Behavior

Precursors of Hydrophilic Polymers.
4[a] The Kinetics of Quaternization of Poly (2-Dimethylaminoethyl Methacrylate) with Methyl Iodide

M. Přádný, S. Ševčík, and P. Vlček

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, CS-162 06 Prague 6, Czechoslovakia

Summary
    The paper deals with a phenomenological description of the kinetics of quaternization of poly(2-dimethylaminoethyl methacrylates) (PDAEM) of various tacticity, brought about by methyl iodide at 11°C in water-ethanol solutions. At a low water content (below 43 mass %) in the mixed solvent the rate constant calculated by the integral method according to the second order increased with conversion of the reaction, while at a higher water content it decreased gradually from the originally high value. In a solvent containing 43 mass % water the rate constant of quaternization was almost independent of conversion, and from the kinetic viewpoint the polymer behaved as a low-molecular weight compound. In all solvents under investigation the isotactic polymer was more reactive than PDAEM having an atactic or syndiotactic structure. The reactivity of the polymers is compared with that of the low-molecular weight model compound, i.e. of 2-dimethylaminoethyl pivalate.

Introduction
    In some cases the reactivity of functional groups bound onto the polymer resembles that of analogous groups in low-molecular weight compounds, in others it is different. The reactivity of a functional group on the polymer chain is affected by many factors, such as steric, electrostatic and polar effects, solvation and interactions between adjacent groups (I). In the literature, attention is most often devoted to hydrolyses of polymer esters and to quaternization reactions of macromolecular amines in connection with the research of polyelectrolytes and ion exchangers.
    Of the quaternization reactions, those investigated in the greatest detail are the reactions of poly(vinylpyridines), poly(4-dimethylaminostyrene) and poly(ethyleneimine) with various alkylation agents (e.g., 2-5). A change in the rate constant of quaternization during the reaction was explained by the role of polymer effects (steric hindrances and electrostatic effect of already reacted and strongly charged groups on the adjacent, still unreacted functional groups). The quaternization kinetics was then usually treated using a second-order equation and the model of adjacent groups. Usually, too the kinetic equation contained three rate constants, k_0, k_1, k_2, characterizing the reactivity of the functional groups with both still unreacted adjacent groups (k_0), and with one (k_1) and two (k_2) already reacted adjacent groups (6,7).
    In this paper, the kinetic behaviour of poly(2-dimethylaminoethyl methacrylate) (PDAEM) in the quaternization reaction with methyl iodide and the effect of tacticity of the polymer on the rate of quaternization are described, and the rate of quaternization of PDAEM is compared with that of a low-molecular weight model compound.

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Experimental Part

    Isotactic and atactic PDAEM and 2-dimethylaminoethyl pivalate were pre-
pared by employing procedures described earlier (8-10). Syndiotactic PDAEM
was prepared by the anionic polymerization of the dry monomer (200 g) with
lithiumaluminium hydride (3 mol.%) in tetrahydrofuran (40% solution) at
-78°C. However, even repeated experiments did not lead to high tacticity
(96 syndiotactic triads) reported in the literature (11). The tacticity
reached by us was 68% of syndio- and 32% of heterotactic triads, $M_w=3 \times 10^4$.

    The quaternization reactions were carried out in an apparatus described
earlier (12). Instead of a feeding device (Fig.C in ref. 12), a glass am-
poule was used. A calibrated reaction flask (12-Fig.A) was filled with the
solvent (ethanol-water), and a weighed amount of the ethanolic polymer sol-
ution of known concentration was added. In the ampoule, a known amount of
methyl iodide was dissolved in the same solvent. After 30 min. of thermo-
stating of both parts of the apparatus to 11.00 ± 0.01°C, the contents of
the ampoule were transferred into the reaction flask, the mixture was
shaken, and at the same time the measurement of the reaction time began.
Than the initial volume of the reaction mixture was read off from the pos-
ition of the meniscus on the scale in the calibrated neck, and a thermo-
stated sampling device was employed (12-Fig.B). The samples were taken
using overpressure produced by syringe. In selected time intervals, the
samples were poured out into titration cells containing 0.1 N sulfuric
acid (50% theoretical excess with respect to amino groups, which stopped
the reaction. The concentration of the iodide ions thus formed was deter-
mined by potentiometric titration with a 0.1 N solution of silver nitrate
using a silver and mercury(II) sulfate electrode, by means of an automatic
titrator consisting of a TTT1 titrator, an automatic ABU 12 burette (0.25
or 2.5 ml in volume), and a recording device Titrigraph SBR 2c (Radiometer
Copenhagen).

