Reactivity of *N*-alkylated cyclic iminoether salts having vinyl groups, 2 [a]

Polymerization and copolymerization of 2-isopropenyl-3-methyl-2-oxazolinium salts

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SUMMARY:
   3-Methyl-2-isopropenyl-2-oxazolinium salts (**4a, b**) were prepared by alkylation of 2-isopropenyl-2-oxazoline (**2**). Their preparation is much easier than that of their vinyl analogues, 3-methyl-2-vinyl-2-oxazolinium salts, which cannot be isolated due to their high tendency to polymerization. **4a**, however, was found, to show a low tendency toward radical and anionic polymerization, but it can be smoothly radically copolymerized with some vinyl monomers. The copolymerization parameters of **4a** were determined and discussed in comparison with those of **2**.

Introduction

2-Alkenyl-2-oxazolines are polymerized by three modes; one is the cationic ring-opening polymerization (Eq. (1a)) to produce the corresponding *N*-acyl derivative of polyethyleneimine[1-3], another one is the cationic polymerization (Eq. (1b)) to give polymers in which the oxazoline ring is preserved[4] and the third one is the radical or anionic polymerization (Eq. (1c)) of the olefinic bond to produce poly[1-(2-oxazolin-2-yl)alkene]s[4-8]. In a previous paper[9] we reported on the fourth mode of polymerization of 2-vinyl-2-oxazoline (**1**) which occurs spontaneously during the process of *N*-alkylation of the oxazoline moiety with strong alkylating agents, such as trialkyloxonium salt, and alkyl sulfate and sulfonate, to produce poly[1-(3-alkyl-2-oxazolinium-

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[a]   Part 1: cf.[9].
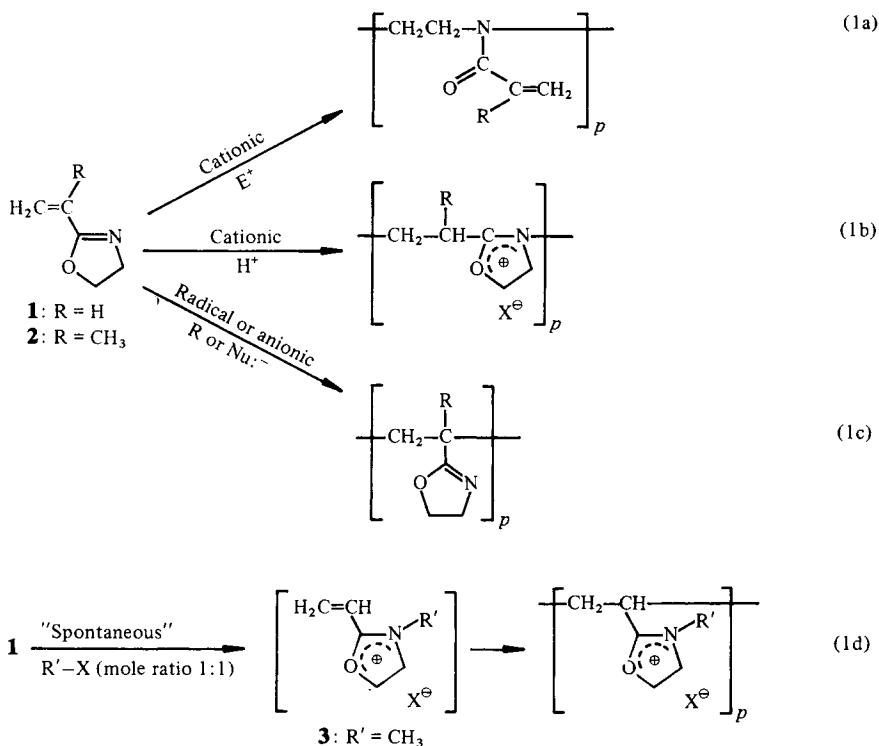
2-yl)ethylene]s (Eq. (1 d)). Therefore, this polymerization was called "spontaneous" polymerization upon quaternization (N-alkylation) on reference to the analogous polymerization of vinylpyridines[10–15]. Concerning the spontaneous polymerization of 1 it has been assumed that the 3-methyl-2-vinyl-2-oxazolinium salt (3), first formed by alkylation of 1, is polymerized by an anionic mechanism via initiation by a nucleophilic attack at the free monomer 1. The intermediate salt could not be isolated because it is too reactive and easily polymerized. The present paper is concerned with the polymerization of 2-isopropenyl-3-methyl-2-oxazolinium salts (4a, b) which can readily be isolated after alkylation of 2-isopropenyl-2-oxazoline (2). In contrast to 1, 2 is not spontaneously polymerized on quaternization. This paper reports on anionic and radical homo- and co-polymerizations of 4a, b. The resulting copolymers with vinyl monomers are of interest since they carry the reactive ionic moiety of oxazolinium salts.

