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# Influence of the Conformation on Chemical Modification of Polymers: Study of the Quaternization of Poly(4-vinylpyridine)[†]

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**Introduction.** The need of polymers and copolymers with more complex architecture for specific applications led to development of the chemical modification of synthetic materials. The reactivity of a functional group onto a polymeric chain is usually different from that of the analogous low molecular compound, and limited modification ratios are often obtained. The parameters influencing the reactivity in homogeneous and pseudohomogeneous systems had already been described in detail by Sherrington[1] and Marechal.[2] A typical example of polymer chemical modification is the quaternization of poly(vinylpyridines) and more specially of poly(4-vinylpyridine) (P4VP).[3] At first, the quaternization rate follows second-order kinetics similar to the quaternization of pyridine; then, in the later stages, a retardation of the reaction is observed. This phenomenon was debated for a long time and attributed to a neighboring group effect inducing either charge building during the reaction or steric hindrance. A model with three rate constants have been proposed to quantify the system.[4] We demonstrated recently that the quaternization reaction does not always go to completion as supposed by the three rate constant model.[3,5] Analysis of the published data shown plateau values much lower than 100%, which depend strongly on temperature. Following this analysis, we propose a simple kinetic model based on a second-order kinetic equation which includes a steric parameter lowering the effective pyridine group concentration capable of reacting.[3] The steric effect was considered as a global effect involving the whole polymer molecule and not as a local effect. The proposed expression describes very well the experimental kinetics published and predicts the observed cessation of reaction. It was suggested that a change in the polymer conformation during the reaction from a free-draining coil to a scarcely permeable globule may account for the effect. Such a conformation or solubility effect may be explained by the change of the solvent quality with the extent of reaction as already proposed by Boucher et al.[6] The recent results of Luca et al.[7] confirm the influence of the solvent. These authors demonstrated that in methanol and dimethylformamide, the quaternization rates of P4VP with ethylchloroacetate are lower than those of its model compound and show an acceleration phenomenon above 25% of extent of reaction. All these results support the point that the major factor influencing the kinetic behavior of the quaternization reaction of P4VP is the polymer−solvent interaction changing as the reaction proceeds.

**Table 1. Preparation of Poly(4-vinylpyridinium) Salts by Spontaneous Polymerization of 4-vinylpyridine in the Presence of Alkylating Agents R−X**

| ref | side group R−X | time (h) | *T* (°C) | [RX] (mol/L) |
|---|---|---|---|---|
| S1 | $(C_6H_5)CH_2{-}Br$ | 24 | 20 | 1.20 |
| | $(C_6H_5)CH_2{-}Br$ | 24 | 0 | 1.20 |
| | $(C_6H_5)CH_2{-}Br$ | 24 | −5 | 1.20 |
| | $(C_6H_5)CH_2{-}Br$ | 24 | −16 | 1.20 |
| | $(C_6H_5)CH_2{-}Br$ | 24 | −30 | 1.20 |
| S2 | $CH_3{-}I$ | 1.25 | 20 | 1.34 |
| | $C_2H_5{-}I$ | 2 | 20 | 1.33 |
| | $C_2H_5{-}I$ | 2 | −5 | 1.33 |
| S3 | $CH_2{=}CH{-}CH_2{-}Br$ | 2 | −5 | 1.47 |
| | $CH_2{=}CH{-}CH_2{-}Br$ | 2 | −30 | 1.47 |
| S4 | $CH_3O(CH_2CH_2O)_3{-}Br$ | 192 | 25 | 1.33 |
| S5 | $HO(CH_2CH_2O)_{26}{-}Ts$ | 312 | 25 | 0.035 |
| S6 | $CH_3O(C_6H_5){-}(C_6H_5)O(CH_2)_6{-}Br$ | 24 | 50 | 0.11 |

The aim of this study is to analyze by light-scattering experiments the conformation of the quaternized P4VP in the reaction solvent. Sulfolane, in which the retardation phenomenon is observed, was used as the solvent since, due to its chemical inertia and its high dielectric constant, it is the most common solvent for quaternization studies. Two strategies may be adopted. Either the conformation is studied as a function of the extent of reaction, or it is studied as a function of the nature of the alkylating agent. In this work, we chose the second approach and analyzed the conformation of a series of samples fully quaternized with very different alkyl and aryl groups. This choice is justified by considering that Boucher et al.[6] already described the influence of the reaction extent by following the change of the viscosity during the quaternization reaction in sulfolane and nitromethane. They showed that the reduced viscosity passes through a maximum at reaction extents of 15% in sulfolane and 30% in nitromethane and then decreases to low values.

