U.P.B. Sci. Bull., Series B, Vol. 71, Iss. 2, 2009 ISSN 1454-2331

SYNTHESIS AND STRUCTURE OF 2-ETHYL-2-OXAZOLINE MACROMONOMERS WITH STYRYL END-GROUPS

Valentin Victor JERCA[1], Florica Adriana NICOLESCU[2], Dan Sorin VASILESCU[3], Ana Maria ALBU[4], Dumitru Mircea VULUGA[5]

S-a realizat sinteza unui macromonomer de poli(2-etil-2-oxazolină) prin polimerizare în soluţie şi în bloc prin „metoda cu iniţiator" folosind p-clorometilstiren. Raportul molar între unităţile oxazolinice şi gruparea stiril variază în funcţie de tehnica de sinteză utilizată. Macromonomerul sintetizat a fost caracterizat calitativ prin spectroscopie FT-IR şi cantitativ prin spectroscopie FT-RMN. Macromonomerul obtinut a fost de asemenea investigat din punct de vedere al stabilităţii termice.

Synthesis of poly(2-ethyl-2-oxazoline) macromonomer having a styryl group as polymerizable function has been performed in bulk as well as in solution by "initiator method" using p-chloromethyl-styrene. The molar ratio between styryl and oxazolinic groups is different depending on the synthesis technique. The resulting macromonomer was analyzed qualitatively by FT-IR and quantitatively by FT-NMR techniques.

The thermal stability of the obtained macromonomer was also investigated by DSC-TGA-MS analysis.

Keywords: 2-ethyl-2-oxazoline macromonomer, cationic polymerization

1. Introduction

Macromonomers are important intermediates for the syntheses of graft and bloc copolymers. A macromonomer is a reactive oligomer or polymer with the molecular weight usually not exceeding $10^3 – 10^4$ Da. Generally, macromonomers can be considered molecules that consist in two parts; one part is the *polymeric chain* influencing its physical properties, while the other part is the *polymerizable*

---

[1] PhD student, Institute of Organic Chemistry "Costin D. Neniţescu", Romanian Academy, Romania, victor_jerca@yahoo.com

[2] PhD student, Institute of Organic Chemistry "Costin D. Neniţescu", Romanian Academy, Romania

[3] Prof., Department of Polymer Science, University POLITEHNICA of Bucharest, Romania

[4] Reader, Institute of Organic Chemistry "Costin D. Neniţescu", Romanian Academy, Department of Polymer Science, University POLITEHNICA of Bucharest, Romania

[5] Researcher, Institute of Organic Chemistry "Costin D. Neniţescu", Romanian Academy, Romania

*(reactive) grou*p influencing chemical reactivity of the macromonomer in polymerizations reactions.

The Change of the chemical structure of the polymer chain provides macromonomers with various properties and influences such parameters like solubility, or glass temperature (T_g). The primary factor affecting the chemical reactivity in polymerization processes is the type of macromonomer end group. The reactivity of macromonomers usually follows the reactivity of the low molecular weight monomer carrying the same functional group [1].

A special class, due to their properties, synthesis and applications are the amphiphilic macromonomers [2-6]. Such macromonomers have a hydrophilic *chain* soluble for example in water, and a hydrophobic *reactive group* insoluble in the mentioned solvent. The use of such macromonomers seems to be of interest, due to their hydrophilic-hydrophobic character; they tend to form micellar or aggregate structures in selective solvents; this feature is very important in practical applications [2-5].

One of the most interesting classes of monomers used for the macromonomer synthesis is that provided by cyclic imino-ethers (2-substituted-2-oxazolines). They can undergo cationic polymerization with various initiators, leading to poly-(N-acylethylenimine) (PROZO) as well as radical polymerization provided they posses a double bond in the side chain [7]. Their versatility is due to both their chemistry and their areas of application. The cationic polymerization of 2-substituted-2-oxazoline has a highly living character under appropriate reaction conditions due to the stability of the onium or covalently bonded propagating species. Through the use of this living character, precisely controlled polymers such as block and graft copolymers, macromonomers, and telechelics have been synthesized [8].

