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Novel Investigations on Kinetics and Polymerization Mechanism of Oxazolines Initiated by Iodine

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ABSTRACT: The cationic ring-opening polymerization of 2-methyl-2-oxazoline (**MOx**) using iodine initiating system was reported. Uncolored polyoxazolines were produced in spite of the use of iodine initiator, well-known dye molecule. Low molecular weight asymmetric telechelic polyoxazolines carrying an acetylimine headgroup and an oxazolinium end group were synthesized, with a good control over the molecular weight. NMR and MALDI−TOF experiments allowed the full determination of the chemical structures of the produced poly(2-methyl-2-oxazoline)s, notably with the acetylimine headgroup, explained by spontaneous α-HI elimination. Finally, to our knowledge, we reported the first detailed mechanism of cationic ring-opening polymerization of 2-methyl-2-oxazoline in acetonitrile according to UV experiments. An ionic-type mechanism was involved with the dissociation of molecular iodine to active initiating species.

Introduction

Poly(oxazoline)s[1,2] are nowadays the subject of great attention due to their properties such as nontoxicity, hydrophilicity, and biocompatibility[3,4] which made them good candidates for biological and biomedical applications[5,6] and the use of poly(2-methyl-oxazoline)s (**POx**)s was even discussed to substitute poly(ethylene oxide).[7] To date, the cationic ring-opening polymerization of 2-oxazolines has been accomplished using many initiators including Lewis acids, such as boron trifluoride, and alkyl esters such as tosylates, triflates and halides as summarized in Scheme 1.[1,8,9] The alkyl halide initiators ranged from chloride[10] and bromide[11] to iodide[12−14] as well as acetyl halide.[15] The alkyl iodide initiators were mostly converted *in situ* from chloride[16−18] or bromide[19] analogues using NaI or KI reactants. The structure of iodide (macro)initiators could also be more sophisticated[20] with, for example, metalloinitiators using Fe(II) and Rh(II) tris(bipyrines),[21] polyhedral oligomeric silsesquioxanes (POSS),[22] gold nanoparticles,[23] or carbon nanotubes.[24]

Widespread used tosylate or iodine initiators showed drawbacks that must be taken in consideration. For instance, the partial initiation from *p*-toluenesulfonic acid (H^+), formed by inadvertent hydrolysis of tosylate initiator[25] led to side products during the polymerization reaction. On the other hand, alkyl iodide initiators proved to be not stable under storage due to the weak C−I bond. They are known to be light-sensitive and temperature-sensitive, and are prone to decomposition to give free iodine (I_2) or hydroiodic acid (HI) by elimination. Riffle and Saegusa studied the polymerization of 2-oxazoline (**Ox**), 2-methyl-2-oxazoline (**MOx**), and 2-ethyl-2-oxazoline (**EtOx**) in presence of MeI and others iodide initiators like benzyl iodide and 1-iodobutane. Saegusa showed the influence of the nucleophilic reactivity of the monomer on the nature of the mechanism, and proved that **MOx** > I^- > **Ox**.[12,26,27] High monomer nucleophilic reactivity promoted covalent mechanism (**Ox** monomer) where the attack of the stronger nucleophile of iodide at the oxazolinium ring led to the covalent-bonded species.[28,29] In the case of **MOx**, the mechanism differed and nucleophilic attack of the monomer at the oxazolinium ring reproduced an oxazolinium ring. Riffle studied the polymerization of **EtOx** in details using various iodide initiators.[30−32] Both covalent and ionic active species were present in these systems. The less reactive alkyl halide, 1-iodobutane, yielded much smaller initiation rate constants than benzyl iodide with incubation period of several hours.

In this contribution, we describe the first polymerization of **MOx** using molecular iodine as initiator, in acetonitrile at 60 °C. The main benefit of the use of I_2 was that no preliminary synthesis was required in comparison with triflate, tosylate and halide initiators. We managed to prepare well-defined poly(2-methyl-2-oxazoline)s with control over the molecular weight and low polydispersities. Additionally, the chemical structures of polymers were fully established as the chain end-groups were clearly identified using NMR and MALDI−TOF analyses. Finally, UV experiments permitted us to report the mechanism of the polymerization of the 2-methyl-2-oxazoline in acetonitrile for the first time in the literature.

Experimental Section

Materials. Molecular iodine, diethyl ether, methanol, chloroform, potassium hydroxide, and calcium hydride (CaH_2) were purchased from ACROS and were used as received. Acetonitrile was dried and distilled according to standard procedures.[33] 2-Methyl-2-oxazoline (**MOx**) was dried, distilled from CaH_2 and stored under a dry nitrogen atmosphere. Deuterated solvents ($CDCl_3$ and CD_3CN) were purchased from SDS and were used without further purification.

