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Kinetics and Mechanism of the Isomerization Polymerization of 2-Methyl-2-oxazoline by Benzyl Chloride and Bromide Initiators. Effect of Halogen Counteranions

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Dedicated to Professor Dr. G. Manecke on his 60th birthday

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SUMMARY:

Kinetic studies of the isomerization polymerization of 2-methyl-2-oxazoline (**2**) initiated with benzyl chloride (**1a**) or bromide (**1b**) were carried out by NMR spectroscopy. The polymerization initiated with **1a** proceeded exclusively via a covalently bonded alkyl chloride species **5**, whereas the polymerization of the system initiated with **1b** proceeded via a oxazolinium bromide **10** as the propagating end. The propagation rate constant k_p with **1a** was about 1/40 of that found with **1b** at 40 °C in CD_3CN. The mechanistic difference is explained by the different nucleophilicities of the counteranions, Cl^- and Br^-. A model compound for the propagation with **1b** as initiator was also examined changing the temperature and the solvent.

ZUSAMMENFASSUNG.

Kinetische Untersuchungen der Isomerisations-Polymerisation von 2-Methyl-2-oxazolin (**2**), initiiert durch Benzylchlorid (**1a**) oder Benzylbromid (**1b**), wurden mit Hilfe der NMR-Spektroskopie durchgeführt. Die mit **1a** ausgelöste Polymerisation verläuft ausschließlich über eine kovalent gebundene Alkylchlorid-Spezies **5**, die mit **1b** initiierte Polymerisation dagegen über ein Oxazoliniumbromid **10** als wachsendes Ende. Die Geschwindigkeitskonstante des Wachstums, k_p, bei 40 °C in CD_3CN, ist im Falle von **1a** ungefähr 1/40 der k_p, die bei der Initiierung mit **1b** gefunden wird. Der mechanistische Unterschied wird mit den verschiedenen Nucleophilien der Gegenanionen Cl^- und

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Br^- erklärt. Eine Modellverbindung für die Wachstumsreaktion mit **1b** als Initiator wurde bei verschiedenen Temperaturen und in verschiedenen Lösungsmitteln untersucht.

Introduction

Recently, we have reported kinetic studies of the isomerization polymerization of 2-methyl-2-oxazoline (**2**) by methyl *p*-toluenesulfonate[1] and iodide[2] initiators. The polymerization of **2** proceeded via oxazolinium propagating species in CD_3CN with both *p*-toluenesulfonate and iodide counteranions[1,2]. The present paper reports the kinetics of the polymerization of **2** by benzyl chloride (**1a**) and bromide (**1b**) initiators, in which the effects of the counteranions on the polymerization were examined. The polymerization initiated with **1a** is a model reaction of the graft polymerization of **2** with chloromethylated polystyrene (crosslinked and non-crosslinked), reported very recently by us[3].

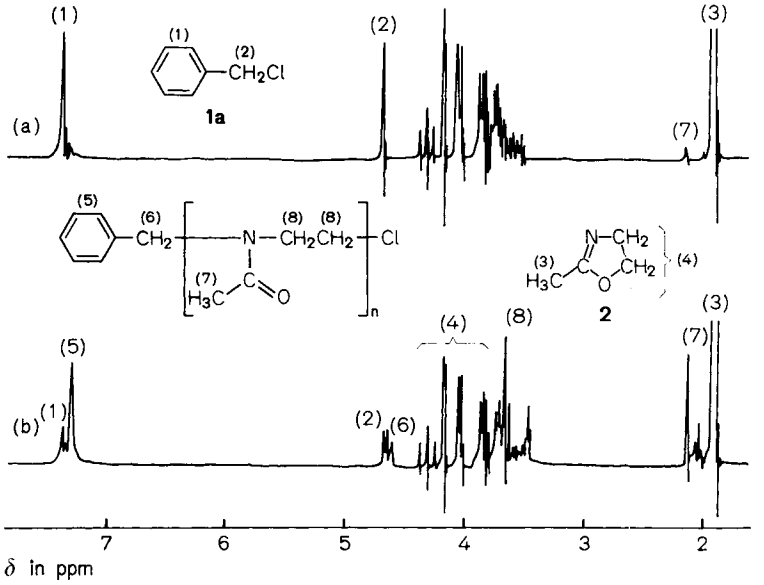


Fig. 1. ^{1}H-NMR spectra of the polymerization system of 2-methyl-2-oxazoline (**2**) initiated by benzyl chloride (**1a**) in CD_3CN at 95 °C. (a): after 5 min; (b): after 102 min

