KINETICS OF QUATERNIZATION REACTIONS OF POLYMERIC AMINES*

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The paper deals with kinetics phenomena occurring in the quaternization of some polymeric amines, such as poly[2-(dimethylamino)ethyl methacrylate], poly{N-[3-(dimethylamino)propyl]--acrylamide}, and poly[2-(dimethylamino)ethyl methacrylate-*co*-2-hydroxyethyl methacrylate], with alkyl halides. The accelerating and slowing-down effects which take place in the alkylation reactions are discussed on the basis of the reaction course, i.e. of the dependence of differential rate constants on the conversion fraction of the reaction. Acceleration of the reaction is affected by the increasing polarity of microsurroundings of the reacting groups, while electrostatic and steric hindrances of the reacted groups slow down the reaction. Conformational effects, chemical and solvation interactions in the polymer–solvent–alkylating agent system and tacticity of the polymer are also operative.

The kinetics of polymeranalogous reactions is most often described using the model of adjacent groups[1], the validity of which has been checked mainly for a series of alkylating reactions of polymeric amines[2] or of hydrolyses of polymeric esters[3]. Such kinetic description is based on an assumption that the rate constants k_0, k_1, k_2 (constants for a functional group surrounded by none, one, or both reacted adjacent groups) do not vary during the reaction, i.e., that the rate constants are independent of the varying ionic strength, of the dielectric constant of the reaction medium, of the conformation and polarity of the macromolecule. If these constants are known, it is possible to determine the structure of intermediates of the polymeranalogous reaction, i.e. the content of triads in a copolymer composed of structural units, both reacted and unreacted. In our preceding paper[4] we came to a conclusion that in the quaternization of poly[2-(dimethylamino)ethyl methacrylate] with methyl iodide in water–ethanolic solutions the assumption of unvarying constants k_0, k_1, k_2 is not satisfied, or that the effect of more remote reacted groups becomes operative, and we suggested an empirical method[5] for determining the reaction course, i.e. the

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dependence of the differential rate constant on conversion of the reaction. The method consisted in that a polynomial of the fourth degree was plotted through experimental data, i.e. through the dependences of conversion fractions on the reaction time or through the dependences of kt vs t values (k is the integral rate constant, t is time), using the least squares method. By differentiating the polynomial, we calculated the differential rate constant as a function of the conversion fraction. The activation energies of the reaction were calculated from reaction courses at various temperatures as a function of the conversion fraction, and subsequently used to discuss effects which are operative in the polymeranalogous reaction.

EXPERIMENTAL

Kinetic data for the quaternization of poly[2-(dimethylamino)ethyl methacrylate] with methyl iodide and benzyl chloride were taken from the literature[6,7]. The quaternization of poly-[2-(dimethylamino)ethyl methacrylate-co-2-hydroxyethyl methacrylate] (PDAEM-HEMA) was measured by using a procedure described earlier[6].

RESULTS AND DISCUSSION

Fig. 1a−b shows dependences of the differential rate constant of quaternization of poly[2-(dimethylamino)ethyl methacrylate] (PDAEM) with methyl iodide in three various water–ethanol solvents and at different temperatures on the conversion fraction. The curves were calculated using a method reported earlier[5]. In Fig. 1 one
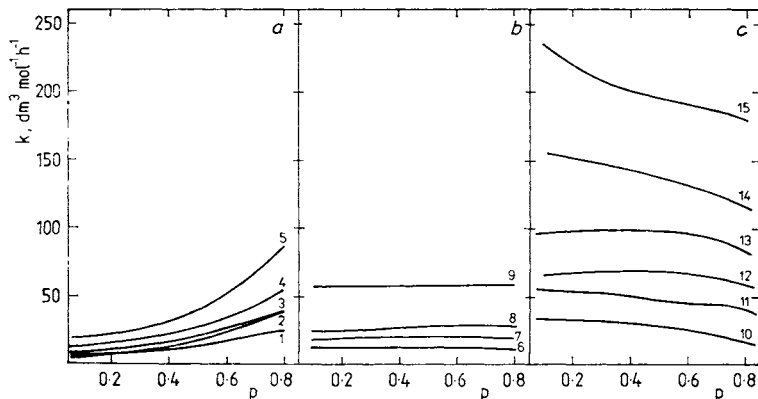

