

POLIMERY

CZASOPISMO POŚWIĘCONE CHEMII, TECHNOLOGII I PRZETWÓRSTWU POLIMERÓW

Reactive surfactants – chemistry and applications. Part II. Surface-active initiators (inisurfs) and surface- -active transfer agents (transurfs)

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Abstract: The aim of this paper is to present recent advances in the technology of surfmers [polymerizable surfactants – in Part I^{**)}], inisurfs (surface-active initiators) and transurfs (surface-active transfer agents). In this part, inisurfs and transurfs are described and discussed. Due to the development of controlled living polymerization, inisurfs and transurfs are becoming more and more significant. Inisurfs are used for atom transfer radical polymerization (ATRP) process and transurfs can be applied for reversible addition fragmentation chain transfer (RAFT) process. Preparation of nanospheres using a transurfs has also been reported.

Keywords: inisurf, surface-active initiator, atom transfer radical polymerization, transurf, surface-active transfer agent, reversible addition fragmentation chain transfer, emulsion polymerization, living polymerization.

Surfaktanty reaktywne – chemia i zastosowania. Cz. II. Powierzchniowo czynne inicjatory (inisurfy) i powierzchniowo czynne środki przeniesienia łańcucha (transurfy)

Streszczenie: Zaprezentowano najnowsze postępy w chemii i technologii reaktywnych surfaktantów: surfmerów [surfaktantów zdolnych do polimeryzacji – w Cz. I^{**)}], inisurfów (powierzchniowo czynnych inicjatorów) oraz transurfów (powierzchniowo czynnych środków przeniesienia łańcucha). W niniejszej części artykułu opisano inisurfy i transurfy, które znajdują zastosowanie m. in. w procesach kontrolowanej polimeryzacji żyjącej; inisurfy – w procesie polimeryzacji rodnikowej z przeniesieniem atomu (ATRP), a transurfy – w procesie polimeryzacji z odwracalnym addycyjno-fragmentacyjnym przeniesieniem łańcucha (RAFT). Transurfy mogą być również zastosowane do otrzymywania nanosfer.

Słowa kluczowe: inisurf, inicjator powierzchniowo czynny, polimeryzacja rodnikowa z przeniesieniem atomu, transurf, powierzchniowo czynny środek przeniesienia łańcucha, polimeryzacja z odwracalnym addycyjno-fragmentacyjnym przeniesieniem łańcucha, polimeryzacja emulsyjna, polimeryzacja żyjąca.

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INISURFS

Surface active initiators, known also as inisurfs or inistabs (INItiator STABilizer) [1], perform double role in polymerization process. They work as an initiator and a surfactant. In some cases, however, it is required to use additional surfactant in the process. Inisurfs form radicals during the polymerization and it may result in reduction of their surface active properties [2].

Structure

Inisurf consists of three parts:

- a hydrophobic moiety;
- a hydrophilic moiety;
- a initiating moiety.

In case of inisurf active in radical polymerization, its molecule can be either symmetrical or asymmetrical. Decomposition of symmetrical inisurf leads to creation of two surface active radicals. In case of asymmetrical inisurf one surface active radical and one non-surface active radical (for instance tertiary butyl or hydroxyl radicals) are produced.

Aside from low molar mass inisurfs, there is also a group of polymeric inisurfs [3].

Properties

There are different inisurfs dedicated for different types of polymerization. There are inisurfs which can initiate radical polymerization, usually containing azo or peroxy initiating moiety. Another group of surface active initiators are inisurfs for ionic polymerization, *e.g.*, dodecylbenzenesulfonic acid, and inisurfs for atom transfer radical polymerization (ATRP).

Inisurfs, as surface active molecules, are characterized by critical micelle concentration (*cmc*) and an area/molecule in the adsorbed state. Due to their ability to form micelles and to accumulate at interfaces, their radical efficiency is much lower than that of the most of conventional initiators. The decomposition behavior is also strongly affected. Radical recombination is very fast due to the low mobility of the adsorbed primary radicals [4, 5].