Results and Discussion

Polymerization initiated with benzyl chloride (**1a**)

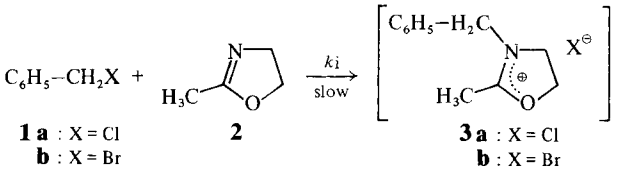
^{1}H-NMR spectroscopy

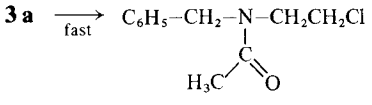
Fig. 1 shows NMR spectra of the polymerization system initiated by **1a** in CD_3CN, taken at reaction times of 5 min (a) and of 102 min (b) at 95 °C, respectively. The initial concentrations of monomer and initiator were 3,33 and 0,667 mol/l, respectively, the mole ratio being 5:1. The peak assignments are given in the Fig. The presence of an oxazolinium ion should be indicated by the signal of the 2-methyl group in the range of $\delta = 2{,}3$–$2{,}5$ ppm[1,2]. In Fig. 1, however, this peak is not detectable. In addition, the triplet between $\delta = 4{,}6$ and 5,1 ppm due to the methylene protons in 5-position of the oxazolinium ion, is not present.

From these findings the propagating end of the product of polymerization of **2**, initiated by **1a**, is concluded to be the covalently bonded *N*-acetyl-*N*-(2-chloroethyl)amino group in **4** or **5**. The course of the polymerization is given as follows:

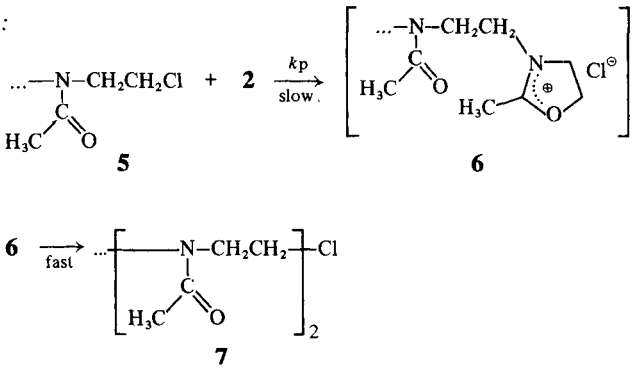
A similar mechanism has been presented for the first time by *Saegusa* et al.[4] for the polymerization of unsubstituted 2-oxazoline with methyl iodide as initiator. The mode of the polymerization of **2** with **1a** as initiator is in a sharp contrast to that of the polymerization with iodide as counter-anion, in which case the propagating species was exclusively an oxazolinium ion in the same solvent. The polymerization course was completely altered with

Initiation:

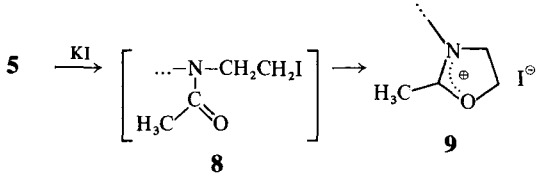




Propagation:



the change of the counteranion from iodide to chloride. The difference of mechanism was further supported by the following experiment. After the polymerization of **2** with **1a** was completed, potassium iodide was added to the system and the mixture was kept at 80°C for 15 h. Two new peaks appeared, i.e., a sharp singlet at $\delta = 2{,}53$ and a triplet at $\delta = 4{,}65$ ppm, which are assigned, respectively, to the methyl protons and the methylene protons in 5-position of an oxazolinium iodide unit, which is formed by a halogen exchange reaction to produce **9**.



