Thermally Induced Cationic Polymerization of 2-Ethyl-2-oxazoline by Benzyl Pyridinium and Anilinium Salts

Halil KIRLIBAL, Yusuf YAĞCI[*]

İstanbul Technical University, Department of Chemistry, Maslak, İstanbul 34469, TURKEY
e-mail: yusuf@itu.edu.tr

N-Benzyl pyridinium (BP), N-benzyl o-cyano pyridinium (BoCP), N-benzyl p-cyanopyridinium (BpCP), N-benzyl N, N-dimethyl anilinium (BDA) and benzyl triphenyl phosphonium (BTP) salts with bromide counter anion, thermal initiators for cationic polymerization, were synthesized and characterized. Their capability to act as initiators for the polymerization of 2-ethyl-2-oxazoline (EOZO) was examined. The postulated mechanism is based on the generation of benzyl bromide by the thermolysis of either BoCP or BDA that reacts with the monomer, EOZO. The polymerization proceeds via an oxazolonium bromide as the propagating end. BP, BoCP and BTP were found to be unreactive towards EOZO.

Key Words: 2-Ethyl-2-oxazoline, pyridinium salts, anilinium salts, phosphonium salts, benzyl bromide, thermally induced cationic polymerization.

Introduction

Initiators that generate reactive species capable of initiating cationic polymerizations by external stimulation, photolysis or heating are extremely important in the control of the initiation step. These external initiators overcome the problems of classical initiators such as heterogeneous polymerization mixture, strong exothermic polymerization and the requirement of low temperatures for polymerization. In recent years, considerable attention has been devoted to thermal or photo-latent systems for the initiation of cationic polymerization[1]. Cationic polymerizations initiated in this way are of great practical interest due to their applicability to the curing of coatings and printing inks, and to resist technology [2].

Cationic polymerization of vinyl and cyclic monomers can be initiated by various initiators such as protonic and Lewis acids, carbocations, and trialkyl oxonium salts [3]. Some of the onium salts are thermolytically activated. However, onium salts with slight differences in the pattern of substitution were mostly used [4]. For example, N-alkoxy pyridinium salts[5] serve as initiators in photoinitiated polymerization whereas N-benzyl pyridinium salts are utilized in thermal polymerization.

---

[*]Corresponding author

2-Oxazolines are 5-membered heterocyclic imino ether compounds. Cationic ring-opening polymerization of cyclic imino ethers generally involves a thermodynamically favorable isomerization of the imino ether groups to the amide.

$$\text{(structure)} \xrightarrow{\text{E}^+} \left(\text{NCH}_2\text{CH}_2 \right)_n \tag{1}$$
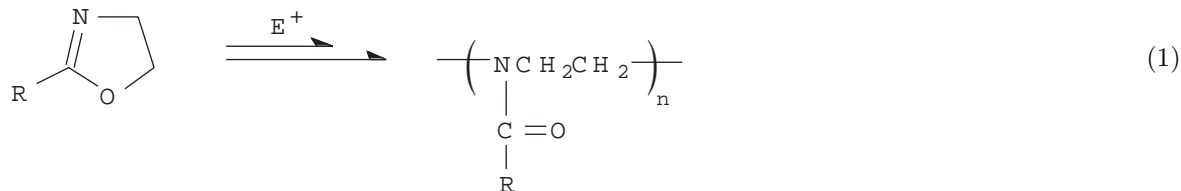
Ring-opening isomerization polymerization of 2-oxazolines aroused a great deal of interest in both polymerization chemistry and in the material design of functional polymers. Numerous studies on 2-oxazoline polymers have been undertaken over the last 30 years. The polymerization of 2-oxazolines has been the subject of several review articles[6−12].

Many different cationic initiators, such as Lewis acids, stable cationic salts, strong protonic acids and their salts, esters of sulfuric, sulfonic and picric acids and acid anhydrides, and alkyl halides, have been employed for the polymerization of 2-oxazolines[13]. Depending upon the type of initiator used, the mechanism of chain growth can be purely cationic, or else involves dipole-dipole interactions. When cationic initiators such as methyl triflate are used, the polymerization is truly cationic. On the other hand, if the monomer is reacted with alkyl halides such as methyl iodide, the polymerization is slower and proceeds via a quite different mechanism, involving propagation reactions between dipoles of opposite signs. In this paper we report on the thermal polymerization of 2-ethyl-2-oxazoline (EOZO) in the presence benzylic salts, namely pyridinium and anilinium salts. Upon heating these salts generate benzyl bromide capable of initiating the cationic polymerization of the oxazoline monomer.