Synthesis of poly (N-acylethylenimine) macromonomers can be carried out by two methods. The first one is based on the living nature of the 2-alkyl-2-oxazoline; the living cationic species is terminated (end-capped) with amine having a vinyl group ("terminator method"). The second one is to employ an initiator having a vinyl group to induce the polymerization ("initiator method") [9]. Acrylic and methacrylic PROZO macromonomers have been obtained by the quantitative termination of the living ends with tri-ethyl-ammonium salt of (meth)acrylic acid to produce PROZO macromonomer [10]. A methacrylamide-type PROZO macromonomer has been synthesized via the terminator method with N,N - di-methyl-amino-propyl-methacrylamide as terminator [11]. These macromonomers have been copolymerized with comonomers with similar polymerization reactivity, such as styrene, methacrylic esters, and amides, to produce graft copolymers with graft PROZO chains. A butadiene-type PROZO macromonomer has been synthesized by the polymerization of 2-oxazolines with 2,3-bis (bromo-methyl)-1,3-butadiene as initiator [12].

A PROZO macromonomer with significantly less reactive polymerizable groups has been synthesized by initiation with vinyl iodo-acetate [13] and subsequently has been copolymerized with vinyl acetate.

A glycol-type PROZO macromonomer has been synthesized by the quantitative termination of the living terminal with diethanolamine [14].

The aim of the present work is the synthesis and characterization of macromonomers via ring-opening polymerization of 2-ethyl-2-oxazoline, bearing a styryl polymerizable group.

2. Experimental

2.1. Materials

2-Ethyl-2-oxazoline (EtOZO, from Aldrich) was purified by cryogenic distillation, chloro-methyl-styrene (CMS, from Aldrich), and N,N-dimethylformamide (DMF, from Fluka), were used as received.

2.2. Procedure

For the macromonomer synthesis we have used two different procedures: in bulk, and in solution respectively.

A typical run was as follows. EtOZO and CMS were dissolved in DMF under argon. The reaction mixture was stirred and heated for 4h at 90^oC.

The resulting macromonomer was separated from the reaction mixture by cryogenic distillation of the solvent and unreacted monomers and the conversion was measured gravimetrically.

2.3. Characterisation

FT-IR spectra were recorded on a Bruker Vertex 70 spectrometer fitted with Harrick MVP2 diamond ATR device. ^1H and ^{13}C FT-NMR spectra were recorded on a Varian Unity 400 spectrometer in $CDCl_3$ at room temperature. The thermo-gravimetric analysis was performed using a simultaneous DSC-TGA apparatus model STA 449C Jupiter Netzsch.

3. Results and discussion

The poly((N-acylethylenimine)-styrene head macromonomer synthesis were performed in agreement with the conditions from Table 1.

Table 1

Substrate compositions

Sample name	Procedure	n_{EtOZO} [mole]	n_{CMS} [mole]	$C_{M\text{-}EtOZO}$ [mol/l]	$C_{M\text{-}CMS}$ [mol/l]
V_M	in solution (DMF)	$4{,}7\cdot10^{-2}$	$6{,}4\cdot10^{-3}$	2,3	0,31
$V_{M\text{-}B}$	bulk	$4{,}7\cdot10^{-2}$	$6{,}4\cdot10^{-3}$	-	-

Both macromonomer structures were analysed by FT-IR spectroscopy. The spectra revealed the presence of a strong ester stretching band $\nu_{C=O}$ centred at 1629 cm^{-1} accounting for a poly(N-acylethyleneimine) structure. Besides this a new $\nu_{C=N^+}$ band at 2415 cm^{-1} appeared due to oxazolinium chloride group.

While IR spectroscopy offers only a qualitative image of the structure of the macromonomer, ^1H NMR and ^{13}C NMR spectra allow quantitative calculations regarding the chain length.

For the macromonomer obtained by solution procedure, ^{13}C NMR spectra (Fig. 1) exhibit signals at 9.67 ppm and at 27 ppm attributed to the methyl and methylene carbon of the side chain. The broad signal at 42-46 ppm is assigned to the methylene carbons of the backbone. The "a" carbon atoms give signals at 51 ppm. The presence of the oxazolinium cation is proved by the presence of the "f" signal protons at 59 ppm.