Kinetics

The instantaneous monomer concentration [M] was calculated from the initial monomer concentration $[M]_0$ and the intensity fraction of peak (3)/(peak (3)+peak (7)) in Fig. 1. The areas of peaks (1) and (5) were utilized to calculate the instantaneous initiator concentration [I]. Fig. 2 shows the time-conversion relationships for monomer and initiator at 105°C. **1a** was consumed within 140 min.

According to the S_N2 mechanism of the polymerization, the rate constants of initiation (k_i) and propagation (k_p) were determined by the integrated forms of Eqs. (1) and (2), respectively[1,2].

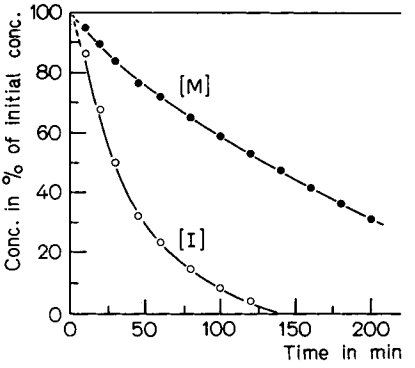


Fig. 2. Time-conversion curves of the polymerization of **2** (M) initiated by **1a** (I) in CD_3CN at 105 °C. Initial concentrations: $[M]_0 = 3{,}33$ mol/l, $[I]_0 = 0{,}667$ mol/l

$$\ln \frac{[I]_0}{[I]} = k_i \int_0^t [M]\,dt \tag{1}$$

$$\frac{\ln([M]_0/[M])}{\int_0^t [I]\,dt} = (k_i - k_p) + k_p \frac{[I]_0 t}{\int_0^t [I]\,dt} \tag{2}$$

After all **1a** has been consumed to form propagating species, the value of k_p results from Eq. (3):

$$\ln \frac{[M]_{t_1}}{[M]_{t_2}} = k_p [I]_0 (t_2 - t_1) \tag{3}$$

Both methods of determination, Eqs. (2) and (3), gave identical values of k_p. The results are given in Tab. 1.

Polymerization initiated with benzyl bromide (**1b**)

^{1}H-NMR spectroscopy

Fig. 3 shows the NMR spectra of the products of polymerization of **2** initiated with **1b** taken at 35 °C after 2 min (a) and 93 min (b). The feed mole ratio of monomer to initiator is 5:1. The assignments of the signals are given in the Fig. A striking difference from the system initiated with **1a** (Fig. 1) is the presence of peaks assignable to an oxazolinium ion. Two peaks at $\delta = 2{,}72$ ((9), n = 0) and 2,54 ppm ((9), $n \geqq 1$) are ascribed to the methyl protons of the *N*-benzyl oxazolinium ring and of the oxazolinium

ring at the growing end. A triplet peak (10) at $\delta = 4{,}82$ ppm is due to the methylene protons in 5-position of the oxazolinium ring. After **1b** was consumed, the ratio of the peak areas (peak (1) + peak (5))/peaks (9) (two peaks) was almost 5:3, indicating that the polymerization proceeded via oxazolinium bromide species **3b** and **10**.

