Reaction Kinetics of Polymer Substituents. Macromolecular Steric Hindrance Effect in Quaternization of Poly(vinylpyridines)

Yves Frère and Philippe Gramain*

Institut Charles Sadron, (CRM-EAHP) CNRS-ULP, 6, rue Boussingault,
67083 Strasbourg Cedex, France

Received December 26, 1991; Revised Manuscript Received February 18, 1992

ABSTRACT: The retardation in the quaternization of poly(vinylpyridines) is of steric origin. Using very voluminous reagents, a steric effect also induces an important limitation to the extent of quaternization which is not included in theoretical treatments of neighboring group effects. A kinetic expression based on the classical second-order equation is proposed. It includes the rate constant k_0 for reaction of a pyridyl group and a macromolecular steric factor β lowering the effective pyridine group concentration capable of reacting. β characterizes the effect of the size and nature of the substituents on the accessibility of the pyridine groups. The expression describes very well the experimental kinetics published and associates to each alkylating agent a steric factor related to its bulkiness. Cessation of the reaction at a given temperature is predicted, in full agreement with experimental results. Possible reasons for such a limitation are discussed, and the change in the polymer conformation from a free-draining coil to a scarcely permeable globule is shown to account for the effect.

Introduction

The chemical modification of synthetic polymers is an important field of polymer chemistry due to the need for new, more complex and varied macromolecular structures useful for specific applications. However, in addition to a possible multiplicity of side reactions, the reactivity of a functional group bound to a polymer is generally modified. This often gives rise to low yields and conversion. Factors affecting reactivity are numerous as detailed in reviews.[1,2] Among them, the so-called neighboring group effects were perhaps the most studied. In fact, the influence of reacted neighbors may be of steric or electrostatic origin, and the distinction may be difficult to pinpoint. In the latter case, they may result in an enhancement or a depression of reactivity. A typical example is the quaternization of poly(vinylpyridines) and more specially of poly(4-vinylpyridine). At first, the quaternization follows second-order kinetics quite similar to the quaternization of pyridine.[3,4] However, in the later stages, retardation of the reaction is observed, attributed by Fuoss et al.[5,6] to a charge buildup during the reaction. Three rate constants are required to quantify the system: k_0, k_1, and k_2. The parameter k_0 is the rate constant for the reaction of a pyridine group flanked by two unreacted groups, whereas k_1 and k_2 refer to groups flanked respectively by one and by two quaternized groups. This model has been developed by Keller[7] and Boucher[8] and applied to the basic hydrolysis of polyacrylamide[9] and, in particular, to the quaternization of P4VP by Boucher and Mollett.[10] Arends[11] suggested that steric hindrance may account for the kinetics of the quaternization of P4VP. Boucher and co-workers[12–14] analyzed the reaction with several alkyl and arylalkyl bromides and concluded that the retardation is mainly due to a steric effect and that the magnitude of the effect increases with increasing size of the organic bromide. They applied successfully the three rate constant model. However, the complexity of the resulting expressions or even of the computer simulations makes a comparison of the theory with the experimental results difficult and inconclusive since, unless the three rate constants can be independently determined,[9] any kinetic curve of P4VP quaternization can be reproduced. We demonstrated recently,[15] by using very voluminous alkylating agents, that the quaternization reaction does not always go to completion as supposed by the three rate constant model, although fully quaternized samples can be easily obtained by spontaneous polymerization.[16] Plateau values much lower than 100% are observed, which depend strongly on temperature. This confirms a very important steric effect and gives support to various observations of a limited conversion[13,14,17,18] with much less voluminous alkylating agents. This prompted us to reanalyze the problem.

In this paper we propose a simple kinetic model based on a second-order kinetic equation which includes a steric parameter. The steric effect is considered as a global effect involving the whole polymer molecule and not a local effect. From the published data, we show that the decreasing rate constant is related to the size of the alkylating agent.

Experimental Section

The data used in this study come from the various kinetics studies published in the literature and from our recent study.[15] To obtain experimental points with good accuracy, large-scale plots were made by controlled magnification of the plots published. Some kinetics were not exploitable because accurate data concerning the concentrations used were lacking.

Results

A quaternization of pyridine derivatives follows second-order kinetics:

$$dx/dt = k_0(a-x)(b-x) \qquad (1)$$

where x is the concentration of halogen ion at time t, a is the initial concentration of base, b is the initial concentration of alkyl halide, and k_0 is the rate constant. Equation 1 integrates to

$$f(t) = (b-a)^{-1} \ln [(1-(a/b)T)/(1-T)] = k_0 t \qquad (2)$$

with a reaction extent $T = x/a$.

