of **5** gives dimeric zwitterion **6**. The subsequent steps of the propagation involve the attack of **5** to **6** to yield a macrozwitterion **7**.

Experimental Section

Reagents. EPO and EPI were prepared by the reactions of ethylene glycol with phenyldichlorophosphine and with phenyl dichlorophosphite in the presence of triethylamine, respectively.[14,15] PS was a commercial reagent, which was dried on molecular sieves 4A and distilled, bp 130–131.5 °C (4 mm). Methyl 3-(phenylmethoxyphosphino)propanesulfonate (**3**) was prepared by the reaction of dimethoxyphenylphosphine with an excess amount of PS at 120 °C for 10 h and was purified by thin-layer chromatography. All solvents were purified by distillation in the usual manner.

Polymerization Procedure and Copolymer Analysis. To 1.5 mol of solvent in a test tube, EPO (or EPI) and PS, 5.0 mmol each, were added at room temperature under nitrogen and the tube was sealed. Then, the mixture was kept at a desired temperature. After the reaction, the reaction mixture was poured into a large amount of benzene to precipitate the copolymer. White glassy material was obtained after drying in vacuo.

Both copolymers of EPO–PS and EPI–PS were very hydroscopic. The calculation of elemental analysis was made on the basis of the formula having occluded water. EPO–PS copolymer: Anal. Calcd for $C_{11}H_{15}O_5PS{\cdot}0.21(H_2O)$: C, 44.93; H, 5.29; P, 10.53. Found: C, 44.64; H, 5.27; P, 10.30. EPI–PS copolymer: Anal. Calcd for $C_{11}H_{15}O_6PS{\cdot}0.27(H_2O)$: C, 42.42; H, 5.50; P, 9.94. Found: C, 42.03; H, 5.46; P, 9.66.

Hydrolysis of Copolymer. To 0.05 g of copolymer was added 0.5 ml of 10% D_2O solution of NaOH at room temperature and the mixture was heated at 90 °C for 5 h. Then the reaction mixture was subjected to NMR measurement.

Methyl 3-(phenylmethoxyphosphono)propanesulfonate (3). **3** was prepared by the reaction of dimethoxyphenylphosphine with PS in chlorobenzene solvent at 120 °C for 14 h. After the reaction, **3** was purified by TLC: a pale yellow, viscous liquid; ir (neat) 1220 ($\nu_{P=O}$), 1360 and 1170 cm^{-1} (ν_{SO_2}); NMR ($CDCl_3$) δ 8.0–7.3 (m, C_6H_5, 5 H), 3.9 (s, $-SO_3CH_3$, 3 H), 3.70 (d, P–OCH_3, 3 H, J_{P-H} = 11 Hz), 3.4–3.1 (m, CH_2S, 2 H), 2.5–1.8 (m, P–CH_2CH_2, 4 H). Anal. Calcd for $C_{11}H_{17}O_5PS$: C, 57.87; H, 7.51; P, 13.57. Found: C, 57.11; H, 7.65; P, 13.39.

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Matrix Polymerization of Ionene–Styrene Sulfonate Complexes. An Interpretation in Terms of "Counterion Condensation"

A. Blumstein and G. Weill*

Department of Chemistry, Polymer Program, University of Lowell,
Lowell, Massachusetts 01854, and Centre de Recherches sur les Macromolécules C.N.R.S.,
Strasbourg, France.

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ABSTRACT: Simple polyelectrolyte theory is applied to the data on the kinetic of polymerization of polystyrenesulfonic acid on templates constituted by ionenes with varying linear charge. It is shown that this model, based on the assumption of a local concentration of "mobile condensed counterions", provides a satisfactory explanation of a number of experiments including the effect of the degree of filling and the influence of added salt.

Much interest has been devoted in the recent years to the matrix polymerization of ionic monomers on polyelectrolyte templates. The fact that the first experiments of Kabanov[1] involving the polymerization of vinylpyridine on polyacids specifically required the formation of a pyridinium salt, as well as some stereospecific effects detected in other systems,[2] has favored the discussion of the experiments in terms of a filling process followed by a nearest neighbor polymerization process. Much attention is then paid to the distance between monomers along the template and to the break in the monomer sequence resulting from a competition with other counterions.

Following a series of investigations by one of us[3] of the polymerization of *p*-styrenesulfonic (pSSA) acid on ionenes with an average charge separation *b* varying from 4.5 to 11.5 Å (Figure 1), it has been shown that the initial rate is a linear function of the linear charge density, which becomes equal to zero for an average distance of 23 Å. This seems to indicate that the concept of stoichiometric site binding of immobilized monomers may be misleading. We have therefore tried to apply to these experiments the general concepts of polyelectrolytes theory.