Analytical Techniques. ^1H and ^{13}C NMR spectra were recorded using a Bruker AC 200 with $CDCl_3$ as solvent. Chemical shifts (^1H NMR) were referenced to the peak of residual $CHCl_3$ at 7.26 ppm. Chemical shifts (^{13}C NMR) were referenced to $CDCl_3$ at 77 ppm. Size exclusion chromatography

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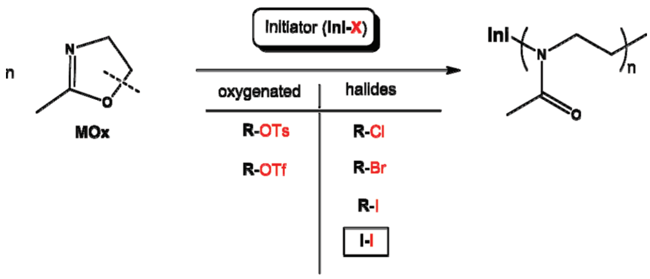
Scheme 1. Cationic Ring-Opening Polymerization of MOx Using Various Initiators



(SEC) was performed on a PL-GPC 50 Plus equipped with an RI refractive index detector. Three PL aquagel−OH columns (25, 7.5, and 4.6 mm ID) were used at 40 °C with a 0.8 mL·min^{-1} flow rate of H_2O/CH_3OH: 7/3 (+ 0.1 M $LiNO_3$), calibrated using PEO standards. Mass spectrometry analyses were conducted with a Bruker Ultra-Flex MALDI−TOF mass spectrometer, equipped with a nitrogen laser (LSI, 337 nm, 10 ns pulse length) and one detector. Mixture of peptides was used for external calibration. The ions were accelerated by a potential of 25 kV and reflected with a 26.3 kV potential. All measurements were recorded in the reflection mode using α-cyano-4-hydroxycinamic acid (HCCA) as matrix with NaI. For each spectrum 300 transients were accumulated. The resolution at m/z = 1650 was 331. The polymer was dissolved in acetonitrile at a concentration of 10 mg.mL^{-1}. UV−visible analyses were conducted with a Perkin-Elmer Lambda 35 UV/vis spectrometer equipped with PTP-1+1 Peltier System. Experimental conditions: $[M]_0 = 2.35 \times 10^{-4}$ M, $[I_2]_0 = 7.88 \times 10^{-6}$ M, 60 °C, and blank = acetonitrile. To avoid any saturation of the absorbance, the reaction mixture was diluted until 2×10^{-4} M instead of 4 M in monomer for a typical polymerization.

Typical Procedure for the Polymerization of the 2-Methyl-2-oxazoline (MOx) using Iodine: POx_{n-1OH}^{-HI}. Targeted Degree of Polymerization: 10. Reactions were carried out under a dry nitrogen atmosphere. Iodine (0.60 g, 2.35 mmol) and **MOx** (2 g, 23.5 mmol) were dissolved in dry acetonitrile (5 mL). The solution was vigorously stirred at 60 °C. The product was quenched by addition of an adequate amount of methanolic potassium hydroxide (0.2 mL, 8.91 M). The flask was maintained for 4 h at 30 °C. After cooling, the polymer was isolated by slow precipitation from cold diethyl ether.

^{1}H NMR ($CDCl_3$) δ (ppm): 7.0−6.7 (m, N = CH), 4.93 (t, N−CH_2 $_{oxazolinium}$), 4.25 (t, O−CH_2 $_{oxazolinium}$), 3.5−3.1 (m, CH_2 POx), 2.6 (s, CH_3 $_{oxazolinium}$), 2.3−2.0 (m, CH_3 POx).

^{13}C NMR ($CDCl_3$) δ (ppm): 176.2 (C=O $_{acetylimine}$), 171.5−169.8 (C=O $_{amide}$), 119.7 (N = CH-$\underline{C}H_2$−N), 117.7 (N=C), 49.3−40.6 (CH_2), 21.8−19.7 (CH_3), 12.3 (CH_3 $_{acetylimine}$).

Determination of the Conversion by ^{1}H NMR Spectroscopy. The conversion from **MOx** to corresponding **POx** was determined by ^{1}H NMR spectroscopy (in deuterated acetonitrile) comparing the signals from the released CH_2 of polymer at 3.5−3.1 ppm with the signals from the remaining CH_2 of monomer at 4.4 and 3.7 ppm.

Results and Discussion

The present study aims at examining (i) the synthesis of well-defined poly(2-methyl-2-oxazoline)s, and (ii) the mechanism of cationic ring-opening polymerization of **MOx** in acetonitrile, in the presence of molecular iodine initiator. The latter was already well-known to act as initiator for cationic polymerization.[34] For example, it was proved that the living/controlled character of the cationic polymerization of numerous monomers such as isobutyl vinyl ether was inefficient in the presence of I_2 and that it was improved by adding others co-initiating species (HI, SO_2, ZnI_2).[35−38] On the other hand, to date, molecular iodine was never applied for the polymerization of oxazolines.

