# Polyoxazolines — mechanism of synthesis and solution properties

**Andrzej Dworak**[1),*)], **Barbara Trzebicka**[1)], **Agnieszka Kowalczuk**[1)],
**Christo Tsvetanov**[2)], **Stanislav Rangelov**[2)]

DOI: dx.doi.org/10.14314/polimery.2014.088

*Dedicated to Professor Stanisław Penczek on the occasion of his 80th birthday*

**Abstract**: Oxazolines and the mechanism of their polymerization have been known for over 40 years. The relatively easy control of the polymerization process of oxazolines, the wide range of oxazoline polymer properties, reaching from strongly hydrophilic through amphiphilic, temperature responding to strongly hydrophobic and last not least their high biocompatibility cause that these polymers are intensively studied and the interest for them seem to increase. In this paper the cationic polymerization of polyoxazolines, especially the problem of the reversible desactivation and reactivation of active centers, the self-organization and response to temperature changes of polyoxazolines is discussed basing upon own research and literature reports. The synthesis of nanocontainers based upon the thermoresponsivity of polyoxazolines for obtaining hollow nanoparticles in nanometer range is also described.

**Keywords**: oxazolines, polymerization mechanism, properties, self-organization, star polymers, thermoresponsive polyoxazolines.

## Polioksazoliny — mechanizm syntezy i właściwości roztworów

**Streszczenie**: Niniejszy przegląd literaturowy dotyczy polimerów oksazolin. Oksazoliny i mechanizm ich polimeryzacji są dobrze znane niemal od 40 lat. Relatywnie łatwa kontrola procesu polimeryzacji oksazolin, szeroki zakres właściwości polimerów od silnie hydrofilowych poprzez amifilowe, reagujące na temperaturę, po silnie hydrofobowe, a także znaczna biozgodność powodują, że polioksazoliny są wciąż intensywnie badane, a w ostatnich latach zainteresowanie tymi polimerami zdaje się rosnąć. W niniejszej pracy, na podstawie własnych prac i danych literaturowych, opisano kationową polimeryzację oksazolin, w szczególności problem odwracalnej dezaktywacji i reaktywacji centrów aktywnych, a także wybrane polimery oksazolin, zarówno liniowe, jak i gwieździste, ich zachowanie w roztworze, samoorganizację i reakcję na zmiany temperatury. Opisano także, wykorzystujące efekt termoczułości polimerów oksazolin, syntezy nanozbiorników — pustych nanocząstek o średnicy kilkuset nanometrów.

**Słowa kluczowe**: oksazoliny, mechanizm polimeryzacji, właściwości, samoorganizacja, polimery gwieździste, termoczułe polioksazoliny.

## INTRODUCTION

Monomeric oxazolines are known as since 1889 [1]. Their synthesis (several routes have been described) is rather simple [2—5]. Oxazolines polymerize easily under the action of cationic initiators. This process is very close to living, opening wide synthetic possibilities and therefore a route to new materials of desired, widely variable properties [6]. The affinity of polyoxazolines to water may be controlled in a wide range by the proper choice of the alkyl substituent at C2 and varies from highly water soluble methyl oxazoline to extremely hydrophobic fluoroalkyl substituted polyoxazolines, making these polymers good objects for studying the water solution properties and the self-organization of amphiphilic polymers in water. The biocompatibility of polyoxazolines is well proven, to an extent that the term "pseudopeptides" has been coined for polyoxazolines [7] to turn attention to the close structural similarity between the polyoxazolines and polypeptides. Polyoxazolines were conjugated to protein and small molecule drugs maintaining their activity [8], grafted onto liposomal bilayers [9], formulated into micelles carriers [10] or immobilized on a surface making antifouling devices [11]. All these factors have caused that the interest in polymerization of oxazolines and resulting polymers, once governed by purely fundamental research, seems to enjoy a renaissance in the last years and is subject of numerous papers, mostly oriented towards possible applications.

---

1) Polish Academy of Sciences, Centre of Polymer and Carbon Materials, PL-41-800 Zabrze, Poland.

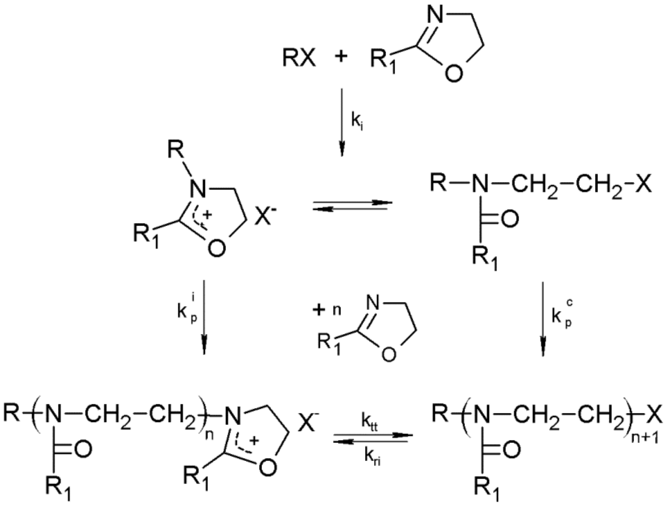
2) Bulgarian Academy of Sciences, Institute of Polymers, 1113 Sophia, Bulgaria.