Results and Discussion

    The integral rate constants (k_i) of quaternization of PDAEM with methyl
iodide were calculated using a second-order kinetic equation:

$$k_i = \frac{1}{t_i(a-b)} \ln \frac{b(a-x)}{a(b-x)} \tag{1}$$

in which a,b are the initial concentrations of methyl iodide and structural
units of the polymer, x is the concentration of reacted structural units,
i.e. the concentration of iodide ions at a time t_i. The data scattering
(especially at low initial concentrations a,b) did not allow us to calcu-
late the differential rate constants which would reflect the instantaneous
reaction course more adequately. The use of a second-order equation in the
kinetic description is justified by the fact that constant k_i is indepen-
dent of the initial concentrations of the polymer and methyl iodide as
proved in Fig.1 which illustrates the dependence of k_i on the conversion*
of quaternization of atactic and isotactic PDAEM at various concentrations
a,b and at various water content in the reaction medium. At the same time,
Fig. 1 gives an idea about the scattering of measured data.

    Similarly to the quaternization reactions of poly(vinylpyridine) (13)
and poly(4-dimethylaminostyren) (4), the rate constants in the case of
PDAEM are independent of the molar mass of the polymer. The polymer was
divided by precipitation into two fractions for which the rate constants
were measured as a function of the conversion of quaternization; no devi-
ations could be observed in the course of the reaction (Fig.2).
*for a>b, the conversion (%) of quaternization p=100 x/b; for a<b, p=100x/a
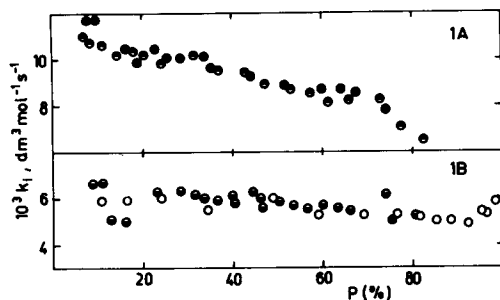
Fig.1 Verification of the validity of second-order kinetic equation. Dependence of the rate constant k_i on conversion p for various concentrations of structural units (a, mol dm^{-3}) of PDAEM and methyl iodide (b, mol dm^{-3}). 1A – atactic PDAEM in the reaction medium with 64 mass % water, 1 B – isotactic PDAEM, water content 44 mass %.
○ a=0,01501; b=0,1296, ◓ a=0,04531, b=0,04091, ◑ a=0,005011; b=0,01118, ● a=0,004853; b=0,001921.

Fig.2 Dependence of the rate constant on the conversion of quaternization of isotactic PDAEM in azeotropic ethanol for the high-molecular weight (●) and low-molecular weight (○) fraction.
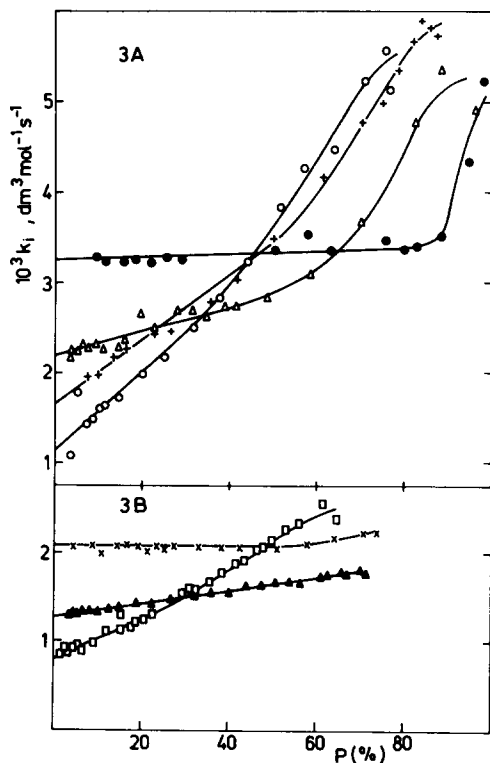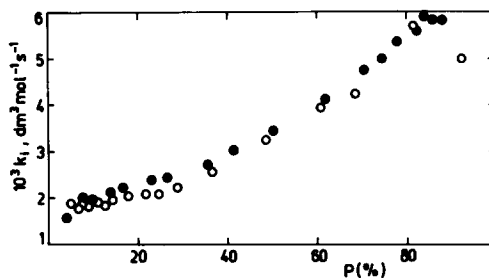

Fig.3 Dependence of the integral rate constant on the conversion of quaternization of isotactic (3A) and syndiotactic (3B) PDAEM at various water content in the reaction medium (mass %):
○ 0,7; + 4,0; △ 10,7; ● 29,9; □ 1,0; ▲ 18,3; ✕ 30,2.