Table 1. Experimental Conditions and Conversion Data for the Polymerization of 2-Methyl-2-oxazoline

run	$[M]_0/[I]_0$	T (°C)	reaction time (min)	conversion (%)
A	10	40	510	100
B	10	60	245	96
C	10	80	120	100
D	30	60	1440	90
E	50	60	4500	91

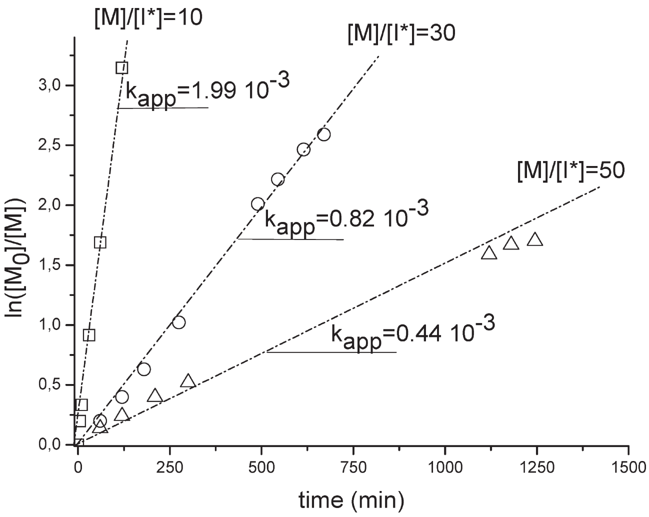


Figure 1. Ln($[M]_0/[M]$) versus time determined by ^{1}H NMR experiment (k_{app} values were expressed in L mol^{-1} s^{-1}).

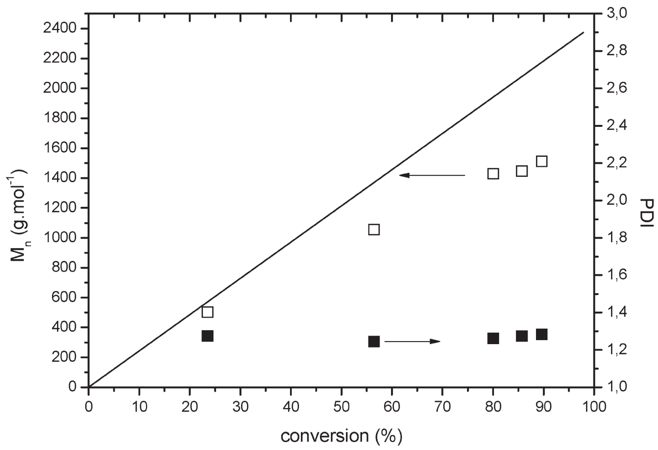
Table 2. Experimental Values of k_{app} for Various $[M]_0/[I]_0$ Ratios

$[M]_0/[I]_0$	slope (s^{-1})	$[I]_0$ (mol L^{-1})	k_{app} (10^{-3} L mol^{-1} s^{-1})
10	4.33×10^{-4}	0.235	1.99
30	6.35×10^{-5}	0.078	0.82
50	2.00×10^{-5}	0.047	0.44
100	7.75×10^{-6}	0.023	0.31

Polymerization Kinetics. A kinetic study of the cationic ring-opening polymerization of 2-methyl-2-oxazoline was first achieved. To avoid any confusion between the terms of initiator and iodine, the abbreviations I* and I were attributed to the initiator and the iodine atom, respectively. **MOx** conversion versus time was first performed by ^{1}H NMR experiment in CD_3CN. The CH_2 monomer protons resonated at δ 4.4 and 3.7 ppm shifts and broadened in the corresponding polymer at 3.5−3.1 ppm. These intensities were used to calculate the monomer concentration as a function of reaction time. The influence of the temperature on kinetic polymerization was studied at 40, 60, and 80 °C. Whatever the temperature, conversions were high and the final reaction time logically decreased with the temperature (Table 1). As expected, the kinetics showed a decrease in polymerization rate with $[M]_0/[I^*]_0$ ratio.

The slope of the ln($[M]_0/[M]$) versus reaction time led to the determination of the rate constant of polymerization (k_{app}) (Figure 1). Theoretically, this k_{app} can be calculated according to eq 1:

$$-\frac{d[M]}{dt} = k_{app}[P^*][M] \qquad (1)$$



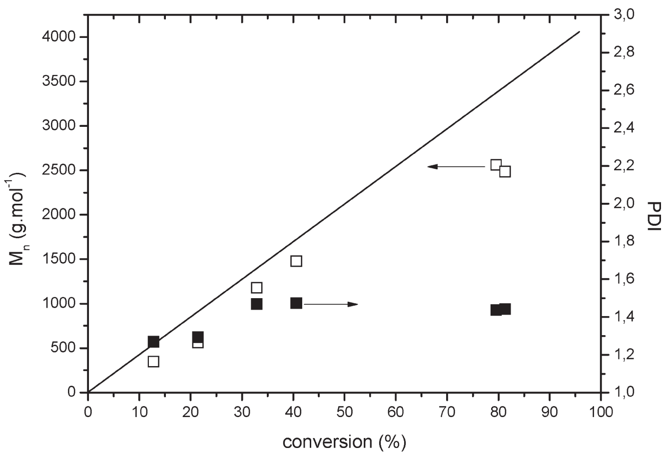


Figure 2. Molecular weight versus conversion determined by size exclusion chromatography (left, $M_{n,th} = 2550\ g\cdot mol^{-1}$; right, $M_{n,th} = 4250\ g\cdot mol^{-1}$).

