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Matrix Polymerization on Polyelectrolyte Backbones: Influence of Monovalent Salts on the Condensed Monomeric Counterions

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ABSTRACT: A detailed investigation of the system [2.2.2],4-ionene-pSSA in the presence of various counterions was undertaken. The affinity of counterions toward the polyelectrolyte was determined by ion-specific potentiometry and the polymerization kinetics of pSSA. A simple equilibrium between "condensed" and "atmospheric" counterions allowed expression of the affinity of the counterions in terms of a ratio of equilibrium constants $K_{\mathrm{pSSA}^-}/K_{\mathrm{C}^-}$, called the "affinity ratio". Good agreement between values of the affinity ratios determined by potentiometry and polymerization kinetics of pSSA was found. This confirms the applicability of the ion-condensation model of the polymerization process on ionene polyelectrolytes. The sequence of ionic selectivity found in water-rich media is $\mathrm{ClO_4^-} > \mathrm{I^-} > \mathrm{Cl^-} > \mathrm{F^-}$. This sequence was found to be strongly dependent on solvent composition (water–2-propanol). An inversion of the sequence is found in 2-propanol-rich media. The affinity changes explain the large influence of solvent composition on the polymerization kinetics of [2.2.2],4-ionene-pSSA. The variation of the affinity of the counterions is explained by their ionic hydration. For organic anions it was found that aromatic sulfonates have an affinity larger than that of aliphatic carboxylates. Here also, the trends can be explained by the differing hydration tendency of carboxylates and sulfonates.

Introduction

In a previous publication[1] the concept of counterion condensation was applied in order to interpret the polymerization kinetics of *p*-styrenesulfonate attached to a [2.2.2],4-ionene polycation matrix (obtained through condensation of 1,4-diazabicyclo[2.2.2]octane and 1,4-dibromobutane) such as given in Figure 1.

In the framework of this model the polymerization on the polyelectrolyte matrix should reflect the properties of the condensed monomeric counterions. The rate of polymerization is considered to be directly dependent on the fraction x of the condensed monomeric counterions. The value of x can be obtained for a given set of experimental conditions (pH, temperature, solvent, initiator concentration) from the dependence of the polymerization rate V_p of *p*-styrenesulfonate ($\mathrm{pSSA^-}$) counterions on the $[\mathrm{pSSA^-}]/[\mathrm{ionene}]$ "filling ratio", r, for $r \leq 1$.

In the present work the relative affinities of various counterions toward the [2.2.2],4-ionene polyelectrolyte are determined by two independent methods. One of these involves the determination of the kinetics of $\mathrm{pSSA^-}$ counterion polymerization, and the other a potentiometric titration of free counterions by means of ion-specific electrodes.

Experimental (conductometric) data show that when r varies from 0 to 1, x varies from 0 to 0.68.[2] Kinetic data[3] indicate that matrix polymerization of ionene-pSSA complex is very sensitive to addition of NaCl, which produces a decrease in the polymerization rate. This effect has also been satisfactorily explained by counterions competing for condensation sites on the matrix.[1] Assuming a simple equilibrium of condensed and "atmospheric" counterions for the competing counterions $\mathrm{C^-}$ and $\mathrm{pSSA^-}$, respectively,

$$\mathrm{pSSA^-} + \mathrm{ionene^+} \rightleftharpoons \text{ionene-pSSA} \tag{1}$$

$$\mathrm{C^-} + \mathrm{ionene^+} \rightleftharpoons \text{ionene-C} \tag{2}$$

From eq 1 and 2 one gets the following equilibrium constants:

$$K_{\mathrm{pSSA}^-} = [\text{ionene-pSSA}]/[\mathrm{ionene^+}][\mathrm{pSSA^-}] \tag{3}$$

$$K_{\mathrm{C}^-} = [\text{ionene-C}]/[\mathrm{ionene^+}][\mathrm{C^-}] \tag{4}$$

From eq 3 and 4 one obtains the "selectivity ratio":

$$\frac{K_{\mathrm{pSSA}^-}}{K_{\mathrm{C}^-}} = \frac{[\mathrm{C^-}][\text{ionene-pSSA}]}{[\mathrm{pSSA^-}][\text{ionene-C}]} \tag{5}$$