Experimental part

Materials: 2-Isopropenyl-2-oxazoline (2) was prepared according to the literature[16,17], purified by repeated distillation at reduced pressure and stored over molecular sieves (4 Å). Trimethyloxonium and triethyloxonium tetrafluoroborates were prepared according to the proce-

dure of Meerwein[18]. Methyl fluorosulfonate was prepared as reported before[19]. Other reagents and solvents were commercial ones, which were purified by conventional methods.

Instrumentation: ^{1}H NMR spectra were recorded on a Hitachi R-20B spectrometer at 60 MHz. ^{13}C NMR spectra were recorded on a Hitachi R-900 Fourier transform spectrometer operating at 22,6 MHz. IR spectra were recorded on a Hitachi 260-20 infrared spectrometer. Melting points were measured by DSC (Rigaku Thermoflex DSC) under nitrogen.

Preparation of 2-isopropenyl-3-methyl-2-oxazolinium salts (**4a, b**): To an ice-cooled solution of the alkylating agent in CH_2Cl_2, an equimolar amount of **2** was added dropwise with vigorous stirring. After the mixture had been maintained at 0 °C for 30 min, a large excess of diethyl ether was added to precipitate the crude oxazolinium salt, which was then purified by repeated recrystallization from dichloromethane/ diethyl ether (vol. ratio 1:1), and finally dried i. vac. All the procedures were carried out under dry nitrogen owing to the hygroscopic property of the salts.

2-Isopropenyl-3-methyl-2-oxazolinium tetrafluoroborate (**4a**): Prepared from **2** and tri-methyloxonium tetrafluoroborate: White needles; m. p. 69 °C.

^{1}H NMR (CD_3CN): δ = 2,10 (t; 3H, CH_3—C), 3,40 (s; 3H, CH_3—N), 4,05 – 4,40 (m; 2H, CH_2—N), 4,79 – 5,17 (m; 2H, CH_2—O), 6,00 (m; 1H, C=CH trans), 6,17 (m; 1H, C=CH cis).

^{13}C NMR (CD_3CN): δ = 19,16 ($\underline{C}H_3$—C=C), 36,43 (CH_3—N), 53,96 (C_4), 71,91 (C_5), 128,16 (C_α), 132,34 (C_β), 174,01 (C_2).

IR (CH_2Cl_2): 1657 (C=N), 1485, 1060, 952 cm^{-1}.

$C_7H_{12}BF_4NO$ (213,0)				
	Calc.	C 39,47	H 5,68	N 6,58
	Found	C 39,36	H 5,76	N 6,52

2-Isopropenyl-3-methyl-2-oxazolinium fluorosulfonate (**4b**): Prepared from **2** and methyl fluorosulfonate: White needles; m. p. 82 °C.

^{1}H NMR (CD_3CN): δ = 2,11 (t; 3H, CH_3—C), 3,42 (s; 3H, CH_3—N), 4,05 – 4,43 (m; 2H, CH_2—N), 4,80 – 5,16 (m; 2H, CH_2—O), 6,00 (m; 1H, C=CH trans), 6,17 (m, 1H, C=CH cis).

^{13}C NMR (CD_3CN): δ = 19,02 ($\underline{C}H_3$—C=C), 36,55 (CH_3—N), 54,21 (C_4), 72,15 (C_5), 128,42 (C_α), 132,47 (C_β), 173,60 (C_2).

