Микрогели являются уникальным классом веществ, которые сочетают в себе свойства макромолекул, поверхностно-активных веществ и коллоидных частиц. Микрогели широко применяются для очистки сточных вод, в системах доставки лекарственных средств, для сушки биодизеля, в технологии регенерации тканей и имплантации, в хроматографии и др. На данный момент разработаны такие методы синтеза микрогелей, как осадительная и суспензионная полимеризация, эмульсионный метод и др. Все эти методы фактически уже стали классикой синтеза микрогелей. Данная публикация является обзором работ по методике синтеза микрогелей на основе полиакриламида и его производных методом обратной эмульсии. Этот метод выбран в связи с рядом преимуществ, таких как высокая степень конверсии мономеров, возможность контроля гранулометрического состава частиц геля во время синтеза, упрощенная процедура сушки готового продукта и др. В статье описаны особенности синтеза, влияющие на размер и форму микрогелей, описаны основные факторы, которые необходимо предусмотреть при планировании синтеза в обратной эмульсии; показана разница между макроэмульсией, наноэмульсией и микроэмульсией. Также приведены основные особенности синтеза микрогела на основе акриламида и его производных: приведены основные ингибиторы свободно-радикальной полимеризации; мономеры, влияющие на свойства микрогеля. Данная статья может быть интересной специалистам, которые только начинают исследования в данном направлении. После изучения публикации читатель сможет спланировать и реализовать эксперимент по синтезу микрогелей на основе полиакриламида методом обратной эмульсии.

Ключевые слова: микрогель, гидрогель, гель, полимер, трехмерная структура, полиакриламид

FUNDAMENTAL PRINCIPLES OF MICROGEL SYNTHESIS BY INVERSE EMULSION METHOD

D.A. Burin, Yu.A. Rozhkova, A.L. Kazantsev

Microgels represent a unique class of compounds that combine the properties of such classes of compounds as colloids, macromolecules and surfactants in a unique way. Microgels are widely used for wastewater treatment, as drug delivery systems, for drying biodiesel, in tissue regeneration and implantation, in chromatography, etc. At this point, such methods of microgel synthesis as the precipitation method, suspension polymerisation and the emulsion method have been developed, which have become traditional in the synthesis of microgels. This publication reviews the inverse emulsion method for microgel synthesis based on polyacrylamide and its derivatives. This method was chosen due to a number of advantages, such as a high degree of monomer conversion, the ability to control the granulometric composition of gel particles during synthesis, a simplified drying procedure for the finished product, etc. The article describes the synthesis features that affect the size and shape of microgels, describes the main factors to consider when planning an inverse emulsion synthesis; shows the difference between macroemulsion, nanoemulsion and microemulsion. The article also presents some aspects of the synthesis of microgel based on
acrylamide and its derivatives: the main free-radical initiators are listed; monomers that affect microgel properties are described. This review may be of interest to specialists who are just starting research in this field. Based on this publication, the reader will be able to plan and conduct an experiment on the synthesis of polyacrylamide-based microgels by the inverse emulsion method.

Key words: microgel, hydrogel, gel, polymer, three-dimension structure, polyacrylamide

INTRODUCTION

Microgels represent a unique and multifunctional class of compounds. IUPAC classifies microgels as cross-linked polymer particles with a size ranging from 0.1 to 100 μm which swell to a certain limited extent in an appropriate solvent [1]. Microgels that swell in water are classified as hydrogels [2]. The swelling of microgels is caused by a shift in the conformation of cross-linked polymer chains as a result of filling of the space between the chains with solvent molecules. The interest in microgels has been actively growing in the last three decades [3]. This is primarily related to the fact that these polymer structures combine the properties of such classes of compounds as colloids, macromolecules and surfactants in a unique way (see Fig. 1) [4]. Swollen microgels behave as colloidal particles, i.e., they have elasticity and a "hairy" surface composed of fragments of polymer chains. The cross-linked three-dimensional polymer structure of microparticles has a macromolecular nature. Due to their size and structural features, microgels are able to reduce surface tension, which is typical for surfactants. This property is manifested even in gels of non-amphiphilic nature [4].

