Makromol. Chem. 178, 2205-2210 (1977)

Institute of Organic Chemistry, University of Mainz, Johann Joachim Becher-Weg 18–20, D-6500 Mainz, W.-Germany

On the Kinetics of the Polymerization of Some Ammonium Methacrylates with Different Alkyl Chain Lengths in Aqueous Solution

Helmut Ringsdorf and Dieter Thunig

(Date of receipt: October 19, 1976)

SUMMARY:

Methacryloyloxyalkyltrimethylammonium chlorides (1a-c) with different alkyl chain lengths were synthesized and polymerized radically with 4,4'-azobis(4-cyanovalerianic acid) and K₂S₂O₈ as initiators. With K₂S₂O₈ as initiator, reaction orders of 0,5 and 1 with respect to initiator and monomer, were found. For the ionic monomers with longer alkyl chains the ratio of rate constants $k_p(2fk_d/k_l)^{0.5}$ was determined over a wide concentration range. It was found that with decreasing monomer concentration the ratio of rate constants increases, which is caused by a diminished termination rate because of an increased electrostatic repulsion of the ionic polymer radicals in dilute solution (increase of dissociation). Methacryloyloxyethyltrimethylammonium chloride (1a) doesn't show this effect. This can be explained by the diminished effective charge of the ammonium group in the preferred gauche conformation of the molecule.

Introduction

Ionic vinyl monomers have been mainly synthesized and polymerized because the obtained ionic homo- and copolymers are used in a variety of industrial products as thickeners, dispersants, flocculants, ion exchange resins, etc. Their suitability for these applications can be referred to the great hydrophilicity and especially to the highly polar character which enable these substances to adsorb other polar compounds, such as dye-stuffs, charged colloidal particles and ions. The unique character of the polymers has finally attracted attention to the monomers itself resulting in some kinetic studies predominantly in aqueous solution¹.

Recently, ionic monomers with large hydrophobic groups have gained special interest again. Such surface active micelle-forming monomers exhibit a kinetically different behavior than ionic monomers not capable of forming aggregations²). The polymers obtained from micellar monomer solutions are expected to have a frozen "micelle-like" molecular structure³).

Micelle formation was also supposed to explain why two completely different polymerization products are obtained from the "spontaneous" polymerization of 4-vinylpyridinium salts⁴⁻⁶). However, a more detailed investigation of this reaction showed that two mechanisms—an anionic and a radical one—are responsible for the formation of the different products and left in doubt whether the assumption of aggregation is necessary^{7,8}).

The results presented in this paper also show that dramatic changes in the kinetics of an ionic monomer must not necessarily be caused by aggregation.

The polymerization kinetics of methacryloyloxyalkyltrimethylammonium chlorides (1) with different alkyl chain lengths (n=2,3,6) are subject of this paper. These compounds don't form micelles as evidenced by their electrical conductivity data. The considerable change found

in the ratio of rate constants $k_p/(k_t^{0,5})$ with increasing chain length must be ascribed to the ionic character of the monomers (k_p =rate constant of polymerization; k_t =rate constant of termination).

H₂C==C(CH₃)--CO₂--(CH₂)_n--
$$\mathring{N}$$
(CH₃)₃Cl⁻
1a: n=2
b: n=3
c: n=6

Results and Discussion

Radically initiated polymerization

Two initiators, potassium peroxodisulfate and 4,4'-azobis(4-cyanovalerianic acid) were used as initiators for starting the polymerization of the methacryloyloxyalkyltrimethylammonium chlorides in aqueous solution. A reaction order of 0,5 with respect to the initiation was found for the potassium peroxodisulfate.

For the 4,4'-azobis(4-cyanovalerianic acid), however, the reaction order n with respect to the initiator increases with increasing monomer concentration $[M]_0$ (n=0,13 for $[M]_0=0,14$ mol/l, n=0,31 for $[M]_0=0,97$ mol/l). The increased deviation from the "square root law" with decreasing monomer concentration can be explained by a preferred chain termination with primary radicals⁹. A possible explanation for this behavior is that the initiator is adsorbed at the polymer molecules, thereby resulting in an increased effective initiator concentration in the immediate vicinity of the polymer radicals.

With potassium peroxodisulfate as initiator a reaction order of one with respect to the monomer was found for all three monomers. This is shown in Fig. 1 where the first order plot for different initial monomer concentrations of methacryloyloxyethyltrimethylammonium



Fig. 1. First order plot of the polymerization of methacryloyloxyethyltrimethylammonium chloride (1a) in aqueous solution for different initial monomer concentrations: (a)=0,14 mol 1^{-1} , (b)=0,48 mol 1^{-1} , (c)=0,97 mol 1^{-1} , (d)=1,28 mol 1^{-1} , (3)=2,35 mol 1^{-1} . Initiator (I): K₂S₂O₈; temp.: 60 °C

chloride (1a) gives straight lines. From the slopes the ratio of rate constants $k_p(2fk_d/k_l)^{0.5}$ can be evaluated (k_d = rate constant of dissociation, f = efficiency factor).