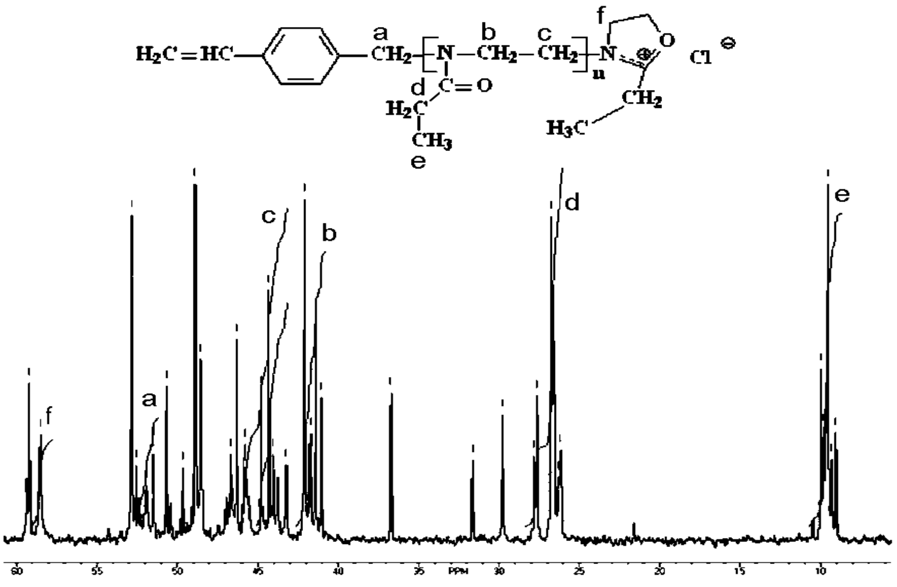

Fig 1. ^{13}C NMR spectrum for EtOZO macromonomer (solution polymerization)

When we used the bulk polymerization procedure, the presence of the oxazolinium cation was no longer proved. Besides this, the macromonomer ^{13}C NMR spectrum (Fig. 2) exhibits the same signals as in the other case typical for the cationic polymerization of the EtOZO.

While ^{13}C NMR spectra allow us to calculate the ratio between styryl and oxazolinic groups the ^{1}H NMR spectrum (Fig. 3) proves that the de-acylation reactions of the side chain are simultaneous.

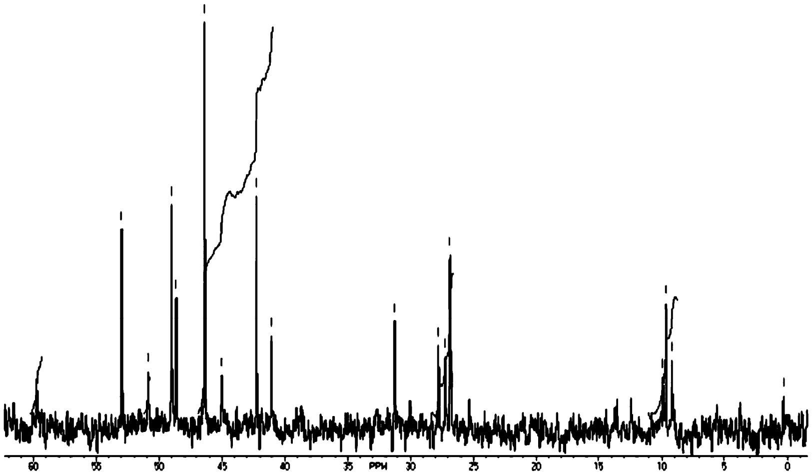

Fig 2. ^{13}C NMR spectrum for EtOZO macromonomer (bulk polymerization)

The "a", "b" protons of the oxazoline polymerized by cationic mechanism give ^{1}H signals between 3.2-3.8 ppm, while "c" protons of the "NH" group are placed at 6.2 ppm. The signal at 10 ppm characteristic to the carboxylic proton is consistent with de-acylation and the integral is equal to "c" signal integral.

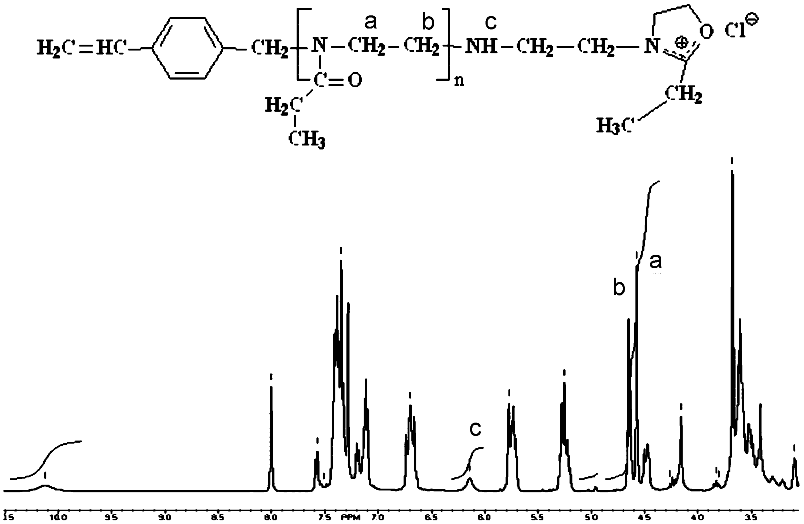

Fig. 3. ^{1}H NMR spectrum for EtOZO macromonomer (solution polymerization)

Using the integrals of these signals we have calculated the macromonomer compositions for both procedures.