Measurements of the rate constants of quaternization of PDAEM showed a strong dependence of the ·reaction course (i.e. the dependence of k_i values on conversion) on the water content in the reaction medium and on the tacticity of the polymer. Fig.3 shows the course of quaternization of isotactic (3A) and syndiotactic (3B) PDAEM in a reaction medium with a low water content (below 43 mass %). The rate constant of both polymers increases with conversion, the increase being steeper for isotactic PDAEM. The k_i vs. p dependence is linear, at least at lower conversions. Extrapolation of k_i to zero conversion gave rate constants of quaternization at the beginning of the reaction (k_o) which characterize the reaction disposition of the original polymer without strongly ionized quaternary ammonium groups. The values of the slopes (s_o) of lienar parts of the k_i vs p dependences decrease monotonically with increasing water content in the mixture; they are summarized in Table 1 for solvents of various composition and for polymers of various tacticity, along with extrapolated k_o values.

In a reaction medium with a high water content (above 43 mass %), where the reaction rate is high compared with the medium rich in ethanol, the rate constant decreased with conversion for all types of PDAEM; the isotactic polymer kept the highest reactivity. Fig.4 demonstrates this reaction course for isotactic and syndiotactic PDAEM. The dependence of the integral rate constant on conversion was linear at least up to a conversion of 65%, even in the range of high water concentrations; extrapolated k_o and s_o values are given in Table 1.
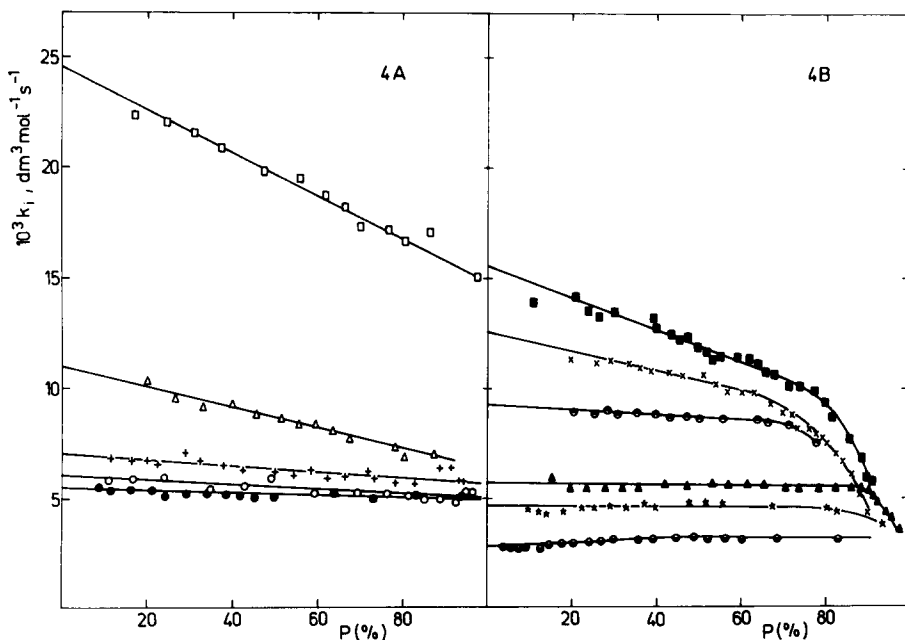

Fig.4 Dependence of the rate constant on the conversion of quaternization of isotactic (4A) and syndiotactic (4B) PDAEM at various water content in the reaction medium (mass %): ● 43,0; ○ 44,0; + 45,4; △ 55,0; ☐ 70,1; ◓ 43,0; ⋆ 51,3; ▲ 55,0; ◓ 61,8; x 66,7; ■ 70,0.

Table 1

Quaternization rate constants k_o ($dm^3mol^{-1}s^{-1}$) extrapolated to zero conversion and the slope s_o ($dm^3mol^{-1}s^{-1}$) of linear parts of the k_i vs p dependence for PDAEM of various tacticity at 11°C and with water in the reaction medium (c_{H_2O}, mass %).