It has been observed that in the emulsion polymerization of styrene, if the inisurf concentration was below the *cmc*, the rate constant of the production of free radicals decreased with the increase of the inisurf concentration. It was recognized as a result of enhanced radical recombination. On the other hand, the inisurf concentration above the *cmc* resulted in an increase of the rate constant of the production of free radicals due to micellar catalysis effects [6].

The location of the radical-generating moiety in the inisurf molecule is important. For the azo-type inisurfs having the initiating moiety attached to the hydrophilic moiety the initiator efficiencies are very low. It is attributed to the fact that azo moiety is located outside of the

micelles. In that case, radicals are generated in the water phase, where monomer concentration is low. It results in domination of termination through recombination [7].

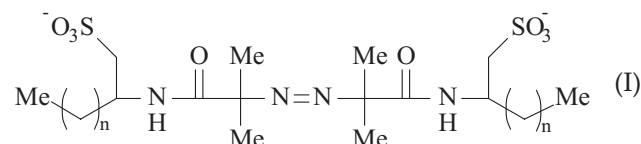
The first inisurfs required a multistep synthesis and were susceptible to hydrolysis. It resulted in higher cost and problems with product purification. Products developed in more recent times are less affected by these two problems. Modern inisurfs can be synthesized even in one step synthesis and do not have hydrolysable groups [2, 8].

Applications

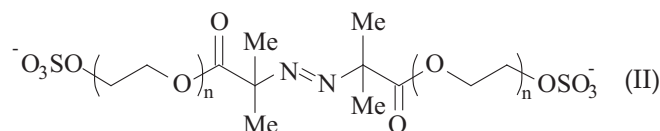
Emulsion polymerization

Inisurfs are used in emulsion polymerization to stabilize emulsion and initiate polymerization process. Additional co-surfactants and co-initiators may be used but it is not necessary in all processes.

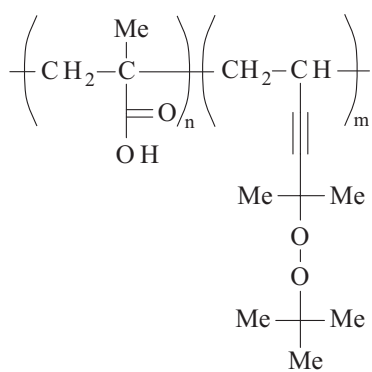
Aslamazova and Tauer [9] synthesized new class of 2,2'-azobis(*N*-2'-methylpropanoyl-2-amino-alkyl-1)-sulfonates [Formula (I)] and investigated their performance in polymerization of styrene.



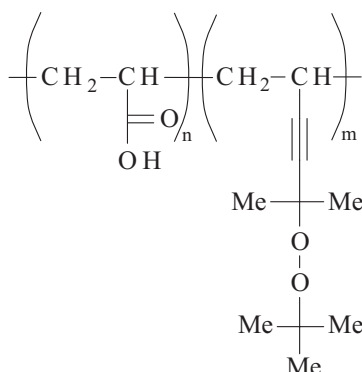
Compounds were obtained *via* one-step modified Ritter reaction. It was determined that these inisurfs are effective for emulsion polymerization if alkyl chain is C₁₄ or longer. The alkyl chain length of an amphiphilic inisurf determines particle stability during the reaction, polymerization rate, and final particle size. The higher surface activity of inisurf results in increased concentration of inisurf on the surface of polymer particles, which leads to an increase of the hydrophilicity of the particles surface and higher stability against coagulation [9]. The same authors compared properties of 2,2'-azobis(*N*-2'-methylpropanoyl-2-amino-alkyl-1)-sulfonates with those of another class of inisurfs – sulfonated poly(ethylene oxide)-azo-initiators [Formula (II)].