*) Author for correspondence; e-mail: andrzej.dworak@cmpw-pan.edu.pl

## LIVING CATIONIC POLYMERIZATION OF OXAZOLINES: ELEMENTARY REACTIONS

Quite early it was established that oxazolines are capable to polymerize under the action of acidic initiators. This process has been studied, giving rise to one of the first well established descriptions of the living cationic ring opening polymerization [12—14].

Already the pioneering works of Saegusa [12], Kagyia [13] and Litt [14] have proven that the mechanism of the polymerization, initiated by numerous kinds of Lewis and protonic acids proceeds, roughly, according to the mechanism shown in Scheme A.



**Scheme A. Polymerization of 2-oxazolines**

Saegusa [12] has shown that during the growth of the chain both kinds of active species: the ionic and the covalent ones coexist in an equilibrium, the position of which depends upon the basicity of the oxazoline monomer and the nucleophilicity of the counter ion. Numerous systems consisting of different oxazolines and initiators bearing counterions of different nucleophilicty have been studied, confirming this finding.

However, the question of the role of both kinds of active centers: the ionic and the covalent ones, in the chain growth, common to most problems of ionic ring opening polymerizations [15], remained open.

The polymerization of oxazolines is a convenient model to study this phenomenon, because the ionic and the covalent active centers give rise to distinct signals in the $^1$H NMR spectrum, as interconversion of ionic to covalent centers is slow enough that the signals are well separated (Fig. 1). It is possible to find a system oxazoline – initiator – counter ion – solvent where this equilibrium can easily be measured [16].

Changing the temperature rapidly the rate at which the equilibrium was reached could be measured. This, together with the data on apparent rate of chain growth related to the ratio of ionic and covalent species, made all rate constants of elementary reactions available with reasonable accuracy.

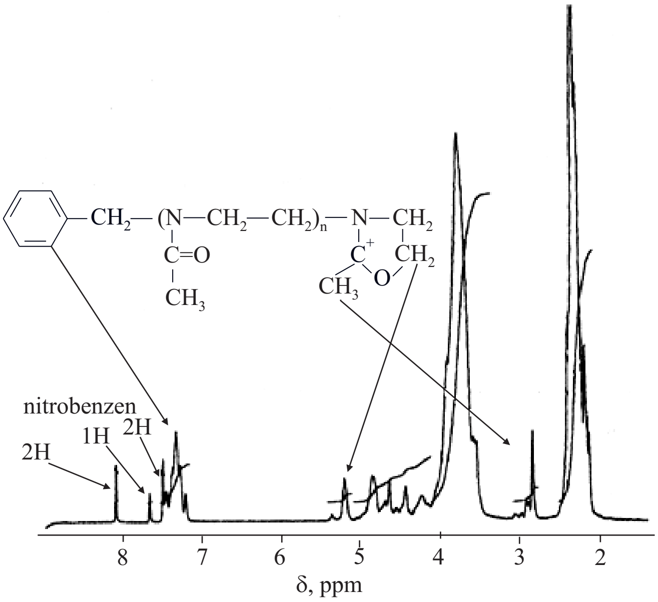


**Fig. 1. $^1$H NMR (600 MHz) spectrum of the living polymer of methyl oxazoline (initiator benzyl bromide(I), solvent nitrobenzene, $[M]_0$ = 1.5 mol/dm$^3$, $[I]_0$ = 0.15 mol/dm$^3$, 25°C) (according to [16])**

The position of the ionic – covalent equilibrium depends upon the monomer and the counter ion and is strongly temperature dependent. With increased temperature the share of covalent centers growths. The chain growth on ionic centers is always much faster than on covalent ones. The growth on cationic centers is almost exclusively responsible for the chain growth, regardless of the temperature and the actual share of their fraction. The covalent centers undergo an intramolecular transformation (without the participation of the monomer) to the ionic ones. The bimolecular conversion, under addition of the monomer, is very slow and of negligible contribution to the growth of the material chain.

Quantitative data on the rate constants of the elementary reactions are thus available. For poly(2-methyl-2-oxazoline) – bromide counter ion in nitrobenzene values shown in Table 1 were obtained [16].

This data may be translated into time-related events.