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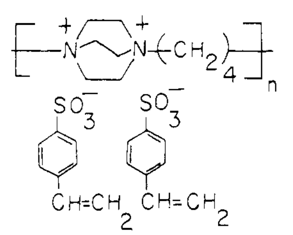

Figure 1. Schematic view of a [2.2.2],4-ionene-pSSA complex.

with [ionene-pSSA] and [ionene-C] representing the concentration of condensed pSSA and C counterions and [pSSA$^-$] and [C$^-$] the concentration of "atmospheric" or "free" pSSA and C counterions, respectively. Introducing the fraction of condensed pSSA ions x = [ionene-pSSA]/P (where P is the concentration of ionene), the fraction of all uncondensed (free) ions $x_0 = ([\text{pSSA}^-] + [\text{C}^-])/([\text{pSSA}]_{\text{tot}} + [\text{C}]_{\text{tot}})$ (where $[\text{pSSA}^-]_{\text{tot}} = [\text{pSSA}^-] + [\text{ionene-pSSA}]$ and $[\text{C}^-]_{\text{tot}} = [\text{C}^-] + [\text{ionene-C}]$), and the "filling ratio" $r = [\text{pSSA}^-]_{\text{tot}}/P$ and assuming the independence of x_0 on the composition of counterions at constant ionic strength and ion valence for a stoichiometric ionene-pSSA complex, one can rewrite eq 5

$$\frac{K_{\text{pSSA}^-}}{K_{\text{C}^-}} = \left\{\frac{[\text{C}^-]_{\text{tot}}}{(1 - x - x_0)P} - 1\right\}\frac{1}{r/x - 1} \tag{6}$$

The larger the selectivity ratio, the larger the affinity of pSSA$^-$ counterions toward the ionene in comparison with C$^-$ counterions while competing for sites in the condensed layer of polyelectrolyte. One can thus by means of the equilibrium constant ratio express the condensation affinities of various counterions. In this paper the techniques described are applied to investigate the relative condensation affinities for a number of monovalent counterions under different conditions.

Experimental Section

Polymerization Kinetics. The details of the experimental procedures have already been published.[3] Here, we just recall their principal features. Ionene bromides are synthesized according to the general technique described by Rembaum.[4] The molecular weight of the ionene bromide was determined by end-group titration (ionizable bromide). It was found to be 3900, corresponding to $\bar{\text{DP}}_n \cong 12$. The ionene bromide is converted into hydroxide and neutralized by freshly purified pSSA in order to achieve a stoichiometric ionene-pSSA complex (r = 1).

The polymerization kinetics have been observed in 10^{-3} M solution in (a) 3/1 (v/v) (79.2/20.8 (w/w) at 20 °C) water-2-propanol and (b) 1/3 (v/v) (29.8/70.2 (w/w) at 20 °C) water-2-propanol, using 10^{-4} M azobis(isobutyronitrile) (AIBN) as initiator. All compositions given in this paper refer to volume per volume parts at 20 °C. 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 were quickly melted and diluted, and the conversions were determined from the absorbance at 2550 Å. The reduction of the initial rate upon addition of various salts was measured. It was shown that the mode of preparation of the system (composed of ionene$^+$, C$^-$, and pSSA$^-$) does not affect the polymerization rate V_p (i.e., the fraction x of pSSA$^-$ ions condensed on the matrix). For example, the rate is strictly the same whether one takes as the initial system a stoichiometric complex of ionene chloride (or bromide) and then adds sodium styrenesulfonate or if one starts with the stoichiometric complex of ionene-p-styrenesulfonate (through neutralization of ionene hydroxide with p-styrenesulfonic acid) and then adds sodium chloride in stoichiometric amounts. This indicates that the establishment of ionic equilibrium in the system composed of the ionene matrix and of the two kinds of counterions is fast and should not be of concern.