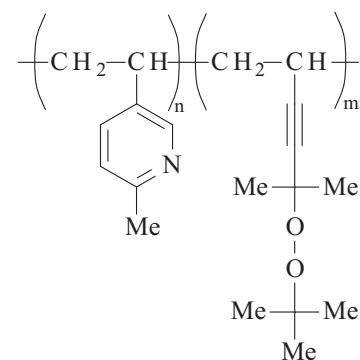
The conducted polymerizations of styrene showed that the surface activity of the inisurfs is more important factor for the polymerization behavior than the decomposition rate of the azo-groups [10]. Compound 2,2'-azobis(*N*-2'-methylpropanoyl-2-amino-alkyl-1)-sulfonates were also used in polymerization of methyl methacrylate [11]. The studies showed that the stability of latexes was influenced also by the hydrophilicity of the polymers. Polystyrene is more hydrophobic than poly(methyl methacrylate) and it has greater zeta-potential. It results in stronger re-



(III)



(IV)



(V)

pulsive forces between the polymer particles and higher latex stability in case of PS. Schipper *et al.* [12] synthesized asymmetrical azo-type inisurf containing the azo moiety attached to the hydrophobic part of the inisurf. This compound was an ethylene oxide-butylene oxide block copolymer esterified with 4-*tert*-butylazo-4-cyanopentanoic acid. It was used in emulsion polymerization of styrene. The resulting PS latex was stable and monodisperse with average diameter of 115 nm.

A large group of inisurfs are polymeric surface active initiators. Voronov *et al.* [13] synthesized a series of polymeric inisurfs with peroxy side groups. They were obtained by copolymerization of a peroxide containing (monomer dimethyl-vinylethynyl-methyl-*tert*-butyl-peroxide) with methacrylic or acrylic acid or 2-methyl-5-vinyl pyridine:

- poly(methacrylic acid-*co*-dimethyl-vinylethynyl-methyl-*tert*-butyl-peroxide) [Formula (III)];
- poly(acrylic acid-*co*-dimethyl-vinylethynyl-methyl-*tert*-butyl-peroxide) [Formula (IV)];
- poly(2-methyl-5-vinyl pyridine-*co*-dimethyl-vinylethynyl-methyl-*tert*-butyl-peroxide) [Formula (V)].

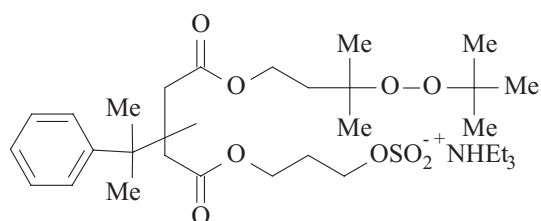
The products were water soluble, surface active and exhibited critical micellar concentration [13]. Another inisurf suitable for obtaining styrene colloid systems and

appropriate for emulsion polymerization was a asymmetrical derivative of cumylsuccinic acid [Formula (VI)] [14].

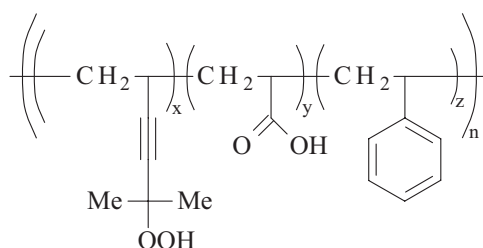
Polymerization of styrene was also carried out using amphiphilic terpolymers with hydroperoxide groups – poly(5-hydroperoxy-5-methyl-1-hexene-3-yne-*co*-acrylic acid-*co*-styrene) [Formula (VII)] – as inisurfs. It was noticed that the particle size of resulting polymer can be controlled by varying inisurf concentration and the reaction temperature. The higher the temperature and the hydroperoxide groups concentration, the smaller the particle size and the greater polymerization rate were observed [15].