**Experimental Part.** 4-Vinylpyridine from Aldrich was distilled over KOH and hydroquinone under vacuum before used. Thiolane 1,1-dioxide (tetramethylene sulfone or sulfolane) was distilled before used. Benzyl bromide, methyl iodide, ethyl iodide, and allyl bromide, all from Aldrich, were used as received without further purification. The synthesis of bromotriethylene glycol monomethyl ether[8] and $\omega$-(4′-methoxy-4-biphenylyloxy)-hexyl bromide[9] were described previously. Poly(ethylene glycol) monotosylate was prepared from PEG ($M_n$ = 1100) and tosyl chloride in $CH_2Cl_2$ in the presence of $NEt_3$ and was purified by a silica chromatographic column ($C_2H_3Cl_3$/EtOH as eluent).

The poly(4-vinylpyridinium) salts were prepared by spontaneous anionic polymerization of 4-vinylpyridine in the presence of the alkylating agents in sealed ampules.[10] Experimental conditions are given in Table 1, and yields ranged from 70 to 90%. The polymers were characterized by $^1H$ NMR spectroscopy and elemental analysis as already described.[10−12] All the samples are fully quaternized.

Light-scattering experiments were carried out in sulfolane and methanol at 26 °C using concentrations in the range $(0{-}3) \times 10^{-3}$ g/cm$^3$. Solutions were purified by centrifugation at 18 000 rpm (SIGMA 3K30 apparatus) for about 2 or 4 h. The measurements were performed with a FICA photogoniometer using verti-

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[†] Dedicated to the memory of the late Dr. Claude Strazielle.

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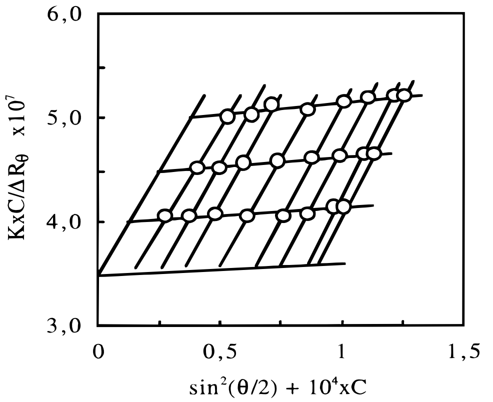

**Figure 1.** Zimm diagram for poly(1-[(4′-methoxy-4-biphenylyloxy)hexyl]-4-vinylpyridinium bromide) (S6) in sulfolane.

cally polarized light (632 nm wavelength). The angular distributions were measured in intervals of 15° in the range 30−150°.

**Results and Discussion.** The polysalts obtained by quaternization of P4VP with alkylating agents may be also obtained by spontaneous polymerization of 4-vinylpyridine (4VP) in the presence of the same alkylating agents. This method of synthesis is particularly simple, leads easily to fully quaternized polymers as first demonstrated by Kabanov,[13] and avoids ambiguity regarding the structure of the quaternized P4VP studied. Studies demonstrate that the mechanism is anionic with an initiation step which depends on the type of alkylating leaving group.[14] With bromide as leaving group, a hard anion, the initiation arises from a nucleophilic attack on the activated double bond of the pyridinium salt. With a softer anion, such as tosylate, the initiation takes place by pyridylethylation in which the lone electron pair of the 4-VP nitrogen attacks the double bond. The termination occurs by reaction of the macrozwitterion with the free alkylating agent. When the temperature of polymerization is lowered, the termination reaction is slowed and higher molecular weight polymers are obtained. Table 1 summarizes the experimental conditions for the preparation of the 13 studied samples.