FIG. 1

Dependence of the differential rate constant (k) on conversion (p) of quaternization of poly[2--(dimethylamino)ethyl methacrylate] with methyl iodide in water–ethanolic mixture. a 4 wt.% water, b 43 wt.% water, c 64 wt.% water, at various temperatures: 11°C curves (1, 6, 10), 15°C (2, 7, 11), 20°C (3, 8, 12), 25°C (4, 13), 30°C (5, 9, 14) and 35·3°C (15)

can see that in the reaction medium of azeotropic ethanol (4 wt.% water) the rate constants at all recorded temperatutes increase with conversion, while in the reaction medium rich in water (64 wt.%) the reactivity decreases and in the reaction medium with 43 wt.% reactivity changes of the polymer during the reaction can be neglected within the limits of experimental error.

At high water content in the mixed solvent with ethanol there is a stronger preferential sorption of water by reactive groups of the macromolecule[8] or by its strongly charged quaternary ammonium reacted structural units, compared with the solvent having a low water content. The dielectric constant of the reaction medium in the immediate surroundings of reacted aminogroups increases during the reaction. According to the simple electrostatic theory of the effect of the dielectric constant on reactivity, the rate constant should increase during the reaction, as has indeed been observed in the reaction medium with a low water content (4 wt.%) in a mixture with ethanol. On the other hand, however, in a medium with a high water content (64 wt.%), where one would expect a still steeper rise, the reactivity decreased with conversion. This means that some other effects are also operative, along with the accelerating effect of the increasing dielectric constant.

The formation of an activated complex in the neighbourhood of an adjacent reacted unit can be represented by Scheme 1. Interactions of the amine and ammonium group with the carbonyl group in the case of esters containing amino
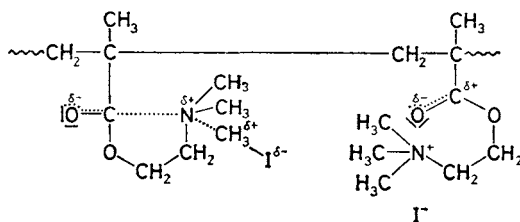
SCHEME 1

groups have been reported earlier[9] and recently verified by spectroscopy[10]. With the reacted ammonium group we have an interaction between the positive charge on the nitrogen atom and the polar carbonyl group. With the unreacted amine group the free electron pair of the nitrogen atom is somewhat delocalized by the carbonyl group, and this interaction is weakened in the formation of an activated complex, because a new covalent N—C bond is formed here.

The increasing polarity of the unreacted structural unit during the reaction due to the preferential sorption of water and to increasing number of positive charges on the macromolecule results in the steric and electrostatic repulsion of the polarized alkylating agent. The formation of an activated complex therefore requires an

increasingly higher activation energy in the course of the reaction. It can be expected that this effect will be less perceptible at lower conversions, when the polarity of the surroundings of uncreacted structural units has not yet significantly increased. Fig. 2 shows the dependence of the activation energy of quaternization of PDAEM in three various reaction media. In the reaction medium with 64 wt.% of water the activation energy increases from the conversion fraction, p, 0·3, in the medium with 43 wt.% the increase sets in from $p = 0·5$, while in azeotropic ethanol it does not begin before $p = 0·65$. In azeotropic ethanol we also observed an important decrease in the activation energy up to $p = 0·65$, which indicates less important steric and electrostatic hindrances in the formation of the activated complex, while at the same time suggesting an important accelerating effect of the increasing dielectric constant.