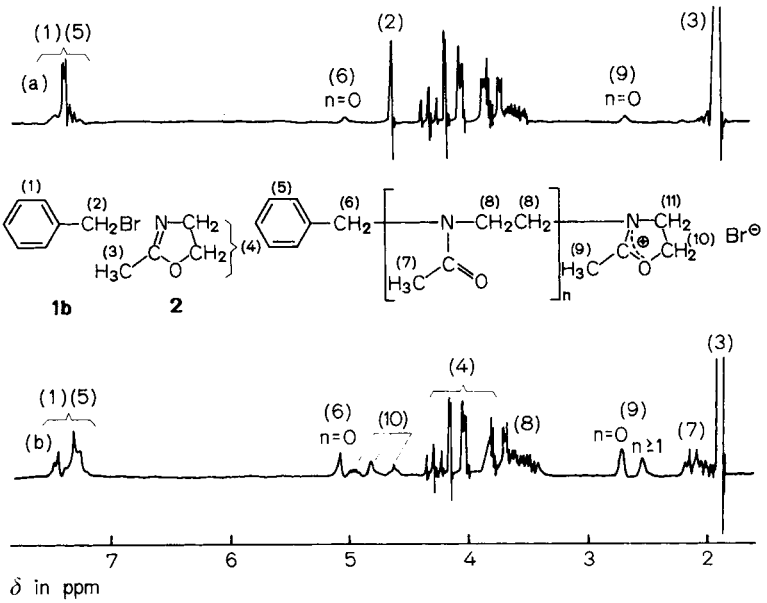


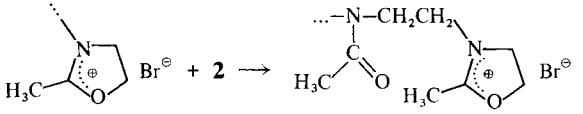
Fig. 3. ^{1}H-NMR spectra of the polymerization system of **2** initiated by benzyl bromide (**1b**) in CD_3CN at 35°C. (a): after 2 min; (b): after 93 min

The following scheme explains the course of the polymerization of **2** initiated with **1b**:

Initiation:

1b + **2** ⟶ **3b**

Propagation:



10 **11**

The above mechanism is the same as that of the polymerization systems initiated by methyl iodide[2] and methyl *p*-toluenesulfonate[1].

Kinetics

Similarly to the system initiated with **1a**, the instantaneous initiator and monomer concentrations ([I] and [M]) were determined. In Fig. 4 the concentration of the oxazolinium ion based on the initial concentration of the monomer is plotted vs. time. Since the mole ratio of **2**/**1b** in the feed is 5,0, it is reasonably assumed that all initiator **1b** was converted into oxazolinium ion as the propagating species. If there were covalently bonded alkyl bromide propagating species its amount would be very small (vide infra).

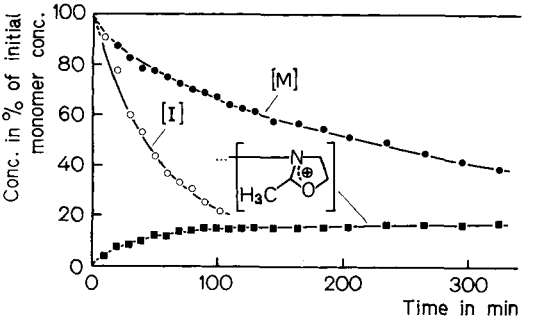


Fig. 4. Time-conversion curves for the polymerization of **2** initiated by **1b** in CD_3CN at 35 °C; $[M]_0 = 3{,}33$ mol/l; $[I]_0 = 0{,}667$ mol/l

A kinetic analysis was made according to Eqs. (1)–(3) (Tab. 1). From the k_i values at 40 °C (Tab. 1) it results that **1b** reacts 130 times faster with **2** than **1a**. The propagation rate of the system initiated with **1b** is 40 times faster than that of the system initiated with **1a**.

Activation parameters and difference of mechanism

Tab. 2 summarizes the k_p values at 40 °C and the activation parameters of both systems along with other ones recently studied. The values of k_p and activation parameters for polymerizations initiated by **1b** are quite close to those initiated by methyl iodide and *p*-toluenesulfonate, showing that the polymerization of **2** progresses according to a similar mechanism with these three initiators. On the other hand, the values of the system initiated

Tab. 1. Rate constants of the polymerization of 2-methyl-2-oxazoline (**2**) initiated by benzyl chloride (**1a**) and benzyl bromide (**1b**) in CD_3CN; $[\mathbf{2}]_0 = 3{,}33$ mol^{-1}, $[I]_0 = 0{,}667$ mol l^{-1}

Initiator	Temp. in °C	$\frac{10^4 \cdot k_i}{l\ mol^{-1}\ s^{-1}}$	$\frac{10^4 \cdot k_p}{l\ mol^{-1}\ s^{-1}}$
1a	40	0,01[a]	0,03[a]
	85	0,47	0,59
	95	0,89	1,0
	105	1,6	1,7
1b	35	1,1	0,81
	40	1,3[b]	1,2[b]
	47	1,6	2,2
	60	—	6,6

[a] Extrapolated value.
[b] Interpolated value.

with **1a** are different from those of the three other systems. The oxazolinium propagating species **10** is 40 times more reactive than the covalently bonded alkyl chloride **5.** This is interesting to compare with the reactivity difference of about 100 in the polymerization of 2-oxazoline by methyl iodide (covalent) and *p*-toluenesulfonate (ionic) initiators[4].