Thus, a plot of f(x) against time is linear, with a slope equal to k_0. Equation 2 supposes that all the bases are accessible. With poly(4-vinylpyridine), departure from linearity after about 20–30% conversion is always observed. With poly(2-vinylpyridine), this deviation starts at a conversion of 4%.[4] Reaction with the voluminous ω-[(4′-methoxybiphenyl-4-yl)oxy]alkyl bromides leads to conversions limited to 70% at 333 K, 23% at 355.5 K, and 4% at 363 K.

0024-9297/92/2225-3184$03.00/0

Table I
Summary of the Kinetic Results for the Quaternization of Poly(vinylpyridines) in Sulfolane

temp, K	a_0 (pyr), mol dm^{-3}	b_0 (reagent), mol dm^{-3}	reagent	ref	10^5K_0, dm^3 mol^{-1} s^{-1}		β	Figure
					ref	this work		
			P4VP					
310	0.0178	0.0028	ω-[(4′-methoxybiphenyl-4-yl)oxy]dodecyl bromide	15		1.33	1.48[f]	7
355.5	0.0124	0.0124		15		42.0	1.25 ± 0.03	7
353				15		36.0	1.31 ± 0.01	7
340				15		23.0	1.40 ± 0.01	7
333				15		15	1.43 ± 0.01	7
363				15		90	1.03 ± 0.02	7
355.5			ω-[(4′-methoxybiphenyl-4-yl)oxy]octyl bromide	15		48.0	1.15 ± 0.03	7
337.5	0.109	0.393	1-bromopropane	18	27.0	18.5	1.10 ± 0.02	2
328	0.114	0.389		18	13.9	10.5	1.14 ± 0.02	2
332.2	0.105	0.382	1-bromo-3-phenylpropane	14	16.00[a]	13.0	1.16 ± 0.02	
340.6				14	28.7[a]	21.0	1.14 ± 0.02	
348.9				14	49.7[a]	37.5	1.11 ± 0.02	
349.2	0.106	0.406	isobutyl bromide	14	301	250	1.07 ± 0.02	5
339.2				14	153	90.0	1.12 ± 0.02	5
325.2				14	55.0	43.0	1.16 ± 0.02	5
305.6	0.035	0.109	allyl bromide	14	356	310	1.07 ± 0.01	1
315.7				14	739	550	1.04 ± 0.01	1
323.7				14	1274	950	1.03 ± 0.01	1
308.4	0.1065	0.392	(2-bromoethyl)benzene	14	1.37[a]	1.1	1.17 ± 0.02	
317.8				14	2.92[a]	2.2	1.13 ± 0.02	
						2.2	1.07 ± 0.02	
323.7				14	4.58[a]	3.6	1.12 ± 0.02	
						3.3	1.05 ± 0.02	
343	0.06	0.23	*n*-butyl bromide	4	29	28	1.10 ± 0.01	
						30	1.15 ± 0.01	
342.7	0.151	0.452	*n*-butyl bromide[b]	13	17.5	16	1.09 ± 0.02	4
313.2	0.042	0.042[c]	benzyl bromide	12	1220[a]	800	1.15 ± 0.01	3
321.2				12	1852[a]	1250	1.13 ± 0.01	3
328.2				12	2820[a]	1800	1.12 ± 0.01	3
339.6	0.107	0.380[d]	*n*-pentyl bromide	14	31	20 or 22	1.13 ± 0.02	6
						22	1.07 ± 0.02	6
306.2	0.0847	0.847	ethyl bromide	12	5.6	4.8	1.03 ± 0.01	4
			P2VP					
343	0.084	0.310	butyl bromide	4	0.39	0.33	2.8 ± 0.1	
			P3VPCH$_3$					
343	0.342	0.541	butyl bromide	4	11[e]	13	1.18 ± 0.01	

[a] Calculated at this temperature from the A_0 and E_0 values given by the authors. [b] In propylene carbonate. [c] b_0 is determined from the kinetics and the k_0 values given by the authors. [d] a_0 and b_0 are determined from the concentration range values given by the authors and the kinetics. [e] From Figure 5 in ref 4. [f] Estimated value in agreement with the experimental results.

Moreover, the quaternization with butyl bromide of samples already partially quaternized with voluminous groups does not lead to complete reaction as observed at the same temperature with pure P4VP. This leads us to suspect a strong steric effect and to suggest that, on the polymeric chain, the accessibility of the pyridine groups decreases as conversion increases, all the more as the size of the alkylating agent is increased. The concentration a_f of the accessible pyridine groups is assumed to be a linear function of x and can be expressed as

$$a_f = a - \beta x \quad \text{with } \beta \geq 1 \tag{3}$$

where β is a macromolecular steric coefficient which describes the effect of the size and the nature of the substituents on the accessibility of the pyridine groups.