Experimental

Materials

2-Ethyl-2-oxazoline (EOZO) used as the monomer was obtained from Merck. It was purified by distillation and stored over molecular sieves. Acetone, used as the solvent in the synthesis of salts, was obtained J.T. Baker. It was purified by distillation before use. Acetonitrile (J.T. Baker) was used as the solvent in polymerization, and the dilution of polymer solutions. It was also used as the solvent in the synthesis of salts. It was purified by distillation before use. Anhydrous diethyl ether (J.T. Baker) was used as the solvent for the precipitation of polymers.

Synthesis of *N*-Benzyl pyridinium bromide (BP)

A mixture of benzyl bromide (3.6 mL, 30 mmol), pyridine (2.5 mL, 30 mmol) and 1.23 g (1.56 mL) of acetonitrile was stirred and maintained at 40 °C for 3 days. After acetonitrile was removed under vacuum, acetone (40 mL) was poured into the mixture to isolate the white bromide salt by filtration. It was then washed copiously with diethyl ether and dried, (yield, 83%). ^{1}H-NMR (D$_2$O, ppm) δ 5.80 (s, 2H, CH$_2$), 7.48 (s, 5H, Ph), 8.02-8.08 (t, 2H, Py), 8.51-8.57 (t, 1H, Py), 8.89-8.91 (d, 2H, Py)

Synthesis of *N*-Benzyl-*o*-cyanopyridinium bromide (BoCP)

A solution of benzyl bromide (3.6 mL, 30 mmol), and *o*-cyanopyridinium (1.56 g, 15 mmol) was stirred and maintained at 40 °C for 2 days. The rest of the procedure was the same as that for the synthesis of BCP, yield, (77.5 %), m.p.: 140 °C, ^{1}H-NMR (D$_2$O, ppm) δ 6.10 (s, 2H, CH$_2$), 7.49 (s, 5H, Ph), 8.35-8.38 (d, 1H, Py), 8.64-8.80 (m, 2H, Py), 9.15-9.18 (d, 1H, Py).

Synthesis of *N*-Benzyl-*p*-cyanopyridinium bromide (BpCP)

A mixture of benzyl bromide (3.6 mL, 30 mmol), and *p*-cyanopyridinium (1.56 g, 15 mmol) was stirred and maintained at 40 °C for 2 days. The rest of the procedure was the same as that for the synthesis of BCP, (yield, 80%), m.p.:205 °C, ^{1}H-NMR (D$_2$O, ppm) δ 5.94 (s, 2H, CH$_2$), 7.53 (s, 5H, Ph), 8.49 (s, 2H, Py), 9.18-9.21 (d, 2H, Py).

Synthesis of *N*-Benzyl-*N, N*-dimethylanilinium bromide (BDA)

A mixture of benzyl bromide (3.6 mL, 30 mmol), N,N-dimethylanilin (3.8 mL, 30 mmol) and 1.23 g (1.56 mL) of acetonitrile was stirred and maintained at 40 °C for 16 hours. The rest of the procedure was the same as that for the synthesis of BCP, (yield, 90%), m.p.:160 °C, ^{1}H-NMR (D$_2$O, ppm) δ 3.65 (s, 6H, 2CH$_3$), 4.97 (s, 2H, CH$_2$), 7.05-7.08 (d, 5H, Ph), 7.31-7.37 (t, 1H, Ph), 7.46-7.51 (t, 2H, Ph),7.62 (s, 2H, Ph).