In a medium rich in water the reaction is also slowed down due to cyclic conformations[11] of side chains of the macromolecule (cf. also Scheme 1). With increasing polarity of the surroundings of unreacted structural units the polar rings become stabilized and the reactivity of the tertiary nitrogen atom is thus decreased, because its free electron pair is somewhat delocalized, due to an interaction with the carbonyl group. In azeotropic ethanol, where particularly in the initial stages of the reaction the reacted ammonium groups are hydrated to a low degree, the cyclic structures are probably not much stabilized, and the slowing-down effect does not occur. With increasing conversion the dielectric constant increases in the surroundings of hydrophilic quaternary ammonium groups due to the preferential sorption of water by reacted groups, which brings about an increase in the rate constant with conversion.

To estimate the effect of adjacent groups, we investigated the kinetics of quaternization of the statistical copolymer of 2-(dimethylamino)ethyl methacrylate with 2-hydroxyethyl methylacrylate (DAEM-HEMA). The content of reactive structural units DAEM was low (4·03 wt.%), in order to guarantee their mutual isolation. The nonreactive comonomer HEMA was chosen because it greatly resembles by its polarity the comonomer DAEM and one component of the solvent (ethanol). Moreover, the resulting copolymer DAEM-HEMA is readily soluble in the solvents under investigation. Fig. 3 shows the reaction course of quaternization of this copolymer with methyl iodide at various water contents in a mixed water–ethanol solvent. Unlike the kinetics of quaternization of the homopolymer PDAEM, we did not observe any acceleration effect in solvents with a low water content (the rate constant even slightly decreased with conversion). The reactive groups are isolated from each other by nonreactive structural HEMA units, so that in the close surroundings of tertiary amino groups the dielectric constant either does not vary too much, or its change is not sufficient to bring about the accelerating effect. On the other hand, at a high water content in the solvent, the decrease in reactivity with conversion remained preserved. Thus, the slowing-down effects are due not only to the adjacent groups — the reactivity is also affected by more distant groups.

Fig. 4 shows the absolute values of the rate constants of quaternization of PDAEM, of the copolymer DAEM-HEMA and of a low-molecular weight model compound, depending on the macroscopic polarity of the reaction medium. 2-Dimethylamino-ethyl pivalate (DAEP) was chosen as a model of the structural unit of PDAEM. From the kinetic standpoint DAEP behaves in an ideal way [a linear dependence of $\ln k$ on Kirkwood's fraction $(D - 1)/(2D + 1)$, where D is the dielectric constant of the reaction medium] and is the least reactive one in all solvents under investigation. The highest reactivity was observed with the homopolymer of PDAEM. This finding supports preceding conclusions, according to which the accelerating effect is due to the preferential sorption of water by the reacted groups in the macromolecule. In the case of partly quaternized PDAEM the increase in the polarity of microsur-
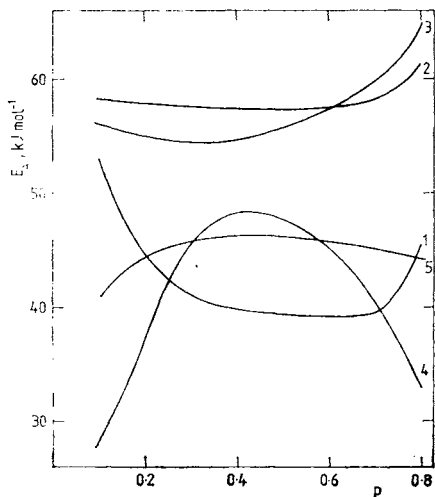
FIG. 2

Dependence of the activation energy (E_A) of quaternization reactions on the conversion fraction. Poly[2-(dimethylamino)ethyl methacrylate] (PDAEM) + methyl iodide in ethanol-water mixture, 4 wt.% (1), 43 wt.% (2), 64 wt.% (3) water, PDAEM + benzyl chloride in DMF (4) and poly{N-[3-(dimethylamino)propyl]acrylamide} (PDAPAA) + + benzyl chloride in N,N-dimethylacetamide (5)
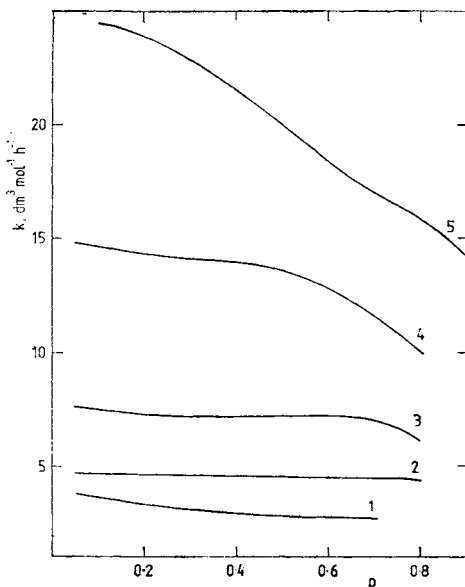
FIG. 3