Another polymeric inisurf mentioned in the literature is poly[1-octene-*co*-maleic anhydride-*co*-methyl-(*tert*-butyl-peroxymethyl maleate)] [Formula (VIII)]. Its sodium salt was used in emulsion polymerization of styrene and poly(methyl methacrylate) and worked effectively both as an initiator and emulsifier [16].

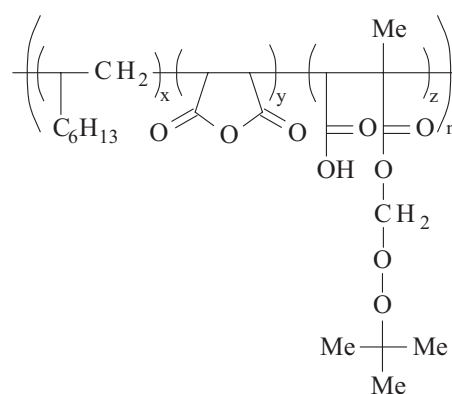
Polymeric inisurf was used for emulsion polymerization of styrene by Tarnavchyk *et al.* [17, 18]. The inisurf was a copolymer of *N*-(*tert*-butylperoxymethyl)acrylamide and maleic anhydride (number average molar mass $\bar{M}_n = 8\,500$ g/mol, dispersity index $DI = 1.68$). The polymerization product was surface-functionalized re-



(VI)



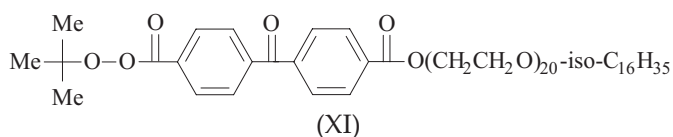
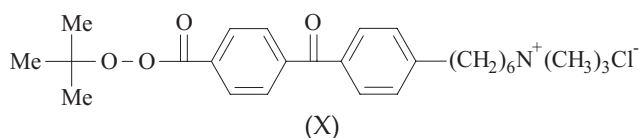
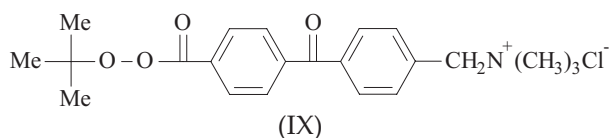
(VII)



(VIII)

active latex particles. Such peroxidized lattice can be potentially used for obtaining polymer particles with core-shell morphology. Another examples of polyperoxide inisurf were presented in other papers [16, 19, 20].

Inisurfs can also be photoactive. Wang *et al.* [21, 22] synthesized three different photoactive inisurfs (phinisurfs): two cationic – [4-(4'-*tert*-butyldioxy carbonylbenzoyl)-benzyl]-trimethylammonium chloride [Formula (IX)]; {6-[4-(4'-*tert*-butyldioxy carbonylbenzoyl)-phenyl]-hexanyl}-trimethylammonium chloride [Formula (X)] – and one non-ionic – isohexadecyl icosaoxyethylene 4-(4'-*tert*-butyldioxy carbonylbenzoyl) benzoate [Formula (XI)] – and used them for the styrene polymerization.



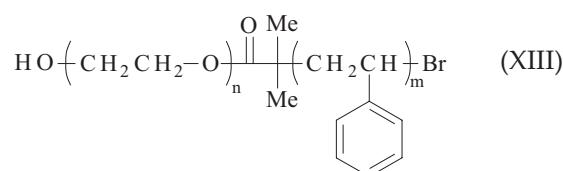
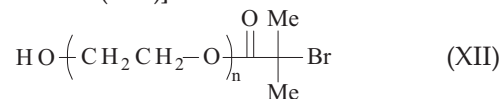
In some of processes, the addition of co-emulsifier is essential. In the cationic polymerization of 1,3,5,7-tetramethylcyclotetrasiloxane using dodecylbenzenesulfonic acid as emulsifier/initiator the addition of neutral co-emulsifier Brij35 [poly(ethylene oxide) dodecyl ether, $\bar{M}_n \sim 1\,200$ g/mol] leads to the formation of linear poly(methylhydrogeno)siloxane of controlled molar mass in the range 7 000–70 000 g/mol with a yield of 90 %. Using inisurf alone resulted in not well-controlled poly(methylhydrogeno)siloxane formation due to cross-linking reactions and poor emulsion stability [23].