Synthesis of *N*-Benzyl-triphenyl phosphonium bromide (BTP)

A mixture of benzyl bromide (0.6 ml, 5 mmol) and triphenylphosphine (1.32 g, 5 mmol) was stirred and maintained at 40 °C for 3 days. The rest of the procedure was the same as that for the synthesis of BCP, (yield, 75.6%), m.p.:310 °C ^{1}H-NMR (D$_2$O, ppm) δ 6.97-7.00 (d, 2H, CH2), 7.23-7.26 (d, 5H, Ph), 7.55-7.88 (m, 15H, 3Ph).
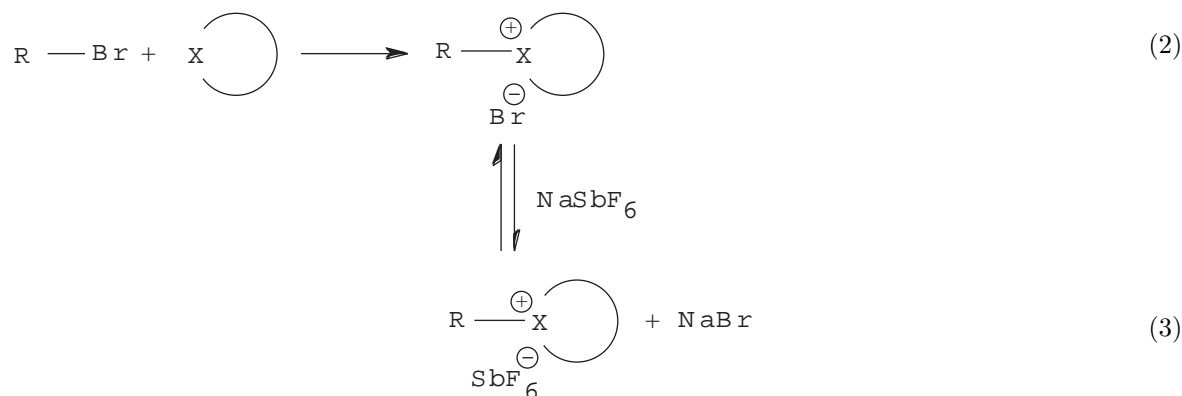
Thermal polymerization

Monomer solutions containing a given amount of the salt in acetonitrile were placed in Pyrex tubes and degassed by bubbling dry nitrogen. Initiation was affected by placing the vessels in an oil bath at 105 °C. At the end of the given time polymer was obtained by precipitation in anhydrous diethyl ether, and filtering and drying in a vacuum oven at 25 °C. Conversions were calculated gravimetrically.

Characterization

GPC measurements were performed with an Agilent1100 RI apparatus equipped with three Waters Styragel columns HR series (4, 3, 2 narrow bore), at a flow rate of 1 mL/min and the temperature of the refractive index detector of 30 °C, and THF as eluent. Molecular weights were calculated using polystyrene standards. ^{1}H-NMR spectra were recorded on a Bruker 250 instrument with D$_2$O and CD$_3$CN as a solvent and tetramethylsilane (TMS) as the internal standard.

Results and Discussion

Synthesis and characterization of the salts having structurally the same cationic moieties were previously reported by Endo et al.[14]. However, as counter ions, inorganic metal complex anions were mostly used. The salts with bromide counter anions were usually formed as an intermediate (Reaction 2) and directly converted to nonnucleophilic ones without isolation (Reaction 3).

$$R \!-\! Br + X \longrightarrow R \!-\! \overset{\oplus}{X} \overset{\ominus}{Br} \tag{2}$$

$$\big\Updownarrow\; NaSbF_6$$

$$R \!-\! \overset{\oplus}{X} \underset{SbF_6}{\ominus} + \; NaBr \tag{3}$$

Thus the salts with bromide counter anions formed by the treatment of benzyl bromide with pyridine, o-cyanopyridine, p-cyanopyridine or dimethyl aniline or triphenyl phosphine were isolated and characterized. A summary of the H-NMR chemical shifts of the aromatic and CH_2 protons belonging to the benzylic moiety is given in Table 1. As can be seen, depending on the nature of the nucleophilic heteroatom and substituents, aromatic protons appear in the 6.98-7.49 ppm range while CH_2 protons resonate at 4.97-7.25 ppm. It is known that these salts equipped with complex metal anions such as SbF_6 were successfully applied for the polymerization of cyclic and vinyl monomers. Upon heating, they undergo a fragmentation to generate benzylic cations stabilized with nonnucleophilic anions.