With (3), the second-order equation (2) becomes

$$F(t) = (\beta b - a)^{-1} \ln [(1 - (a/b)T)/(1 - \beta T)] = k_0 t \tag{4}$$

β can be easily estimated if the quaternization reaction is conducted up to its maximum T_M ($T_M = \beta^{-1}$). To estimate β, we first obtain k_0 from the earlier stages of the reaction and search, by iteration, for the β value which fits best the later stages of the reaction. This is conveniently accomplished by a comparison of the experimental values T and the T calculated according to relation 5.

Table I lists k_0 and β values for 30 published kinetics studies carried out in sulfolane (except for one in propylene carbonate) with P4VP, P2VP, or P3VPCH$_3$. In the same table, the k_0 values found according to (4) are compared to the k_0 values given by the authors. Except for one value, all the authors' values are overestimated. This is easily explained by the difficulty in determining the initial slope of the kinetics in the absence of a satisfying theoretical expression.

The 30 experimental kinetics results obtained at different temperatures and for different alkylating agents are compared to the theoretical ones by plotting T versus time according to (4). Typical examples are shown in Figures 1–7. The agreement is very good except in the cases of pentyl bromide and (2-bromoethyl)benzene (at 323.7 and 317.8 K) for which at higher conversions (the absolute errors are larger) some discontinuity is observed. This is illustrated in Figure 6 with *n*-pentyl bromide, where two possible values of β are considered (full and dashed theoretical lines with respectively $\beta = 1.13$ and 1.07). We see from Figure 8, discussed later, that the higher β value is the most probable.

Quite interesting also is the examination of the nitrogen position in the pendant pyridine. Loucheux et al. studied the quaternization of P4VP, P2VP, and P3VPCH$_3$ with *n*-butyl bromide under the same conditions.[4] Results (not shown) are in full agreement with β values of respectively

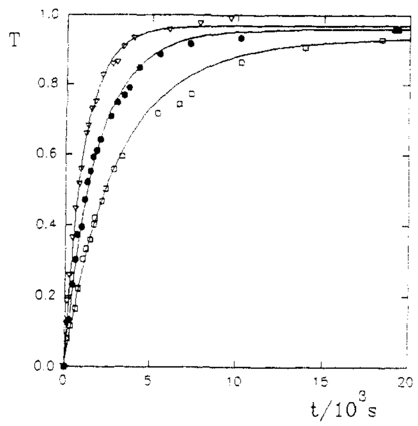

Figure 1. Quaternization of P4VP with allyl bromide at 323.7 (▽), 315.7 (●), and 305.6 K (□) in sulfolane. The curves are theoretical [β = 1.03 (▽), 1.04 (●), and 1.07 (□)].

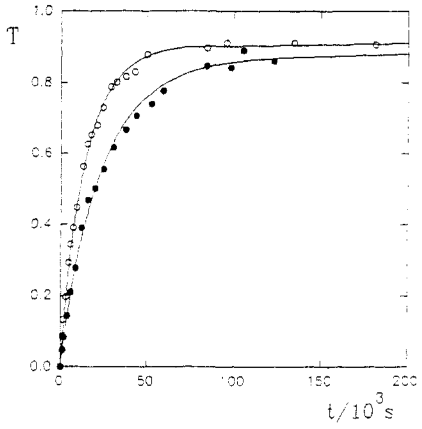

Figure 2. Quaternization of P4VP with 1-bromopropane at 337.5 (○) and 328.0 K (●) in sulfolane. The curves are theoretical [β = 1.10 (○) and 1.14 (●)].

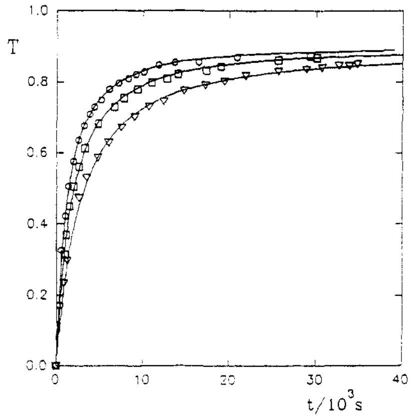

Figure 3. Quaternization of P4VP with benzyl bromide at 328.2 (○), 321.2 (□), and 313.2 K (▽) in sulfolane. The curves are theoretical [β = 1.12 (○), 1.13 (□), and 1.15 (▽)].

1.10, 2.8, and 1.18, strongly correlated to the accessibility of the nitrogen atom.