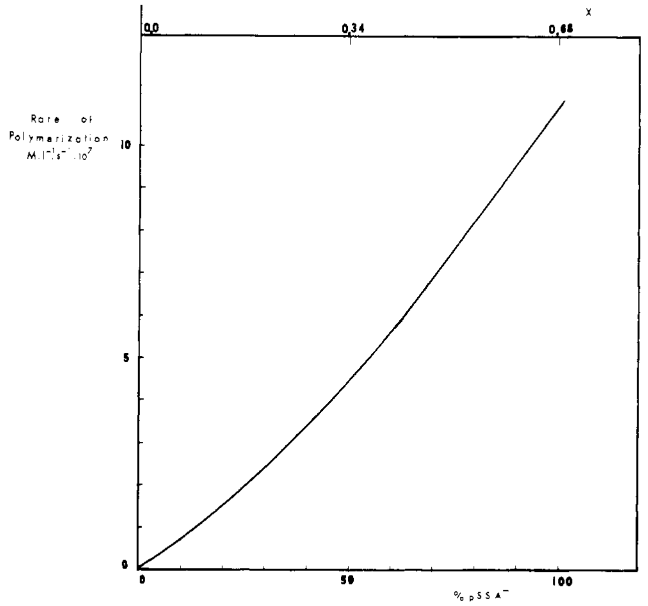

Figure 2. Rate of polymerization of [2.2.2],4-ionene-pSSA complex as a function of % pSSA$^-$ counterions. Lower scale at [pSSA$^-$] + [Br$^-$] = 2×10^{-3} M. The upper scale gives the corresponding fraction of condensed pSSA$^-$ ions, x. Composition: [[2.2.2],4-ionene$^+$] = 1×10^{-3} M, [pSSA$^-$] + [Br$^-$] = 2×10^{-3} M, [Na$^+$] = 1×10^{-3} M; [AIBN] = 1×10^{-4} M; solvent 75/25 (v/v) H_2O–$CH_3CH(OH)CH_3$; pH 7.0, temperature 70 ± 0.1 °C.

Table I
Selectivity Ratios ($K_{\text{pSSA}^-}/K_{\text{C}^-}$) for Various Ions[a]

counterion C$^-$	$10^{-7}V_p$, M·L^{-1}·s^{-1}	x	$K_{\text{pSSA}^-}/K_{\text{C}^-}$ polymn kinetics	$K_{\text{pSSA}^-}/K_{\text{C}^-}$ potentiometry
F^-	6.4 ± 0.3	0.476	3.54	2.2
Cl^-	4.8 ± 0.2	0.405	1.79	
Br^-	3.4 ± 0.2	0.340	1.00	1.4
I^-	3.3 ± 0.3	0.327	0.89	
ClO_4^-	3.2 ± 0.4	0.320	0.84	
SCN^-	5.1 ± 0.1	0.418	2.02	
IO_3^-	4.8 ± 0.1	0.403	1.76	
$CH_3SO_3^-$	5.5 ± 0.3	0.437	2.42	1.8
$C_2H_5SO_3^-$	5.4 ± 0.2	0.435	2.37	
$C_6H_5SO_3^-$	4.8 ± 0.3	0.408	1.84	1.5
p-$CH_3C_6H_4SO_3^-$	4.6 ± 0.2	0.398	1.68	1.6
$C_2H_5COO^-$	7.0 ± 0.4	0.502	4.66	6.23
$CH_3CHClCOO^-$	6.5 ± 0.3	0.479	3.65	4.0
$(CH_3)_2CHCOO^-$	6.4 ± 0.4	0.475	3.51	4.4

[a] [[2.2.2],4-ionene-pSSA] = 1×10^{-3} M, [NaC] = 1×10^{-3} M; [AIBN] = 1×10^{-4} M; pH 7.0, temperature 70 ± 0.1 °C; solvent 75/25 (v/v) water-2-propanol.

The value of x (the fraction of the condensed pSSA$^-$ counterions) is obtained from a curve giving the polymerization rate V_p as a function of x (Figure 2). This calibration curve is established on the assumption that the affinity of Br$^-$ toward the ionene approximately equals that of pSSA$^-$ (see Table I and compare values of selectivity by potentiometry). The calibration curve is then obtained by plotting the polymerization rate of pSSA at various compositions of [pSSA$^-$] and [Br$^-$] (for a constant total counterion concentration equal to 2×10^{-3} M or twice the concentration of ionene at 70 °C) as a function of the fraction of the condensed counterions x, assuming that the composition of the condensed layer of counterions is roughly equal to the total composition of counterions introduced in the solution. The value x = 0.68 was obtained by conductometry[2] for a pSSA$^-$ concentration of 2×10^{-3} M. On the basis of the above assumptions one can vary x from 0 to 0.68 by increasing the molar fraction of pSSA$^-$ from 0 to 1.