Under these conditions the growing sites are stabilized with the nonnucleophilic counter anions, which cannot undergo ion splitting and chain terminating reactions. In the present work, we use the cationic salts possessing nucleophilic bromide ion as initiators for cationic polymerization. In accordance with the initiating role of benzyl bromide in oxazoline polymerization, it was attempted to generate such species indirectly with external stimulation such as thermal treatment. The results of thermal polymerization of EOZO using various salts are given in Table 2. Unsubstituted benzyl pyridinium salt, BP is ineffective in the initiation of polymerization. Similarly, p-CN derivative also does not induce polymerization.

Interestingly, the conversion to polymer is highest when the cyano group is in the orto position. In general, the p-CN substituted benzyl pyridinium salt has often been used for cationic polymerizations. It is more reactive than the corresponding unsubstituted N-benzyl pyridinium salt, but suffers from the disadvantage of requiring high temperatures for a successful polymerization. Other analogs with p-substituents in the pyridinium moiety show a worse performance in cationic polymerization[15−16]. Therefore, we employed only the CN substituted salt in our studies. If the pyridinium ring is substituted by o-CN instead of p-CN, the thermal sensitivity is drastically improved, increasing the activity by a factor of 20 to 30[17]. The effect of the o-CN substituent was attributed to both steric and electronic factors. Our results are also in agreement with those obtained with salts possessing nonnucleophilic counter anions.

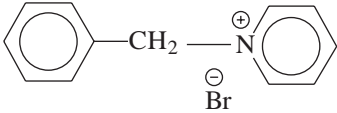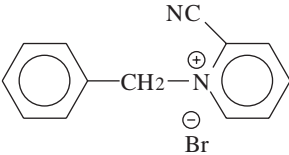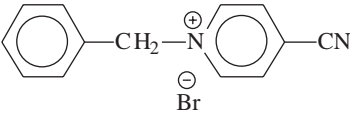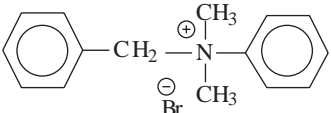**Table 1.** Benzylic protons appearing in the ^{1}H-NMR spectrum of the salts used.
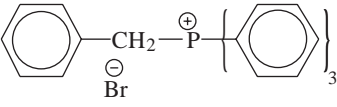
Salt	Structure	Aromatic protons (ppm)	CH$_2$ protons (ppm)
BP		7.48	5.80
BoCP		7.49	6.10
BpCP		7.53	5.94
BDA		7.07	4.97
BTP		6.98	7.25

Table 2. Thermally initiated cationic polymerization of EOZO[a] in acetonitrile by cationic salts.

Run	Initiator[b]	Time (h)	Temp. (°C)	Conv.	Mn[c]	Mn/Mw[c]
1	BP	6	105	-	-	-
2	BpCP	6	105	-	-	-
3	BoCP	6	105	70	3500	1.92
4	BoCP	24	105	71.5	3300	1.68
5	BDA	6	105	55	1100	1.45
6	BTP	6	105	-	-	-

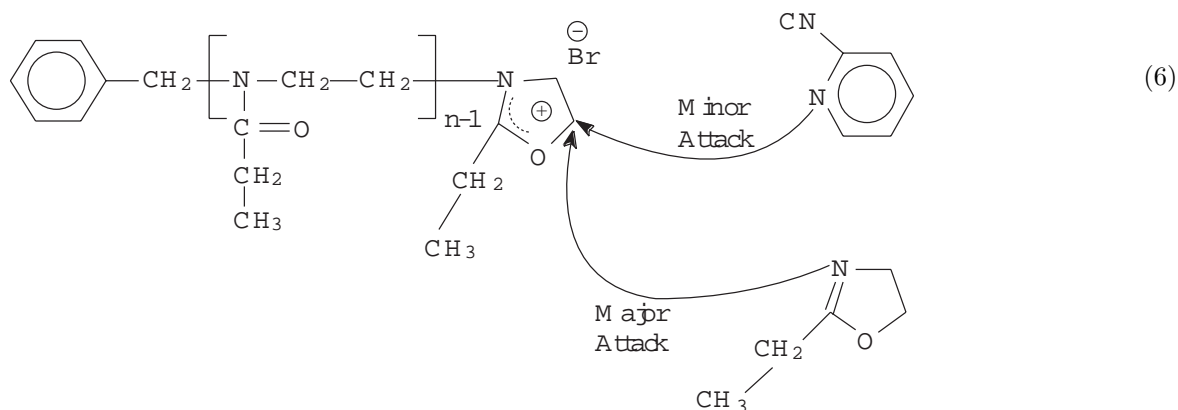[a] Concentration of EOZO: 6.6 M
[b] Concentration of initiator: 5×10^{-3}M
[c] Determined by GPC