In Figure 8, the variations of β with temperature are presented. This plot summarizes all the results discussed here concerning P4VP. Three important observations can be made:

(i) The more voluminous the grafted alkylating agent is, the higher is the β value.

(ii) For all the alkylating agents, β decreases with rising temperature. In the range of temperature 300–345 K, the variation of β can be considered linear, and the slopes are identical for all the alkylating agents. This demonstrates that the variation of β is strongly correlated to the P4VP backbone; the accessible volume around the pyridine groups increases with T, while the volume of the alkylating agent is hardly affected by temperature. The elevation of temperature results in a better accessibility of the nitrogen groups along the chain.

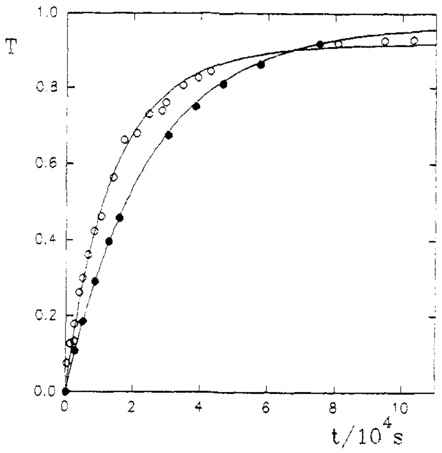

Figure 4. Quaternization of P4VP with ethyl bromide at 306.2 K (●) in sulfolane and with *n*-butyl bromide at 342.7 K (○) in propylene carbonate. The curves are theoretical [β = 1.03 (●) and 1.09 (○)].

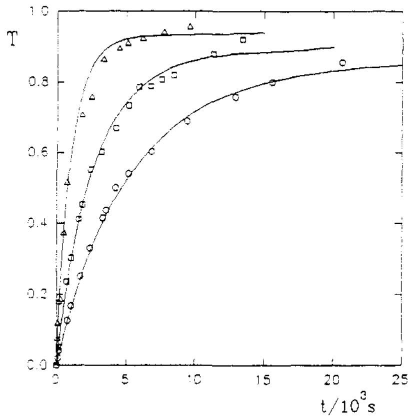

Figure 5. Quaternization of P4VP with isobutyl bromide at 349.2 (△), 339.2 (□), and 325.2 K (○) in sulfolane. The curves are theoretical [β = 1.07 (△), 1.12 (□), and 1.16 (○)].

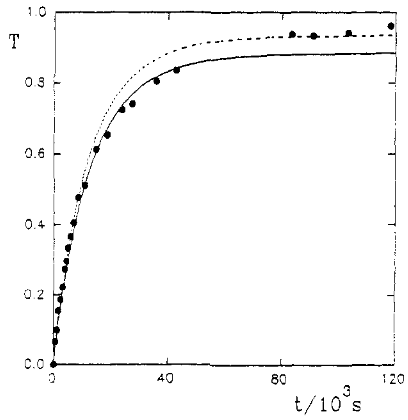

Figure 6. Quaternization of P4VP with *n*-pentyl bromide at 339.6 K in sulfolane. The curves are theoretical [β = 1.07 (- - -) and 1.13 (—)].

(iii) At higher temperature, above 350 K, the few examples available (points 6, 9, 10, and 11) show a sudden and rapid decrease of β observed with voluminous reagents and more particularly with the mesogenic alkylating agents. It is important to note that in the same temperature range, the variation of k_0 is monotonous and follows closely the Arrhenius law (Figure 9) similar to all the other reactants studied, with an activation energy of 58.4 kJ

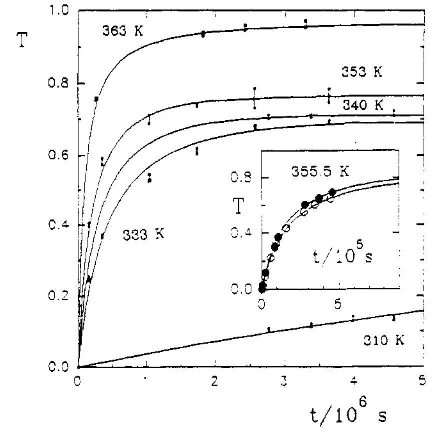

Figure 7. Quaternization of P4VP with ω-[(4'-methoxybiphenyl-4-yl)oxy]dodecyl bromide at various temperatures in sulfolane. The curves are theoretical [β = 1.03 at 363 K, 1.31 at 353 K, 1.40 at 340 K, 1.43 at 333 K, and 1.48 at 310 K]. In the insert, β = 1.25 for ω-[(4'-methoxybiphenyl-4-yl)oxy]dodecyl bromide (●) and 1.15 for ω-[(4'-methoxybiphenyl-4-yl)oxy]octyl bromide (○).