Fig. 2 gives a summarized view of the ratio of rate constants obtained for all three investigated monomers **1a–c** as a function of the initial monomer concentration.



Fig. 2. Polymerization of methacryloyloxyalkyltrimethylammonium salts (1) in water. (\circ): 1c; (\triangle): 1b; (\Box): 1a. Initiator: K₂S₂O₈; temp.: 60°C

The ratio of the rate constants shows a marked dependence on the length of the carbon chain and on monomer concentration. The largest difference is observed in dilute solution where, contrary to 1a, a steep increase of the ratio of the rate constants is found for the methacryloyloxyhexyltrimethylammonium salt (1c) and to some extent for the methacryloyloxy-propyltrimethylammonium salt (1b). For monomer concentrations higher than 0.5 mol/l, the rate constants of all three monomers seem to be independent of the monomer concentration.

Since 1a and 1c show no significant differences in the concentration dependence of the electrical conductivities (they behave more like inorganic 1,1-electrolytes than like ionic detergents), significant differences in aggregation of the two monomers can be ruled out^{10} . Therefore, it is evident that electrostatic effects are a more plausible explanation for the experimental results. Since the equally charged species must approach each other in each elementary step of the polymerization, the electrostatic effects are strongest in dilute water solution, where the electrolytes, monomers and polymers are highly dissociated:



The value of $k_p(2fk_d/k_t)^{0.5}$ was found to be predominantly influenced by variations of k_t —caused for instance by changes of the solvent viscosity^{11,12} or by an increase in the volume of the monomer substituent¹³. Referring to these findings the steep increase of $k_p(2fk_d/k_t)^{0.5}$ for compound **1c** can be explained by a decrease in k_t , because the terminating radicals are repelling each other.

This effect has also been observed for sodium methacryloyloxyethylsulfonate in dilute aqueous solution. There was no increase when the dissociation was suppressed by the addition of foreign salt¹⁴).

1a represents an exceptionel case in its kinetical behavior. No increase of $k_p (2fk_d/k_t)^{0.5}$ on dilution was observed. The reason for this can be that the molecule exists in a gauche conformation where an interaction of the non-bonded electron pair of the ester oxygen with the positively charged ammonium group is possible as shown in structure **A**. The consequence is that the effective positive charge is diminished.



Experimental Part

Monomers

The monomeric salts, methacryloyloxyethyltrimethylammonium chloride (1a) and methacryloyloxypropyltrimethylammonium chloride (1b) were donated by the Röhm Company, Darmstadt, W.-Germany. For the kinetic studies the salts were recrystallized twice from ethylacetate/ethanol (2:1) without heating, followed by an addition of ether.

Methacryloyloxyethyltrimethylammonium chloride (1a): mp 170-171 °C (polymerization).

C ₉ H ₁₈ ClNO ₂ (207,7)	Calc.	C 52,08	H 8,74	N 6,74	Cl 17,07
	Found	C 51,70	H 8,83	N 6,77	Cl 17,29

Methacryloyloxypropyltrimethylammonium chloride (1b): mp 162–163 °C (polymerization).

C ₁₀ H ₂₀ ClNO ₂ (221,7)	Calc.	C 54,17	H 9,09	N 6,32	Cl 15,99
	Found	C 54,14	H 8,95	N 6,14	Cl 15,74

Methacryloyloxyhexyltrimethylammonium chloride (1c): It was synthesized by passing methylchloride gas through 500 ml of boiling acetone (0,1 g Phenothiazine was added). Simultaneously a solution

of 0,1 mol (22 g) of 6-dimethylaminohexyl methacrylate in 100 ml of acetone was slowly added. The precipitate was recrystallized twice from acetone. Yield: 21 g (80%), mp 135–136 °C.

C₁₃H₂₆ClNO₂ (263,8) Calc. C 59,19 H 9,93 Cl 13,44 N 5,31 Found C 59,33 H 9,73 Cl 12,93 N 5,38

6-Dimethylaminohexyl methacrylate: Two solutions -36.3 g (0.25 mol) of 6-dimethylaminohexanol and 26.3 g (0.25 mol) of methacryloylchloride dissolved in 30 ml of dry methylene chloride, respectively were slowly and simultaneously added to a vigorous stirred solution of 0.5 g of 1.3-dinitrobenzene in 50 ml methylene chloride. By cooling with ice and regulation of the addition rate the temperature was kept below 10°C.

The solution was treated twice with 50 ml of 2 N aqueous sodium hydrogen carbonate solution and twice with 50 ml of water. After drying over sodium sulfate the solvent was removed i. vac. The residue was distilled, bp 80-82 °C (≈ 0.3 mbar); n_D^{20} 1,4500 [Lit.¹⁹: bp 109-114 °C (2 mm); n_D^{20} 1,4480]. Yield: 27,5 g (52%).

For analysis 6-dimethylaminohexyl methacrylate was quaternized with methyl iodide: dec.-p. 137°C.