Activation parameters of the polymerization of **2** initiated by **1a** are rather close to those of the polymerization of 2-oxazoline with methyl iodide. In both cases the propagating ends are covalent species.

The rate determining step of the propagation is the formation of the unstable oxazolinium chloride intermediate **6** by reaction of the two dipoles **5** and **2.**

Relatively low values of $\Delta E^{\neq}$ (favorable) and A (unfavorable) for the system initiated with **1a** are compatible with the mechanism[4].

The difference of the polymerization mechanism of **2** is probably explained by the difference of the nucleophilic reactivity of the two counteranions. According to *Fuchs* and *Mahendran*[5] the nucleophilic reactivity in an aprotic solvent such as dimethyl sulfoxide is in the following order: $Cl^- > Br^- > I^- > OTos^-$ *). A strong nucleophile such as chloride anion rapidly attacks the 2-methyl-2-oxazolinium ion in CD_3CN to produce the covalent alkyl chloride species **5.** A weaker nucleophile such as bromide anion, however, does not

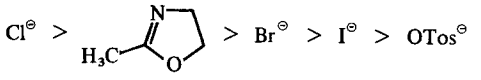
*) Tos: *p*-toluene sulfonyl.

Tab. 2. Rate constants and activation parameters of the polymerizations of 2-methyl-2-oxazoline (**2**) and of 2-oxazoline in CD_3CN. $[M]_0 = 3{,}33$ mol l^{-1}; $[I]_0 = 0{,}667$ mol l^{-1}

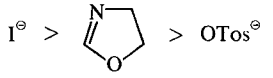
	Polymerization of **2** with				2-oxazoline with	
	1a[a]	**1b**[a]	CH_3I[b]	CH_3OTos[c]	CH_3I[d]	CH_3OTos[d]
$10^4 \cdot k_p/(l\ mol^{-1}\ s^{-1})$ at 40 °C	0,03	1,2	1,14	1,17	0,18	19
$\Delta E^{\neq}$/(kcal mol^{-1})	14,8	17,1	17,4	19,1	13,5	25
(in kJ mol^{-1})	(62,0)	(71,6)	(72,9)	(80,0)	(56,5)	(104,7)
$A/(l\ mol^{-1}\ s^{-1})$	$6{,}5 \cdot 10^4$	$1{,}1 \cdot 10^8$	$1{,}7 \cdot 10^8$	$1{,}9 \cdot 10^9$	$5{,}0 \cdot 10^4$	$7{,}5 \cdot 10^{14}$
Propagating species	covalent	ionic	ionic	ionic	covalent	ionic

[a] This work. [b] cf.[2]. [c] Tos = *p*-toluenesulfonyl; cf.[1]. [d] cf.[4].

undergo a similar course and hence the polymerization proceeds via oxazolinium bromide species **10.** From these results the order of nucleophilicity in the polymerization of **2** is as follows:



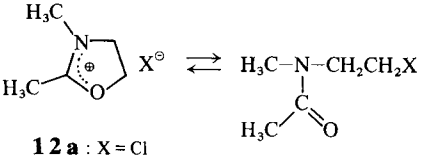
This is interesting to compare with the order in the polymerization of 2-oxazoline[6]:



Analysis of the equilibrium with model compounds

In the polymerization of **2** initiated with **1a** the presence of the propagating oxazolinium chloride was excluded by NMR. In the system initiated with **1b** the concentration of oxazolinium bromide species was almost equal to the consumed initiator. However, it was not possible to exclude the presence of a very small amount of the covalently bonded alkyl bromide as propagating species even if characteristic signals of the species could not be detected, since they would be overlapped with other signals (Fig. 3). To examine this point in more detail the equilibrium of a model compound was studied.