Table 3. Experimental and Theoretical Values of DP_n and M_n

run	temp (°C)	time (min)	$DP_{n,th}$ [a]	conv (%)	$M_{n,th}$ (g/mol)	$DP_{n,SEC}$ [b]	$M_{n,SEC}$ [b] (g/mol)	PDI_{SEC} [b]
1	40	850	10	89	800	6	550	1.3
2	80	30	10	83	800	8	650	1.3
3	60	180	10	82	800	7.5	600	1.2
4	60	360	20	80	1700	12.5	1000	1.3
5	60	420	30	80	2550	18	1550	1.2
6	60	1400	40	81	3400	29	2500	1.5
7	60	1400	100	52	8500	20	1700	1.6

[a] $DP_{n,th}$ = [M]/[I*] × convn. [b] From SEC data in $MeOH/H_2O$: 3/7 relative to PEO standards.

where [M] and [P*] are the concentrations of the monomer and propagating species, respectively. Assuming that the concentration of propagating species was equal to the initial initiator concentration $[I]_0$, eq 1 was integrated in eq 2. In the last equation $[I]_0$ replaced $[I^*]_0$ because it was not known whether each iodine molecule initiated one polymer chain.

$$\ln \frac{[M]_0}{[M]_t} = k_{app}[I]_0 t \quad (2)$$

$Ln([M]_0/[M])$ versus time was found to be linear as evidenced in Figure 1. This linear behavior showed that the concentration of active chains remained constant throughout the polymerization indicating that termination reactions were not significant. We noted that the k_{app} values depended on $[I]_0$ and decreased with $[M]_0/[I]_0$. The trend revealed that [I*] did not linearly scale with $[I]_0$ (Table 2). The difference between [I*] and [I] increased with $[M]_0/[I]_0$. Additionally, for the same [M]/[I] ratio, the rate constant propagation for the cationic polymerization of **MOx** using iodine initiator (0.82×10^{-3} L mol^{-1} s^{-1}) was consistent with the values obtained for MeOTs and MeI initiators, in dimethylacetamide (2.40×10^{-3} and 2.22×10^{-3} L mol^{-1} s^{-1}, respectively).[39] From the graphical resolution of the Arrhenius equation (eq 3) the frequency factor and the activation energy were deduced for the **MOx**/I_2/CH_3CN system. The calculation of kp from $Ln([M]_0/[M])$ = f(t) at 40, 60, and 80 °C was achieved. The values fitted with the literature data [system; Ea (KJ mol^{-1}); A (L mol^{-1} s^{-1})]. Our initiator system seemed more reactive than the MeI initiator, with the following values: [**MOx**/I_2/CH_3CN; 60.0; 3.5×10^6] and [**MOx**/MeI/CH_3CN; 72.9; 1.7×10^8].[12,40]

$$k_p = A e^{-E_a/RT} \quad (3)$$

All obtained polymers were characterized by size exclusion chromatography to determine the molecular weights and the polydispersity indexes (PDI). The molecular weight versus global conversion was reported in Figure 2 for two different theoretical molecular weights (2550 and 4250 $g\cdot mol^{-1}$). The M_n values increased linearly until 80% conversion showing the control of the polymerization reaction. For higher conversion, the experimental values deviated from the targeted ones probably due to the presence of transfer reactions. The study of the mechanism revealed the HI was released at the beginning of the polymerization (according to the MALDI−TOF and NMR parts). HI could reinitiate new chains, could induce transfer reactions, and might explain the limited DPs even if the HI initiated chains were not detected by MALDI−TOF spectroscopy.

The influence of the temperature on the molecular weight was studied at 40, 60, and 80 °C (Table 3 runs 1−3). The lowest value of polydispersity index was obtained at 60 °C. As a consequence, a series of **POx** polymers were synthesized at this temperature, with a $[M]_0/[I^*]_0$ ratio ranging from 10 to 100 (Table 3 runs 3−7). In all cases, the molecular weight distribution of the obtained poly(2-methyl-2-oxazoline)s was lower than 1.5. Up to an [M]/[I*] ratio of 40, the molecular weights versus DP_n increased linearly as depicted in Figure 3. As already mentioned in the literature, the deviation could be attributed to polymer adsorption onto some component of the SEC apparatus.[41] For higher M_n values, the decrease of molecular weight and the enhancement of molecular weight distribution meant the presence of transfer reactions (Table 3 run 7). We concluded that the synthesis of high molecular weight polyoxazolines using iodine was limited, as already described for others initiators.[42]

Chain-End Functionalities. Determination by MALDI−TOF and NMR Measurements. It is important to notice that polymerization reactions were stopped at about 80% conversion for the determination of chain-end functionalities in order to minimize transfer. Moreover, for the sake of clarification of this work, the following abbreviation was attributed to each possible chain end-group, taking into account the head and end groups of the poly(2-methyl-2-oxazoline) considered chain:

$$\mathrm{POx}^{\text{head group}}_{\text{end group}}$$

In many cases ^{1}H NMR analysis was suitable for the determination of end-groups and also permitted to identify the type of mechanism. The cationic ring-opening polymerization of oxazoline proved to proceed via two different types of species, i.e. ionic and covalent types, depending on the nature of the initiator and on the monomer.[1] Ionic and covalent polymerization mechanisms were explained by the balance of nucleophilicities between monomers and X^- counteranions. In both mechanisms the first step dealt with the reaction between the RX initiator and the **MOx** monomer (Step A of Scheme 2). In the case of the covalent mechanism, a further step occurred with the reaction between the initiation product and the X^- counteranion (Step B of Scheme 2).