As stated previously, benzyl pyridinium type salts generate benzylic cations upon thermolysis. Due to the high nucleophilicity of the bromide counter anion, benzyl bromide is expected to be formed. The cationic polymerization of EOZO then proceeds in the manner described for the initiating system using benzyl bromide. The general reactions concerning benzyl bromide formation and subsequent polymerization are given below for the case of BoCP:

$$(4)$$

$$(5)$$
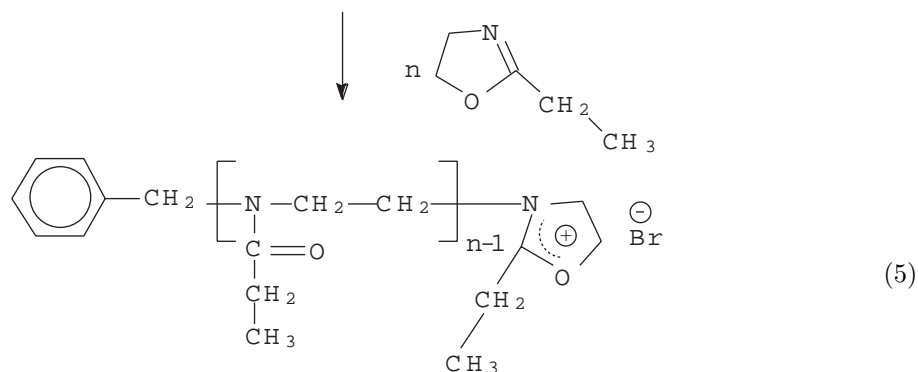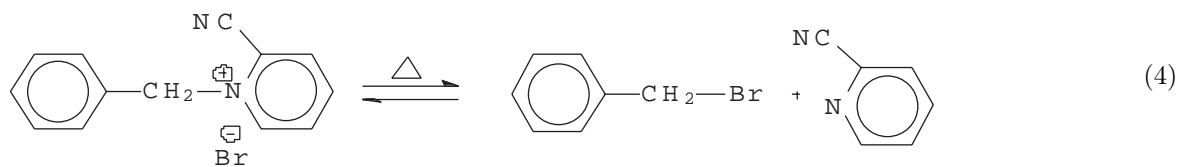
It is also interesting to note the reactivity of BDA. These salts are known to generate benzylic cations in a similar way. Similar high reactivity of both pyridinium and anilinium salts was observed in the polymerization of epoxy type monomers[1].

It should be pointed out that prolonged thermolysis times do not increase the yield or molecular weight (see Table 2, runs 3 and 4). This is probably related to the termination of polymerization by free pyridine groups formed in the thermolysis. This behavior was investigated in detail by Endo et al.[14]. According to Endo, the attack of pyridine groups in the early stages of the polymerization is only a minor process (Reaction 6).

$$(6)$$

However, when the concentration of pyridine increases it may become the major attack and polymerization may be terminated (reaction 7).