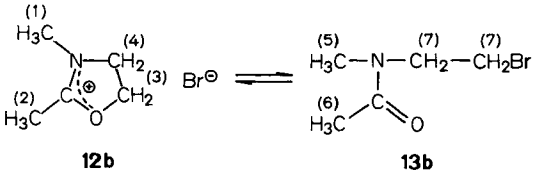
2,3-Dimethyloxazolinium bromide **12b** was prepared as a model compound of the propagating end in the polymerization of **2** initiated with **1b**. A 0,6 mol/l solution of **12b** in $CHCl_3$, CD_3CN, or CD_3NO_2 was subjected to NMR measurement at various temperatures.



12a : X = Cl
b : X = Br
c : X = I

13a : X = Cl
b : X = Br
c : X = I

Fig. 5 shows the NMR spectrum of **12b** in CD_3CN at 35 °C and the signal assignments, **12b** is clearly in equilibrium with **13b,** although the equilibrium



12b **13b**

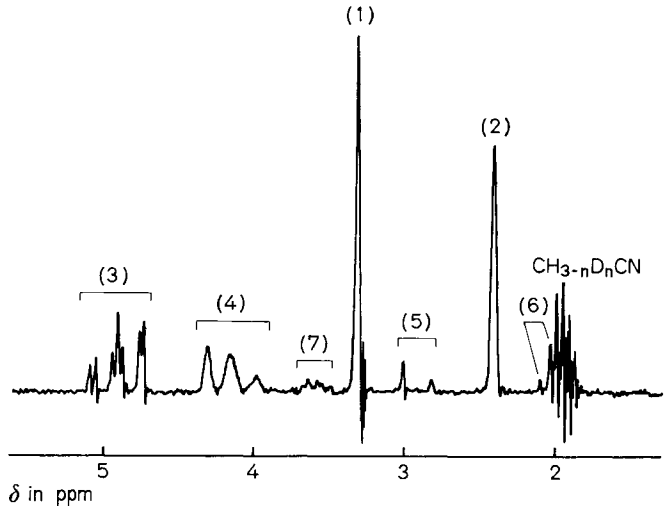


Fig. 5. ^{1}H-NMR spectrum of **12b** at 35 °C in CD_3CN

constant $K = [\mathbf{13b}]/[\mathbf{12b}]$ is small in CD_3CN. The equilibrium **12b** $\rightleftarrows$ **13b** was also observed in $CHCl_3$ and CD_3NO_2. Tab. 3 shows values of K together with values of ΔH and ΔS defined as Eq. (4):

$$\Delta G = \Delta H - T\Delta S = -RT\ln K \tag{4}$$

The fraction of **13b** decreases with the increase of the solvent polarity, e.g. the ionic species **12b** is stabilized in a polar solvent.

In order to examine a series of halogen counter anions, *N*-(2-chloroethyl)-*N*-methylacetamide **13a** was prepared. A 0,6 mol/l solution of **13a** in CD_3CN did not show the presence of the ionic species **12a** in the temperature range of 35–105 °C. The oxazolinium iodide **12c** on the other hand, was present only in the ionic form, **13c** being not involved at all[2]. Thus, **12b** with the bromide counter anion is the intermediate case between **12a** and **12c** with chloride and iodide anions.

Tab. 3 (a) Equilibrium constants $K = [\mathbf{13b}]/[\mathbf{12b}]$ in various solvents

Temp.	K in $CHCl_3$ (percentage of **13b**)	K in CD_3CN (percentage of **13b**)	K in CD_3NO_2 (percentage of **13b**)
35	0,25 (20)	0,10 (9,2)	0,07 (6,8)
60	0,58 (37)	0,20 (17)	0,12 (11)
80	1,2 (54)	0,32 (24)	0,17 (15)

(b) Corresponding enthalpy and entropy values

	Solvent		
	$CHCl_3$	CD_3CN	CD_3NO_2
ΔH/(kcal mol^{-1})	7,4	5,5	4,1
(in kJ mol^{-1})	(31,0)	(23,0)	(17,2)
ΔS/(cal mol^{-1} K^{-1})	21	13	8,1
(in J mol^{-1} K^{-1})	(87,9)	(54,4)	(33,9)

From the above findings it is still difficult to determine the precise concentration of the covalently bonded alkyl bromide in the polymerization of **2** by **1b**. However, it is safe to say that the alkyl bromide species is involved in very small quantity (less than the error in the NMR determination), if present at all.