Ion-Specific Potentiometry. The activity measurements of bromide ions in solution were made with an Orion ion-specific bromide electrode (Model 94-35A) and an Orion single-junction

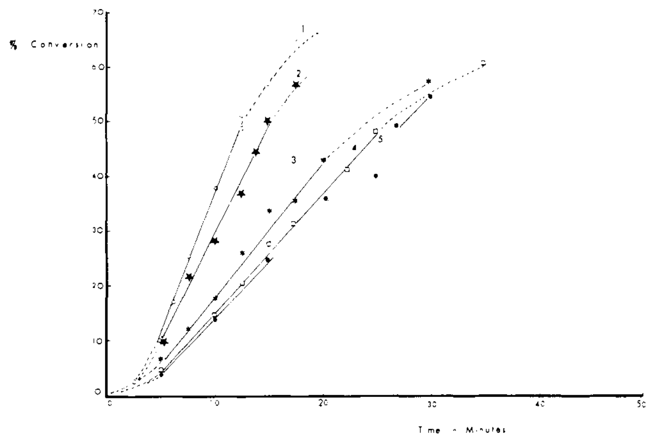

Figure 3. Conversion as a function of time for polymerization of [2.2.2],4-ionene-pSSA complex in the presence of equivalent amounts of competing monovalent electrolyte. Composition: [[2.2.2],4-ionene] = [$pSSA^-$] = 1×10^{-3} M, [NaC] = 1×10^{-3} M; [AIBN] = 1×10^{-4} M; solvent 75/25 (v/v) $H_2O–CH_3CH(OH)CH_3$; pH 7.0, temperature 70 ± 0.1 °C. Curve 1, no added salt; curve 2, NaF; curve 3, NaCl; curve 4, NaBr; curve 5, NaI.

reference electrode (Model 9001). The measurements were carried out with an Orion potentiometer (Type 407-A) at 20 °C.

We measured the activity of bromide ions in solutions of ionene bromide to which we had added either an equivalent amount of salt of the counterions studied or an equivalent amount of sodium bromide. These solutions were prepared from initial stock solutions of ionene bromide and different sodium salts of concentration equal to 5×10^{-3} N in water. Water and 2-propanol were added in quantities necessary to obtain a final concentration of ionene bromide and sodium salt of the competing counterion each equal to 10^{-3} N in a given water–2-propanol composition.

Before starting the measurements, we ascertained the linearity of the electrode ($E = f(c)$) in the interval of ionic concentrations for different solvent (water–2-propanol) compositions with three standard solutions of NaBr of concentrations equal to 5×10^{-4}, 10^{-3}, and 2×10^{-3} M. Also the noninterference of the ions investigated with the ion-specific bromide electrode was checked. Measurements were made initially in aqueous solutions. After each measurement the standard solutions were rechecked for the stabilization of the electrode. The solvent composition was changed stepwise to that rich in 2-propanol, allowing enough time for stabilization for each measurement.

From the activity measurement (equated to the concentration) of the Br^- ion in the mixture ionene-Br–NaBr, the total fraction of counterions not condensed on the ionene, x_0, can be calculated at the ionic strength used in this work. The activity of Br^- ions in mixtures of ionene-Br and NaC can similarly give the fraction of condensed bromide counterions. The condensed and free fractions of Br^- and C^- ions and consequently the ratio K_{Br^-}/K_{C^-} and also $K_{pSSA^-}/K_{C^-} = (K_{pSSA^-}/K_{Br^-})(K_{Br^-}/K_{C^-})$ can be deduced (on the assumption that the total number of condensed counterions does not change with the nature of the counterions at constant valence and ionic strength).