IR (MeCN): 1660 (C=N), 1283 (S=O), 715, 565 cm^{-1}.

$C_7H_{12}FNO_4S$ (225,2)				
	Calc.	C 37,33	H 5,37	N 6,22
	Found	C 37,14	H 5,54	N 6,38

Procedure for radical polymerization: A typical procedure was as follows. In a tube equipped with a three-way stop-cock and a magnetic stirrer bar, 3 mmol of **4a** and 0,09 mmol of AIBN were allowed to dissolve in 1 ml of *N,N*-dimethylacetamide (DMAc). The solution was then maintained at 60 °C for 50 h. After the reaction, the mixture was poured into 50 ml of CH_2Cl_2 to precipitate the polymeric product. The precipitate was isolated by decantation which was purified further by repeated reprecipitation from acetonitrile (solvent) to CH_2Cl_2 (non-solvent), and dried i. vac. A pale yellow solid polymer was obtained; yield: 0,10 g (16%).

The supernatant layers of repeated re-precipitations were combined and concentrated by evaporation to recover unreacted **4a**. All the procedures were carried out under nitrogen.

5 [poly(**4a**)]: Pale yellow, powdery solid.

^{1}H NMR (CD_3CN): δ = 1,1 – 1,8 (3H, CH_3—C), 1,9 – 2,8 (2H, CH_2), 3,3 – 3,8 (3H, CH_3—N), 4,0 – 4,7 (2H, CH_2—N), 4,8 – 5,3 (2H, CH_2—O).

IR (Nujol): 1640 (C=N), 1300, 1050 (B—F), 718 cm^{-1}.

$(C_7H_{12}BF_4NO)_n$ (213,0)$_n$				
	Calc.	C 39,47	H 5,68	N 6,58
	Found	C 39,46	H 6,05	N 6,63

Procedure for radical copolymerization: A typical example, carried out under nitrogen, was as follows. In a tube equipped with a three-way stop-cock and a magnetic stirrer bar, 1,00 mmol

of **4a**, 0,16 mmol of AIBN, and 4,33 mmol of methyl acrylate (MA) were dissolved in 3 ml of DMF. The solution was kept at 60 °C for 30 h. The mixture was then poured into 50 ml of CH_2Cl_2 to precipitate the copolymer, which was isolated as described above. Yield of pale yellow solid copolymer: 0,20 g (91%).

The supernatant layers of repeated precipitation were combined and concentrated by evaporation. No additional polymeric material was obtained from the supernatant layer.

Poly(**4a**-*co*-MA): ^{1}H NMR (CD$_3$CN): δ = 0,9 – 1,4 (CH$_3$—C), 1,5 – 2,5 (CH$_2$—C and CH—C(O)), 2,8 – 3,7 (CH$_3$—N and CH$_3$—O), 3,9 – 4,2 (CH$_2$—N), 4,4 – 4,9 (CH$_2$—O).

IR (KBr): 2940, 2870, 1730 (C=O), 1640 (C=N), 1435, 1160, 1055 (B—F), 727 cm^{-1}.

Poly[**4a**-*co*-MMA]: ^{1}H NMR (CD$_3$CN): δ = 0,8 – 1,2 (CH$_3$—C), 1,4 – 2,1 (CH$_2$—C), 3,0 – 3,6 (CH$_3$—N and CH$_3$—O), 3,8 – 4,3 (CH$_2$—N), 4,4 – 4,9 (CH$_2$—O).

IR (KBr): 2990, 2945, 1735 (C=O), 1630 (C=N), 1445, 1235, 1140, 1057 (B—F), 985, 745 cm^{-1}.

Poly[**4a**-*co*-VAc]: ^{1}H NMR (CD$_3$CN): δ = 0,9 – 1,6 (CH$_3$—C), 1,7 – 2,8 (CH$_3$—C(O) and CH$_2$—C), 3,0 – 3,6 (CH$_3$—N), 3,8 – 4,4 (CH$_2$—N), 4,5 – 5,1 (CH$_2$—O and CH—O).