D.A. Burin, Yu.A. Rozhkova, A.L. Kazantsev

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Due to their unique properties, microgels are used in a wide range of applications. For example, gels are widely used for wastewater treatment [5, 6], as drug delivery systems [7, 8], for drying biodiesel [9, 10], in tissue regeneration and implantation [11-13], in chromatography [14], etc. A number of review publications on the variety of application fields of microgels have already been published [15-17]. The authors of this publication are developing gels (microgels) for oil recovery stimulation based on cross-linked polyacrylamide. Previously, we also published a detailed review of microgels used for oil recovery stimulation [3].

The goal of this brief review is to analyze the available periodic literature on the synthesis of permanently structured microgels based on acrylamide and its derivatives by the inverse emulsion method. This article may be useful to specialists who are just starting research in this field. Since this review is narrowly focused, it consists of only two main sections: a method of forming an inverse emulsion and its main types and aspects of inverse emulsion synthesis of microgels based on acrylamide and its derivatives.

**METHODOLOGY**

This review is based on publications found in international databases such as Scopus, Springer and WoS by the following keywords: synthesis of microgels, emulsion polymerization, polyacrylamide synthesis. This review is narrowly focused and based on more than 90 studied publications.

**MICROGEL SYNTHESIS BY INVERSE EMULSION METHOD**

One of the commonly used methods of microgel synthesis is inverse emulsion polymerization [18]. This method, in its classical form, consists of synthesis of cross-linked polymer particles in a two-phase system comprising a water phase and an organic phase. These phases are combined into an emulsion by reducing surface tension with the introduction of surfactants that act as an emulsifier. The type of emulsifier to be used and the phase ratio are influenced by the nature of the initial monomers: if the monomers used can be dissolved in an organic medium, the synthesis is conducted by the direct emulsion method, if the monomers used are water-soluble, the polymerization is carried out by the inverse emulsion method. Therefore, each particle of the cross-linked polymer is synthesized in isolated micro- or nanoreactors, being micelles whose walls are lined with surfactants [19, 20].

The microgel synthesis by the emulsification method is preferable for several reasons. This approach allows to obtain particles of specified sizes (from 0.1 to 1000 µm) [18]. In addition to that, the polymerization and crosslinking process runs with the maximum degree of conversion [21]. The production technology is easy to execute. The advantages of microgel synthesis by the emulsification method also include: control of the heating of the reaction environment, the granulated product can be obtained without grinding; the product can be easily dried, and the resulting gels have an excellent capacity to absorb water [22].

The article [23] thoroughly describes the process of free radical polymerization, according to which polymerization of polyacrylamide and its derivatives is carried out. The main stages of this process include initiation, propagation, termination and chain transfer reactions.

Consequently, in order to obtain microgels in an emulsion, we need such process components as: disperse and dispersion medium, emulsifiers and co-emulsifiers, polymerization initiators and, of course, monomers and crosslinkers. By using the example of polyacrylamide microgels, the following technological stages of synthesis can be identified:

1) preparation of the water (disperse) phase: preparation of a mixture of monomers, crosslinkers;
2) preparation of the organic (dispersion) phase: selection of a hydrocarbon solvent, selection and introduction of an emulsifier mixture;
3) preparation of the emulsion by introducing the water phase into the organic phase while constantly stirring;
4) initiation of a free radical reaction (can be initiated by chemical or physical method);
5) polymerization;
6) separation of the obtained microgels by decantation, filtration or another method.

The size of the cross-linked polymer particles can be changed by adjusting the granularity of the emulsion. Table 1 shows the classification of emulsions by the micelle size.

