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The lectures presented at the
**15th Bratislava International Conference
on Polymers,
Non-Conventional Polymer Dispersions**



Held in Smolenice, Slovakia – June 25–28, 2001

Symposium Editor

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Preface

The 15th Bratislava International Conference on Polymers continues the series of Bratislava meetings organized by Polymer Institute of the Slovak Academy of Sciences (SAS). The International Symposium on Non-Conventional Polymer Dispersions is thus the second one, following the successful Symposium on Polymer Dispersions in Smolenice (Slovakia) 1990 both organized by Department of Polymerization Reactions of Polymer Institute, SAS. The Symposium was sponsored by the International Union of Pure and Applied Chemistry and supported by the Slovak Grand Agency (VEGA) of SAS and participants themselves. The meeting took place at the fairy-tale-looking castle of Smolenice located about 65 km north of Slovakian capital, Bratislava.

The conference honoured the forty-year scientific contribution of Dr Jaroslav Bartoň, the former Director of the Polymer Institute, to the development of free-radical polymerization in homogeneous and heterogeneous media. Active participants from different countries have generated a friendly working atmosphere and presented main and contributed lectures and posters. The speakers were recognized experts in the field.

The main topics of the Symposium included.

- Microemulsion, miniemulsion and multiple emulsion polymerizations
- Association and polymerization behavior of amphiphilic macromonomers, graft copolymers and macroinitiators in polar media
- Novel and non-conventional polymer products and polymer dispersions, prepared by radical polymerization

The Symposium included invited plenary lectures, contributed lectures and poster presentations. This meeting was a international one: lectures and posters were presented in English by scientists from the Czech Republic, France, Germany, Hungary, Italy, Japan, Russia, Turkey, Taiwan and Slovakia. The plenary and contributed lectures were presented by eminent scientist and by well-known active researchers of younger generations. The Symposium featured a dynamic poster section which included presentations by many participants, especially young scientists, and was accompanied by very lively discussions. A short account on the materials presented at the Symposium was published in the Book of Abstracts. Regrettably, this volume does not cover all the new and interesting results presented at the Symposium since not all the authors were able to present their lectures for publication in this volume (some of the material had been published earlier or submitted elsewhere). However, it provides a good representation of the scope of the meeting and the main topics of the discussion.

The microsymposium aimed to cover the study of the kinetics and mechanism of free-radical polymerization of conventional and non-conventional (macro)monomers in disperse systems (nanostructured media, micellar solutions, microemulsions, miniemulsions, dispersions, double emulsions, etc). The scope of the conference covered the preparation of polymer particles ranging from a few tens of nanometers to the millimetre size, kinetics of particle formation and the advanced design of particle structure. The synthetic approaches using microemulsions, miniemulsions and classical (multi-) emulsions were extensively discussed. Specialty products included magnetic, conducting and coloured colloids, thermosensitive

microparticles, submicron-sized polymer microgels, polymerizable surfactants, waterborne coatings, photo-initiators for emulsion polymerization, amphiphilic block, graft and comb-like copolymers, hollow microspheres and other objects with unique properties.

Polymerization in nanostructured media (normal micelles, micelle-forming monomers and microemulsions) allowed the preparation of functionalized polymers carrying hydrophobic and/or ionic sites. The nature, number and size of these sites were modulated so that it was possible to prepare polymers with widely differing properties and therefore able to be used in a number of applications. Different processes of polymerisation in nanostructured media allowed the preparation of a wide variety of stimuli-responsive polymers whose properties can be varied by tuning external parameters such as temperature, pH, ionic strength and shear rate. Microemulsions are deemed to be novel chemical nanoreactors for producing nanostructured materials such as polymers, ceramics and inorganic/polymer nanocomposites. Polymerization in microemulsions is a relatively new but attractive field, because it can produce nanoscale polymer particles with extraordinarily high molecular weights. The enormous number of nanodroplets in both o/w and w/o microemulsions or water channels in bicontinuous microemulsions is the potential loci for fast polymerization to produce non-traditional polymer nanoparticles. Although latex particles are small, polymers of molar mass exceeding one million can readily be obtained from these systems. The present kinetic models, however, deviate strongly from the experimental kinetic and colloidal data, and this deviation increases with conversion. One of the possible reasons for such a deviation is the competition between the active and non-active polymer particles for monomer and emulsifier. However, a consistent kinetic picture of this polymerization system is still missing.