Experimental Part

Reagents: 2-Methyl-2-oxazoline (**2**), a commercial reagent, was purified by dist. under nitrogen. Commercial reagents benzyl chloride (**1a**) and benzyl bromide (**1b**) were purified by dist. i. vac. CD_3CN (Merck) was dried on molecular sieves 4A.

N-(2-chloroethyl)-N-methylacetamide (**13a**): A mixture of 2-methylaminoethanol (21,3 g; 0,284 mol), acetic acid (17,1 g; 0,284 mol) and xylene (20 ml) was refluxed for 17 h. After the xylene/water mixture was dist. off, the product was dist. i. vac. Yield of *N*-(2-hydroxyethyl)-*N*-methylacetamide: 65%; bp 111,5–113,5 °C (at $\approx$ 1 mbar).

NMR ($CDCl_3$): $\delta = 2{,}09$ (d; 3H, $COCH_3$), 2,99 (d; 3H, NCH_3), 3,55 (m; 4H, CH_2CH_2), and 4,25 ppm (s; 1H, OH).

To a stirred mixture of *N*-(2-hydroxyethyl)-*N*-methylacetamide (10 g; 85 mmol), 10 ml of benzene, 15,8 ml of triethylamine and 30 ml of chloroform, a solution of thionyl chloride (8,2 ml) in benzene (10 ml) was added dropwise at 10 °C. The mixture was stirred at 50 °C for 4 h and was kept overnight at room temp. The precipitate of triethylammonium chloride was isolated by filtration and washed with a small portion of benzene.

The filtrate and washings were combined and concentrated i. vac. The crystalline material was washed with benzene. This procedure was repeated three times, and triethylammonium chloride was almost removed. The remaining solution was distilled i. vac. Yield of **13a**: 40%; bp 77,5–79,5 °C (at ≈2,2 mbar).

NMR ($CDCl_3$): $\delta = 2{,}11$ (d; 3H, $COCH_3$), 2,98 (d; 3H, NCH_3), and 3,62 ppm (s; 4H, CH_2CH_2).

NMR (CD_3CN): $\delta = 2{,}05$ (d; 3H, $COCH_3$), 2,96 (d; 3H, NCH_3), and 3,73 ppm (m; 4H, CH_2CH_2).

IR (neat): 1650 cm^{-1} (s; C=O).

$C_5H_{10}ClNO$	(135,6)	Calc.	C 44,29	H 7,43	Cl 26,15	N 10,33
		Found	C 44,23	H 7,45	Cl 25,97	N 10,33

2,3-Dimethyl-2-oxazolinium bromide (**12b**): To a stirred solution of *N*-(2-hydroxyethyl)-*N*-methylacetamide (2,1 g; 17,9 mmol) in benzene (8 ml) was slowly added at 5–10 °C under nitrogen, a mixture of phosphorous tribromide (1,7 g; 6,3 mmol), and 2 ml of benzene. The solution was stirred at room temp. for 5 h to give a white precipitate, which was isolated by decantation. The solid was recrystallized from a benzene/chloroform (4:1) mixture to give white hygroscopic crystals; yield: 20%.

IR (Nujol): 1680 (C=N—), 1282 (C—O—C), and 976 cm^{-1} (skeletal).

$C_5H_{10}BrNO \cdot (H_2O)_{1,3}$	(203,5)	Calc.	C 29,51	H 6,24	N 6,88
		Found	C 29,73	H 6,42	N 6,77

Polymerization and NMR measurement: The whole operation was carried out under nitrogen. **2**, CD_3CN, and initiator were placed in an NMR tube at 0 °C in the desired conc. of monomer and initiator, i.e., $[M]_0 = 3{,}33$ mol/l and $[I]_0 = 0{,}667$ mol/l. The tube was sealed and the polymerization was carried out at a constant temp. The instantaneous concentrations of monomer, initiator, and the propagating species were determined from NMR spectra recorded at different reaction times on a "Hitachi-Perkin Elmer R-20B" NMR spectrometer (60 MHz). The NMR experimental error was ±5%.

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