^{13}C NMR (CD$_3$CN): δ = 16,4 – 20,8 (C̲H$_3$—C(O) and CH$_3$—C̲—), 33,4 – 38,3 (CH$_3$—N), 40,3 – 45,7 (C̲H$_2$—C), 54,7 – 56,1 (CH$_2$—N), 65,4 – 66,3 (CH—O), 69,6 – 71,3 (CH$_2$—O), 171,2 (C=O), 178,5 – 179,9 (C=N).

IR (Nujol): 1730 (C=O), 1630 (C=N), 1240, 1060, (B—F), 720 cm^{-1}.

Poly[**4a**-*co*-St]: ^{1}H NMR (DMSO-d$_6$): δ = 0,7 – 4,5 (a very broad peak), 6,0 – 7,7 (phenyl).

IR (KBr): 3060, 3015, 2920, 1635, 1482, 1450, 1280, 1050 (B—F), 760, 705 cm^{-1}.

Acylation of poly[2-(2-oxazolin-2-yl)propylene]: All procedures were carried out under nitrogen. A solution of 1,54 g of trimethyloxonium tetrafluoroborate (10,4 mmol) in 10 ml of acetonitrile was vigorously stirred at – 20 °C, to which a solution of 0,580 g (5,2 mmol) of poly-[2-(2-oxazolin-2-yl)propylene]$^{9)}$ ([η] = 0,21) in 10 ml of acetonitrile was added slowly. After the addition was over, the mixture was stirred at – 20 °C for 1 h and at 0 °C for additional 2 h to complete the reaction. Then, the mixture was poured into 100 ml of dichloromethane to precipitate the product. The precipitate was isolated by decantation and purified further by repeated reprecipitation from acetonitrile (solvent) into dichloromethane (non-solvent), and dried i. vac. at 60 °C. A pale yellow solid polymer was obtained; yield: 0,76 g. The solubility of the product transmuted by crosslinking between oxazolinium ring and unreacted oxazoline ring during the drying process. The resulting polymer is insoluble in common organic solvents and swells in water and DMF. From the result of elemental analyses, the degree of methylation of oxazolinium group of the product was estimated to be 46%.

Determination of monomer reactivity ratios: The monomer reactivity ratios of **4a** were determined for its copolymerizations with MA and with VAc. In addition, the reactivity of **2** in the copolymerization with MA was examined for comparison. In most runs of the copolymerizations, the conversions of the monomers were below 10%. The copolymer composition was examined by ^{1}H NMR rather than by elemental analyses, because the copolymers are very hygroscopic. The results are summarized in Tab. 1.

Results and discussion

Preparation of 2-isopropenyl-3-methyl-2-oxazolinium salts (**4a, b**)

2-Isopropenyl-3-methyl-2-oxazolinium tetrafluoroborate (**4a**) and fluorosulfonate (**4b**) were prepared by the reaction of **2** with the corresponding alkylating agents at 0 °C.

The conversions were almost quantitative, but the yield of isolated product ($\approx$ 90%) were a little lower due to the loss during the purification procedure. Both salts are hygroscopic, white needles soluble in methylene chloride, acetonitrile, DMF and other aprotic polar solvents. Their structures were reasonably established by both
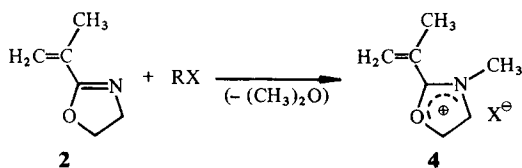
$$\text{RX: BF}_4\text{O(CH}_3)_3 \text{ or FSO}_3\text{CH}_3$$

(2)

	4a	b	c
X	BF$_4$	FSO$_3$	HSO$_4$

spectroscopic and analytical data (see Exptl. part). This type of compounds could not be prepared by conventional alkylating agents of relatively low reactivity such as methyl iodide and tosylate. These alkylating agents react with **2** at higher temperatures ($>50\,°C$) causing cationic ring-opening polymerization.