$$(7)$$
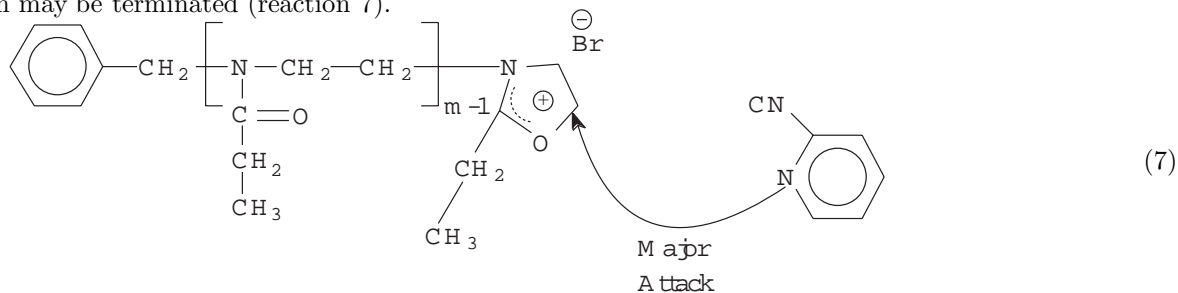
Phosphonium salts are not capable of initiating the cationic polymerization of EOZO. This behavior may be attributed to the different thermolysis mechanisms of phosphonium salts.

$$(8)$$

$$(9)$$
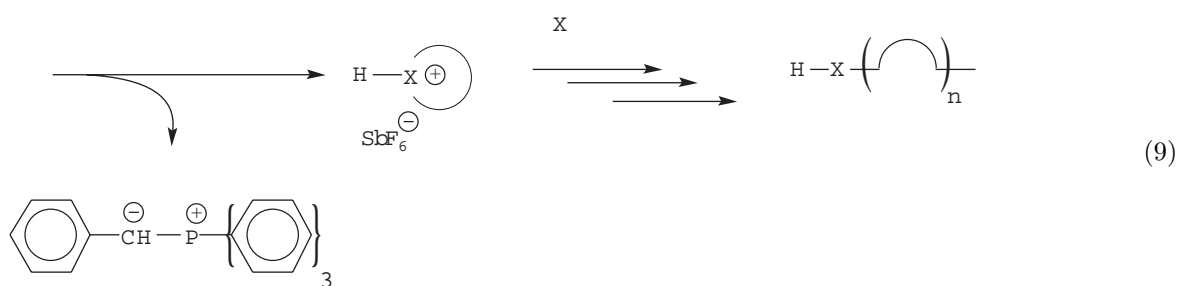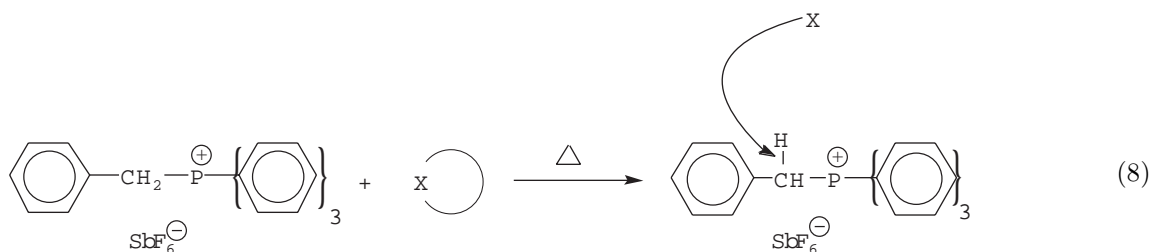
In order to confirm the polymerization mechanisms, spectral investigations of the polymers were performed. Figure 1 shows the ^{1}H-NMR spectrum of the polymer obtained by thermal initiation using BDP.

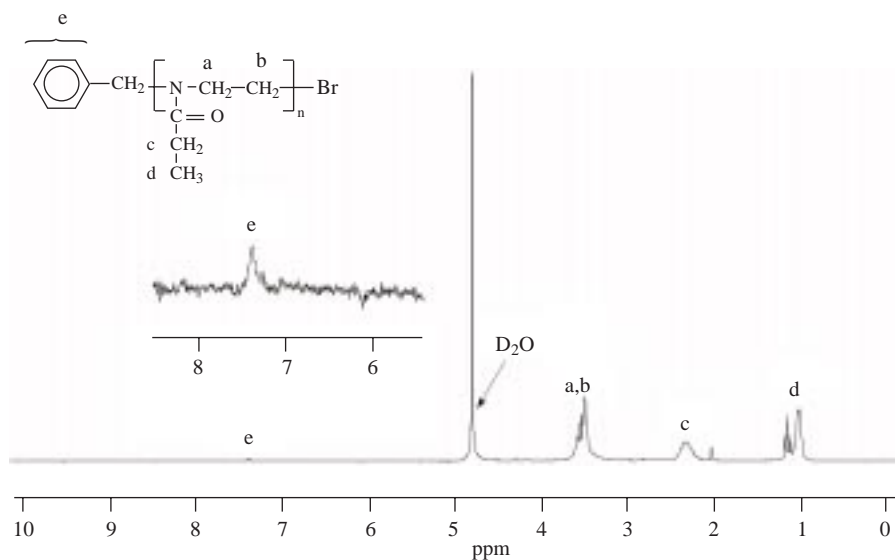**Figure 1.** ^{1}H-NMR spectrum of polyEOZO obtained by using (BDA) N-Benzyl-N,N-dimethylanilinium bromide (6 h).