The study of the conformation in solution of all these samples was first carried out by light scattering (LS) in sulfolane. Among the solvents also used in quaternization reactions and showing retardation effects (dimethylformamide, nitromethane, propylene carbonate, 2,4-dimethyl sulfolane), sulfolane was chosen since it is the preferred solvent for the studies of the P4VP quaternization kinetics. Indeed, sulfolane has a dielectric constant sufficiently high to give useful rates while avoiding side reactions. In addition, the difference in the refractive indexes of the polysalts and sulfolane, a critical parameter for the LS experiments, is sufficient to ensure accurate LS analysis.

Figures 1 and 2 represent the Zimm plots obtained in sulfolane with two polysalts bearing quite different grafts, respectively the S6 sample bearing a mesogenic side-group and the S5 sample with PEG grafts. These diagrams are representative of all the studied samples. They present quite normal groups of parallel straight lines without deviations or abnormal curvatures characteristics of the presence of large particles such as aggregates resulting of physical entanglements. In Table 2, the data calculated from the LS diagram of each samples are reported. They show the weight-average molecular weight ($M_w$), the radius of gyration ($R_g$), the second virial coefficient ($A_2$), and the dissymmetry factor ($Z$).

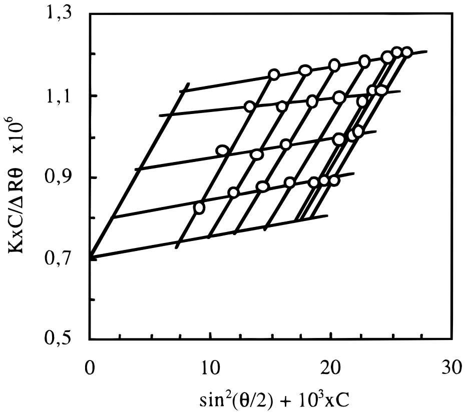

**Figure 2.** Zimm diagram for poly(1-[poly(ethylene oxide)]-4-vinylpyridinium tosylate) (S5) in sulfolane.

Unexpected very high molecular weights are obtained, and except for the S4 and S5 samples containing respectively methyl triethyleneglycol and PEG grafts, the radii of gyration are too low to be determined (<100 Å). Moreover, the values of the dissymmetry factor $Z$ are found to be near to 1, showing that the polymer samples present no dissymmetry. The low values of the second virial coefficient $A_2$ are indicative of the poor solvent quality of sulfolane. Preferential segment−segment interactions occur over segment−solvent interactions. All these characteristics are in agreement with the presence of particles with a dense globular conformation, a result of well-defined intermolecular associations of the quaternized macromolecules. Moreover, the results of Table 2 show that these associations occur whatever the size and the nature of the alkylating agent.

To confirm the presence of these associations, LS experiments were performed in methanol, a solvent expected to be of better quality than sulfolane for most of the polysalts. Table 2 summarizes the calculated data for seven of the samples, which were quite soluble in methanol. Normal Zimm plots are also observed as shown in Figure 3 for the S5 sample (the same polymer as in Figure 2). The obtained molecular weights are much lower than those in sulfolane and correspond to the expected values considering the polymerization mechanism. In particular, they increase with the lowering of the polymerization temperature as expected for an anionic process. The better quality of the methanol as solvent for these samples is confirmed by the values of the second virial coefficient 10 times higher or more than in sulfolane. All the obtained values are indicative of a normal behavior with well-dispersed macromolecular solutions. Comparison with the data obtained in sulfolane confirms the formation of contracted associations in sulfolane. In the last column of Table 2, the average number $N$ of molecules per association in sulfolane is reported ($N = M_w$ in sulfolane/$M_w$ in methanol). Comparison of the results obtained with S1 samples polymerized at different temperatures shows that the high molecular weights promote the formation of larger associations. This may be of importance when the effect of the molecular weight of the P4VP chain on the quaternization kinetics is considered.