With the vinyl homologue **1**, the corresponding salt **3** could not be isolated because it entered into spontaneous polymerization upon alkylation[9]. Compared with **3**, **4a** and **4b** are less reactive toward nucleophiles. Due to their low reactivity they can be isolated from **2**.

Tab. 1.   Copolymerizations of **4a** and **2** (M$_1$) with methyl acrylate (MA) and with vinyl acetate (VAc)[a]

Feed M$_1$ /M$_2$	M$_1$ feed in mol-%	Polymerization time in h	Copolymer yield in %	M$_1$ content in mol-%
	25,0	1	5,4	28,8
	33,0	0,5	7,7	35,1
	38,7	0,5	7,8	41,2
4a/MA	50,1	1	9,0	44,9
	58,4	1	6,6	53,2
	70,0	2	8,6	59,2
	80,0	2	11,1	61,8
	19,5	2	8,1	54,0
	30	2	7,0	54,3
4a/VAc	40,2	2	12,1	54,3
	49,5	4	9,9	54,4
	59,8	4	14,3	62,0
	69,9	4	6,4	67,1
	19,5	0,5	4,4	40,8
	28,6	1	8,1	48,3
	38,3	1	6,8	57,5
2/MA	49,7	2	8,9	67,5
	59,0	2	8,4	77,1
	70,2	2	8,6	83,5
	80,8	2	8,9	89,9

[a]   Initiator: AIBN (2 mol-%); $T = 60\,°C$.

Radical and anionic polymerizations of **4a**

The salt **4a** was subjected to radical and anionic polymerizations under various conditions using only aprotic polar solvents because of their inertness and sufficient solubilizing ability toward **4a**. The results are shown in Tab. 2.

Under usual radical polymerization conditions using AIBN as initiator, poly[2-(3-methyl-2-oxazolinium-2-yl)propylene] (**5**) with low solution viscosity was obtained in poor yield. A considerable amount of monomer was left unreacted. In Fig. 1 the ^{1}H NMR spectrum of **5** is compared with that of **4a**.

$$\text{4a} \xrightarrow{\text{Cat.}} \left[\text{5} \right]_n \xrightarrow[\text{2. aq. NaOH}]{\text{1. (CH}_3)_3\text{CNH}_2} \left[\text{6} \right]_n \quad (3)$$
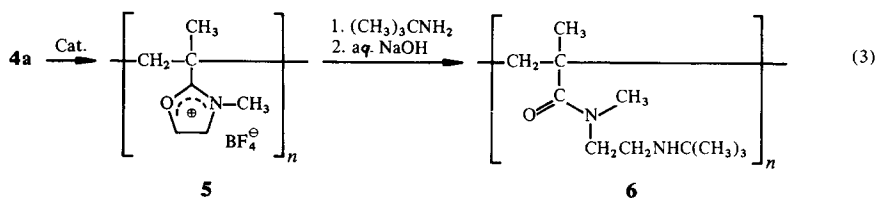
Tab. 2. Conditions and results of the homopolymerization of **4a**

Run No.	Initiator (mol-%)	Solv.	Temp. in °C	Time in h	Yield in %	η_{sp}/C [a] $\overline{\text{dl} \cdot \text{g}^{-1}}$
1	AIBN (3)	DMF	60	50	11	0,043
2	AIBN (3)	DMAc	80	50	13	0,042
3	AIBN (3)	[b]	80	50	4	0,066
4	AIBN (2)	—	70	10	0	—
5	[c]	—	R.t.	24	7	0,038
6	$(C_2H_5)_3N$ (5)	DMF	80	20	10	0,033
7	Pyridine (3)	DMF	0	50	0	—
8	$(C_6H_5)_3P$ (5)	DMF	80	20	9	—

[a] $C = 0,12$ g/dl, in 2% NaI/CH$_3$CN; $T = 30$ °C.
[b] Mixed solvent CH$_2$Cl$_2$/DMF (vol. ratio 3:1).
[c] ^{60}Co radiation; $5 \cdot 10^5$ rad/h.

From the peaks assigned (see Exptl. part), it is obvious that polymer **5** contains pendant 3-methyl-2-oxazolinium groups.