The spectrum represents characteristic signals of the polymer, i.e. -CH$_3$ protons at 1.0-1.1 ppm, -CO-CH$_2$-protons at 2.2-2.4 ppm, and -CH$_2$-CH$_2$- protons at 3.4-3.6 ppm. Moreover, aromatic protons of the

benzylic group appear in the 7.50 ppm region, indicating the incorporation of benzylic moiety and therefore, initiation by benzyl bromide.

We also examined the ^{1}H-NMR spectra of the polymerization mixture. In this case, polymerizations were performed in an NMR tube containing deutoro acetonitrile, monomer and the initiating salt. In the ^{1}H-NMR spectra recorded before and after the 6 h polymerization time, the new peaks appearing in the range 2.4-3.6 ppm correspond to the propagating oxonium ions[18] (Figure 2).
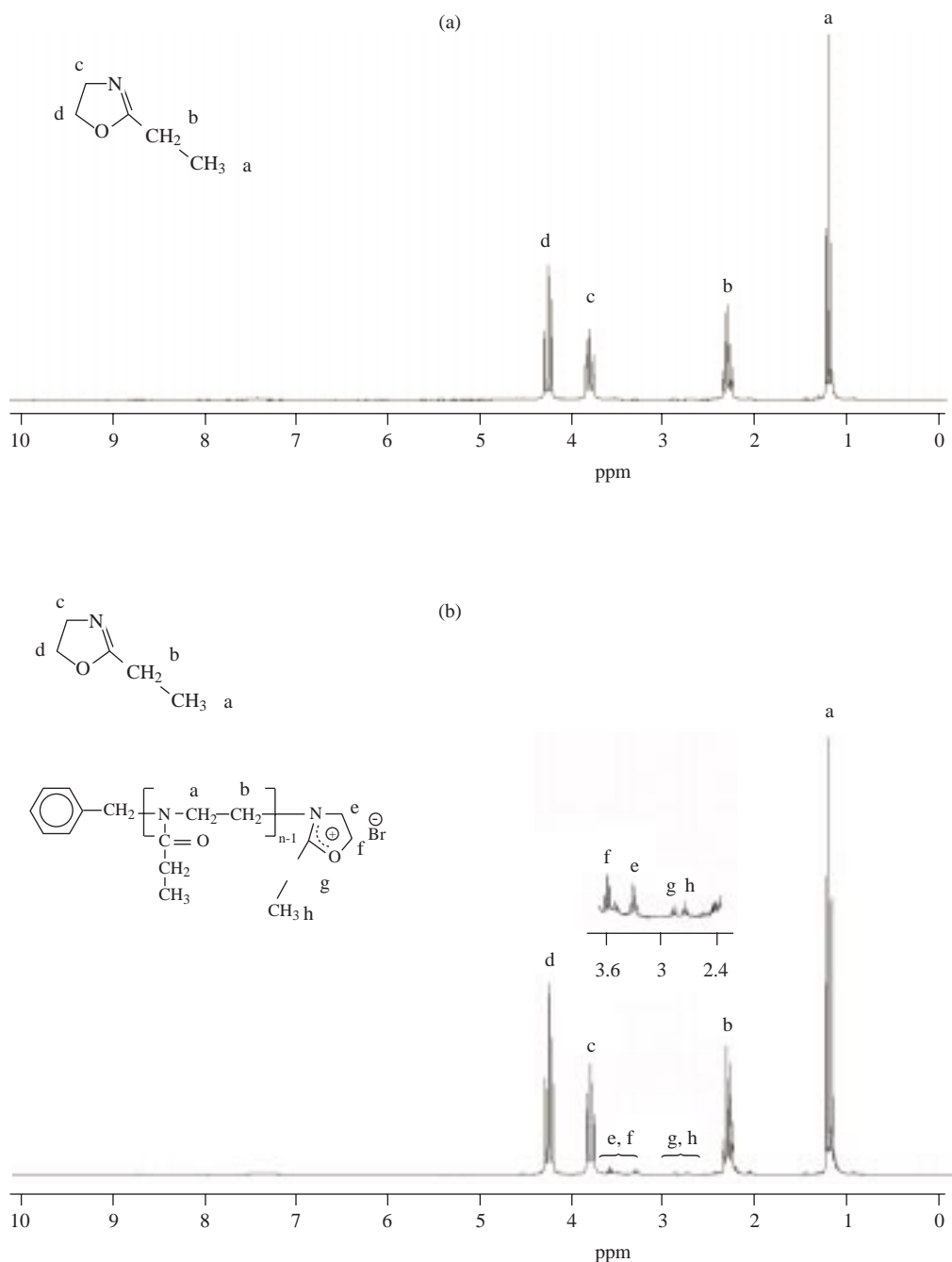