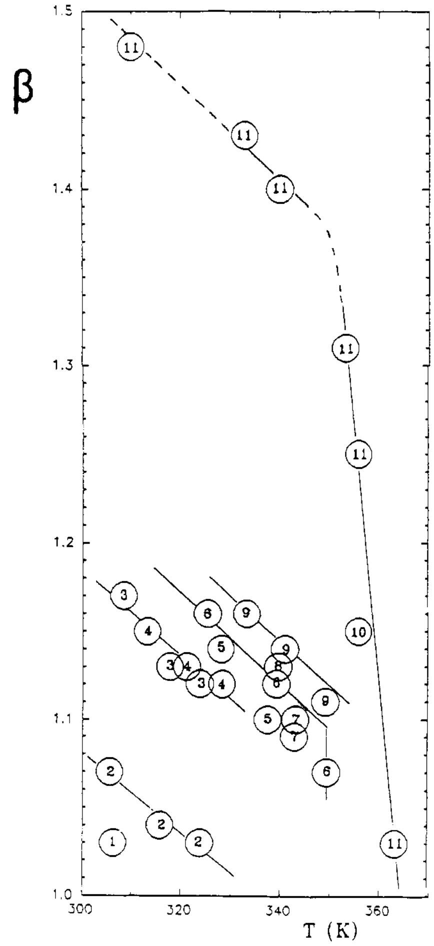

Figure 8. Temperature dependence of β: (1) ethyl bromide; (2) allyl bromide; (3) (2-bromoethyl)benzene; (4) benzyl bromide; (5) 1-bromopropane; (6) isobutyl bromide; (7) n-butyl bromide; (8) n-pentyl bromide; (9) 1-bromo-3-phenylpropane; (10) ω-[(4'-methoxybiphenyl-4-yl)oxy]octyl bromide; (11) ω-[(4'-methoxy-4-biphenyl-4-yl)oxy]dodecyl bromide.

mol^{-1}, not very different from the average value of 65.9 kJ mol^{-1} observed with smaller alkylating agents. This shows that the observed variation of β mainly reflects a property of the macromolecular coil.

Discussion

The kinetic expression proposed in this paper fully describes the quaternization reaction by two parameters

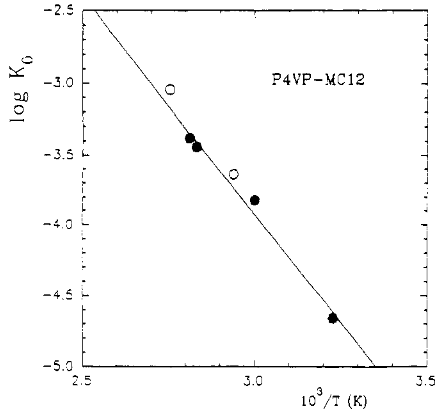

Figure 9. Temperature dependence of k_0 for the quaternization of P4VP with ω-[(4'-methoxybiphenyl-4-yl)oxy]dodecyl bromide in sulfolane. (○) Estimated from the plateau values.

k_0 and β, where k_0 characterizes the reactivity of the pyridyl group with the reactant and β describes a steric hindrance related to the size and nature of the reactant and to some properties of the macromolecular coil. In the following, we will analyze these parameters.

The Rate Constant k_0. To compare the rate constant of the quaternization reaction with pyridine derivatives and poly(vinylpyridines), it is useful to remember factors affecting k_0, other than temperature and dielectric constant of the reaction medium.

The kinetics of quaternization of pyridine derivatives in sulfolane were mainly studied by Coleman and Fuoss,[5] Boucher et al.,[18] and Morcellet-Sauvage and Loucheux.[4] The reaction follows second-order kinetics, but only few data exist on the influence of the type of organic bromide (chemical nature and steric hindrance) and of the pyridine derivative (basic character and steric hindrance). There is evidence that differences in reactivity of an isolated pyridyl group depend on the nature of the substituents on the α- and β-carbons of the organic bromides.[14,19] π-Bond overlap between atoms on the α-carbon enhances the rate constants (e.g., allyl and benzyl bromide). Steric hindrance of the organic bromides depends mainly on the substituents on the α- and β-carbons. The steric hindrance is lower with methyl and ethyl bromides (higher reactivity) and becomes constant for linear alkyl bromides with three or more methylene groups (k_0 constant).