Experimental Section

The details of the experimental procedures being already published elsewhere,[3] we just recall their principal features. Ionene bromides have been synthesized according to general techniques described by Rembaum.[4] They are converted into hydroxide using an excess of freshly precipitated silver hydroxide and neutralized by freshly purified pSSA, for the stoichiometric complex, *r* = 1, or, for other degrees

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* Centre de Recherches sur les Macromolécules C.N.R.S.

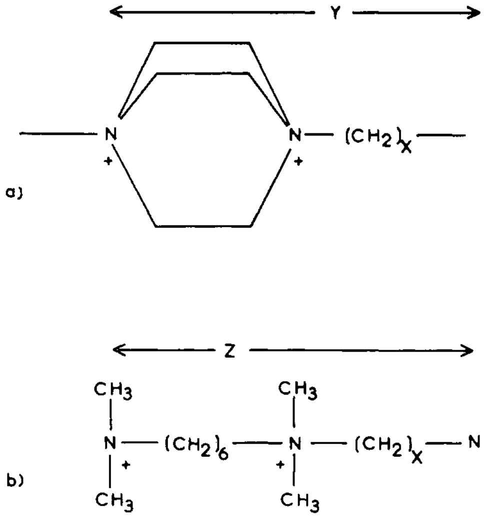

Figure 1. Type of ionenes used as templates: (a) $x = 4, y = 9.0$ Å; $x = 6, y = 11.5$ Å; $x = 8, y = 14.0$ Å; (b) $x = 6, z = 18.0$ Å; $x = 10, z = 23.0$ Å.

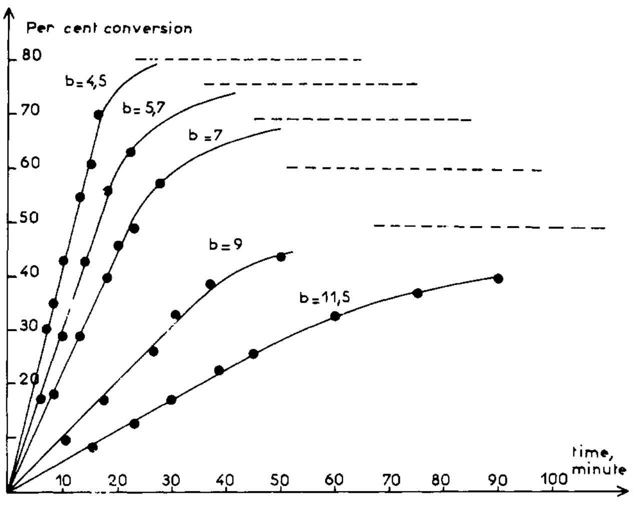

Figure 2. Conversion vs. time for the polymerization of the stoichiometric complexe of pSSA with several ionenes of average charge distance b (in Å). Dotted asymptotes correspond to calculated limiting degrees of conversion for fast polymerization (see text).

of filling r, after addition of a given quantity of pSSA, brought to pH 7 by addition of sulfuric acid or sodium hydroxide. The polymerization kinetics has been observed on 10^{-3} M solution in a 3:1 part water–2-propanol solvent mixture, to increase the solubility of the polymerized complex, using 10^{-4} M azobis(isobutyronitrile) as an initiator. Polymerization tubes, thoroughly degassed, were kept at a constant temperature of 70 C. The polymerization was stopped by freezing the tube in liquid nitrogen; the frozen solutions are then quickly melted and diluted, and the degree of conversion was determined from the absorbance at 2550 Å. Polymerization rates have been measured for stoichiometric complexes of pSSA with polyionenes of increasing charge densities, up to high degrees of conversion (Figure 2). The effect of the degree of filling on the initial rate has been studied for the (222)4 polyionene which has the highest linear charge. It should be noted that the polymer–template complex precipitates during the polymerization. This is likely to affect the bimolecular radical termination and in the case of an excess of free monomer, which can diffuse into a precipitated phase, the net result is an increase in the overall rate. The reduction of the initial rate upon addition of NaCl has been measured on the stoiechiometric complex with the (222)4 polyionene (Table I).

Basic Features for the Application of Polyelectrolyte Theory

According to the work of Lifson and Katchalsky,[5] Oosawa,[6] and Manning,[7] the distribution of counterions in a polyelectrolyte solution is dominated by the phenomenon of "counterion condensation". Such a condensation takes place as soon as the average distance between charges e along the linearly extended polymer is smaller than a critical distance b_0 which makes the characteristic (non dimensional) charging parameter $\lambda = e^2Z/\epsilon kTb > 1$ (ϵ being the dielectric constant and Z the valence of the counterion). A fraction x of counterion approximately given by $1 - \lambda^{-1}$ remains in a small volume around the polyelectrolyte where the electric potential Ψ is such that $e\Psi/kT \gg 1$, the rest being free in the outer volume. Among the condensed counterions, depending on short-range forces and entropic factors, one has to distinguish between "site binding" (formation of an ion pair with a loss of hydration and a restricted mobility) and "atmospheric trapping", which should not affect considerably the mobility of the counterion along the cylindrical equipotentials. The concentration of counterions is nonuniform in the volume of high electric potential but decreases with the radial distance to the polymer. The fraction of condensed counterions is practically independent of the presence of added salt (additivity law).