<table>
<thead>
<tr>
<th>Form</th>
<th>Droplet/micelle size</th>
<th>Stability</th>
<th>Polymerization</th>
<th>Microemulsion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical</td>
<td>1-100 µm</td>
<td>Thermodynamically unstable emulsion</td>
<td>High (more than 40%)</td>
<td>10-100 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thermodynamically unstable emulsion</td>
<td>Low (10-20%)</td>
<td>10-100 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Thermodynamically stable emulsion</td>
<td>Low (less than 10%)</td>
<td>10-100 nm</td>
</tr>
</tbody>
</table>

Table 1. Классификация эмульсий по размеру мицелл

In the international periodicals, examples of the microgel synthesis in macroemulsions, miniemulsions (nanoemulsions) and microemulsions can be found [24]. The principles of emulsion polymerization for all three types of emulsions are similar, including the use of the same reagents (continuous phase, water and emulsifier).

Synthesis of Microgels in Macroemulsion

During the microemulsion polymerization (also known as classical emulsion polymerization), droplets of significant size (1-100 µm) are obtained. This process is characterized by low stability, which requires intensive stirring during synthesis in order to prevent disintegration and decomposition of the system. At the initial stage, the emulsion consists of an emulsifier micelle and a monomer droplet. Unlike miniemulsions and microemulsions, the formation of polymer-monomer particles can occur at the same time in droplets, micelles and in a continuous phase.

The authors of the article [25] thoroughly describe the process of polymerization in a macroemulsion which consists of three stages. At the first stage, particles are formed and micelles disappear. At the second stage, micelles disappear and particles grow due to the diffusion of monomers in the dispersion medium.

At the third stage, the polymerization process is completed, which is followed by the addition of residual monomers that were in droplets, micelles, growing polymer particles, as well as in the dispersion medium. The authors also draw attention to some patterns during polymerization in the inverse emulsion associated with an increase in the emulsifier concentration. With an increase in the emulsifier concentration, the amount of monomers in the droplets decreases, and monomers concentrate in the formed micelles. The article also shows that the polymerization rate tends to decrease with an increase in the emulsifier concentration.

Synthesis of Microgels in Miniemulsions (Nanoemulsions)

In the course of working on this review, we wanted to distinguish between the terms "miniemulsion", "microemulsion" and "nanoemulsion". These terms were widely used long before their explicit definition was given. The term "microemulsion" was first mentioned more than half a century ago [26], while the term "nanoemulsion" was used in the article [27] much later – in 1996. While studying various reference sources, we found out that the particles of nanoemulsions are larger than those of microemulsions. Such colloidal dispersions as submicronic emulsions, ultradisperse emulsions and miniemulsions later became known as "nanoemulsions". The terms "nanoemulsion" and "miniemulsion" are synonyms by nature [28-30].

In various reference sources, the upper limit of the miniemulsion particle size is defined as 100 nm [31, 32], 200 nm [33, 34], 500 nm [35, 36]. After reviewing the literature sources, we came to a conclusion that the average size of droplets in miniemulsions can vary from 50 to 500 nm. For miniemulsion polymerization, it is particularly important to add an osmotic agent emulsion. In order to stabilize the miniemulsion and prevent the growth of droplets due to Ostwald ripening, it is particularly important to find the right osmotic agent. Emulsifiers, solid nanoparticles (Pickering emulsions) and other components that influence the surface tension (for example, electrolytes) may act as an osmotic agent [37-40]. One of the features of miniemulsions is their kinetic stability due to the state of dynamic balance between the growth and melting of mini-droplets. However, over time the structure of the miniemulsion changes for one of the reasons: Ostwald ripening, flocculation, coalescence and/or gravity separation. These changes may manifest as changes in particle size distribution, overall microstructure, foam formation, or phase separation during storage.

Synthesis of Microgels in Microemulsions

Microemulsions are considered to be the most thermodynamically stable systems in which the surface
tension and the interfacial energy of the phases are close to zero [41].

The droplet size in a microemulsion is in the range of 10-100 nm. One of the significant disadvantages of microemulsions in comparison with miniemulsions is the need to use more emulsifier in order to stabilize droplets. Compared with miniemulsions, microemulsions are thermodynamically more stable and do not change their structure over time. If the structure and properties of colloidal dispersion remain constant during storage, it is a microemulsion, if they change, then it is a miniemulsion.