Results and Discussion

Inorganic Ions. A set of typical conversion vs. time curves for a stoichiometric [2.2.2],4-ionene-pSSA complex in the presence of 10^{-3} M halogen salt is given in Figure 3. It is easy to see that the polymerization rate is strongly influenced by the nature of the counterion. This effect is illustrated in Figure 4 in which the polymerization rate V_p is plotted against the crystallographic radius of the counterion in two solvents of different dielectric constant (solvent 1, 75/25 (v/v) water–2-propanol, $D = 50.6$; solvent 2, 25/75 (v/v) water–2-propanol, $D = 20.1$).

It is apparent that in the solvent rich in water the effectiveness of various halogen ions in depressing the rate of polymerization proceeds in the order $I^- > Br^- > Cl^- > F^-$. In the solvent with 75% 2-propanol ($D = 20.1$) a reversal of the order takes place, with F^- being the most effective depressant and I^- the least effective. From the depression of V_p one can obtain the fraction x of $pSSA^-$ ions condensed on the ionene matrix in the presence of 10^{-3} M concentration of halogen ions (see Figure 2). The fraction of displaced monomeric counterions is then $1 - x_0 - x$. Figure 5 shows that $1 - x_0 - x$ assumes a linear increase with the crystallographic radius of the competing halogen ion. Such a dependence can be qualitatively explained by the state of hydration of the ion, which is higher for ions with a high charge/radius ratio in the solvent rich in water. Thus F^- is more hydrated and less competitive than I^- in displacing $pSSA^-$ counterions. Within media with a low water content (in which less hydration takes place) this trend is reversed. Table I gives values of V_p, x, and K_{pSSA^-}/K_{C^-} for various counterions.

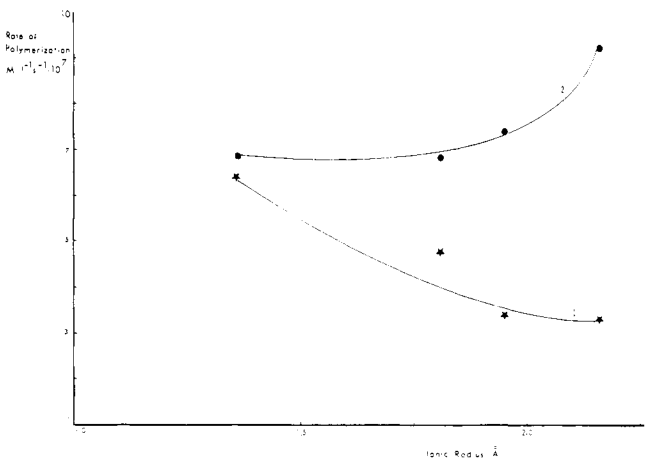

Figure 4. Rate of polymerization of the stoichiometric complex of [2.2.2],4-ionene-pSSA in the presence of competing monovalent anions (added in equimolar amounts) as a function of the ionic radius: curve 1, 75/25 (v/v) water–2-propanol; curve 2, 25/75 (v/v) water–2-propanol.

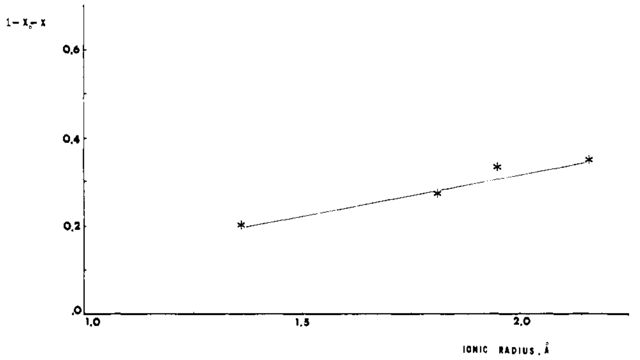

Figure 5. Fraction of monomeric $pSSA^-$ ions displaced from the condensed layer of $pSSA^-$ ions on [2.2.2],4-ionene, $1 - x_0 - x$, by an equimolar amount of competing counterions as a function of the ionic radius of the competing counterion. Solvent 75/25 (v/v) water–2-propanol.