In contrast with the conventional microemulsion techniques, latexes with particles from 10 to 100 nm are efficiently obtained with Ausimont techniques of polymerization using perfluoropolyether microemulsions. In comparison with other cases of polytetrafluoroethylene (PTFE) microemulsion polymerization, where low conversions and high surfactant concentration are used, with Ausimont technology PTFE particles of small size are produced at high conversion and with a relatively low surfactant content. Moreover, this technique allows one to control not only the size of the PTFE particles, but also to change their morphology in order to get rod-like particles or spherical ones.

Polymerization in miniemulsions is a new polymerization technique which allows the preparation of submicron-sized latex particles within the range $100 \text{ nm} < \text{particle radius} < 500 \text{ nm}$. The growth of the nanodroplets can effectively be suppressed by using a strong hydrophobe and an effective emulsifier. The hydrophobe acts as an osmotic agent which stabilizes the system against Ostwald ripening. Based on the quantitative understanding of miniemulsions, the process allows the creation of new particle structures. These stable monomer droplets have an extremely large surface area and can compete effectively with the monomer-swollen micelles for oligomeric radicals. The accumulation of hydrophobe (polystyrene, PSt) in the monomer phase during the classical emulsion polymerisation can increase the stability of monomer droplets. The increased stability of monomer

droplets is accompanied with the depressed transfer of monomer to the reaction loci and the rate of polymerization. Under such conditions, the emulsion polymerization system can preserve monomer droplets up to high conversion.

Emulsifier-free emulsion (dispersion in the absence of stabilizer) polymerization and copolymerization of hydrophobic monomers with hydrophilic or amphiphilic macromonomers in polar media led to the formation of the monodisperse polymer particles. The macromonomer technique was used to prepare a variety of core-corona polymeric particles and then used for different particle-surface modifications. Amphiphilic (macro)monomers and/or the amphiphilic graft copolymers obtained by the copolymerization of hydrophilic (macro)monomer and hydrophobic conventional comonomer present all the typical properties of conventional emulsifiers. In addition, these surface-active compounds contain reactive groups due to which the surface-active group is chemically bound to the polymer (particle) matrix. In this manner, these reactive emulsifiers are bound to the particle surface and therefore they are prevented from subsequent migration. Polymerization of amphiphilic PEO-type macromonomers in water was very fast and afforded the preparation of a regularly, highly branched comb polymers. This was discussed in terms of the organized aggregation of macromonomer into micelles. The polymerization increased with increasing hydrophobicity of the polymerizing alkyl-styryl (methacryloyl) group. Furthermore, the PEO macroinimers are used for the synthesis of various kinds of functional graft copolymers. The ability of macromonomer and macroinimers to get involved in a copolymerisation is controlled by their molecular weight, the type of reaction media and reactivity ratios of (co)monomers.

Emulsifier mixtures used for industrial application often contain non-ionic emulsifiers. The excellent ability of non-ionics to solubilize and disperse hydrophobic soils such as fats, mineral oils, etc. in water leads to their extensive use. The electrostatic stabilization provided by anionic emulsifiers improves latex stability at high temperatures, while the steric stabilization provided by non-ionic emulsifiers enhances the chemical and freeze-thaw stability of latex products.

Polymerizable surfactants have been developed for use as reactive emulsifiers in emulsion polymerizations. Although they are exclusively utilized in emulsion polymerizations, they also have potential application in other disperse systems. Surfactant containing both the anionic groups and poly(oxyethylene) chain can make electrostatic and steric contributions to particle stabilization. Polymerizable surfactants adsorb onto solid materials from their aqueous solutions to form monolayers at the surface of organic solids at saturation. When polymer particles capable of absorbing vinyl monomers such as styrene and acrylates are used as the solid material, the emulsifier monolayers can be fixed by the copolymerization with the monomers within the particle. The immobilization of the surfactants adsorbed onto organic pigments can be applied to the preparation of waterborne inks with good storage stability.

The amphiphilic PST/polyethylene oxide (PEO) block copolymers were reported to be efficient stabilizers in the emulsion polymerization of vinyl acetate. An increase in PEO content increased the polymerization rate and the particle size. The rate of polymerization increased strongly with increasing both the initiator and emulsifier concentration. The increased content of PEO chains in the copolymer decreased

the mentioned reaction orders but increased the activation energy. This is attributed to the thick interfacial layer formed by PEO chains which makes barrier for entering radicals. The barrier varies with the chain length of PEO units.