It may not be so obvious in practice, since the properties of microemulsions may change due to chemical degradation or microbial contamination, while the properties of miniemulsions may not change for a long period of time due to high kinetic stability [42].

Typically, miniemulsions contain spherical particles due to high Laplace pressure, whereas microemulsions can form spherical or non-spherical particles due to ultra-low surface tension. Therefore, a miniemulsion may be distinguished from a microemulsion by measuring the shape of the particles, for example, by using scattering methods (neutron, X-ray or light scattering) or microscopy (electronically). If the system contains non-spherical particles, most likely it is a microemulsion. If the system contains spherical particles, it may be either a microemulsion or a miniemulsion.

**FEATURES OF THE INVERSE EMULSION SYNTHESIS OF MICROGELS BASED ON ACRYLAMIDE AND ITS DERIVATIVES**

When planning the microgel synthesis, special attention should be paid to the following system components:

- monomers and co-monomers to impart the necessary physical and chemical properties of microgels;
- disperse medium in which the reaction will occur;
- initiating system to start the polymerization process;
- emulsifier system to stabilize the emulsion and adjust the average size of microgels.

Further, each of the components of the emulsion during the synthesis is described in more detail.

**Choosing Monomers for the Microgel Synthesis via Inverse Emulsion**

Choosing monomers, including co-monomers, for emulsion polymerization is a key step in the microgel synthesis. Depending on the area of application and purpose of the synthesized microgels, different monomers of various functionality can be used.

### Table 2

Substances used as acrylamide comonomers

<table>
<thead>
<tr>
<th>Formula</th>
<th>Function</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylamide</td>
<td>Scaffolding monomer</td>
<td>[43]</td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>Scaffolding monomer, improving of hydrophilic properties</td>
<td>[44,45]</td>
</tr>
<tr>
<td>2-acrylamido-2-metilpropan sulfonic acid</td>
<td>Scaffolding monomer, resistance to the high temperatures</td>
<td>[46]</td>
</tr>
<tr>
<td>N,N'-methylene-bis(acrylamide)</td>
<td>Cross-linking monomer</td>
<td>[47,48]</td>
</tr>
<tr>
<td>3-(methacryloyloxy) propyl trimethoxysilane</td>
<td>Reinforcing co-monomer for SiO2 incapsulation</td>
<td>[49,50]</td>
</tr>
<tr>
<td>Acryloyloxy coumarin</td>
<td>Fluorescent violet color</td>
<td>[51]</td>
</tr>
<tr>
<td>Allyl-Rhodamine B</td>
<td>Fluorescent red color</td>
<td>[52]</td>
</tr>
<tr>
<td>Oxyfluorescein</td>
<td>Fluorescent green color</td>
<td>[53]</td>
</tr>
</tbody>
</table>
The most common type of connection is "head to tail" due to overcoming large activation barriers. These three types of connection are characterized by resistance to acids, alkalis, as well as other reagents.

The "tail-to-tail" polymer units are characterized by the lowest rate of alkaline hydrolysis, while the highest rate is typical for the "head to head" position.

The initiation process starts the polymerization reaction. The reaction can be initiated by physical methods, for example, by exposing monomers to various types of radiation [61, 62], ultraviolet light [63], visible light [64], ultrasound [65, 66], electric current [67, 68]. It is also possible to start the free radical polymerization process by using special substances (initiators) that can decompose into radicals. Physical and chemical methods have recently been used together more often, allowing to select various combinations of the process.

One example of such combination is the thermal homolytic decomposition of unstable substances, i.e., decomposition of initiators into radicals.

In order to increase the degree of monomer conversion, oxidation-reduction (redox) reactions are used when conducting the process at room temperatures and even at low temperatures. Thus, the by-products of a redox reaction act as free radicals which initiate the process of free radical polymerization. Table 3 shows common initiators used in the polymerization of acrylamide and its derivatives.