The degree of polymerization was estimated by measuring the molecular weight of the reaction product **6** from **5** with *tert*-butylamine, as reported before[9]. The highest value of the degree of polymerization was found to be ≈ 20 (for Run No. 1 Tab. 2). Although the polymerization reaction was not optimized, it was found that the yield decreases at temperatures lower than 60 °C and higher than 80 °C. The bulk polymerization of **4a** in the melt (Run No. 4) produced no polymeric product. In the experi-

ment of irradiation polymerization (Run No. 5), the crystalline salt of **4a** was exposed to a ^{60}Co source at $\approx 5 \cdot 10^5$ rad/h. The color of the salt changed from white to brown after 1 day of irradiation resulting only a small amount of polymeric product.
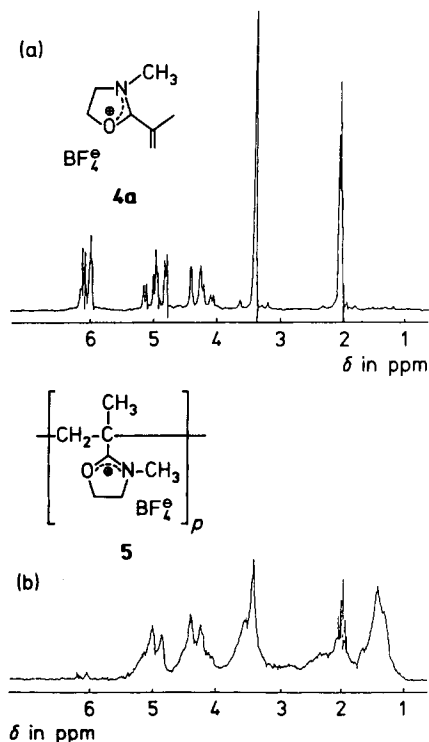

Fig. 1. ^{1}H NMR spectra of **4a** (a), and **5** (b)

Anionic polymerization of **4a** was then examined using amines and phosphines as initiators. As shown in Tab. 2, triethylamine and triphenylphosphine are effective as initiators of polymerization, while pyridine is not. However, the yield and the solution viscosity of the product were as low as those of the product obtained by radical polymerization, though the structure of the polymers is substantially identical. In the spontaneous polymerization of **1**[9], the intermediate **3** is highly electrophilic and hence polymerized by such weak bases as pyridine. Monomer **1** itself may be polymerized even at 0 °C and in a non-polar solvent by weak bases. In contrast, less electrophilic **4a** is polymerized only by stronger bases.

As described above, **4a** shows poor homopolymerizability in both radical and anionic polymerizations. This result may interestingly be compared with that obtained with **2**. Radical polymerization of **2** with AIBN as initiator (0,5 mol-%) in DMF affords poly[2-(2-oxazolin-2-yl)propylene] with high molecular weight in 72% yield under relatively mild conditions at 60 °C for 50 h. This polymer was alkylated with $(CH_3)_3OBF_4$ to give polymer **5**. However, quantitative conversion was hardly

attained. Reasons for the poor polymerizability of **4a** might be the electrostatic repulsion between oxazolinium cations, and the steric hindrance of the isopropenyl group. Concerning the steric hindrance, it is to be quoted that *N,N*-disubstituted methacrylamide (corresponding to **4a**) is not polymerizable, whereas *N*-monosubstituted methacrylamide and *N,N*-disubstituted acrylamide (corresponding to **2** and **3**, respectively) can be polymerized. The chain propagation of **3**[20 – 22] was found to be sterically hindered.

Radical copolymerizations

Radical copolymerizations of **4a** with some vinyl monomers were examined. Tab. 3 shows some of the preliminary results of copolymerizations with a feed fraction of **4a** less than 1/3. In the copolymerizations with methyl acrylate (MA), methyl methacrylate (MMA) and vinyl acetate (VAc), **4a** was incorporated successfully in the copolymers. Their structures were determined by ^{1}H NMR (see Exptl. part), from which the copolymer compositions were estimated. The rate of copolymerization was slow at 60 °C (Runs No. 1 and 5). The yields are considerably higher, however, at higher temperatures using relatively large amounts of AIBN (Runs No. 2, 4 and 7).