The cationic propagating species of an oxazolinium salt was not fragile and could be isolated. Thus, the ionic-type mechanism was detected by NMR technique showing the oxazolinium group. The presence of typical peaks of oxazolinium species were detected at 4.9 and 4.4 ppm corresponding to CH_2−O and CH_2−N, respectively.[12] Similar results were obtained in our case, clearly demonstrating that an ionic-type mechanism was involved for the CROP of **MOx** using iodine (Figure 4). An additional signal was displayed around 7.0 ppm and was attributed to the C*H*=N proton of an acetylimine group obtained by the elimination of hydroiodic acid (HI) at the end-group of the polymer chain.

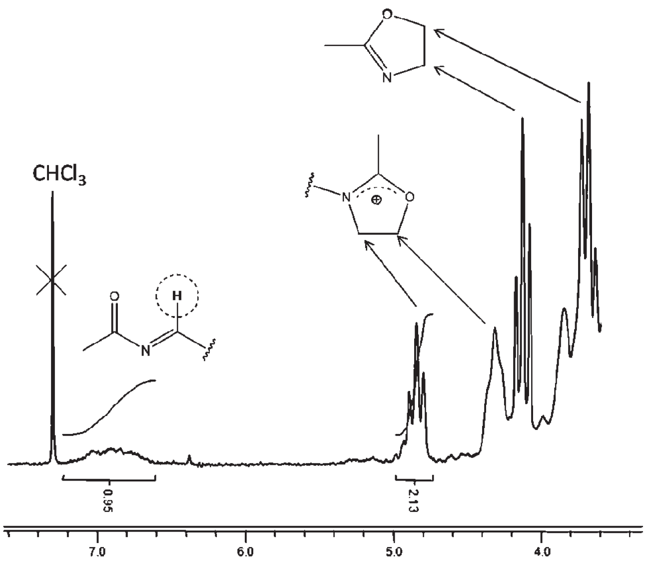


Figure 4. ^{1}H NMR spectrum of the poly(2-methyl-2-oxazoline)s showing both the ionic mechanism of the polymerization and the elimination of HI.

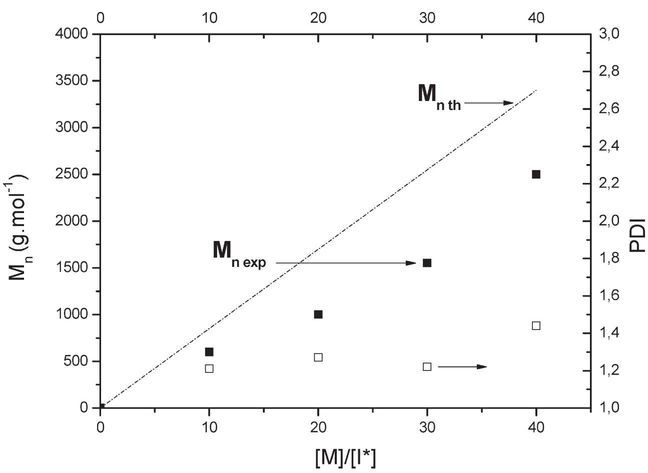
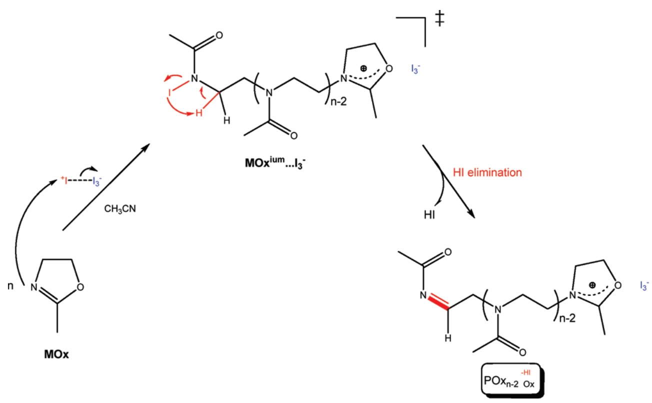


Figure 3. M_n and polydispersity indexes obtained by means of SEC for **MOx** initiated by iodine.