### Table 3

<table>
<thead>
<tr>
<th>Substance/compound</th>
<th>Formula</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen peroxide</td>
<td>H₂O₂</td>
<td>[69]</td>
</tr>
<tr>
<td>Benzoyl peroxide</td>
<td>Ph-C(O)-O-O-C(O)-Ph</td>
<td>[70]</td>
</tr>
<tr>
<td>2,2'-azo-bis-isobutyronitrile</td>
<td>(CH₃)₂CN=NC(CH₃)₂</td>
<td>[71]</td>
</tr>
<tr>
<td>Dialkyltriazene compounds</td>
<td>RN=N–NR₁R₂</td>
<td>[72]</td>
</tr>
<tr>
<td>Azobisisobutyronitrile (azobis-isobutyric acid dinitrile)</td>
<td>C₆H₁₂N₄</td>
<td>[70, 73, 74]</td>
</tr>
<tr>
<td>Potassium peroxodisulfate</td>
<td>K₂S₂O₈</td>
<td>[75]</td>
</tr>
<tr>
<td>Ammonium persulfate</td>
<td>(NH₄)₂S₂O₈</td>
<td>[76, 77]</td>
</tr>
<tr>
<td>Ammonium (potassium) persulphate/sodium sulphite</td>
<td>(NH₄)₂S₂O₈/ K₂S₂O₈ + Na₂SO₃</td>
<td>[78-81]</td>
</tr>
</tbody>
</table>
Choosing an Emulsifying System

One of the most important technological matters when using emulsions for the preparation of microgels is their stabilization. Thermodynamic instability causes the destruction of emulsions due to the tendency of dispersed liquid droplets to merge together (coalescence), which leads to complete disintegration of the two-phase system. In order to prevent coalescence, special stabilizing substances called emulsifiers are used. They form adsorption protective films on the surface of dispersed liquid droplets that prevent coalescence. Therefore, in order to obtain a stable inverse emulsion, the most important step of preparation is to choose the "disperse medium – emulsifier system".

The requirements for the disperse medium during the inverse emulsion synthesis are water-insoluble hydrocarbons with a known value of the hydrophilic-lipophilic balance. Based on the HLB value of the disperse medium, the composition of the surfactants is selected so that the HLB value of the surfactant system is equal to that of the disperse medium.

The purpose of surfactants acting as emulsifiers is to saturate the phase interface. The following are the basic principles of selecting an emulsifying composition for the synthesis process, as well as the most common and available emulsifiers for polymerization reactions conducted in order to obtain microgels through inverse emulsion.

As is commonly known, a surfactant molecule consists of two parts – a hydrophilic head and a hydrophobic tail. The main characteristic of surfactants that describes the hydrophilicity or lipophilicity of a surfactant is a unitless value – hydrophilic-lipophilic balance (HLB).

Based on the size of the hydrocarbon tail or the polar group, it is possible to define which phase the surfactant prefers. The HLB value describes the protruding of surfactant molecule into the oil or water phase (see Fig. 4).

For the synthesis of inverse emulsions, colloidal surfactants are used. In these surfactants, \((b + v\Psi) < a\), i.e., the available energy of interaction of surfactant molecules with the hydrocarbon phase tends to a minimum, and with the water phase – to a maximum.

In practice, the use of one emulsifier is less effective compared to an emulsifier system: one with a higher HLB value, the other with a lower one.

Thus, in 1949 Griffin developed the classification of emulsifiers based on the HLB values [82] (Table 4). HLB values > 10 indicate hydrophilic surfactants that can be used for direct emulsion synthesis. Accordingly, lower HLB values are typical for inverse emulsions.

In 1954, Griffin also determined the HLB values for commercially available surfactants [83]. Among them were sorbitan esters (Span) and polysorbate esters (Tween) which are widely used and remain popular to this day (Table 4). This is mainly because these esters are well studied, cheap, biologically compatible and available on the market [84]. The authors of this article use Tween 60 as one of the emulsifiers in the preparation of microgels.