In the copolymerization with styrene (St), the conversions of both monomers were quite rapid, but the structure of the polymeric product was complex, i. e., no oxazolinium ring was present (see Exptl. part). With isobutyl vinyl ether (BVE), no polymeric material was produced. The combination of these two monomers produced a dark-blue color, which may be due to a charge transfer complex. The behavior of **4a** in copolymerization reactions is similar to that of *N*-vinylpyridinium salts, except for the fact that the *N*-vinylpyridinium salts show poor copolymerizability with VAc[23].

The above copolymers as well as the homopolymer of **5** are polyelectrolytes. Thus, an anomalous behavior of the solution viscosity was observed. Fig. 2 shows the change of viscosity with the concentration for homopolymer **5** (Tab. 2, No. 1) and copolymers of **4a** with MA (Tab. 3, No. 2 and 3).

Copolymerization parameters

The monomer reactivity ratios for **4a** and **2** were determined for the copolymerizations with MA and with VAc. Fig. 3 shows the relationship between monomer and copolymer composition. It is of interest that the system **4a**/VAc exhibits an alternating tendency, whereas the system **4a**/MA shows a characteristic curve for the copolymerization between two monomers of similar reactivities.

In the system **2**/MA, the homo-propagation of **2** is preferred. The monomer reactivity ratios of r_1 (for **4a** and **2**) and r_2 (for comonomers) were calculated according to the Kelen-Tüdős method[24], from which the *Q-e* values of **4a** and **2** were evaluated. The values of **4a** and **2** are shown in Tab. 4, where the corresponding values of related monomers, the 1:1 complex of **2** with zinc chloride (2-ZnCl$_2$)[7], 2-methyl-5-vinylpyridine (MVP), and 1,2-dimethyl-5-pyridinium methyl sulfate (DPMS) are given for comparison.

Tab. 3.   Conditions and results of the radical copolymerizations of **4a** with several vinyl monomers

Run No.	Comono-mer[a]	**4a** Feed in mol-%	AIBN content in mol-%	Temp. in °C	Time in h	Yield in %	**4a** content in mol-%	$\dfrac{\eta_{sp}/C}{dl \cdot g^{-1}}$ [b]
1	MA	25	0,5	60	5	14	29	0,084
2	MA	9,1	3	85	17	87	7,8	0,16
3	MA	17	3	85	17	94	17	0,15
4	MMA	33	2	80	50	86	29	0,096
5	VAc	30	0,5	60	5	9	52	0,061
6	VAc	33	2	80	50	54	47	0,072
7	St	17	0,5	60	5	58	c)	—
8	BVE	30	2	70	120	0	—	—

[a] MA: methyl acrylate; MMA: methyl methacrylate; VAc: vinyl acetate; St: styrene; BVE: isobutyl vinyl ether.

[b] $C = 0,25$ g/dl, in 2% NaI/CH_3CN; $T = 30\,°C$.

[c] The structure of the copolymer could not be determined.

Fig. 2.   Relationship between viscosity and concentration of **5** (Tab. 3, Run 1) (○) and poly(**4a**-*co*-MA) [Tab. 3, Run 2 (●) and Run 3 (◑)]. Solvent: CH_3CN; $T = 30\,°C$
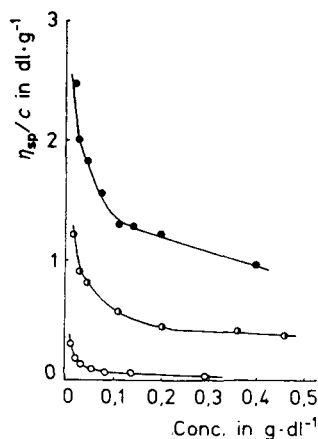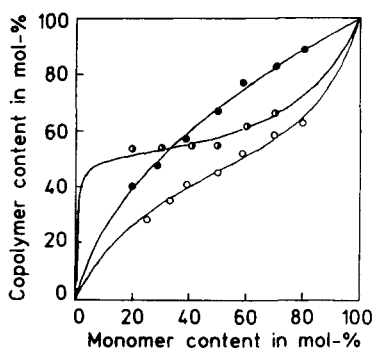