C ₁₃ H ₂₆ INO ₂ (355,3)	Calc.	C 43,95	H 7,38	N 3,94	1 35,72
	Found	C 43,74	H 7,57	N 3,85	I 36.06

6-Dimethylaminohexanol: A mixture of 273 g (2 mol) of 6-chlorohexanol and 650 ml of a 40% aq. dimethylamine solution was heated 24 h in a steel autoclave at 100 °C. To the reaction product 200 g of a 50% aq. potassium hydroxide solution was added. The solution was extracted four times with 200 ml of benzene, then it was dried over potassium carbonate, the solvent was removed and the residue was distilled. bp 120 °C ($\approx 16 \text{ mbar}$); n_D^{25} 1,4458 [Lit.²⁰]: bp 115 °C (14 mm); n_D^{25} 1,4462]. Yield: 218 g (75%).

For analysis 6-dimethylaminohexanol was quaternized with methyl iodide: mp 124°C.

C ₉ H ₂₂ INO	Calc.	C 37,64	H 7,72	N 4,89	I 44,19
	Found	C 38,03	H 7,91	N 4,66	I 44,28

6-Chlorohexanol: It was synthesized by esterification of 1,6-hexanediol with hydrogenchloride²¹⁾.

Methacryloylchloride was synthesized from methacrylic acid by exchange of the acid chloride function by benzoylchloride²²⁾.

Kinetic studies

Samples of the salts (1a-1c) and the aqueous solution of the initiator were separately degassed three times and mixed i. vac. The dilatometers were either filled i. vac. using a special apparatus similar to that of *Baer*²³⁾ or under a steady stream of nitrogen with a pipette. The volumes of the dilatometer had been between 2,5 and 12 ml and were connected by a ground joint with either a 50 or a 100 μ l capillary. Polymerization temperatures were kept constant within ± 0.02 °C.

In order to get a conversion-volume contraction relationship the polymerization was quenched by cooling in ice, the solution was diluted and the residual UV-absorption determined.

- ¹⁾ "Functional Monomers", Ed. by. R. H. Yocum and E. B. Nyquist, Marcel Dekker, New York 1973 (I), 1974 (II), Vol. I and II
- ²¹ J. C. Salamone, P. Taylor, B. Snider, S. C. Israel, Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem. 15 (1), 462 (1974)
- ³⁾ K. Kammer, H. G. Elias, Kolloid Z. Z. Polym. 250, 344 (1972)
- ⁴⁾ I. Mielke, H. Ringsdorf, J. Polym. Sci., Part C, **31**, 107 (1970)
- ⁵⁾ I. Mielke, H. Ringsdorf, Makromol. Chem. 153, 307 (1972)
- ⁶⁾ V. Martin, H. Ringsdorf, H. Ritter, W. Sutter, Makromol. Chem. 176, 2029 (1975)
- ⁷⁾ V. Martin, W. Sutter, H. Ringsdorf, Makromol. Chem. 177, 89 (1976)
- ⁸⁾ V. Martin, H. Ringsdorf, D. Thunig, "Midland Macromolecular Monographs", Gordon and Breach Science Publishers Ltd., New York, Vol. 111, p. 175
- 9) J. C. Bevington, "Radical Polymerisation", Academic Press, New York 1961, p. 148-152
- ¹⁰⁾ D. Thunig, Ph. D.-Thesis, University of Mainz, W.-Germany

- ¹¹⁾ A. M. North, G. A. Reed, J. Polym. Sci., Part A, 1, 1311 (1963)
- ¹²⁾ G. V. Schulz, Chem. Technol. 3, 220 (1973)
- ¹³⁾ N. A. Platé, A. G. Ponomarenko, Polym. Sci. USSR (Engl. Transl.) 16, 3067 (1974)
- ¹⁴⁾ D. A. Kangas, J. Polym. Sci., Part A-1, 8, 1813 (1970)
- ¹⁵⁾ A. F. Casy, M. M. Hossan, E. C. Wu, J. Pharm. Sci. 60, 67 (1971)
- ¹⁶⁾ R. J. Cushley, H. G. Moutner, Tetrahedron 26, 2151 (1970)
- ¹⁷⁾ C. C. J. Culvenor, N. S. Ham, Chem. Commun. 1966, 537
- ¹⁸⁾ H. Kunz, Justus Liebigs Ann. Chem. 1973, 2001
- ¹⁹⁾ M. A. Korshunov, F. N. Bodnaryuk, Zh. Org. Khim. 4, 1023 (1968)
- ²⁰⁾ B. C. Barrass, R. W. Brimblecombe, P. Rick, Joan V. Taylor, Brit. J. Pharmacol. 39, 40 (1970)
- ²¹⁾ A. Müller, W. Vanc, Monatsh. Chem. **77 B**, 259 (1947)
- ²²⁾ G. H. Stempel, R. P. Cross, R. P. Mariella, J. Am. Chem. Soc. 72, 2299 (1950)
- ²³⁾ M. Baer, J. A. Caskey, A. L. Fricke, Makromol. Chem. 158, 27 (1972)