Figure 2. ^{1}H-NMR spectrum of polyEOZO obtained by using (BoCP) *N*-Benzyl-*o*-cyanopyridinium bromide in CD₃CN at 105 °C (a): after 20 min (b): after 6 h.

In conclusion, it was shown that cationic polymerization of EOZO can be thermally induced by *o*-cyanopyridinium and dimethylanilinium salts with bromide anion. Spectral investigations suggest that benzyl bromide formed from the thermal dissociation of the salts is responsible for the initiation, and the polymerization proceeds via an oxazolinium bromide as the propagating end.

Acknowledgment

References

1. Y. Yagci and T. Endo, **Adv Polym Sci., 127,** 59 (1997).

2. Y. Yagci and I. Reetz , **Prog Polym Sci., 23,** 1485 (1998).

3. J.P. Kennedy, **Carbocationic Polymerization** Wiley Interscience, New York, (1982).

4. K. Takuma and T. Endo, **J. Japan Soc. Colour Mat. 67,** 574 (1994).

5. Y. Yagci, A. Kornowski and W. Schnabel, **J. Polym. Sci. Part A: Polym. Chem., 30**, 1987 (1992).

6. T. Seagusa and S. Kobayashi, **Macromolecular Science, International Review of Science, Phys. Chem.Series 2**, Vol 8, Ch 4, Butterworth, London (1975).

7. T. Seagusa and S. Kobayashi, **Encyclopedia of Polymer Science and Technology**, Vol. 1, p. 220, John Wiley & Sons, New York (1986).

8. S. Kobayashi and T. Seagusa, **Ring Opening Polymerization**, Vol. 2, Ch. 11, Essex (1984).

9. S. Kobayashi and T. Seagusa, **Encylopedia of Polymer Science and Technology**, Vol. 4, p 525, John Wiley & Sons, New York (1986).

10. T. Seagusa and Y. Chujo, **Frontiers of Macromolecular Science**, p. 119, Blackwell Scientific Publication, Oxford (1989).

11. S. Kobayashi, **Prog.Polym.Sci**., 15, 751 (1990).

12. Y. Chujo and T. Seagusa, **Ring Opening Polymerization,** p. 239, Hanser, Munich (1993).

13. T.S. Bal, A. Cox, T.J. Kemp and P. Pinot de Moire, **Polymer, 21**, 423 (1980).

14. S.B. Lee, T. Takata and T. Endo, **Macromolecules, 24,** 2689 (1991).

15. H. Uno, T. Takata and T. Endo, **Chem. Lett**., 935 (1988).

16. H. Uno, T. Endo, **J. Polym. Sci. Part C: Polym. Lett. Ed. 26,** 453 (1988).

17. S.B. Lee, T. Takata, and T. Endo, **Macromolecules, 24,** 431 (1990).

18. T. Saegusa, S. Kobayashi and A. Yamada, **Makromol. Chem, 177,** 2271 (1976).