Table I

	Rate of polymerization, mol l.$^{-1}$ s^{-1}	r from Figure 4	x
No added NaCl	$7.3 \pm 0.2 \times 10^{-4}$	1	0.8
10^{-3} M added NaCl	$4.3 \pm 0.15 \times 10^{-4}$	0.78	0.58
210^{-3} M added NaCl	$3.3 \pm 0.1 \times 10^{-4}$	0.69	0.49

Table II

Ionene	b, Å	λ	x
[2.2.2],4-	4.5	5.1	0.805
[2.2.2],6-	5.7	4	0.75
[2.2.2],8-	7	3.28	0.695
6,6	9	2.56	0.61
6,10	11.5	2	0.50

Mixing counterions of different chemical nature may lead to selective effects, especially if "site binding" is more favored for one type of counterion or if condensation is energetically favored for one species of higher valency.

In the framework of this model, polyelectrolyte matrix polymerization should reflect the properties of the largely mobile condensed phase and the discussion of polymerization rates in terms of distances between immobilized monomers and sequence interruption should be replaced by a discussion of the effect of the mean linear charge density on the fraction and local concentration of condensed monomeric counterions, in the presence or absence of other competing counterions.

We offer such a discussion of the results of ref 3, the expectation for a quantitative agreement being however limited by: the finite length of the template, the finite concentration, and the use of a water–2-propanol mixture with possible selective adsorption effects which make the local value of ϵ even more ill defined than in pure water.

Discussion

(1) We Start with the Linear Dependence of the Initial Rate of Polymerization as a Function of the Linear Charge Density. These rates have been obtained from the percent conversion vs. time curves plotted in Figure 2 for the radical polymerization of the stoichiometric complexes of pSSA on five different ionenes.[3] They are reported in Figure 3 as a function of the average number of charges per 10 Å. According to the "ion condensation" model the rate of polymerization should be (neglecting the polymerization of the very dilute free counterions) proportional to the mean local concentration, i.e., to the fraction of condensed counterions

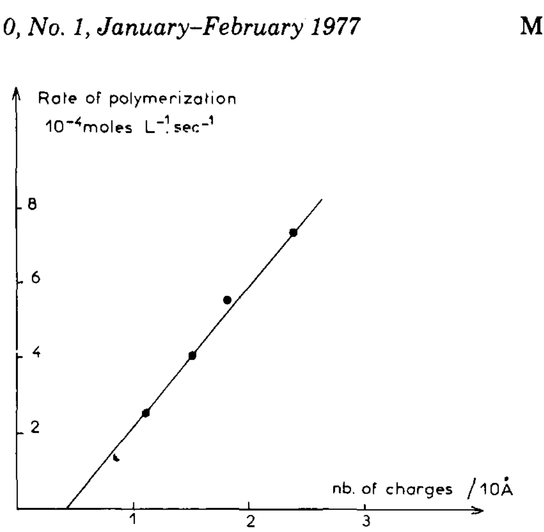

Figure 3. Initial rate of polymerization vs. linear charge density (number of charges/10 Å).

x divided by the average distance between charges b. Taking the above expression for x with $Z = 1$ one gets a dependence according to $1/b - \epsilon kT/e^2$, i.e., linear in $1/b$ or the number of charges/Å. From the experimental dependence one gets an average distance for zero rate $b_0 = 23$ Å from which one gets $\epsilon = 25$, a reasonable value taking into account the presence of 2-propanol and the bulkiness of the counterion.

(2) The Influence of the Degree of Filling of Template on Polymerization Rate for the [2.2.2]-4-Ionene. The dependence of the initial rate of polymerization as a function of the pSSA/ionene ratio r has been plotted in Figure 4.[7] For that ionene, assuming $\epsilon = 25$ one gets $\lambda = 5.1$ and $x = 0.80$. Since the divalent SO_4^{2-} competing with the monomer at degrees of filling <1 is preferentially condensed, the amount of condensed monomer should vary linearly from 0 to 0.80 when the degree of filling r varies from $(1 - x) = 0.20$ to 1. Indeed, despite the small number of experimental points, it is plausible to extrapolate the data of Figure 4 to zero at a degree of filling close to 0.20 since one expects the rate dependence with the filling factor to present an upward curvature. This is due to the concentration profile in the counterion atmosphere. SO_4^{2-} are trapped (or bound) in the region of higher potential while the styrenesulfonic monomer is rejected in the outer part of the cylindrical volume. The mean local concentration in monomer varies therefore more rapidly than the number of condensed styrenesulfonic counterions. The results obtained for $r > 1$ cannot be treated in a similar way, due to the effect of precipitation mentioned above.