Simple calculations based upon data in Table 1 yield information about the time periods at which the elementary events occur. At 25 °C in nitrobenzene the cationic active centers transform to the covalent ones *via* the collapse of the ion par (*i.e.* intramolecularly) each 250 s. During that time 0.006 molecules of the monomer are added (each addition happens every 11 hours, a rather slow growth). After the reversible termination, the collapse of the ion pair, the active centers stays in the covalent form for 154 s, before the intramolecular reinitiation occurs. The covalent center, the bromide, may also be reactivated in a bimolecular reaction with the monomer. This reaction is extremely slow, it happens every $5 \cdot 10^5$ s. This time

**Table 1. Thermodynamic and kinetic parameters of the polymerization of 2-methyl-2-oxazoline with bromide counter ion in nitrobenzene**

| Parameter | $k$[1], $K$[2] | $\Delta H$, $\Delta E$, $\Delta S$ |
|---|---|---|
| Equilibrium constant ionic-covalent centers | 1.62 | $\Delta H$=-22.0 kJ/mol, $\Delta S$=-70 J/ mol·deg |
| Rate constant of reinitiation | $6.5 \cdot 10^{-3}$ $s^{-1}$ | $\Delta E$=42.3 kJ/mol |
| Rate constant of temporary termination | $4.0 \cdot 10^{-3}$ $s^{-1}$ | $\Delta E$=65.3 kJ/mol |
| Fraction of ionic active centers | 55 % | $\Delta E$=80.0 kJ/mol |
| Rate constant of propagation on ionic active centers | $4.2 \cdot 10^{-5}$ $dm^3$ $mol^{-1}s^{-1}$ | $\Delta E$=60.0 kJ/mol |
| Rate constant of propagation on covalent active centers | $< 2 \cdot 10^{-6}$ $dm^3$ $mol^{-1}s^{-1}$ | ≈60 kJ/mol |

[1] $k$ — rate constant, [2] $K$ — equilibrium constant.

shortens of course with monomer concentration. The calculated monomer concentration, at which the rate of bimolecular reactivation (the rate of chain growth on covalent centers) would become equal to the rate of the intramolecular reinitiation, is *ca*. 1000 mol/dm$^3$, which by far exceeds the concentration of the monomer in bulk.

## SYNTHESES OF 2-OXAZOLINE POLYMERS AND MATERIALS BASED UPON THEM

The rather in-depth knowledge of the mechanism of the cationic polymerization of oxazolines indicates that this process may easily be controlled. The active centers are not very reactive and therefore rather stable, the side reactions (transfer or termination) may be suppressed. This, together with confirmed or expected interesting properties of the products opened ways to the syntheses of materials based upon them, some will be outlined below.

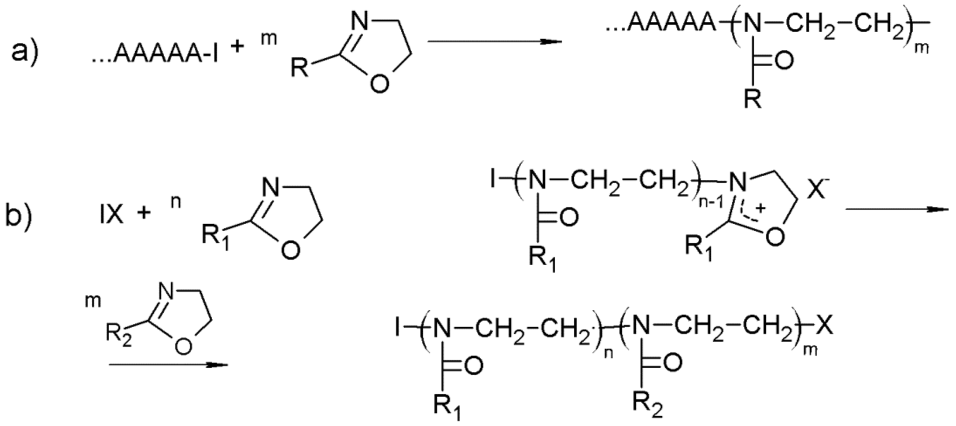
### Copolymers of oxazolines

Block copolymers of different oxazolines or oxazolines and other monomers, both vinyl and heterocyclic, have been synthesized, mostly by subsequent monomer addition using the living character of the polymerization of oxazolines or applying the macroinitiator technique [17—19] (Scheme B).