Atom transfer radical polymerization (ATRP) in miniemulsion

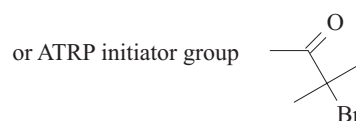
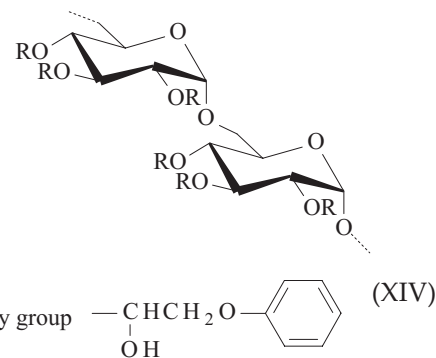
Reversible-deactivation radical polymerization (or controlled radical polymerization) is a method for preparation of copolymers with precise architecture, microstructure, and controlled molar mass. Among many types of this reaction, atom transfer radical polymerization is perhaps one of the most successful techniques. Very good method for achieving good control over ATRP process is to conduct it in dispersed media. In miniemulsion process, polymerization is located in monomer droplets. As a final product, polymer nanodispersion of particles, which size distribution is almost a copy of the initial monomer emulsion, can be obtained [24]. To ensure good stability of produced latex, inisurfs can be employed.

Li *et al.* [25] synthesized PEO homopolymer with ATRP initiator group [Formula (XII)]. It was used to generate *in*

situ a copolymer with butyl acrylate acting as a stabilizer. Amphiphilic block copolymers of poly(ethylene oxide) (PEO) and polystyrene (PS) having ATRP initiator group at one end to work as initiators in AGET (activator generated by electron transfer) ATRP of butyl acrylate was also synthesized [Formula (XIII)].



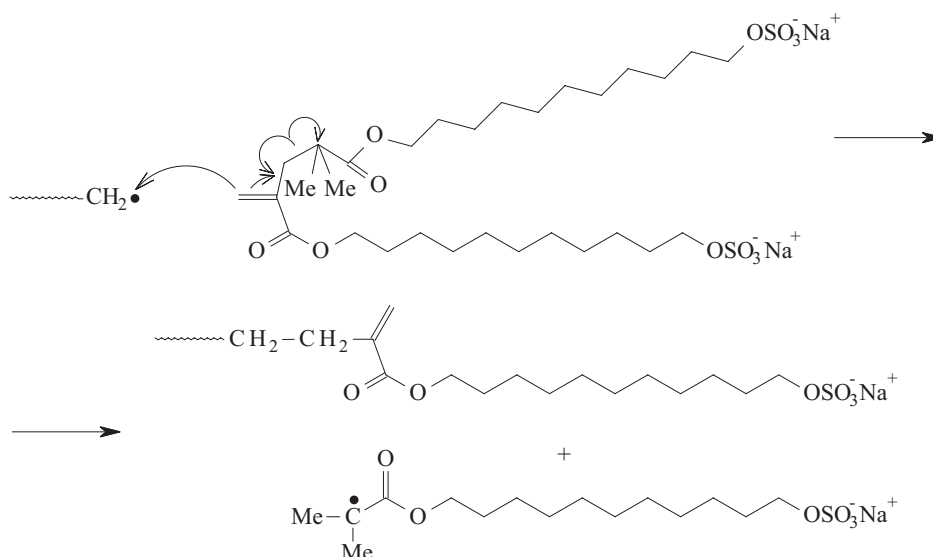
Polymerizations both with PEO-PS and PEO homopolymer as inisurfs were successful. Stable latexes were obtained. PEO-PS with ATRP initiator group was also used for miniemulsion polymerization of butyl methacrylate [26] and copolymerization of butyl methacrylate with dimethacrylate monomers [27, 28]. Wu *et al.* [24] synthesized dextran-based inisurf having phenoxy hydrophobic groups and ATRP initiator groups [Formula (XIV)]. It was used for AGET ATRP of *n*-butyl acrylate. Stable latexes were obtained, no free surfactant remained in the final product.