Conversion dependence of the differential rate constant of quaternization of poly[2-(dimethylamino)ethyl methacrylate-co-2-hydroxyethyl methacrylate] (4·03 mole %) with methyl iodide at 11°C in water-ethanolic mixtures: 4 wt.% (1), 28 wt.% (2), 43 wt.% (3), 55 wt.% (4), 64 wt.% (5) water

roundings of the reacting group is larger than that observed with the copolymer DAEM-HEMA, where the amino groups are separated from each other by non-reactive HEMA units.

The preferential sorption of the more polar component of the mixed solvent by reacted groups of the macromolecule is probably not the only cause of the accelerating phenomena. During the quaternization of PDAEM with methyl iodide in anhydrous tetrahydrofuran (THF) or acetone, we also observed acceleration during the reaction (Fig. 5). Although in these one-component solvents no preferential sorption can take place, the charges formed raise the polarity of microsurroundings of amine groups, and the reactivity of the latter increases until the polymer begins to precipitate. On the contrary, in dimethylformamide (DMF), where the reaction is quite fast, no acceleration of the reaction could be observed (Fig. 5): the reaction was slowed down. Thus, the solvent has a basic effect on the absolute reaction rate and on the accelerating or slowing-down phenomena being predominant in the reaction. The dielectric constant of DMF $(D = 36.7)$ is approximately the same as in a water–ethanol mixture containing 28 wt.% water, where the reactivity increases with conversion. This is why the effect of the dielectric constant is not the only cause of the complicated phenomena observed here, but probably there occur such interactions between solvent and activated complex or the starting polymer which originate in the chemical nature of the solvent. The kinetic data measured by us do not provide any further details about these interactions, however.
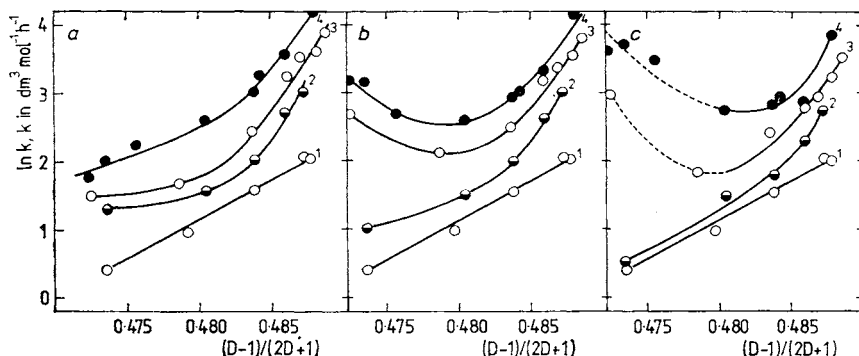

FIG. 4

Dependence of the logarithm of the differential rate constant on Kirkwood's fraction at 11°C and on conversion fractions 0·1 (a), 0·5 (b), 0·8 (c) in the quaternization of 2-(dimethylamino)-ethyl pivalate (1), poly[2-(dimethylamino)ethyl methacrylate-co-2-hydroxyethyl methacrylate] (2), atactic PDAEM (3) and isotactic PDAEM (4) with methyl iodide. D is the dielectric constant of the solvent. In the hatched part the reaction was not homogeneous, the solution was turbid