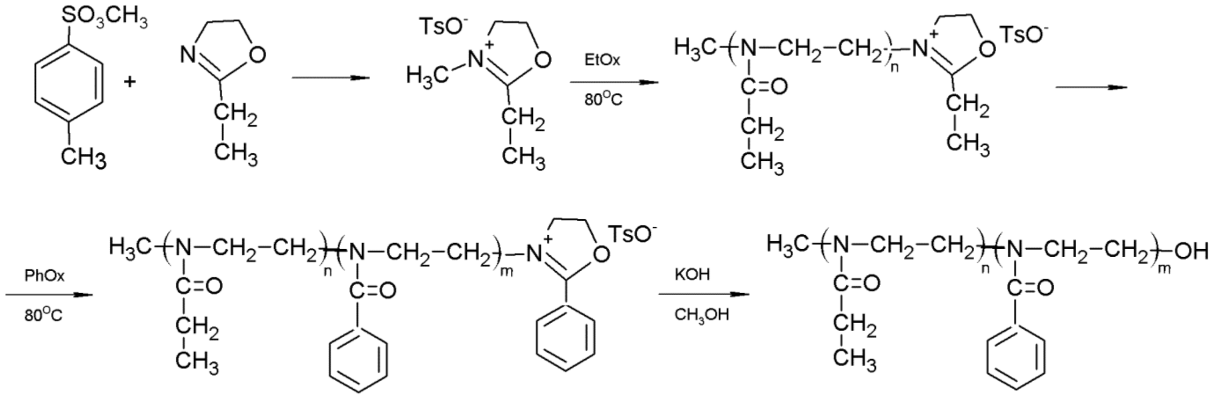
Different macroinitiators have been used in the macroinitiator technique, amongst others chloroformates or carboxylic acid chlorides [20, 21]. The block copolymers of oxazolines alone have most frequently been synthesized by subsequent monomer addition, using the active centers at the end of the more basic (more reactive) oxazoline to initiate the polymerization of the second block. Living character of the process and large differences in reactivities of oxazolines made even a rather unique "one pot" synthesis of block copolymers possible: methyl- and phenyl oxazoline were mixed and the polymerization initiated [22]. After the more reactive monomer was consumed the temperature was increased causing that the block of the less reactive monomer was formed.

The affinity to water of polymers of oxazolines depends strongly upon the substituent in the 2 position: polymers of methyl oxazoline are water soluble, ethyl or isopropyl oxazoline thermoresponsive, while longer alkyl or phenyl substituent imparts a strong hydrophobic character. Combining both blocks makes amphiphilic copolymers available and give rise to studies of their behavior in water systems, also to studies of their self-organization [23—28].

Trzebicka *et al.* [29] have synthesized poly(2-ethyl-2-oxazoline)-block-poly(2-phenyl-2-oxazoline) of different poly(2-phenyl-2-oxazoline) length (Scheme C) and studied their behavior in water.



**Scheme B. Strategies for syntheses of oxazoline block copolymers a) by macroinitiator b) by subsequent monomer addition**



**Scheme C. Synthesis of poly(2-ethyl-2-oxazoline)-*block*-poly(2-phenyl-2-oxazoline) (n = 60, m = 4, 12, 37)**

Amphiphilic block copolymers frequently self-organize in water. However, not always micelles are formed. Frequently, aggregation occurs to large, rather isotropic structures.

Here, the copolymer with the shortest hydrophobic 2-phenyl-2-oxazoline block (4 units) formed highly hydrated clusters. Their structure was destroyed upon spin-coating. The increase of the length of the hydrophobic segment to 12 or 37 2-phenyl-2-oxazoline units resulted in 50—150 nm aggregates depending on the concentration of polymer solution. Such structures are however of limited stability. They may disintegrate even under the action of relatively weak shear forces, depending on copolymer composition yielding single macromolecules (m = 4), mixtures of aggregates and micelles (m = 12) or well-defined stable micelles of 20 nm diameter (m = 37) [29]. Behavior of studied copolymers is schematically shown in Fig. 2.

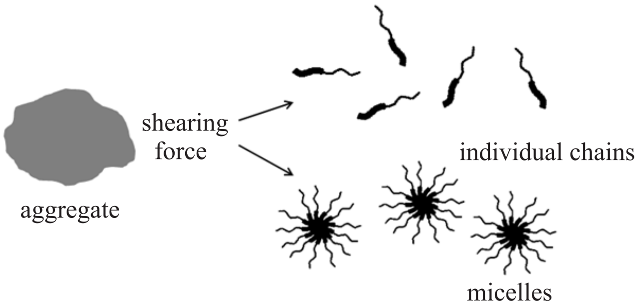


**Fig. 2. Behavior of poly(2-ethyl-2-oxazoline)-*block*-poly(2-phenyl-2-oxazoline) aggregates in water under the action of shear forces**

## Star polymers of oxazolines

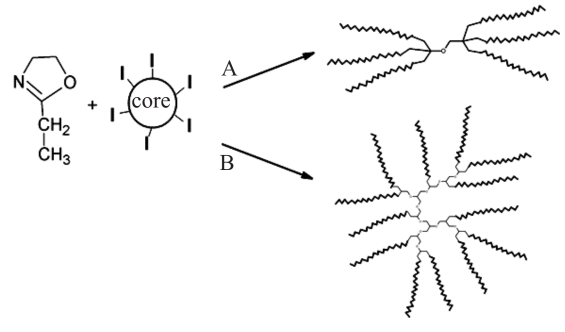
Efficient and rather fast initiation of the polymerization of oxazolines makes the synthesis of the star polymers having polyoxazoline arms by the "core-first" technique easily accessible. In this method, cores containing initiating groups are used to initiate the polymerization of arm-forming monomers (for reviews, see *e.g.* [30—31]).