				Polymer				
	isotactic			syndiotactic			atactic	
c_{H_2O}	10^3k_o	10^5s_o	c_{H_2O}	10^3k_o	10^5s_o	c_{H_2O}	10^3k_o	10^5s_o
0.7	1.15	4.4	1.0	0.80	2.1	1.0	0.96	1.3
4.0	1.65	3.8	18.3	1.26	0.75	21.5	1.52	0.72
10.7	2.20	1.3	30.2	2.03	0.16	43.0	3.81	0.12
29.9	3.25	0.25	43.0	2.80	0.07	57.5	7.57	-1.5
43.0	5.51	-0.86	51.3	5.40	-0.07	64.0	11.2	-4.2
44.0	5.61	-1.2	55.0	5.60	-0.07	70.1	12.6	-4.3
45.4	7.08	-1.6	61.8	9.20	-0.28	75.9	15.7	-4.3
55.0	11.0	-6.5	66.7	12.5	-1.6			
70.1	24.3	-9.3	70.0	15.5	-7.2			

The atactic polymer approaches syndiotactic PDAEM by its tacticity, and its reactivity is therefore also similar. The reaction courses are summarized in Fig.5, and the extrapolated k_o and s_o values are given in Table 1.

For the description of the quaternization of low-molecular weight amines in mixed solvents, the validity of a linear dependence of the logarithm of rate constant on $\frac{D-1}{2D+1}$ (Kirkwood's relation) where D is the dielectric constant of the solvent, has been confirmed in the literature many times. In this study, too, the validity of this relation has been verified for the low-molecular model of the structural unit of PDAEM (i.e. for 2-dimethyl-aminoethyl pivalate), as shown in Fig.6. For all polymers, however, a steep rise in reactivity was observed in solvents containing more than 43 mass % water. Fig.6 also shows the lowest reactivity of the low-molecular weight model compound compared with all polymers under study.

In the quaternization reactions of poly(vinylpyridines) (2), poly(4-dimethylaminostyrene) (4) and poly(ethyleneimine) (5), the reactivity decreased with conversion of the reaction, while, e.g., in the amination reactions of chloromethylated polystyrene (15) acceleration effects appeared, the cause of which was seen in the different electrostatic and steric effect of the already reacted groups on the adjacent, still unreacted ones. Also in our case these effects will probably be operative simultaneously, with the acceleration effects predominating in media poor in water. Their essential feature might be preferential sorption of one component of the solvent on the macromolecule in the course of the reaction (sorption of water on the forming ammonium groups) or conformational changes of the side chains. The prevalent deceleration phenomena in water-rich media may be based on electrostatic and steric hindrances of adjacent groups described in the literature earlier. These effects will be examined in a further paper.
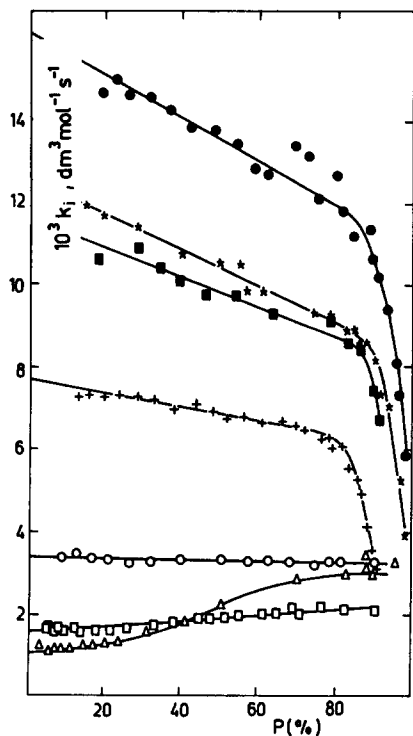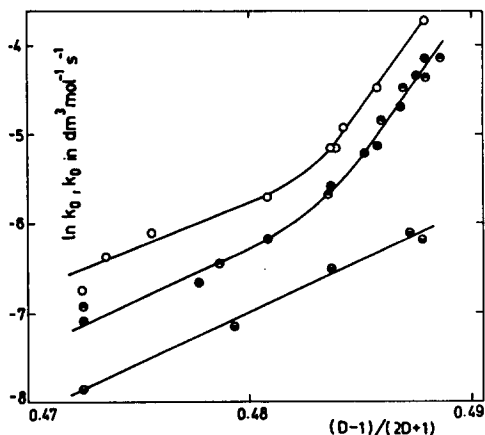
Fig.5 Dependence of the rate constant on the conversion of quaternization of atactic PDAEM at various water content in the reaction medium (mass %) Δ 1.0; ☐ 21.5; ○ 43.0; + 57,5; ■ 64.0; ✶ 70.1; ● 70.9.

Fig.6 Dependence of the logarithm of rate constant on $(D-1)/(2D+1)$, where D is the dielectric constant of the reaction medium: ○ isotactic, ● syndiotactic, ◐ atactic PDAEM, ◓ 2-dimethylaminoethyl pivalate.

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