Scheme 3. Elimination of Hydroiodic Acid during the Polymerization Reaction



Scheme 2. Covalent and Ionic Mechanism Types for the Cationic Ring-Opening Polymerization of MOx

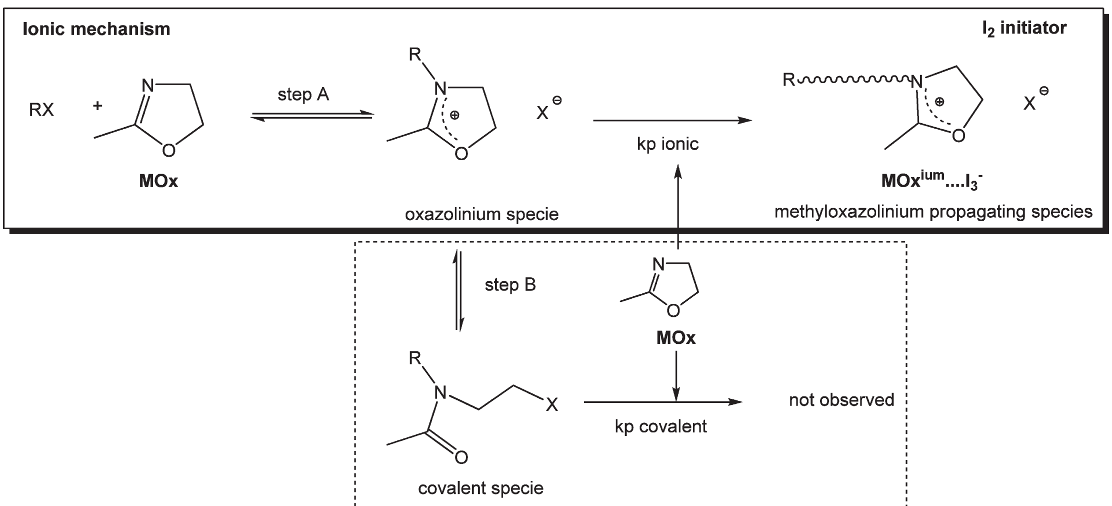


Table 4. Analytical Data Derived from MALDI−TOF MS Spectroscopy[a]

assignment	$RM_{formula}$	ΔM_{exp}[b]	RM_{th}[b]	RM_{exp}[b]	$M_{p,th}$[b]	$M_{p,exp}$[b]	calculation
POx_{n-2Ox}^{-HI}	$C_8H_{13}N_2O_2I$	85.05	296.10	296.10	976.90	976.50	$85.10(n-2) + RM$
POx_{nOH}^{I}	IOH	85.06	143.91	144.02	824.71	824.50	$85.10n + RM$
POx_{n-1OH}^{-HI}	$C_4H_7NO_2$	85.05	101.10	101.00	781.90	781.40	$85.10(n-1) + RM$

[a] ΔM = mass of the monomer unit. ΔM_{th} = 85.10 g·mol^{-1}. RM = residual mass. [b] Value expressed in g mol^{-1}.

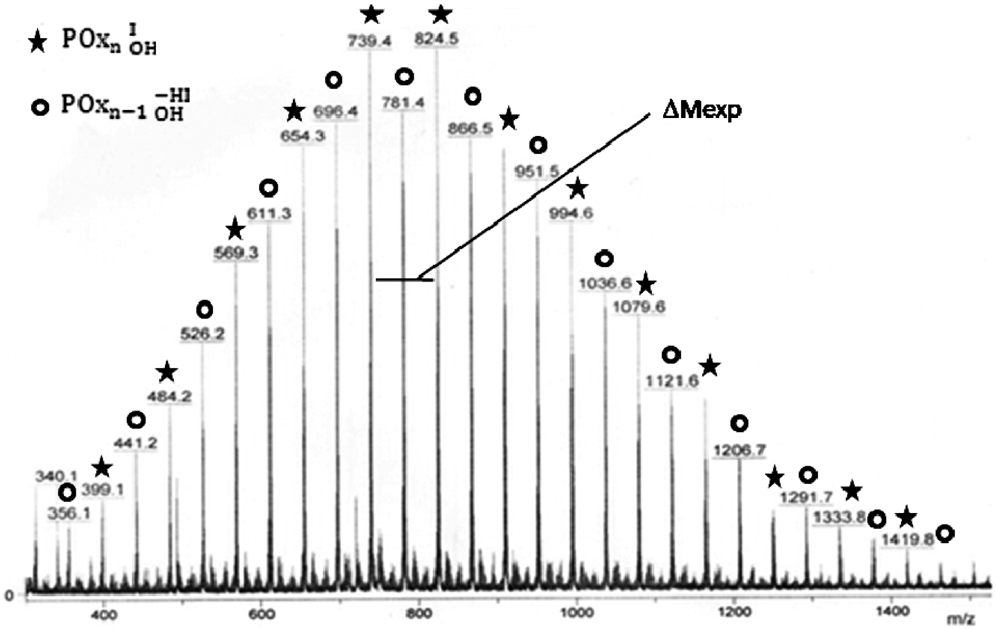
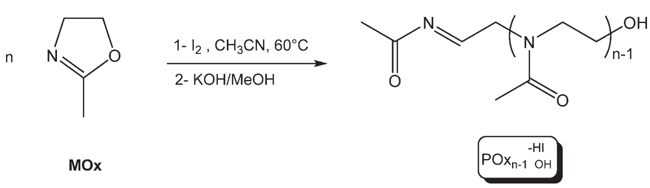


Figure 5. MALDI−TOF mass spectrum of **POx** after the termination reaction by the potassium hydroxide.