Heterogeneous aqueous-phase polymerization initiated by a redox initiator offers some unique features with respect to the preparation of amphiphilic block copolymers. The redox system generates radicals at polymer chain ends that subsequently form during the polymerization polymeric micelles or polymer particles as isolated reaction loci where the block copolymer formation takes place. Thus, the radical heterogeneous polymerisation is suitable for the synthesis of specialty polymers such as amphiphilic block copolymers. The blocks are built sequentially in a way that the hydrophobic blocks are formed during the heterophase polymerization. The hydrophilic blocks acts as polymeric stabilizers and the hydrophobic blocks form the cores of the particles or micelles. For example, an interesting class of block copolymers contains a poly(*N*-isopropylacrylamide) block causing the thermo-reversible change in the properties of the particles. Another interesting class are double hydrophilic block copolymers consisting of two different hydrophilic blocks.

A non-seeded semibatch emulsion copolymerization was used for the preparation of different colloid copolymers containing hydroxyl, carboxyl, amide and alkoxy-methylamide functional groups. Any application of synthetic latexes requires the specific properties of a latex in its colloidal state, during its application, as well as properties of a polymer latex after application. Very specific properties are required for latex application as a binder in waterborne paints – good colloidal stability in the process of a paint application, good film-forming properties in the process of film formation from the discrete particles and, usually a crosslinking ability for further treatment of the coating film. A need exists for waterborne polymer compositions which undergo crosslinking upon film formation to impart one or more desired properties to the resulting coatings. Functional groups help to increase colloidal stability of polymer dispersions, increase polarity and improve adhesion properties of polymer films.

In the synthesis of latexes for use in waterborne coatings, the benefits of using reactive surfactants are now well-known. Improvements are obtained in the stability of the latexes, due to the fact that they are not desorbed from the particle surface. The film properties are also better, particularly when the films are exposed to humidity, where the water rebound has decreased significantly. One group contains a series of anionic surfmers (polymeric surfactants) prepared upon reacting a polymerizable alcohol with either maleic or succinic sulfosuccinic anhydride. The other contains a series of non-ionic block copolymer surfmers. Transurfs, with an addition – fragmentation mechanism, is the subject of the next group, etc.

Water-soluble synthetic polyelectrolytes are polymers of continuously growing interest due to their manifold applications in industrial processes. An important part of the polyelectrolyte is the block copolymers consisting of charged blocks with cationic and betaine structures as well as of uncharged blocks of different hydrophilicity/hydrophobicity. The synthesis of these block copolymers was carried out by free-radical polymerization as well as by functionalization of reactive

precursor polymers. By employing surface-active monomers, a new type of micellar polymers bearing unusual properties form.

Hollow microspheres show many attractive characteristics, for example, thermal resistance, low density, thermal insulation, and optical opacity due to their small air-void. They can be used in various fields such as paint, ink, paper-coating, face-foundation, etc. Submicron-sized hollow particles can be prepared by utilizing phase-separation between polystyrene (PSt) and poly(methyl methacrylate) (PMMA) at the second stage in seeded-emulsion polymerization. The hollowed particles were also prepared with seeded-dispersion polymerization using a dynamic swelling method. The uniform PMMA hollow particles of around 10 μm were prepared by one-step polymerization, a combining membrane-emulsification technique and a subsequent swelling process.

Submicron-sized polymer microgels have been prepared by emulsion polymerization of or copolymerization of multifunctional monomers. The particle size was controlled to some extent by varying the initiator, emulsifier, and/or monomer concentrations. However, the particle-size control is very complex and remains an area of interest. In this system, the micellar nucleation, the homogeneous nucleation, and the coagulative nucleation may, in principle, be operating simultaneously. Thus, information on the locus of initiation and particle formation is a necessary prerequisite for understanding the polymerization process in the emulsion system containing multifunctional monomers. The network-formation process in the free-radical monovinyl/divinyl emulsion copolymerization involves four reactions of a growing polymer radical: 1) intermolecular propagation with two types of monomer, 2) intramolecular cyclization leading to the formation of small ring or large loop structures, 3) intermolecular crosslinking with the prepolymer to form an effective crosslink, eventually leading to the gel, and 4) intramolecular crosslinking leading to the formation of multiple crosslinks leading to microgelation.