We can see from Table I that Br^-, I^-, and ClO_4^- have a similar ability to condense on the matrix (solvent 75/25 (v/v) water–2-propanol). The values of the selectivity ratio K_{pSSA^-}/K_{C^-} obtained from polymerization kinetics are quite comparable to the values obtained by ion-specific potentiometry.

It must be pointed out that the values of the selectivity ratios in Table I are given to serve only as a comparison between the selectivity of various counterions toward ionene. They have been obtained by assuming an invariance of the fraction of condensed counterions (with composition of counterions), which is not rigorously exact. Furthermore, we have assumed that the affinity of the Br^- counterion (taken as reference) is the same as that of the

Table II
Rate of Polymerization of the Ionene-pSSA Complex (in 75/25 2-Propanol-Water) in the Presence of Various Salts (NaC)[a]

counterion C^-	none	F^-	Cl^-	Br^-	I^-
$10^{-7}V_p$, $M \cdot L^{-1} \cdot s^{-1}$	17.8 ± 1.2	6.9 ± 0.4	7.4 ± 0.3	7.4 ± 0.2	10.7 ± 0.8

[a] [[2.2.2],4-ionene-pSSA] = 1×10^{-3} M, [NaC] = 1×10^{-3} M; [AIBN] = 1×10^{-4} M; pH 7.0, temperature 70 °C.

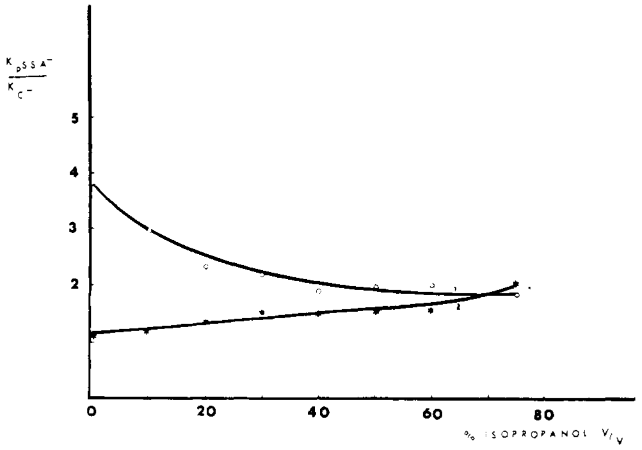

Figure 6. Selectivity ratio K_{pSSA^-}/K_{C^-} (obtained by ion-specific potentiometry) as a function solvent composition: curve 1, C^- is F^-; curve 2, C^- is Br^-.

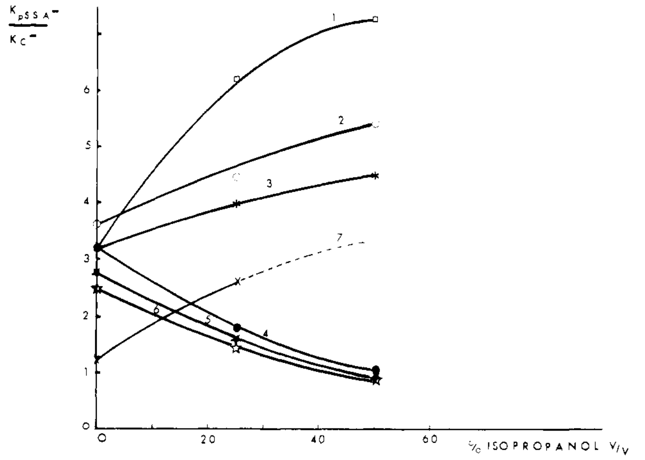

Figure 7. Selectivity ratio K_{pSSA^-}/K_{C^-} (obtained by ion-specific potentiometry) for various organic anions as a function of solvent composition: curve 1, propionate; curve 2, 2-methylpropionate; curve 3, 2-chloropropionate; curve 4, methanesulfonate; curve 5, p-toluenesulfonate; curve 6, benzenesulfonate; curve 7, 4-biphenylcarboxylate.

$pSSA^-$ ion, which is only an approximation; for example, the value of K_{pSSA^-}/K_{C^-} in Table I for ClO_4^- is 0.84, quite close to 1, and does not allow us to conclude that ClO_4^- is more condensed than $pSSA^-$.