Scheme 4. Poly(2-methyl-2-oxazoline) after the Termination Reaction by the Potassium Hydroxide



The HI elimination was explained by the weakness of the N−I bond, and led to the formation of more stable conjugated specie as shown in Scheme 3. The peak corresponding to the C*H*= appeared from the beginning of the polymerization and its integration kept constant with regard to oxazolinium group during the polymerization process. We concluded that the spontaneous α-HI elimination occurred at the very beginning of the polymerization and revealed the existence of the POx_{n-2OX}^{-HI}, corresponding to a polyoxazoline main chain with an acetylimine headgroup and an oxazolinium end group. By the integration of respective ^{1}H NMR signals the CH=N/oxazolinium ratio was 89%. This ratio was underestimated since a complete broken of N−I was supposed. Thus, the covalent route represented lower than 11% and the ionic species were the most important ones. ^{13}C NMR spectroscopy confirmed this POx_{n-2OX}^{-HI} chemical structure with signals at 171.5−169.8 ppm for the carbonyl group of the **POx** main chain whereas the downfield peak at 176.2 ppm was assigned to the C=O acetylimine group. Peaks at 119.7 and 117.7 ppm were attributed to the units adjacent to imine group and CH=N, respectively. Finally, peaks at 21.8−19.7 and 12.3 ppm were assigned to **POx** main chain and the methyl group of acetylimine, respectively.

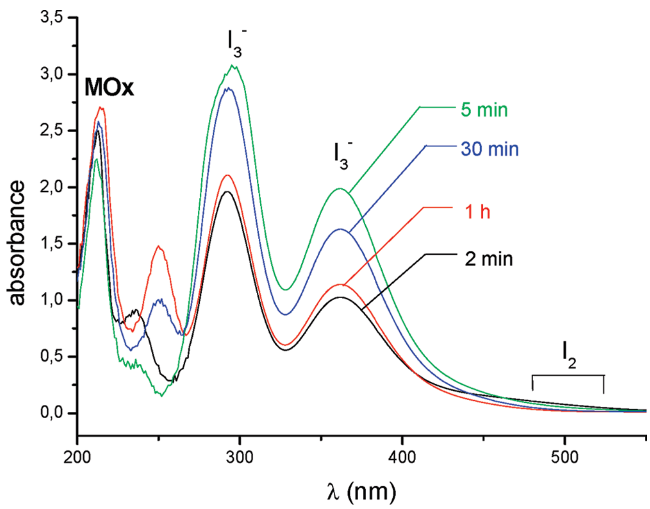


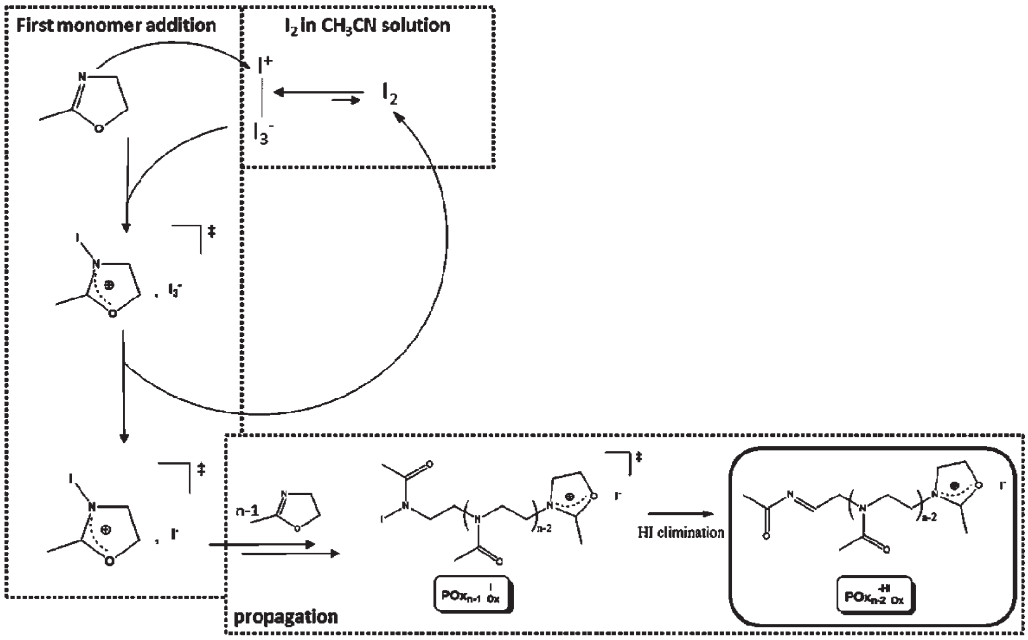
Figure 6. UV−vis spectra as a function of time for the polymerization of **MOx** in acetonitrile using iodine.

MALDI−TOF mass spectroscopy was used to confirm the nature of the **POx** end-groups and to study the polymerization mechanism. The theoretical values were compared to the experimental ones (M, RM and ΔM) as summarized in Table 4. The theoretical mass was expressed following the eq 4:

$$M_{th} = \Delta M_{th} \times n + RM_{th} \qquad (4)$$

where M_{th} is the calculated mass of the polymer of degree of polymerization nearest to the measured value, ΔM_{th} is the mass of the monomer unit, and RM_{th} represents the

Scheme 5. Proposed Mechanism of MOx Polymerization Using Iodine Initiator



calculated residual mass. The determined M_p values (mass at peak maximum of the most intensive signal) and the number-average molecular weight (M_n) are also given in Table 4.