NMR analyses reveal the following aspects:

- The molar ratio between CMS and EtOZO in the macromonomer obtained in solution is n_{CMS}/n_{EtOZO}= 1:5;
- The molar ratio between CMS and EtOZO in the macromonomer when the polymerization takes place in bulk is n_{CMS}/n_{EtOZO}= 1:4 without being noticed the presence of the oxazolinium cation (the absence of the signal generated by "f" proton);
- There is one de-acylated oxazolinic unit for both procedures.

Based on these aspects we may conclude that DMF separates the charges and allows ionic propagation, while in bulk the propagation is mainly covalent due to the fast attack of the counter ion over the oxazolinium cation. This hypothesis is also sustained by the lower yield (60%) for bulk polymerization as compared with the solution polymerization (92%).

In order to study the macromonomer thermal stability to see if it can be used as a stabilizer in dispersed systems we performed DSC-TGA analysis. (Fig. 4). The DSC curve revealed a melting-like transition at 87.4°C. The TGA curve exhibits four distinct degradation steps with almost equal enthalpies which can be assigned to stepwise de-polymerization.

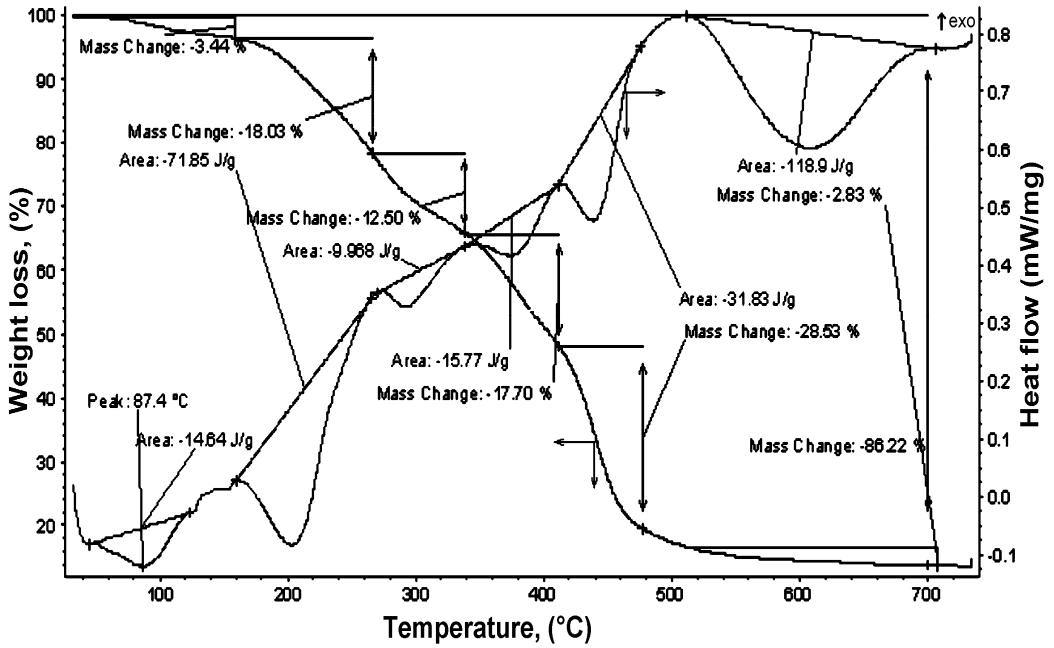

Fig. 4. Thermal analysis for solution for EtOZO macromonomer (solution polymerization)

4. Conclusions

A poly((N-acylethylenimine)-styrene head macromonomer was synthesized by two methods: solution polymerization and bulk polymerization. Its structure was confirmed by FT-IR and FT- NMR analyses.