Fig. 3.   Monomer-copolymer composition curves for the systems **4a**/MA (○), **4a**(VAc (◑), and **2**/MA (●)

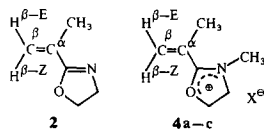Tab. 4. Copolymerization parameters of **2** and **4a**

M_1	M_2	Solvent	r_1	r_2	Q_1	e_1
4a	MA	DMF	0,27	0,50	2,0	2,0
4a	VAc	DMF	0,38	0,009	1,7	2,2
2	MA	DMF	2,10	0,41	1,3	1,0
2[a]	St	Benzene	0,55	0,49	0,81	0,35
2-ZnCl₂ [b]	St	Benzene	4,60	0,009	28	1,0
MVP[c]	MMA	None	0,46	0,61	1,04	− 0,7
DPMS[d]	MMA	CH_3OH[e]	1,8	0,12	9,0	1,6

a) Ref.[7].

b) Complex of **2** with zinc chloride (1 : 1), from ref.[7].

c) 2-Methyl-5-vinylpyridine, from ref.[25].

d) 1,2-Dimethyl-5-vinylpyridinium methyl sulfate, from ref.[26].

e) 70 wt.-%.

In general the r_1 values for **4a** are below 0,5 and lower than those of other comonomers cited for reference. This finding is compatible with a low homo-polymerizability of **4a**.

As shown in previous studies on the reactivities of cationic salts of vinyl monomers, the values of r_1 and r_2 as well as the values of Q and e are considerably affected by both the comonomer and the solvent utilized[23, 25, 27]. In the case of **4a**, the solvent effect could not be studied in detail due to the restricted selection of the solvents. With regard to both Q and e values for **4a**, they were very similar in two sets of copolymerization. In comparison with **2**, a significant increase in both Q and e values

Tab. 5. Change of chemical shifts of isopropenyl groups of **2**, **4a**, **4b** and **4c** in the ^1H and ^{13}C NMR spectra

Sample	Chemical shift (change of chemical shift)			
	^1H NMR δ in ppm		^{13}C NMR δ in ppm	
	$H^{\beta-E}$	$H^{\beta-Z}$	C^α	C^β
2	5,67	5,27	134,36	121,53
4a	6,17 (+ 0,50)	6,00 (+ 0,73)	128,16 (− 6,20)	132,34 (+ 10,81)
4b	6,17 (+ 0,50)	6,00 (+ 0,73)	128,42 (− 5,94)	132,47 (+ 10,94)
4c[a]	6,39 (+ 0,72)	6,14 (+ 0,87)	127,30 (− 7,06)	134,50 (+ 12,97)

a) 2-Isopropenyl-2-oxazolinium hydrogen sulfate, from ref.[4].

was noted for **4a**. An analogous relation has been reported between MVP and DPMS. The increase of Q and e values was also reported for 2-ZnCl$_2$.

The higher e value of **4a** than that of 2-ZnCl$_2$ is due to the large electron withdrawing effect of the oxazolinium cation.

From the chemical shift of the isopropenyl groups of **2** and **4a** in the ^{1}H and ^{13}C NMR spectra, the apparent electron density on each carbon may be estimated. The results are shown in Tab. 5.

The low-field shift of the proton and C$^\beta$ signals and the up-field of C$^\alpha$ were observed for both **4a** and protonated **2** (**4c**)[4]. The big deshielding at the β-position is compatible with the high e value, although the deshielding of this position in **4a** is smaller than that in the hydrogen sulfate salt **4c**, probably due to the electron donation by the methyl group. The lower polymerizability of **4a** may be expected from the large shielding at C$^\alpha$ which destabilizes the radical at the α-carbon atom. The radical polymerization of **4c** has not been studied yet.

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