In Figure 6 the selectivity ratio K_{pSSA^-}/K_{C^-} is plotted as a function of composition of the binary (water–2-propanol) solvent for F^- and Br^-. One can see an increase in the affinity of the F^- counterion (decrease of K_{pSSA^-}/K_{C^-}) and the decrease of the affinity of Br^- counterion (increase of K_{pSSA^-}/K_{Br^-}) as the 2-propanol content increases. This trend leads eventually to an inversion of affinities toward ionene between F^- and Br^- for media with low water content such that $F^- > Cl^- \sim Br^- > 1$ (see Table II).

Organic Ions. It is apparent from Table I that the organic anions studied can be placed in two categories: sulfonic and carboxylic. The former have a higher affinity for ionene than the latter. Here also the values of K_{pSSA^-}/K_{C^-} obtained by the two independent methods are in reasonable agreement.

Figure 7 shows the variation of ion selectivity ratio K_{pSSA^-}/K_{C^-} as a function of 2-propanol concentration. One observes a decrease of the ratio for sulfonates and an increase of the ratio for carboxylates with increasing 2-propanol concentration. In pure water the differences in the affinity of all counterions studied are not very large. In mixtures of 2-propanol and water the affinities of carboxylates and sulfonates diverge. The affinity of the individual carboxylates decreases (K_{pSSA^-}/K_{C^-} increases) in the order chloropropionate > isobutyrate > propionate. Figure 7 shows that the affinity of organic counterions toward the [2.2.2],4-ionene depends on both the nature of the ionic group (COO^- or SO_3^-) and the nature of the hydrophobic moiety (aliphatic or aromatic). The aromatic sulfonates have clearly an affinity larger than that of aliphatic carboxylates. There is not much difference between the aromatic and aliphatic sulfonates, in particular in solvents rich in 2-propanol. In contrast to sulfonates, large differences between aliphatic and aromatic carboxylates exist, especially in water-rich solvents. Thus it appears that in solvents rich in 2-propanol the ionic group is the main affinity factor, while in water the nature of the hydrophobic moiety becomes important. The diverging trends in the curves of Figure 7 between carboxylates and sulfonates could be related to their hydration tendency, which is stronger in carboxylates than in sulfonates. It could indicate therefore a partition of the solvent composition in the vicinity of the [2.2.2],4-ionene in favor of the 2-propanol, which in turn would attract preferentially the sulfonate ion toward the ionene.

Conclusion

The detailed investigation of the system [2.2.2],4-ionene-$pSSA^-$ in the presence of various counterions undertaken in this work confirms the basic validity of the classical concept of electrostatic equilibrium between condensed and atmospheric ions as applied to the polymerization kinetics of monomeric counterions proposed previously.[1] The values of the affinity ratio reported in this work are considerably improved by using as reference a monovalent ion of similar affinity (Br^-). The selectivity ratios obtained from two independent methods are in good agreement. This confirms the applicability of the ion condensation model in the polymerization process. The large influence of the nature of the counterion on the polymerization kinetics can satisfactorily be explained by a dynamic competition of counterions.

The composition of the solvent (water–2-propanol) influences the kinetics through the change of affinity of the counterions toward the ionene, which in turn can be explained by ionic hydration. The sequence of ionic selectivity $ClO_4^- > I^- > Cl^- > F^-$ in water-rich solvents agrees well with the sequence of affinity found for strongly basic ion-exchange resins in water.[5] This sequence is to be expected if the affinity of ions depends on their hydration energy.[6] The affinity sequence inversion found by polymerization kinetics can be therefore attributed to the variation of the extent of hydration of counterion and of the ionic sites in solvents of different water–2-propanol content.