The interest in hybrid polymer-inorganic materials as well as that in the dispersion of inorganics in fluids led to an increased number of studies combining these fields. It emerged in getting hybrid polymer-inorganics as particles dispersed in organic solvents, in polar solvents-water mixtures or even water. The hybrids can be generated by forming silica, in the presence of polymers or by performing the polymerization of monomers in the presence of performed silica. The bonds between polymer and inorganic compound are thought to be formed by the copolymerization of unsaturated monomers on the surface of silica particles. Hybrid materials were obtained by sol-gel reaction of silane derivatives combined with free-radical polymerization of Vac. The change of the glass-transition temperature and thermal stability of the polymers in the presence of the inorganic core proved the existence of polymer-inorganic hybrids.

The feasibility of efficient particle growth during the seed polymerization by controlling electrostatic charges between the seed particles and the secondary monomer/initiator was demonstrated within a range of experimental conditions: agitation, seed particle size, amount of emulsifier and secondary monomer to seed polymer weight ratio.

The symposium focused on current developments in the radical polymerization in the micellar media and synthesis of novel (surface-active) polymer products. It

attracted an excellent attendance, reflecting the strong and wide-spread interest in the field of preparation of non-conventional polymer dispersions and stimulated mutual interactions between researchers working on similar display technologies. Both an interesting venue of the conference and well-organized scientific and social program added to the success of the event as quoted by participants.

This brief review of the materials of the Symposium including those presented in this volume shows that the main interest in the investigation of the preparation of non-traditional polymer dispersions and polymer products lies in the nature of the reaction loci, particle nucleation and particle-growth events.

We believe that the 15th Bratislava International Conference on Polymers or the 2nd on Radical Polymerization in Disperse Systems (Non-Conventional Polymer Dispersions) contributed significantly to the understanding of the particle nucleation and polymerization mechanisms in the radical polymerization in disperse systems used for the preparation of non-conventional polymer dispersions and novel polymer products.

I. Capek

Chairman

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Kinetics and Mechanisms of O/W Microemulsion Polymerization of Styrene

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Summary: To clarify the kinetics and mechanisms of o/w microemulsion polymerization, the o/w microemulsion polymerizations of styrene were carried out with different kinds and types of initiators and surfactants. The number of polymer particles and the molecular weight of polymer formed were not affected by the kinds and types of initiators and surfactants. The rate of polymerization with different kinds of azo-type oil-soluble initiators with widely different water-solubility was almost the same, but was much lower than that with KPS. A kinetic model proposed by us could mostly explain the kinetic behavior except for the difference in the polymerization rate with KPS and that with oil-soluble initiators.

Introduction

Polymerization in microemulsion (microemulsion polymerization) is a relatively new, but an attractive field, because it can produce nano-scale polymer particles with extraordinary high molecular weight polymer. Many papers have been published to date on the o/w microemulsion polymerization of styrene (St), and some models for kinetics and mechanisms of the o/w microemulsion polymerization have been proposed. However, a consistent kinetic picture of this polymerization system is still missing. In order to clarify the kinetic picture of the o/w microemulsion polymerization of St in more detail, the o/w microemulsion polymerizations of St were conducted by changing the type of initiators (water-soluble and oil-soluble initiators) and also by changing the type of emulsifiers (anionic and cationic).

Experimental Part

Materials

Anionic and cationic emulsifiers used were sodium lauryl sulfate (NaLS, Nacalai) and dodecyl trimethyl ammonium bromide (DTAB, Tokyo Kasei), respectively. 1-Pentanol (Wako) was used as cosurfactant in the case where NaLS was used as surfactant. Water-soluble initiator used was potassium persulfate (KPS, Wako). Oil-soluble initiators with widely different water-solubility used were 2,2'-Azobis(2-methyl-butynitrile) (V-59),

2,2'-Azobis (methyl 2-methylpropionate) (V-601), 2,2'-Azobis(2-methyl-propionitrile) (V-60=AIBN), 2,2'-Azobis(4-hydroxybutyl 2-methylpropionate) (HB-AIBE), respectively. They are all obtained from Wako Pure Chemical Industries Ltd. Their water-solubilities and partition coefficients between the monomer (St) and water phases, λ were measured at 25°C by the same method as described in the previous paper^[1], and are listed in Table 1.