In the 1960s, D. Davis proposed a scale of HLB numbers ranging from 0 (lipophilic surfactants) to 40 (hydrophilic surfactants) (Table 4) [85]. It should be noted that oil-soluble surfactants are more effective stabilizers of inverse emulsions.

Davis’ approach is based on functional groups of molecules, i.e., each group of atoms has a group number by adding which an HLB value is calculated according to the formula (1):

\[
\text{HLB}_{\text{surf}} = 7 + \sum (\text{hydrophilic group numbers}) - \sum (\text{lipophilic group numbers})
\]

(1)

The diagram illustrates a surfactant at the interface between water and oil phases. \((b + v\Psi)\) is the affinity of the non-polar part of the surfactant molecule to the hydrocarbon liquid (available energy of the interaction of the hydrocarbon tail with the oil phase); \(b\) is a unitless value depending on the nature of the surfactant; \(\Psi\) is the available energy of interaction per one \(\text{CH}_2\) group in the hydrocarbon radical; \(v\) is the number of \(\text{CH}_2\) groups in the hydrocarbon radical; \(a\) is the affinity of the polar group to water.
The hydrophilic-lipophilic balance of the emulsifier system should correspond to that of the organic solvent. Griffin’s formula (2) is used to select a suitable emulsifier system:

$$HLB_{sys} = \frac{W_A HLB_A + W_B HLB_B}{W_A + W_B}$$

(2)

where $HLB_{sys}$ is the HLB value of the surfactant system which ensures a stable emulsion; $W_A$ is the amount of emulsifier A; $W_B$ is the amount of emulsifier B.

The formation of micelles by surfactant molecules is the main reason why these substances are used as emulsifiers.

The more fully the emulsifier molecules get adsorbed on the surface of the phase interface, the lower surface tension value $\sigma$ can be obtained.

To stabilize inverse emulsions, the dispersion interaction of hydrophobic radicals and the minimum area of polar groups are to be reduced, in order to concentrate the adsorption layer to the maximum extent possible. A low value of the surface tension indicates instability of the inverse emulsion.

The formation of micelles at the phase interface ensures the absence of interaction between lyophilic and lyophobic groups, which leads to a decrease in the available energy of the system. The emulsifier properties will depend on the form of surfactants – micellar or molecular [86].

The micelles are formed at a critical concentration of micelle formation (CCM) and at very small concentrations of surfactants [87]. Various factors contribute to the CCM: the structure of surfactants, temperature, pH value, etc. The CCM value increases with the growth of the hydrophilic part of the chain, at the same time, the number of molecules in a micelle decreases due to the increased energy of the hydrophilic part and decreased surface tension at the phase interface [88]. The increase or decrease in the CCM value with temperature depends on the nature of surfactants (ionic or non-ionic structure). For non-ionic surfactants containing the ethoxylated part, the CCM value decreases due to dehydration of the hydrophilic fragment with increasing temperature [89]. An increase in temperature intensifies the disaggregating effect of the heat motion, and consequently, decreases the size of the micelles and increases the CCM [90].

The formation of droplets and disruption of the surface of the phase interface drastically reduce the surface tension without having a significant effect on the emulsion viscosity.

Emulsifiers contribute to these processes, i.e., with an increase in the concentration of emulsifying agents, $\sigma$ tends to a minimum value [91]. However, after reaching certain minimum value of $\sigma$, an increase in concentration will no longer affect the droplet size and emulsion stability, which means that emulsification will not be effective [92].