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Chirality of Polyvinyl Compounds. 2. An Asymmetric Copolymerization

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ABSTRACT: Optically active polymers or copolymers of 1-substituted olefins with structural chirality in the main chain were previously unknown and not expected to occur. By symmetry considerations, three types of structure are deduced where optical activity due to chirality of the main chain is to be expected. One of these, the structure resulting from asymmetric copolymerization, was realized. For this, two monomeric units were fixed stereospecifically at a chiral template molecule and during radical polymerization another comonomer was polymerized diastereoselectively with these two. After the template was split off, linear optically active copolymers with asymmetric triads were obtained. D-Mannitol 1,2:3,4:5,6-tris-*O*-[(4-vinylphenyl)boronate] (**5a**), 3,4-*O*-isopropylidene-D-mannitol 1,2:5,6-bis-*O*[(4-vinylphenyl)boronate] (**6**), and D-mannitol 3,4-*O*-carbonate 1,2:5,6-bis-*O*-[(4-vinylphenyl)boronate] (**7**) were thus successfully used in copolymerization with methyl methacrylate or styrene. D-Mannitol 3,4-di-*O*-benzyl ether 1,2:5,6-bis-*O*-[(4-vinylphenyl)boronate] (**8**), methyl α-D-mannopyranoside 2,3:4,6-bis-*O*-[(4-vinylphenyl)boronate] (**9**), or D-glucitol tris-*O*-[(4-vinylphenyl)boronate] (**10**), which have another conformational arrangement of the (4-vinylphenyl)boronate residues, did not give optically active copolymers after the template was split off. A possible reaction mechanism for this new type of copolymerization is discussed.

I. Introduction

During our investigations on enzyme analogue built polymers,[1] the question arose as to whether vinyl monomers in the presence of optically active templates can form optically active polymers whose optical activity depends on the chirality of the main chain. According to previous findings[2] optical activity is not expected to occur in usual polyvinyl compounds, since in each step of the polymerization of a 1-substituted olefin, a chiral center is formed from a prochiral center, but in atactic polymers with an irregularly alternating *R* and *S* configuration and in syndiotactic polymers with a regularly alternating *R* and *S* configuration. Chains of this type could indeed be chiral, but the optical activity is intramolecularly compensated and therefore not measurable. Isotactic polymers (**1**, Chart I) could begin with an *R* or with an *S* configuration, with formation of two enantiomorphic chains. If, however, the difference in the end groups can be neglected ($RCH_2 \simeq R'$), as is always permissible in the case of longer chain lengths, the molecule possesses a reflection plane (i.e., it is a mesoform) and does not show any optical activity.[2]

In accordance with this, as yet no optically active polyvinyl or polyvinylidene compounds are known whose optical activity depends on the chiral structure of the main chain;[3] indeed, there are numerous examples where the optical activity arises from chiral side chains.[2]

On the other hand, for polymers from 1,2-disubstituted olefins like homopolymers from benzofuran[2,4] or alternating copolymers from maleic acid,[2,5] the occurrence of chirality in the main chain is to be expected, and many optically active polymers have already thus been obtained by asymmetric induction.[2]

The same holds true with polymers from substituted 1,3-dienes,[2,6] where also optical activity due to chirality of the main chain can be achieved.

Recently, we deduced by symmetry considerations three types of structure where optical activity due to chirality of the main chain is expected in vinyl or vinylidene polymers.[7] One possibility would be the head-to-head polymerization of the monomers, in which 1,2-disubstituted chiral segments can be formed (**2**) with a structure similar to that of the copolymers of the 1,2-disubstituted monomers. Chirality in the main chain would also be possible if the substituents near the center of an isotactic polymer chain change to the other side of the main chain with respect to the Fischer projection (**3**). Since each part of the chain has in itself a strong isotactic structure, we propose the designation inverse-diblock isotacic for this type of arrangement. With identical chain ends, **3** has one twofold symmetry axis and is therefore chiral as a whole. Whether this type of polymer can exhibit a measurable optical activity is now investigated by an attempted directed synthesis of this type.

While the concept inverse-diblock isotactic applies for homo- as well as copolymers, there should also be a type of chirality of polymer chains that can occur only in copolymers. **4** represents one example of several possibilities. In these copolymers triad I, as well as the other two possible triads, is asymmetric, and polymers of this type should show optical activity. In this context, it must be remembered that optical activity should already occur if the structures **2**, **3**, and **4** are only partially realized in the chains.

Another quite different possibility of chirality in polymer chains has been realized very recently. Okamoto et al.[8a] described the preparation of optically active, isotactic poly(triphenylmethyl methacrylate) in a one-handed helical conformation by anionic polymerization in the

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