Table 1. Properties of oil-soluble initiators used.

Name	Structural formula	λ^a at 25°C	$k_d f [10^{-7} \text{ s}^{-1}]$	% in water phase ^{b)}
V-59	$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{N}=\text{C}-\text{CH}_2\text{CH}_3 \\ \\ \text{CN} \end{array} \right)_2$	2560	8.4	0.6 %
V-601	$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{N}=\text{C}-\text{CH}_3 \\ \\ \text{CO}_2\text{CH}_3 \end{array} \right)_2$	595	13	2.4 %
AIBN	$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{N}=\text{C}-\text{CH}_3 \\ \\ \text{CN} \end{array} \right)_2$	120	8.4	11.1 %
HB-AIBE	$\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{N}=\text{C}-\text{CH}_3 \\ \\ \text{CO}_2(\text{CH}_2)_4\text{OH} \end{array} \right)_2$	2.8	29	84.2 %

a) Partition coefficient between St and water phases ($\lambda = [I]_{\text{oil}}/[I]_{\text{water}}$).

b) % of initiator dissolved in the water phase.

The values of thermal decomposition rate constant times the initiator efficiency, $k_d f$ at 50°C for V-59, V-601 and HB-AIBE, relative to that for AIBN were determined by comparing the rate of bulk polymerization of St initiated by each initiator at 50°C with that initiated at 50°C by AIBN, the $k_d f$ value of which is already known,^[1] and are listed in Table 1.

Procedure of Polymerization and Characterization

All polymerizations were carried out at 50°C under a high purity nitrogen atmosphere (purity >> 99.995%). The recipe for the polymerization used in this study is shown in Table 2.

Table 2. Recipe of the O/W microemulsion polymerization of St employed.

Styrene	20.65 g ;	Water	350g ;	Initiator	variable ;
(1) Surfactant	NaLS	38.5g ;	Cosurfactant	1-pentanol	16.36g ;
(2) Surfactant	DTAB	54.9g ;	Cosurfactant	none	

The monomer conversion was determined gravimetrically with methanol as precipitant for polystyrene (PSt). The molecular weight of PSt produced was measured by gel-permeation chromatography. The volume average diameter of polymer particles produced was determined by transmission electron microscopy.

Results and Discussion

Polymerization with anionic emulsifier (NaLS) and water-soluble initiator (KPS)^[2,3]

In our microemulsion polymerization systems, the amounts of monomer and emulsifier initially charged are usually comparable. Therefore, the number of micelles left in the system at any stage of the reaction is regarded to be far greater during the whole course of the polymerization than the total number of polymer particles so far produced (N_T). Full and Puig et al.^[4] have directly demonstrated from SANS spectra of polymerized St microemulsions that only less than 1% of the monomer-swollen micelles present in the parent St microemulsion forms polymer particles, the rest coexisting with polymer particles as empty micelles. So, we proposed a simple mathematical kinetic model based on the following kinetic picture^[2,3]: (A) Almost all the radicals in the water phase diffuse into monomer-swollen micelles, at least in the beginning of the reaction, to transform them into polymer particles containing a growing radical (active polymer particles), (B) with negligible radical termination in the water phase and (C) with negligible radical entry into the preformed polymer particles. Considering the kinetic picture given by (C), we can deduce that (D) all chain-stopping events in the active polymer particles are the chain transfer to monomer or some chain transfer agent, and (E) growth of the polymer particles is stopped only when the low-molecular weight radical generated by the chain transfer reaction desorbs out from the particles.

According to the kinetic picture presented above, the monomer conversion, X_m can be derived in the following way. Since loss of radicals via bimolecular termination is negligible and almost all the radicals in the water phase participate in forming new polymer particles, the number of the active polymer particles N^* is roughly equal to the total number of radicals generated so far from the beginning of the polymerization and can be expressed as:

$$N^* = r_i t \quad (1)$$

where r_i is the generation rate of radicals effective for nucleating new polymer particles and t is the reaction time. In the case where water soluble initiator like KPS is used, effective radical generation rate can be expressed as:

$$r_i = 2 k_d f I_0 N_A / M_I \quad (2)$$

where I_0 is the amount of initiator charged initially in unit of g/cc-water, N_A is the Avogadro's