Different polyfunctional macroinitiators have been applied to obtain stars with polyoxazoline arms: trichloroformates [33, 34], tetrakis(bromomethyl)ethylene [35], halomethylated silsequioxane [36, 37], or derivatives of cyclotriphosphazene [38]. There are also reports about the synthesis of the multiarm polyoxazoline stars using halogenated hyperbranched cores as initiators [39, 40].

Kowalczuk *et al.* [41, 42] obtained a series of six and 13 arm star polymers of ethyl oxazoline (Fig. 3) initiating the polymerization with dipentaerythritol hexakis(4-nitrobenzene sulfonate) or nitrotoluenesulphonic acid esters of hyperbranched polyglycidol. They have proven the structure of obtained stars and looked into their solution behavior, comparing the viscosity data obtained for such stars with those of linear counterparts.

It is known that the viscosities of the solutions of star polymers are lower than those of linear counterparts. The theoretical predictions of the solution behavior is however difficult. Even flexible chains behave differently in confined environment, bound to the star core, then as separated chains in solution.

The well-defined poly(2-ethyl-2-oxazoline) stars of different molar masses and 6 or 13 arms were used to



A=core: dipentaerythrityl hexakis(4-nitrobenzene sulfonate)
(6 initiating groups)
B=core: tosylated hyperbranched polyglicydol (13 initiating groups)
I=initiating groups

**Fig. 3. Synthesis of 6 and 13 arm poly(2-ethyl-2-oxazoline) stars**

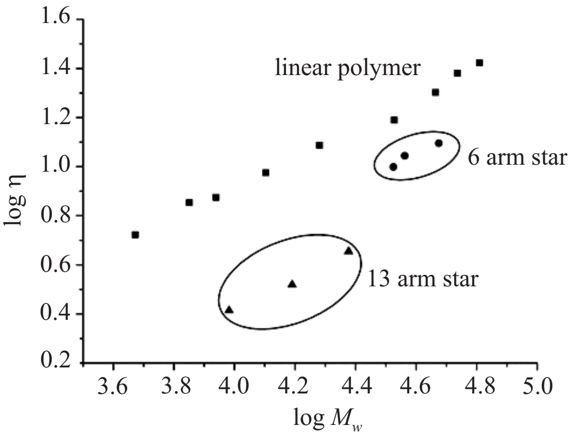


**Fig. 4. Intrinsic viscosity vs. molar mass of linear (squares), 6 arms (circles) and 13 arms (triangles) poly(2-ethyl-2-oxazoline)**

look into this problem [41]. For comparison, intrinsic viscosities of linear polyoxazolines of narrow molar mass distribution were measured. In this way, the parameters in the Mark-Houwink-Sakurada equations for all studied linear and star poly(2-ethyl-2-oxazoline)s were obtained using the plots shown in Fig. 4.

It turned out that, as may even intuitively be expected, the molar masses of star polymers (triangles and circles in Figure 4) are significantly lower than the molar masses of their linear counterparts (squares in Fig. 4). However, the intrinsic viscosities of the star polymer solutions change with the molar mass in very much the same way, as measured for their linear counterparts (similar a value in M-H-S equation). This confirms the assumption, that the chains bound at one end to the core behave like freely moving in solution, when a certain lower limit of their length is exceeded. The growth of the star macromolecules by extending the arms (not by adding to the core more arms of the same length) influences the solution in the same manner as the growth of the length of the individual macromolecules would.

The precision of the experimental results made also the value of the shrinking parameter $g'$ ($g' = [\eta]_{\text{branched}} / [\eta]_{\text{linear} \,|\, \text{at the same } M}$) available. This parameter was established to 0.60 for the 6 arm stars and to 0.32 for the 13 arm stars, similar to the values predicted by Roovers [43] and Douglas [44].

## Thermoresponsive polyoxazolines

Many polymers exhibit limited solubility in water. They are water soluble below a certain temperature and precipitate, when this temperature, called cloud point temperature $T_{CP}$, is exceeded. This behavior, widely studied and used for many purposes, is due to the limited stability of hydrogen bonds, responsible for the formation of the hydration sphere, which keeps the macromolecules in solution. When enough energy is supplied to the system, the hydrogen bonds dissociate, the solvation sphere is destroyed and the driving force for the solubility becomes too weak for the polymer to stay dissolved [45].