(3) The Influence of Added NaCl on the Initial Polymerization Rate of a Stoichiometric Mixture with the [2.2.2]-4-Ionene. Addition of ClNa results in a decrease in the polymerization rate as shown in Table I, in which the filling degrees r corresponding to the rate, as interpolated on the curve of Figure 4, and the fraction of bound pSSA x equal to $(r - x_0)$ where x_0 is the fraction of uncondensed counterions, which, from the above results, has been taken equal to 0.20, have also been reported. A decrease in rate is easily understood on the basis of the competition between Cl^- and pSSA counterions. Would, however, both be equally bound, one would expect x to vary by a factor equal to the ratio of the concentrations of pSSA to the total concentration in anions, i.e., respectively $\frac{1}{2}$ and $\frac{1}{3}$ for the two additions of NaCl. The much higher values of x reveal large preferential condensation of pSSA as compared to Cl^-. Assuming (a) a simple equilibrium of the counterions with constants K_{Cl^-} and K_{pSSA} and (b) the independence of x_0 upon addition of NaCl (additivity law), one calculates easily the following relation giving the fraction x of bound pSSA as a function of the ratio of the concentration of added salt Cl_{tot} to the concentration in ionene charged groups P

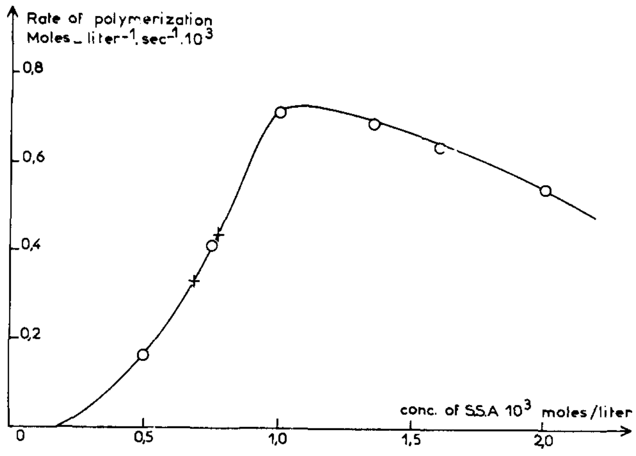

Figure 4. Dependence of the rate of polymerization of pSSA on the pSSA/ionene ratio r. Crosses correspond to the effective r for stoichiometric complexes with added ClNa (see text).

$$\frac{[Cl_{tot}]}{(1 - x_0 - x)P} - 1 = \frac{K_{pSSA}}{K_{Cl^-}}\left(\frac{r}{x} - 1\right)$$

with $x_0 = 0.2$, $r = 1$, $P = 10^{-3}$, and $K_{pSSA}/K_{Cl^-} = 4.85$, one gets for $[Cl_{tot}] = 10^{-3}$ $x = 0.58$ and for $[Cl_{tot}] = 2 \times 10^{-3}$ $x = 0.48$ in excellent agreement with the values in the table.

(4) Decrease of the Rate of Polymerization with the Degree of Conversion for Different Ionenes (Figure 2). A further test of the model can be obtained from the value of the degree of conversion at which the polymerization rate decreases, which is very dependent upon the linear charge of the ionene. If one assumes that only the condensed fraction x of monomer can polymerize rapidly, this rate should tend to zero at a degree of conversion equal to x. Assuming the value of ϵ calculated above, the fraction x of condensed monomer for a stoichiometric complex with the different ionenes has been calculated. The values are given in Table II and have been reported as horizontal asymptotes on Figure 2; the prediction seems reasonable.

It is obvious that all these facts do not constitute a proof that the model of polyelectrolyte matrix polymerization based on the assumption of a local concentration of "mobile condensed counterions" is in all cases to be preferred to the model of sequential polymerization of immobilized counterions. It may well depend upon the relative importance of "site binding" and "atmospheric trapping". But the use of these concepts of polyelectrolyte theory suggest to directly characterize the fraction of condensed counterions, both by thermodynamic (activity or osmotic coefficients) and spectroscopic (^{13}C NMR) measurements, in order to clear the relation between the polymerization rate and the structure of the counterion atmosphere. It must be added that there is no contradiction with a possible stereoregulating effect of the matrix; as soon as a small n-mer is formed, it will, due to its higher charge, give a close complex with the template; the addition of a further monomer on the active end can then be oriented by the matrix.

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