The fact that the dielectric constant is not the only cause of the kinetic behaviour of PDAEM is also indicated by the nonlinear character of the $\ln k$ vs $(D - 1)/(2D - 1)$ dependence for water–ethanolic reaction medium; if there is a change in the solvent, i.e., if DMF, THF or acetone is used, the experimental points are so scattered (Fig. 6) that no correlation could be found for them. It has been pointed out earlier that the effect of the dielectric constant need not predominate in the quaternization reactions[12]. The chemical nature of effects occurring in the alkylating reactions has already been pointed out by Muchin et al.[13] In the quaternization of PDAEM, where a polymer bearing strong charges arises from the low-polar polymer through a stage of the polar transition state, such chemical interactions seem quite likely to occur.

At higher conversions, the $\ln k$ vs $(D - 1)/(2D + 1)$ dependence describing the quaternization of PDAEM contains a pronounced minimum (Fig. 4); at a low water content (<43 wt.%) in the mixed solvent the reactivity decreases with the dielectric constant. This fact also shows the limited effect of the dielectric constant
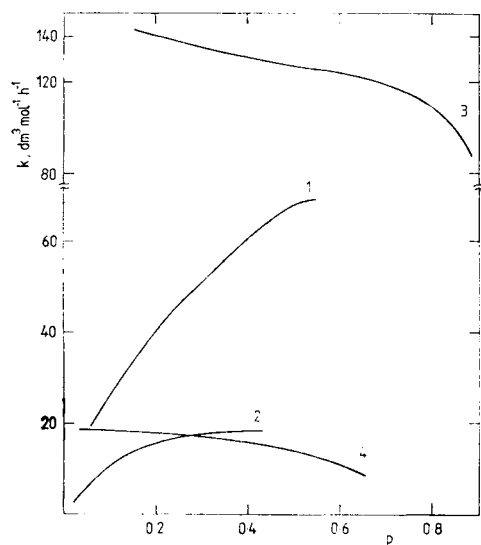

FIG. 5

Conversion dependence of the differential rate constant of quaternization of poly[2--(dimethylamino)ethyl methacrylate] with methyl iodide at 11°C in acetone (1), THF (2), DMF (3), and THF–water mixture (50·8 wt.% water) (4)
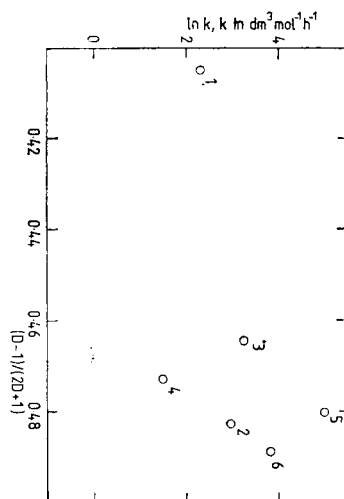
FIG. 6

Differential rate constants of quaternization of poly[2-(dimethylamino)ethyl methacrylate] with methyl iodide at 11°C and conversion fraction 0·1 in various solvents: THF (1), THF–water (50·8 wt.% water) (2), acetone (3), azeotropic ethanol (4), DMF (5) and ethanol–water mixture (70·9 wt.% water) (6)

in the quaternization reaction. The dielectric constant as a macroscopic quantity is probably only little connected by its size with the polarity of microsurroundings of the reacting parts. Moreover, polarity of the microsurroundings is affected by the reacted close structural units bearing a positive charge, or sometimes also iodide counterions.

Isotactic PDAEM behaves similarly to atactic PDAEM, but the former is the most reactive of the compounds investigated in this study (Fig. 4). This finding has already been attributed to the higher basicity, and thus nucleophilicity of the isotactic polymer[8].

The character of the reaction also depends on the choice of the alkylating agent. Fig. 7 shows dependences of the differential rate constants of quaternization of PDAEM with benzyl chloride in DMF at various temperatures. Here, the reaction is always accelerated; the content and strength of some interactions and the kinetics of elementary processes probably differ from those observed in reactions carried out in ethanol–water mixtures using methyl iodide. The curves in Fig. 7 were used to calculate the activation energies of individual conversions given in Fig. 2. While the E_A vs conversion dependence always has a minimum if mixed water–ethanol solvents are used, with DMF as the reaction medium there is a distinct maximum at the conversion 0·42.