Poly(2-ethyl-2-oxazoline) is known to exhibit such property. The transition temperature depends rather strongly upon the molar mass (and, at lower molar masses, upon the kind of the end groups) and varies from 80 °C for $M_n$ of *ca.* 10 000 to 65 °C for $M_n$ of *ca.* 60 000 [46].

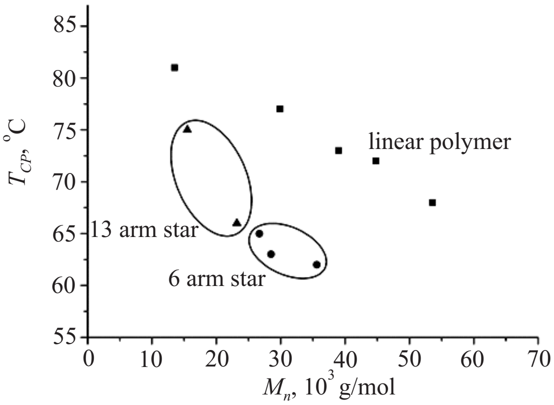


**Fig. 5. Cloud point temperatures of water solutions of linear (squares), 6 arms (circles) and 13 arms (triangles) poly(2-ethyl-2-oxazoline)**

It was found that also the star polymers of 2-ethyl-2-oxazoline exhibit such properties [41]. Also here the transition temperature is molar mass dependent and falls with increasing molar mass, even faster than in the case of linear poly(2-ethyl-2-oxazolines). The cloud point temperature changes depend also upon the topology: for the star polymers it is by *ca.* 10 to 20 °C lower than for linear chains (Fig. 5).

## Thermoresponsive polyoxazolines as templates for hollow nanoparticles

Polymeric vesicles consisting of a solvent (usually water) reservoir surrounded by a polymer layer are interesting structures, also because of their envisaged ability to serve as transporting vehicle for active species, first of all biologically active compounds. When the outer layer is not covalently stabilized, the advantages are diminished by the possibility of the disintegration caused by external factors, like pH, ionic strength, temperature *ea*. There is a need for nanoreservoirs with stable, but semipermeable walls.

Different approaches have been described for the synthesis of such nanoreservoirs [47—51]. Most of them calls for the use of a sacrificial template, a nanoparticle on which the outer layer would be formed and which would be removed after it fulfilled its role. Searching for an optimal solution we have proposed to use the effect of thermoresponsivity for preparing stable, hollow nanoparticles.

Above phase transition temperature thermoresponsive polymers form in semi-dilute water solution fairly large particles usually precipitating from the solution. However when proper conditions are chosen (polymer molar mass and concentration, heating rate, presence of surfactants) [52—55] the size of the formed particles may be controlled, so that particles of several hundred nanometer diameter and uniform distribution of sizes are formed. Such particles, frequently called mesoglobules, exhibit interesting properties due to large surface – volume ratio and their dimensions, determining the pathway in physiological systems.

The idea of the proposed synthetic route is shown in Fig. 6.

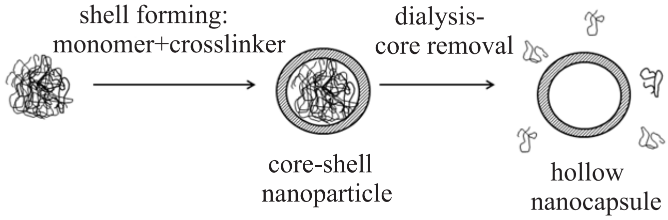


**Fig. 6. The route to hollow nanoparticles using thermoresponsive template**

At first, the template is formed using the thermoresponsivity of the dissolved polymer. Proper control of the conditions should yields mesoglobules of the desired size. Still keeping the temperature above the cloud point another monomer and possibly a crosslinker is added. The polymerization is initiated and, when the resulting polymer is not water soluble, the shell is formed.

The core has to be removed. To do so, the temperature is lowered below the cloud point temperature of the core forming polymer. The polymer of the core becomes water soluble and diffuses out of the interior, a process driven by the concentration gradient of the core polymer in the interior and outside of the polymer.

Our first attempt was concentrated on poly(*N*-isopropyl acryl amide) as template forming polymer and poly(hydroxyl ethyl methacrylate) for the shell formation [56]. Nanoparticles of lose interior were obtained. However, only *ca*. 40 % of the core polymer could be removed from the interior of the particle, either because it has been grafted onto the shell polymer during the radical polymerization or because of the tight core structure.

The application of thermoresponsive polyoxazolines to form the nanoparticle templates is the solution of choice.

Poly(2-isopropyl-2-oxazoline) was chosen [57] to obtain the template because it exhibit the cloud point temperature of *ca*. 37 °C [45], thus making the preparation of mesoglobules easier.