Other examples of inisurfs applications for ATRP in emulsion were reported in a number of papers [29–34].

TRANSURFS

Transurfs combine properties of transfer agents and surfactants. They were introduced in 1995 by Vidal *et al.* [35] to be used for emulsion polymerization of styrene. Transurfs with dithio-cleavable group can be used for living free-radical polymerization by reversible addition-fragmentation chain transfer (RAFT). This type of controlled/living free-radical polymerization can be used for many monomers and resulting polymers have low polydispersities, usually lower than 1.2 [36].



Scheme A

Structure

Transurfs have a cleavable group, which allows them to perform their role as transfer agents. They also have hydrophilic and hydrophobic moieties, which give them surface-active properties. Transurfs, similarly to surfmers and inisurfs, can be divided into three groups: cationic, anionic, and non-ionic, regarding the type of the hydrophilic moiety.

At first, most of transurfs were based on this group. The development of RAFT method caused a rapid increase of number of publications concerning dithio-based transurfs, which can be used as amphiphilic RAFT agents to conduct living free-radical emulsion polymerization.

Properties

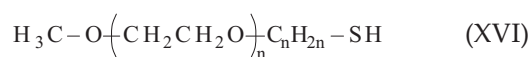
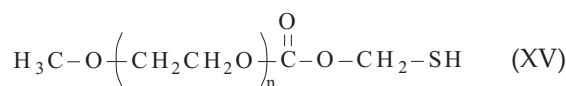
Transurfs, similarly to other groups of reactive surfactants, must not greatly change the molecular weight or particle size distribution [37]. To meet this condition, transurf should be incorporated toward the end of the polymerization [38]. Transurf should also have good surface-activity similar to conventional surfactants used for emulsion polymerization. Transurfs, additionally to their role as transfer agents and surfactants, work also as co-initiators and, in case of RAFT process, terminators. Due to this fact, they are sometimes referred to as SURINIFERTERS (SURfactant, INItiator, transFER agent, TERminator) or surface-active INIFERs (INItiator, transFER agent) [39].

Transurfs used for RAFT process must meet one more condition. They must be able to reversibly attach to the growing polymer chain, so that the reversible addition-fragmentation mechanism could take place.

Applications

Emulsion polymerization

First transurfs presented in the literature were thiol-ended non-ionic surfactants [Formulas (XV)–(XVI)] [40].



They were used for emulsion polymerization of styrene with *t*-butyl hydroperoxide [39] or water soluble azo initiator [35]. In both cases stable latex was obtained, but transurf incorporation rate was about 25 and 40 %, respectively.

Different type of transurf was synthesized by Wilkinson *et al.* [41] and used for emulsion polymerization of methyl methacrylate [37]. The synthesized anionic transurf, 2,4-bis(sodium 10-sulfate decanoxycarbonyl)-4-methylpent-1-ene, was a dimeric molecule with “bola-form” – (α,ω) structure. The addition-fragmentation mechanism for this transurf is presented on Scheme A.