Key requirements for emulsifiers:

- reduction of surface tension up to 5 mN/m for emulsions prepared by stirring, and up to 0.5 mN/m for emulsions that do not require intensive stirring;
- sufficiently fast adsorption on droplets, formation of a thin layer that does not change during collisions of droplets and prevents coagulation and coalescence;
- specific molecular structure with polar and non-polar groups;
- good dissolution in a dispersion medium;
- development of a certain electrokinetic potential in the emulsion;
- effect on the emulsion viscosity;
- showing emulsifying properties even in small quantities;

<table>
<thead>
<tr>
<th>Emulsifier and some functional groups of emulsifier</th>
<th>HLB values</th>
</tr>
</thead>
<tbody>
<tr>
<td>inverse emulsions (water/oil)</td>
<td>4-6</td>
</tr>
<tr>
<td>wetting agents</td>
<td>7-9</td>
</tr>
<tr>
<td>direct emulsions (oil/water)</td>
<td>8-18</td>
</tr>
<tr>
<td>cleaning agents (detergents)</td>
<td>13-15</td>
</tr>
<tr>
<td>solubilising agents</td>
<td>15-18</td>
</tr>
</tbody>
</table>

### Table 4

**HLB values of different emulsifiers and some functional groups of emulsifiers**

Таблица 4. Значения HLB различных эмульгаторов и некоторых функциональных групп эмульгаторов

<table>
<thead>
<tr>
<th>Emulsifier and some functional groups of emulsifier</th>
<th>HLB values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Span 85</td>
<td>1.8</td>
</tr>
<tr>
<td>Span 65</td>
<td>2.1</td>
</tr>
<tr>
<td>Span 80</td>
<td>4.3</td>
</tr>
<tr>
<td>Span 60</td>
<td>4.7</td>
</tr>
<tr>
<td>Span 40</td>
<td>6.7</td>
</tr>
<tr>
<td>Span 20</td>
<td>8.6</td>
</tr>
<tr>
<td>Tween 61</td>
<td>9.6</td>
</tr>
<tr>
<td>Tween 81</td>
<td>10.0</td>
</tr>
<tr>
<td>Tween 65</td>
<td>10.5</td>
</tr>
<tr>
<td>Tween 85</td>
<td>11.0</td>
</tr>
<tr>
<td>Tween 21</td>
<td>13.3</td>
</tr>
<tr>
<td>Tween 60</td>
<td>14.9</td>
</tr>
<tr>
<td>Tween 80</td>
<td>15.0</td>
</tr>
<tr>
<td>Tween 40</td>
<td>15.6</td>
</tr>
<tr>
<td>Tween 20</td>
<td>16.7</td>
</tr>
<tr>
<td>-COOK</td>
<td>21.1</td>
</tr>
<tr>
<td>-COONa</td>
<td>19.1</td>
</tr>
<tr>
<td>-COOH</td>
<td>2.4</td>
</tr>
<tr>
<td>-OH</td>
<td>1.9</td>
</tr>
<tr>
<td>=O</td>
<td>1.3</td>
</tr>
<tr>
<td>=CH</td>
<td></td>
</tr>
<tr>
<td>=CH₃</td>
<td></td>
</tr>
<tr>
<td>=CH₂</td>
<td></td>
</tr>
<tr>
<td>=C=C</td>
<td>0.475</td>
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D.A. Burin, Yu.A. Rozhkova, A.L. Kazantsev


13
• low price;
• safe to handle and non-toxic [93].

CONCLUSION

This article is an opening review based on which the reader can form a general idea of the principle of the microgel synthesis through inverse emulsion. We made efforts to clarify the confusion with respect to the terminology by explaining the difference between macroemulsion, miniemulsion, nanoemulsion, and microemulsion. We also described the features of the microgel synthesis in these emulsions and how each of the approaches affects the size and shape of microgels. In the second part of the review, we went into the details on the main components of the system which need to be selected before synthesis: we gave a list of monomers with their functions, presented a list of suitable systems for initiating the polymerization reaction, and also analyzed how to correctly select and calculate a composition of emulsifiers when choosing a specific disperse medium. We hope that this review will help a starting specialist to quickly get a sense of this field of research and serve as a useful aid in developing and synthesizing microgels with specified properties.

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DECLARATION OF INTERESTS

The authors declare the absence a conflict of interest warranting disclosure in this article.

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