In the first step, 2-isopropyl-2-oxazoline was polymerized using methyl *p*-tosylate, a cationic initiator. Polymers of desired low molar mass from 3000 to 9000 and narrow molar mass distribution were obtained.

The route shown in Fig. 6 was applied to prepare hollow particles using poly(2-isopropyl-2-oxazoline). Conditions were searched to obtain nanoparticles of desired diameter and narrow distribution of diameters to serve as templates. A surfactant, sodium dodecyl sulfate was added and the a very rapid heating was applied using nanoprecipitation – the solution of the thermoresponsive poly(2-isopropyl-2-oxazoline) was dropped into a large amount of hot water, kept well above the cloud point of the core forming polymer. Narrowly distributed nanoparticles of *ca*. 400 nm diameter were obtained.

These particles were used as templates to form the shell. *N*-isopropyl acryl amide and a crosslinker were introduced and the polymerization was initiated. As the temperature was kept above the phase transition of poly(*N*-isopropyl acryl amide) the formed polymer, insoluble under such condition, covered the template with a shell of *ca*. 50 nm thickness.

To remove the sacrificial core the system was cooled down to 20 °C. Poly(2-isopropyl-2-oxazoline) became water soluble, diffused through the shell and could be remove by dialysis. *Ca*. 80 % of the template material was removed, yielding hollow nanoparticles, as evidenced by TEM.

*ACKNOWLEDGMENT*

*A.D. appreciates the help of Professor Stanislaw Penczek, who pointed out to him the possibility of studying the ionic — covalent equilibria in the polymerization of oxazolines and offered many significant advices during this part of research.*

## REFERENCES

[1] Gabriel S.: *Ber. Dtsch. Chem. Ges*. **1889**, *22*, 2220. [2] Schollkopf U., Jentsch R., Madawita K., Harms R.: *Liebigs Ann. Chem*. **1976**, *11*, 2105. [3] Rausch D. M., Pathel M. M.: *Synth. Commun*. **1985**, *15*, 675. [4] Witte H., Seeliger W.: *Liebigs Ann. Chem*. **1974**, *6*, 996. [5] Moller H., Fristad W., Krause H. J.: *Fat Sci. Technol*. **1993**, *95*, 151. [6] Rossegger E., Schenk V., Wiesbrock F.: *Polymers* **2013**, *5*, 956. [7] Aoi K., Suzuki H., Okada M.: *Macromolecules* **1992**, *25*, 7073. [8] Luxenhofer R., Han Y., Schultz A., Tong J.: *Macromol. Rapid. Commun.* **2012**, *33*, 1613. [9] Woodle M. C., Engbers C. M., Zalipsky C.: *Bioconjugate Chem.* **1994**, *5*, 493. [10] Lee S. C., Kim C., Kwon I. C., Chung H.: *J. Controlled Release* **2003**, *89*, 437.

[11] Zhang N., Pompe T., Amin I., Luxenhofer R.: *Macromol. Biosci.* **2012**, *12*, 926. [12] Saegusa T., Ikeda, H., Fuji H.: *Macromolecules* **1972**, *5*, 354. [13] Kagiya T., Narisawa S., Maeda T., Fukai K.: *J. Polym. Sci. Polym. Lett*. **1967**, *B4*, 441. [14] Bassiri T. G., Levy A., Litt M. H.: *J. Polym. Sci. Polym. Lett*. **1967**, *5*, 871. [15] Penczek S., Duda A., Kubisa P., Słomkowski S.: „Ionic AND coordination ring-opening polymerization”, in “Macromolecular Engineering: Precise, Synthesis, Material, Properties, Applications”, Vol.

1, (Eds. Matyjaszewski K., Gnanou Y., Leibler L.) Wiley VCH, Weinheim 2007, pp. 103—160. [16] Dworak A.: *Macromol. Chem. Phys*. **1998**, *199*, 1843. [17] Aoi K., Okada M.: *Prog. Polym. Sci*. **1996**, *21*, 151. [18] Hoogenboom R., Fijten M. W. M., Schubert U. S.: *J. Polym. Sci., Part A* **2004**, *42*, 1830. [19] Hoogenboom R.: *Angew. Chem. Int. Ed*. **2009**, *48*, 7978. [20] Dworak A., Schulz R. C.: *Macromol. Chem*. **1985**, *192*, 437.

