not perfectly rigid but flexible to some extent. The persistence length of the AA-added solution is 50–30% shorter than that of the NaCl-added one, although the ionic strengths of these solutions are the same; the strongly

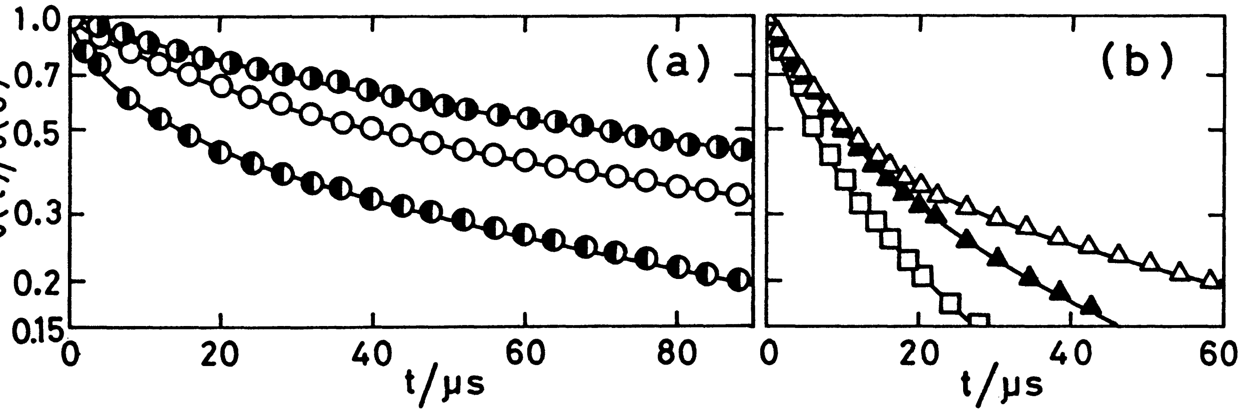

Fig. 2. Field-free decay curves of PSS in aqueous solutions. The normalized phase retardation; $\delta(t)/\delta(0)$, was plotted against the decay time t on a semilogarithmic scale. Field strengths in kV/cm and counterions are 1.6 (○, Na^+ only), 7.7 (◐, Na^+ only), 5.6 (◑, Na^+ with 50% glycerol, C_p = 0.33 mmol/dm^3), 6.2 (△, Na^+ with 0.11 mM NaCl), 8.9 (▲, Na^+ containing 0.11 mM AA), and 6.7 (□, Mg^{2+} only).

Table 1. The Relaxation Time and Persistence Length of PSS in Aqueous Solutions with Various Additives Obtained from the Decay Process

Sample	Observed $\langle\tau\rangle_{EB}/\mu s$		Persistence length/Å	
	low field[a)]	high field[b)]	low field[a)]	high field[b)]
NaPSS	100 (99)[c)]	49 (49)[c)]	322	169
NaPSS-NaCl	53 (53)	28 (28)	181	105
NaPSS-glycerol	134 (16)	105 (12)	67	56
NaPSS-AA	21 (21)	17 (17)	84	71
MgPSS	18 (18)	—	74	—
CaPSS	19 (19)	—	77	—

a) Field strength E = 1.6—5.6 kV/cm. b) E = 7.7—11.5 kV/cm.
c) Values in parentheses are $\langle\tau\rangle_{EB}/\eta_0$ in $10^{-3}Pa^{-1}$.

interacting AA cations contract the PSS chain significantly. More surprising, however, is the effect of the divalent counterions: The backbone chains of Mg- and CaPSS seem to be coiled or bent by effective charge neutralization of the sulfonate group.

In conclusion, the electric field orientation of the ionized PSS chains with various additives results from the formation of counterion-induced dipole moment on the polymer backbone chain. The induction of this moment is much faster than the overall rotation of the PSS chain. The rigidity of the chain diminishes greatly by the charge neutralization of sulfonate groups by divalent counterions or by tight-binding AA cations. The usefulness of the RPEB technique in the study of ionized polyelectrolytes has been demonstrated.

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