Further evidence of the influence of the quality of the solvent on the formation of associations is provided by LS experiments carried out in sulfolane with progressive

**Table 2. Light-Scattering Chain Parameters of Poly(4-vinylpyridinium) Salts Determined in Sulfolane (S) and in Methanol (M): Weight-Average Molecular Weight, $M_w$; Radius of Gyration, $R_g$; Second Virial Coefficient, $A_2$; Dissymmetry Factor, $Z$; Polymerization Temperature, $T$ (°C)**

| ref | side group R−X | $T$ (°C) | LS solvent | $\bar{M}_w \times 10^{-3}$ | $R_g$[a] (Å) | $Z$ | $A_2 \times 10^4$ | $N$[b] |
|---|---|---|---|---|---|---|---|---|
| S1 | $(C_6H_5)CH_2{-}Br$ | 20 | S | 420 | < | 1 | 2.35 | 20 |
| | | | M | 21,2 | < | 1 | 44,4 | |
| | $(C_6H_5)CH_2{-}Br$ | 0 | S | 695 | < | 1 | 2.45 | 28 |
| | | | M | 24,6 | < | 1 | 23,9 | |
| | $(C_6H_5)CH_2{-}Br$ | −5 | S | 280 | < | 1 | 4.01 | 74 |
| | | | M | 37,7 | < | 1 | 61,9 | |
| | $(C_6H_5)CH_2{-}Br$ | −16 | S | 520 | < | 1 | 1.97 | 85 |
| | | | M | 61,3 | < | 1 | 81,4 | |
| | $(C_6H_5)CH_2{-}Br$ | −30 | S | 640 | < | 1 | 1.42 | 62 |
| | | | M | 103,0 | < | 1 | 85,9 | |
| S2 | $CH_3{-}I$ | 20 | S | 153 | < | 1.07 | 13.5 | |
| | $C_2H_5{-}I$ | 20 | S | 180 | < | 1 | 4.20 | |
| | $C_2H_5{-}I$ | −5 | S | 840 | < | 1 | 1.90 | |
| S3 | $CH_2{=}CHCH_2{-}Br$ | −5 | S | 275 | < | 1 | 0.045 | |
| | $CH_2{=}CHCH_2{-}Br$ | −30 | S | 480 | < | 1 | 6.17 | |
| S4 | $CH_3(OCH_2CH_2)_3{-}Br$ | 25 | S | 137 | 185 | | 2.19 | 2.7 |
| | | | M | 51,2 | 95,3 | | 24.6 | |
| S5 | $HO(CH_2CH_2O)_{26}{-}Ts$ | 25 | S | 142 | 229 | | 0.262 | 4.3 |
| | | | M | 325,0 | 560 | | 5.27 | |
| S6 | $CH_3O(C_6H_5)(C_6H_5)O(CH_2)_6{-}Br$ | 50 | S | 270 | < | 1 | 1.2 | |

[a] Key: < means lower than 100 Å. [b] $N$ is the average number of associations in sulfolane ($N = M_w$ in sulfolane/$M_w$ in methanol).

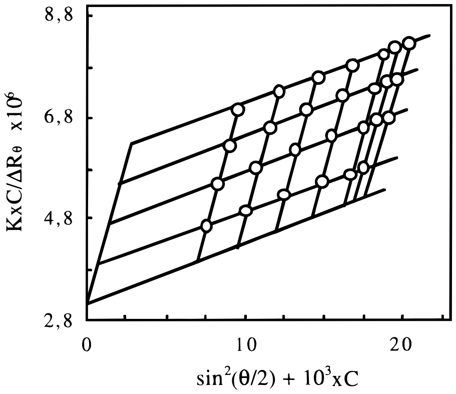

**Figure 3.** Zimm diagram for poly(1-[poly(ethylene oxide)]-4-vinylpyridinium tosylate) (S5) in methanol.

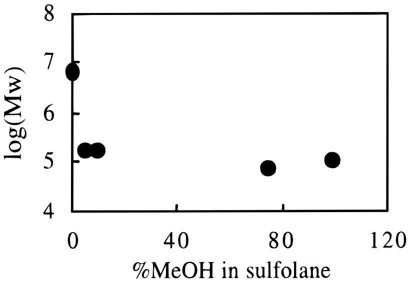

**Figure 4.** Variation of the molecular weight ($M_w$) of poly(1-benzyl-4-vinylpyridinium bromide) (S1-30 °C) with the percentage of methanol added in sulfolane.

addition of methanol. Figures 4 and 5 represent respectively the molecular weight and $A_2$ variations versus the amount of methanol added to sulfolane for the S1-30 °C sample. In agreement with the observed increase of $A_2$ corresponding to the increase of the solvent quality, the associations disappear as soon as 5−10% methanol is added. This methanol amount is obviously sufficient to solvate the pyridinium ions and to decrease the strong intermolecular interactions. This result may explain the acceleration of the quaternization rate observed by Luca et al. in methanol. The electrostatic repulsions between the pyridinium groups will tend to expand the coils, making easier the diffusion of the alkylating agent.