[21] Dworak A., Schulz R. C.: *Macromol. Symp*. **1994**, *85*, 203. [22] Saegusa T., Chujo Y., Aoi K., Miyamoto M.: *Makromol. Chem. Macromol. Symp*. **1990**, *32*, 1. [23] Wiesbrock F, Hoogenboom R., Leenen M., Van Nispen S. F. G. M., *et al*.: *Macromolecules* **2005**, *38*, 7957. [24] Hoogenboom R.: *Macromol. Chem. Phys*. **2007**, *208*, 18. [25] Hoogenboom R., Wiesbrock F., Leenen M. A. M., Meier M. A. R.: *J. Comb. Chem*. **2005**, *7* (1), 10. [26] Hoogenboom R., Wiesbrock F., Leenen M. A. M., Thijs H. M. L., *et al*.: *Macromolecules* **2007**, *40* (8), 2837. [27] Fustin C. A., Lefevre N., Hoogenboom R., Schubert U. S.: *Macromol. Chem. Phys*. **2007**, *208* (18), 2026. [28] Fustin C. A., Huang H., Hoogenboom R., Wiesbrock F., *et al*.: *Soft Matter* **2007**, *3*, 79. [29] Trzebicka B., Koseva N., Mitova V., Dworak A.: *Polymer* **2010**, *51*, 2486. [30] Gao H., Matyjaszewski K.: *Prog. Polym. Sci*. **2009**, *34*, 317.

[31] Hadjichristidis N., Iatrou H., Pitsikalis M., Mays J.: *Prog. Polym. Sci*. **2006**, *31*, 1068. [32] Hadjichristidis N., Pitsikalis M., Iatrou H.: “Polymers with star-related structures” in “Macromolecular Engineering, Precise Synthesis, Material, Properties, Applications” (Eds. Matyjaszewski K., Gnanou Y., Leiber L.) Wiley, New York 2007, pp. 909—972. [33] Dworak A., Schulz R. C.: *Polimery* **1992**, *37*, 325. [34] Dworak A., Schulz R. C.: *Macromol. Chem*. **1991**, *192*, 437. [35] Kobayashi S., Uyama H., Narita Y., Ishiyama J.: *Macromolecules* **1992**, *25*, 3232. [36] Shen J., Zheng S.: *J. Polym. Sci., Part B* **2006**, *44*, 942. [37] Kim K., Ouchi Y., Chujo Y.: *Polym. Bull*. 2003, 49, 341. [38] Chang Y., Ji H., Han M., Rhee S.: *Macromolecules* **1994**, *27*, 1376. [39] Weberskich R., Hettich R., Nuyken O., Schmaljohann D.: *Macromol. Chem. Phys*. **1999**, *200*, 863. [40] Nuyken O., Weberskich R., Bortenschlager M., Schonfelder D.: *Macromol. Symp*. **2004**, *215*, 215.

[41] Kowalczuk A., Kronek J., Bosowska K., Trzebicka B., Dworak A.: *Polym. Int*. **2011**, *60*, 1001. [42] Dworak A., Trzebicka B., Kowalczuk A., Utrata-Wesolek A.: *Polimery* **2012**, *57*, 441. [43] Roovers J.: “Dilute solution properties of regular star polymers” in “Star and hyperbranched polymers”(Eds. Mishra M. K., Kobayashi S.) Marcel Dekker, New York 1999, 285—341. [44] Douglas J., Roovers J., Freed K.: *Macromolecules* **1990**, *23*, 4168. [45] Aseyev V., Tenhu H., Winnik M.: *Adv. Polym. Sci*. **2011**, *242*, 29. [46] Christova D., Velichkova R., Loos W., Goethals E.: *Polymer* **2003**, *44*, 2255. [47] Jiang P., Bertone J. F., Colvin V. L.: *Science* **2001**, *291*, 453. [48] Huang H., Remsen E. E., Kowalewski T., Wooley K. L.: *J. Am. Chem. Soc*. **1999**, *121*, 3805. [49] Nardin C., Hirt T., Leukel J., Meier W.: *Langmuir* **2000**, *16*, 1035. [50] Gittins D. I., Caruso F.: *Adv. Mater*. **2000**, *12*, 1947.

[51] Jang J., Ha H.: *Langmuir* **2002**, *18*, 5613. [52] Trzebicka B., Szweda D., Rangelov S., *et al*.: *J. Polym. Sci., Part A*. **2013**, *51*, 614. [53] Trzcinska R., Szweda D., Rangelov S., *et al*.: *J. Polym. Sci., Part A* **2012**, *50*, 3104. [54] Toncheva-Moncheva N., Dimitrov P., Tsvetanov C. B.: *Polym. Bull*. **2011**, *67*, 1335. [55] Trzebicka B., Weda P., Utrata-Wesolek A., *et al*.: *J. Polym. Sci., Part A* **2010**, *48*, 4074. [56] Weda P., Trzebicka B., Dworak A., Tsvetanov C. B.: *Polymer* **2008**, *49*, 1467. [57] Toncheva N., Tsvetanov C. B., Rangelov S., Trzebicka B., Dworak A.: *Polymer in press*.