Examination of the tables of basicity[20] shows that the position and the number of the alkyl substituents on the pyridine ring affect the basicity of the molecules, and therefore its reactivity, much more than the size of the substituent; k_0 increases with basicity as shown in Figure 10, where k_0 values obtained at 343 K in sulfolane are plotted against the basicity constants k_a at 298 K for the reaction of n-butyl bromide with pyridine, 4-methylpyridine, 4-ethylpyridine, and 4-isopropylpyridine. The steric hindrance around the nitrogen is also an important factor. A methyl or ethyl group in the 2-position strongly decreases k_0. This is illustrated also in Figure 10, where the dependence of k_a on k_0 is compared for substitutions in the second or fourth positions. When compared at the same basicity, k_0 values for the 2-ethyl and 5-ethyl-2-methyl derivatives are respectively 35 and 10 times lower that those for the same derivatives in the 4-position.

The above observations are noteworthy when the behavior of pyridine groups attached to a polymeric backbone is considered. They explain the difference in the reactivity of P4VP with the different reactants. In particular, for the eight alkyl reagents including the mesogenic molecules shown in Table I, we find a constant value for k_0 ($2.8 \times 10^{-4} \pm 1 \times 10^{-4}$ dm^3/mol·s at 343 K).

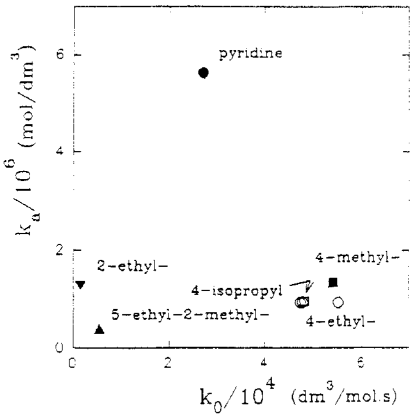

Figure 10. Dependence of k_0 for the quaternization of pyridine derivatives at 343 K in sulfolane versus pK_a of the base at 298 K.[4,5,20]

They explain also the difference of the reactivity of P4VP ($k_0 = 28 \times 10^{-5}$), P2VP ($k_0 = 0.33 \times 10^{-5}$), and P3VPCH$_3$ ($k_0 = 13 \times 10^{-5}$) with butyl bromide. P2VP has the lower basicity and the higher steric hindrance, leading to a very low k_0 value. P3VPCH$_3$ has the higher basicity but exhibits an important steric hindrance, and P4VP has an intermediate basicity and no steric hindrance.

The above analysis shows that the variation of the k_0 values obtained with the polymers in Table I are simply explained without taking into account the polymeric structure. The strong observed dependence of β on the size of the reactant and on temperature can only be attributed to a polymer effect.

The β Steric Factor. Figure 8 shows that β increases regularly with the number of carbon atoms of the grafted alkylating agents except for two jumps, the first one between two and three carbons and the second one between 1-bromo-3-phenylpropane and the mesogenic reactant. Two reasons may explain this variation. The steric hindrance of the reactants already discussed probably induces the same effect once grafted on the polymer; however, its influence seems minor and cannot explain the increase of β observed with the linear alkyl reactants and particularly with the mesogenic molecules. It is obvious that the increase in size and increase in nonpolar character of the reactants are determining factors. The rodlike structure of the mesogenic molecules may also have an important contribution. If we except the contribution of the steric hindrance associated to the reactants themselves, our results show that β and k_0 hardly depend on each other. This is illustrated in Figure 4. The k_0 for ethyl bromide in sulfolane at 306.2 K is lower than for *n*-butyl bromide at 342.7 K in propylene carbonate but leads to a higher maximum conversion T_M (lower β value).

One might argue that the limited conversion of the reaction depends on the stereoregularity of the polymer. The reaction of the pyridyl group would be affected by its "tactic placement" with respect to its neighbors, particulary when one or both of the neighbors have already reacted. The accessibility of a central member of the isotactic triads would be lower than for hetero or syndio triads, and the effect would increase once one neighbor has reacted and becomes very important when both have reacted. No precise data of the tacticity of the polymers used in the works quoted have been published, but all except one have been prepared by a radical process and no great difference in the tacticity of the samples is to be expected. Although Boucher found no difference between free-radical- or sodium-initiated samples, no characterization of the tacticity was carried out.[12] In our experiments with mesogenic reactants, the starting P4VP (^{13}C NMR in methanol at 50 °C) contained 27.3, 30.6, and 42.1% of iso-, syndio-, and heterotactic triads and 48.35 and 51.65% of iso- and syndiotactic diads. Such data are difficult to reconcile with the slowdown of the reaction after only 10–20% substitution and with the 30% inaccessible groups experimentally demonstrated, even by supposing that all the central pyridyl groups of the isotactic triads are unreactive. Although an effect of tacticity is quite likely, its contribution to the whole effect must be minor. Experiments are needed to elucidate the point.