The quaternization of poly(vinylpyridine) (PVP) is a polymeranalogous reaction which is very often used in the investigation[2]. In this case, slowing down of the reaction has always been observed, and has been assigned to electrostatic and steric effects of the adjacent reacted groups, which could be described by means of rate constants k_0, k_1, k_2. It has even been observed in the reaction of PVP with propyl bromide and benzyl bromide[2] that the relative slowing down does not depend on the character of the solvent. Although this finding is not a general one (e.g., in the
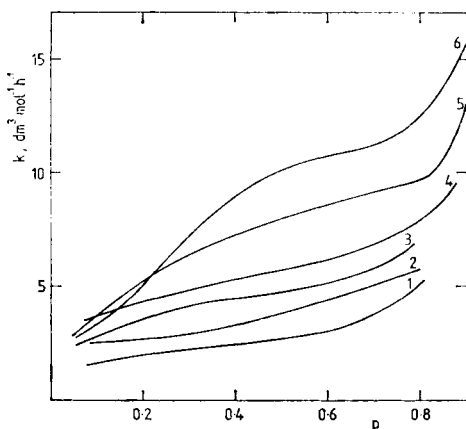

FIG. 7

Conversion dependence of the differential rate constant of quaternization of poly[2-(dimethylamino)ethyl methacrylate] with benzyl chloride in DMF: 50°C (1), 55°C (2), 60°C (3), 65°C (4), 70°C (5), and 75°C (6)

quaternization of PVP in a mixture of DMF and tetrahydrothiophene-1,1-dioxide[14] the slowing down effect is less pronounced with increasing amount of DMF, in pure DMF there is no slowing down at all, similarly to methanol[15]), it seems that from the kinetic standpoint the quaternization of PVP is much simpler compared with PDAEM. Similarly, the quaternization reactions of poly[4-(dimethylaminomethyl)-styrene] were slowed down[16], and the kinetic behaviour could be described in terms of the theory of adjacent groups. The predominant role played by the reacted adjacent groups in such reactions is also indicated by the fact that the kinetics of quaternization of copolymers with a lower content of reactive tertiary amino groups is second-order, and no slowing down occurs in the reaction[17,18].

Differences between the kinetic behaviour of PDAEM and PVP may be explained by the interactions between side chains of PDAEM already mentioned, or by their interactions with the solvent, or also with the alkylating agent. While in the case of PVP the groups capable of alkylation are near the macromolecular backbone, with which they are connected by a rigid aromatic ring, PDAEM contains reactive sites on a flexible chain with polar bonds and with a large number of possible conformations. For instance, cyclic conformations according to Scheme 1 cannot appear with PVP at all, and solvation phenomena will also probably be much weaker here than with polar side chains of PDAEM.

Dragan et al.[7] investigated the quaternization reactions of poly{N-[3-(dimethyl-amino)propyl]acrylamide} (PDAPAA) and observed an accelerating effect similar to that observed with PDAEM. These polymers are quite similar, and a similar kinetic behaviour can also be anticipated. Fig. 2 shows the reaction course of the activation energy of quaternization of PDAPAA with benzyl chloride, which has a maximum, similarly to the quaternization reaction of PDAEM with the same alkylating agent.

CONCLUSION

The following processes and phenomena may become operative in the quaternization of polymers containing amino groups:

1) Accelerating effects in water-poor media due to the increasing dielectric constant of microsurroundings of the reacting amino groups and to the rise in polarity as a consequence of the positive charges arising on the macromolecule.

2) Slowing down effects of adjacent or more remote reacted structural units. The slowing down is also affected by cyclic conformations of side chains of PDAEM and PDAPAA.

3) Chemical interactions in the polymer–solvent–alkylating agent system, solvation of the polymer and of the alkylating agent which depends on the chemical quality of the solvent.

4) Tacticity of the polymer.

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