The polyoxazoline chemical structures were analyzed before and after the termination stage by potassium hydroxide (Scheme 4). Spectra were recorded in reflectron mode using Na^+ cations in an α-cyano-4-hydroxycinamic acid matrix. The detected ions were MNa^+ type. Two distributions of peaks from m/z in the range of 356 (n = 3; $\mathrm{POx}_{n-1\,\mathrm{OH}}^{-\mathrm{HI}}$) to 1419 Da ($n$ = 13, $\mathrm{POx}_{n-1\,\mathrm{OH}}^{\mathrm{I}}$) were observed with an interval between two principal peaks of the same family being 85.10, which corresponded to the molecular weight of the 2-methyl-2-oxazoline monomeric unit. Before the termination stage $\mathrm{POx}_{n-2\,\mathrm{Ox}}^{-\mathrm{HI}}$ was detected with HI α-elimination and oxazolinium headgroup according to ^{1}H NMR experiment (Figure 4). The MALDI−TOF mass study confirmed the HI elimination during the polymerization stage with a good correlation between theoretical and experimental M_n values. We noted the agreement between RM_{exp} and RM_{th} values as well as the close value of $M_{p,exp}$ and $M_{p,th}$. In the MALDI−TOF mass spectrum of **POx** terminated by the potassium hydroxide, a monomodal distribution was attributed to $\mathrm{POx}_{n-1\,\mathrm{OH}}^{-\mathrm{HI}}$ where a scission of HI labile group occurred. No other family was mentioned thus no side reaction was detected. In order to avoid a complete HI scission and to show the N−I bond an experiment was achieved in the darkness. A multimodal distribution displayed two different populations of the same intensity as compiled in Figure 5. $\mathrm{POx}_{n\,\mathrm{OH}}^{\mathrm{I}}$ corresponded to the substitution of oxazolinium head chain by the hydroxyl group.

Finally, the originality in this work was also due to the obtaining of uncolored poly(2-methyl-2-oxazoline)s despite the use of iodine as initiator. This was achieved by both the addition of the potassium hydroxide and the elimination of hydroiodic acid during the polymerization reaction. Iodine was easily eliminated to afford well-defined products with an acetylimine headgroup and a hydroxyl end group.

Investigations on the Polymerization Mechanism by UV Experiments. During the polymerization process the evolution of iodide species was monitored by UV spectroscopy as a function of time (Figure 6). The electronic spectrum of iodine was first recorded in cyclohexane and acetonitrile to evaluate the influence of the dielectric constant D on iodine. Both solvents have a dielectric constant of 2.0 and 37.5 and a dipole moment of 0 and 3.84 D, respectively.[43] In nonpolar solvent, the absorption band of free iodine was observed at 480−600 nm. In the very polar and polarizable acetonitrile, the absorption of iodine disappeared and additional transition appeared before the addition of **MOx**.[44] This indicated that acetonitrile interacted with iodine according to partial bimolecular initiation and that other iodide species were formed such as triiodide anion.[45,46] The presence of the latter was clearly shown by UV experiments with the absorption bands at 290 and 366 nm whereas the pentaiodide anion did not appear at 442 nm.[47] The addition of **MOx** induced a total shift of the equilibrium toward I_3^- and I^+ and gave oxazolinium species with triiodide counteranion: **MOx^{ium}···I_3^-**. This trend was suggested by the increase of the typical bands of I_3^- and the disappearance of iodine band as soon as the addition of **MOx**. The I^+ species acted as active initiator species and reacted with the nitrogen atom of monomeric unit. After 5 min of reaction the decrease of I_3^- species bands could be explained by the conversion of triiodide to I^-. The conversion released molecular iodine and produced I_3^- and I^+ ions which reacted with **MOx** again. This step should explain the relatively large polydispersity index around 1.2−1.4 caused by a long time of initiation stage. The UV experiments concluded on the partial ionization of I_2 to I^+ and I_3^- in a polar solvent and the complete conversion with the addition of **MOx** (Scheme 5). Then the active species I^+ reacted with **MOx** and I_3^- was converted into an I^- counteranion. The released iodine was ionized into I^+ and I_3^- until complete depletion of iodine. The next stage was the propagation with the formation of $\mathrm{POx}_{n-2\,\mathrm{Ox}}^{-\mathrm{HI}}$.

Conclusion

Low molecular weight poly(2-methyl-2-oxazoline)s were synthesized with good control over the chain length and low polydispersity using molecular iodine as initiating system. The main kinetic features were described. The polyoxazoline end-groups were also identified using NMR and MALDI−TOF MS measurements which notably showed the formation of N−I bond as headgroup of the polymer chain. The spontaneous α-HI elimination due to the unstable N−I bond was also demonstrated and uncolored products were isolated. The mechanism of the cationic ring-opening polymerization of **MOx** was finally discussed. All experimental results allowed us to propose an ionic-type mechanism for the ring-opening polymerization of 2-methyl-2-oxazoline in acetonitrile.

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