According to our model, which supposes a global steric effect, the β values are related to the average accessible volume around a pyridine group which, under the same experimental conditions, must depend only on temperature and conversion. A global effect of polymer molecules has been already proposed and analyzed by Boucher et al.[13] as a possible explanation for the decrease in the rate, in addition to a neighboring group effect. Many of the arguments developed below were already given by these authors.

The decrease in the reaction rate and complete cessation may be explained if one supposes an influence of the conformation of the polymeric coil on its reactivity. Thus, in a good solvent, in which the coil is expanded, the reactivity should be higher than in a Θ solvent, in which the coil is collapsed. Unfortunately, the choice of solvent for the quaternization reactions is restricted. The solvent has to have a dielectric constant sufficiently high to give useful rates while avoiding side reactions. Among the solvents most often used—dimethylformamide, nitromethane, propylene carbonate, 2,4-dimethylsulfolane, and sulfolane—sulfolane gives the best results (rapid kinetics, absence of side reactions). It is difficult under these conditions to study the influence of the nature of the solvent. However, published data are illustrative. With *n*-propyl bromide, results obtained in sulfolane and propylene carbonate are identical although, in the latter solvent, a cessation of the reaction at 95–97% substitution is observed.[13] Also, whereas the presence of salt in sulfolane has no significant influence, salt in propylene carbonate increases the retardation with the appearance of clouding as the reaction proceeds, which indicates that the reacting medium has reached Θ conditions. The same effect was noted in nitromethane.[13] These results suggest a dependence of the rate on the quality of the solvent. More illustrative is the change in the reduced viscosity during the reaction with *n*-butyl bromide in propylene carbonate. Boucher[13] found that the viscosity passes through a maximum at about 15% conversion and decreases rapidly thereafter. The same behavior was observed with poly(4-vinylpyridinium hydrochloride) in methanol,[21] with *n*-octyl bromide in water,[22] and with *n*-butyl bromide in nitromethane with random copolymers of styrene and 4-vinyl-*N*-butylpyridinium.[21] The interpretation is obvious: at first, electrostatic repulsions tend to expand the coil together with increasing alkylation, but the solvent power of the medium diminishes rapidly and the polymer dimensions are reduced. With the influence of the nonpolar alkyl groups, internal phase separation may occur until the formation of a globular conformation, a phenomenon well demonstrated with systems having incompatible sequences such as polysoaps and block-type or comblike copolymers. The reaction may not only be retarded but completely stopped. In the majority of incompatible systems, an increase of temperature leads to a decrease of the repulsive interactions and to an increase of solvation. The increase of the accessibility (β^{-1}) with increasing temperature may be thus understood. According to this interpretation, the β parameter should be related not only to the geometrical size of the reactant but also to the induced change of conformation of the coil due to the interactions of the grafts with the backbone and the solvent. The irregular variation of β with the size of the reactant (Figure 8) becomes understandable since these interactions depend on the chemical nature of the grafts. The effect is obviously reinforced when substituents are voluminous and promote internal phase separation. In a segregated conformation, the solvation and permeability of the coil are strongly restricted, and exclusion of the reactant from the inside of the coil may occur, leading to a decrease of the reaction rate up to complete cessation. The results of experiments of postquaternization described previously[15] are in agreement with this model. In these experiments, P4VP samples containing already 21.9, 31.1, and 54.7% groups quaternized with a ω-[(4′-methoxybiphenyl-4-yl)oxy]dodecyl bromide were reacted with an excess of *n*-butyl bromide at 355.5 K over 24 h, conditions where nearly fully quaternized samples are obtained with pure P4VP. The ratios obtained for *n*-butyl substitution were respectively 40.5, 36.0, and 27.9%, much lower than predicted. Obviously, the first reaction with a mesogenic group induced a contraction of the coil, preventing the further "normal" grafting of *n*-butyl bromide.

The above analysis shows that the hydrodynamic volume of the polymer coil has a complicated dependence on the extent of the quaternization reaction. The expansion of the coil at the first stages of the reaction implies that the reactivity of the pyridine residues is at least constant in this domain. This is in agreement with the general observation of the appearance of the retardation of the reaction after only 20–30% conversion. Our treatment, which supposes a constant value of β for the entire kinetics, is obviously not applicable in the initial stages. Further development of the model based on a clearer significance of β should include a variation of this parameter with the extent of the reaction. However, two important remarks may be made: (i) it is very likely that the more voluminous and nonpolar the alkylating agent is, the earlier the appearance of the contraction of the polymeric coil and (ii) eq 4 shows that the influence of β on T is weak in the initial stages, too weak to be experimentally observed under the usual conditions, and becomes significant after about 30% conversion. This last point is illustrated in Figure 6, where a 6% variation of β ($\pm 2\%$) hardly affects the slope of the theoretical kinetics up to about 30%. Both remarks may explain the good agreement between the experimental results and the theoretical treatment supposing β constant.