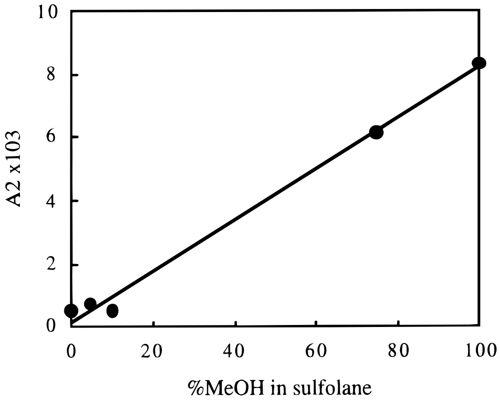

**Figure 5.** Variation of the second virial coefficient $A_2$ with the percentage of methanol added in sulfolane for poly(1-benzyl 4-vinylpyridinium bromide) (S1-30 °C).

The obtained LS results concern only the conformation of fully quaternized samples. However, associated with the viscosity experiments of Boucher recalled in the Introduction, the results allow to one describe the evolution of the coil conformation during the quaternization reaction. Up to a quaternization ratio of about 15% in sulfolane, the reduced viscosity of the solution increases due to the electrostatic repulsions which favor the coil expansion and lead to quaternization kinetics similar to that of pyridine. For higher quaternization ratios, a rapid decrease of the viscosity was observed due to the poorer quality of the solvent for the partly grafted coils. Upon further quaternization, the coils collapse and associate. As a consequence of associations, significant restriction of internal diffusion appears and steric effects become very important. It results in an important lowering of the quaternization rate and even cessation of the reaction before complete quaternization. When the results obtained with alkyl agents of different sizes and polarities are considered, it is obvious that the main parameter governing the association formation is the appearance of ions on the chains. In solvents with low polarity, intramolecular ion-pairing is dominant and internal phase separation may occur, leading to the formation of globular associations and to eventual precipitation.

**Conclusion.** Many experimental studies have shown the influence of the polymer conformation and of the changes in conformation on the polymer reactivity.[2] Although the quaternization kinetics of P4VP have been extensively studied, the importance of this phenomena for this reaction has never been fully demonstrated. The results of the LS experiments clearly demonstrate the formation in sulfolane of dense and globular associations between the fully quaternized P4VP molecules while in methanol random free coils are observed. Although the present study is limited to fully quaternized P4VP, the results together with those of Boucher demonstrate that the main factor influencing the quaternization kinetics is the polymer conformation. It is worth remarking that the steric effect related to the size of the quaternization agent and well demonstrated in various works[3,4,6,15] is not the intrinsic factor but, according to the present results, appears as a consequence of the formation of dense associations able to considerably reduce the diffusion of the reagents inside the coils. The association formation explains quite well the limitation to the extent of reaction. Unless a preferential adsorption of the reagent occurs, the reactivity of such globules becomes governed by the internal diffusion of the reagent. Under such conditions, the quaternization rates of P4VP may become quite low and cannot be compared any more to that of pyridine.

This study confirms our previous conclusions deduced from the analysis of more than 30 quaternization kinetics and supports the proposed quaternization model.[3] In this model, as recalled in the Introduction, the steric effect was considered as a global effect involving the whole polymer molecule and not a local effect. The proposed expression predicted the observed cessations of reaction and introduced a parameter $\beta$ describing the restriction of diffusion of the reagents inside the P4VP coils. The fact that, for one system, a constant value for $\beta$ was able to well describe the quaternization kinetics seems to demonstrate that the collapse of the P4VP chains and the association formation are not a progressive phenomenon but occur rather abruptly.

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