The chain length and conversion were depending on reaction technique. Four ethyleneimine units to one styrene in bulk, and five to one in solution were obtained. The solution procedure proved to be better than the bulk procedure, leading to a higher conversion and molecular weight for the macromonomer, due to the DMF presence that allows the separation of the charges.

Specific de-acylation of poly(N-acylethylenimine) chain was proved to take place in both cases.

The DSC-TGA analysis showed an melting temperature of 87.4°C for the macromonomer and sustained the ratio found between EtOZO and CMS from FT-NMR analyses.

Acknowledgment

The authors are deeply indebted to National Council for Scientific Research for their generous financial support within the project entitled "Materiale cu structura macromoleculara care contin cromofori legati chimic"; PN II, code CNCSIS 86.

REFERENCES

[1] *K. Ito*, „Polymeric design by macromonomer technique", in Prog. Polym. Sci., **vol.23**, no.4, 1998, pp. 581-620.

[2] *K. Ito, K. Tanaka, H. Tanaka, G. Imai, S. Kawaguchi, S .Itsuno*, "Poly(ethy1ene oxide) macromonomers. 7. Micellar polymerization in water", in Macromolecules, **vol. 24**, no. 9**,** 1991, pp. 2348-2354.

[3] *D. Chao, S. Itsuno, K. Ito*, "Poly(ethylene oxide) macromonomers IX. Synthesis and polymerization of macromonomers carrying styryl end groups with enhanced hydrophobicity", in Polym. J., **vol. 23,** no. 9, 1991, pp. 1045-1052.

[4] *S. Kawaguchi, A. Yekta, J. Duhamel*, *M. Winnik, K. Ito*, "Fluorescence probe study of micelle formation of poly(ethylene oxide) macromonomers in water", in J. Phys. Chem., **vol. 98**, no. 32, 1994, pp. 7891-7898.

[5] *K. Ito, K. Hashimura, S. Itsuno, E. Yamada*, "Poly(ethylene oxide) macromonomers. 8. Preparation and polymerization of ω-hydroxypoly(ethylene oxide) macromonomers", in Macromolecules, **vol. 24**, no. 14, 1991, pp. 3977-3981.

[6] *M. Maniruzzman, S. Kawaguchi, K. Ito*, "Micellar copolymerization of styrene with poly(ethylene oxide) macromonomer in water: Approach to unimolecular nanoparticles via pseudo-living radical polymerization", in Macromolecules, **vol. 33,** no. 5, 2000, pp. 1583-1592.

[7] *V. V. Jerca, A. F. Nicolescu, A.-M. Albu, D. M. Vuluga*, "Polymer architectures based on oxazoline monomers" in Molecular Crystals and Liquid Crystals, **vol. 483**, 2008, pp. 78-88.

[8] *S.Kobayashi, H. Uyama*, "Polymerization of cyclic imino ethers: from its discovery to the present state of the art", in J. Polym. Sci. Part A: Polym Chem, **vol. 40**, no. 2, 2002, pp. 192-209.

[9] *S. Kobayashi, M. Kaku, S. Sawada, and T. Saegusa,* "Synthesis of poly (2-methyl-2-oxazoline) macromers", in Polym. Bull., **vol. 13**, no. 5, 1985, pp.447-451.

[10] *S. Kobayashi, E. Masuda, S. Shoda, Y. Shimano*, "Synthesis of acryl- and methacryl-type macromonomers and telechelics by utilizing living polymerization of 2-oxazolines", in Macromolecules, **vol. 22**, no. 7, 1989, pp. 2878-2884.

[11] *R.C.Schulz, E.Schwarzenbach*, "Macromonomers on the basis of 2-phenyl-2-oxazoline", in Makromol. Chem. Macromol. Symp., **vol. 13-14** , 1988, pp. 495-505.

[12] *S. Kobayashi, H. Uyama, Y. Narita*, "Synthesis and polymerization of butadiene-type poly(2-oxazoline) macromonomers", in Makromol. Chem.Rapid Commun., **vol.13**, no. 7, 1992, pp. 337-341.

[13] *H. Uyama, S. Kobayashi*, "Synthesis of poly(2-oxazoline) macromonomers having a vinyl ester group", in Macromolecules, **vol. 24**, no. 2, 1991, pp. 614-615.

[14] *S. Kobayashi, H. Uyama, H. Shirasaka,* "Synthesis and polymerization of poly(2-oxazoline) macromonomers having a glycol group", in Makromol. Chem. Rapid Commun, **vol. 11**, no. 1, 1990, pp. 11-14.