This scheme describing a conformational and exclusion effect during quaternization reactions is confirmed by published data and by our knowledge of such systems. It is in full agreement with the "steric effect" demonstrated in this paper and included in the proposed model. If tactic and electrostatic effects cannot be completely excluded, they have certainly a minor influence. Further experiments are needed to give a clearer theoretical significance to β. Characterization of the change of the conformation of the polymeric coil during the quaternization reactions is necessary to correlate a possible variation of the steric factor β with the conversion of the reaction and with the molecular weight of the starting P4VP. This last parameter, which may be of importance, has not been studied since the work of Fuoss et al.,[6] who noticed a slight tendency for the rate to increase with increasing molecular weight.

References and Notes

(1) Sherrington, D. C. *Encyclopedia of Polymer Science and Engineering*; Mark, H. F., et al., Eds.; John Wiley: New York, 1988; Vol. 4, p 101.

(2) Maréchal, E. *Comprehensive Polymer Science*; Bevington, A., Ed.; Pergamon Press: New York, 1989; Vol. 6 (1), p 24.

(3) Brown, H. C.; Cahn, A. *J. Am. Chem. Soc.* **1955**, *77*, 1715.

(4) Morcellet-Sauvage, J.; Loucheux, C. *Makromol. Chem.* **1975**, *176*, 315.

(5) Coleman, B. D.; Fuoss, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 5472.

(6) Fuoss, R. M.; Watanabe, M.; Coleman, B. D. *J. Polym. Sci.* **1960**, *48*, 5.

(7) Keller, J. B. *J. Chem. Phys.* **1963**, *38*, 325.

(8) Boucher, E. A. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 2295.

(9) Sawant, S.; Morawetz, H. *Macromolecules* **1984**, *17*, 2427.

(10) Boucher, E. A.; Mollett, C. C. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 75.

(11) Arends, C. B. *J. Chem. Phys.* **1963**, *39*, 1903.

(12) Boucher, E. A.; Groves, J. A.; Mollett, C. C.; Fletcher, P. W. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1629.

(13) Boucher, E. A.; Khosravi-Babadi, E.; Mollett, C. C. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 1728.

(14) Boucher, E. A.; Mollett, C. C. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 75.

(15) Navarro-Rodriguez, D.; Frère, Y.; Gramain, Ph. *J. Polym. Sci., Polym. Chem. Ed.*, in press.

(16) Navarro-Rodriguez, D.; Frère, Y.; Gramain, Ph. *Makromol. Chem.* **1991**, *192*, 2975.

(17) Platé, N. A. *Pure Appl. Chem.* **1976**, *46*, 49.

(18) Boucher, E. A.; Mollett, C. C. *J. Polym. Sci., Polym. Phys. Ed.* **1977**, *15*, 283.

(19) Boucher, E. A.; Khosravi-Babadi, E.; Mollett, C. C. *J. Chem. Soc., Faraday Trans. 1* **1978**, *74*, 427.

(20) Rappoport, Z. *Handbook of Tables for Organic Compound Identification*, 3rd ed.; CRC Press: Boca Raton, FL, 1967.

(21) Fuoss, R. M. *Discuss. Faraday Soc.* **1951**, *11*, 125.

(22) Ghesquiere, D.; Chachaty, C.; Ban, B.; Loucheux, C. *Makromol. Chem.* **1976**, *177*, 1601.

Registry No. P4VP, 25232-41-1; P2VP, 25014-15-7; P3VPCH$_3$, 25038-86-2; $Br(CH_2)_{12}O(C_6H_4\text{-}p\text{-})_2OCH_3$, 134254-01-6; $Br(CH_2)_8O(C_6H_4\text{-}p\text{-})_2OCH_3$, 134253-99-9; $Br(CH_2)_3H$, 106-94-5; $Br(CH_2)_3Ph$, 637-59-2; *i*-BuBr, 78-77-3; $H_2C{=}CHCH_2Br$, 106-95-6; $Br(CH_2)_2Ph$, 103-63-9; $BrCH_2Ph$, 100-39-0; $Br(CH_2)_5H$, 110-53-2; $Br(CH_2)_2H$, 74-96-4.