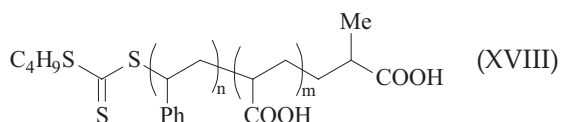
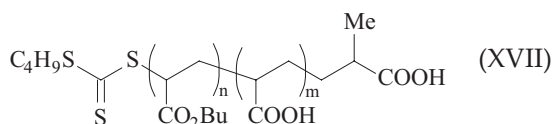
The polymerization of methyl methacrylate using the transurf led to formation of polymer with very broad molar mass distribution and lower \overline{M}_n than in case of the experiment with conventional surfactant – sodium dodecyl sulfate. Polymerization rate was lowered and particle size diameter almost doubled compared to control experiment.

Another anionic transurf, sodium ω -mercapto-decane sulfonate, was also used for emulsion polymerization of styrene [42]. The technique allows controlling surface chemistry independently of particle size. The products were extremely stable colloids containing only sulfonate ionic surface functional groups.

RAFT process in emulsion

The development of RAFT process in emulsion resulted in a new class of transurfs designed for this method. They act both as RAFT agents and surfactant. Examples of such transurfs can be found in a number of papers: 4-thio-

benzoyl sulfanylmethyl benzoate [43, 44], RAFT-capped-poly[(acrylic acid)-*block*-styrene] [45], quaternary ammonium-based transurfs [46, 47], RAFT-capped-poly[(ethylene oxide)-*block*-(2-methoxyethyl acrylate)] [48], RAFT-capped-poly(acrylic acid) [49]. Formulas (XVII) and (XVIII) present examples of amphiphilic macro RAFT agents.

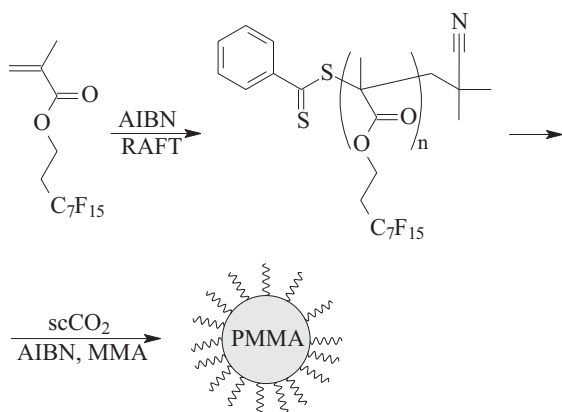


Amphiphilic macro RAFT agents were used for mini-emulsion polymerization [50, 51]. The irreversible adsorption of transurfs on the droplets surface results in forming an insoluble monolayer and stabilizes the mini-emulsion. The molecular mass control was stabilized. The process allows obtaining a polymer with low dispersity index.

Nanospheres preparation

Ishizuka *et al.* [52] used a transurf, RAFT-capped-poly[(hydroxypropyl methacrylamide)-*block*-styrene], to obtain hollow polymer nanospheres [52]. The process was carried out in inverse miniemulsion. Resulting polymeric nanocapsules had average diameters below 300 nm. They can be potentially used for drug delivery systems.

A fluorinated macro RAFT agent was used by Zong *et al.* [53] to obtain spherical particles by dispersion polymerization of methyl methacrylate (MMA) in supercritical CO_2 (sc CO_2) with azobisisobutyronitrile (AIBN) as a radical initiator (Scheme B). The particles exhibit a core-shell structure with a fluorine-rich region on the periphery of the particle.



Scheme B

CONCLUSIONS

Reactive surfactants are a rapidly developing group of chemical compounds. Inisurfs and transurfs are less popular than surfmers, but their importance is increasing with

the development of controlled living polymerization. Inisurfs combine surface active properties and the ability to initiate polymerization process. Their application is impeded by the fact, that their concentration quickly decreases during polymerization. Inisurfs can be used not only for emulsion polymerization, but also for ATRP. Transurfs are transfer agents with surface-active properties. Transurfs are especially useful for conducting RAFT process in emulsion. They can be also used for nanospheres preparation.

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