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Synthesis and investigation of properties of cryogel based on polyacrylic acid

This work is focused on synthesis of different ratios of cryogel based on polyacrylic acid in order to obtain the best results of cryogel in the most right moment. Studying of physico-chemical properties of obtained cryogel includes determination of equilibrium swelling, density, obtaining photographs by atomic force microscope, scanning electron and optical microscopes.

Key words: synthesis, properties, cryogel.

Introduction

Nowadays one of the main aims of scientists is an easy synthesis – processing of cryogels by available synthesis methods. The basic subject to be considered on obtaining polymeric materials is economically available, effective, ecologically harmless polymer synthesis methods. Gel materials belong to polymeric cryogels, which polymeric and monomeric bases are formed in not deeply frozen solutions. Set point of superficial processing is about ten degrees lower than set point of solvent. The systems obtained on the basis of this processing show two-phase systems which in a solid phase of crystals play role of porogen. And the other remained volume of liquid in a microphase, that is forms a cryogelic matrix for a concentrated solution of the dissolved substance [1].

Cryotrop gel formation of polymeric system happens at not deep freezing, at remaining in the frozen state and late disolution of colloid – dispers solutions or solutions containing monomeric and polymeric representatives which can give potential gel. The formed polymeric materials under these conditions got the name of cryogel (from Greek «cryos» – a frost and ice) [2] and has specific features in comparison with sample of gels formed at temperatures above than a solvent crystallization point [2-3].

Experimental part

Cryogel was synthesized on base of 10% polyacrylic acid (PAA) obtained by gelatin reaction (Fig.1.). As crosslinking agent was used N,N'-methylene–bis-acryl amide and as initiator was used ammonium persulphate, sodium metabisulphite, sodium hydroxide, and water. Radical polymerization was carried out at -30°C temperature for 24 hours. Cryogelic solvents have some specific features in comparison with sample gels formed at higher temperature than their crystallization point [4-5].

Morphological structure of cryogel was studied by pictures of optical microscope, atomic force microscope and scanning electron microscope. The equilibrium swelling kinetics were researched, and the influence of external factors such as pH and temperature on it was found.

Sorption property of 10% PAA cryogels was studied. 10 μg/ml concentration of lead nitrate salt solution was used as sorbate. Metal entered into cryogel by sorption immobilization method, and between some period of time took aliquots and determined numerical values on atomic-absorption spectrometer AAS Shimadzu 6200 (Japan).

Research results discussion

On a basis of PAA chemically crosslinked cryogel was synthesized. Obtained cryogel had density 1,4674 g/cm^3 and yield 90%. In order to see more exact picture of morphology and structure the 10% PAA cryogel was studied by using scanning electron microscope (SEM) equipment in different sizes (μm, nm). As a result, information obtained allows us to notice that cryogel consists of homogeneous microstructure unit (Fig.2). From Figure 2 we can see that formed cryogel was porous.

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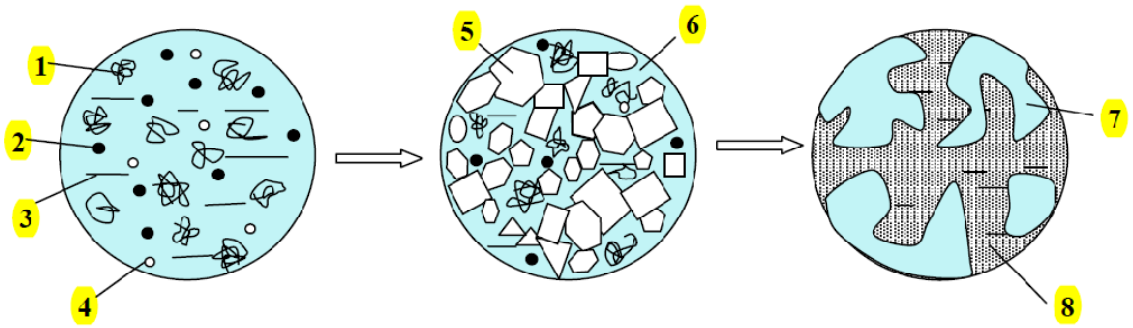
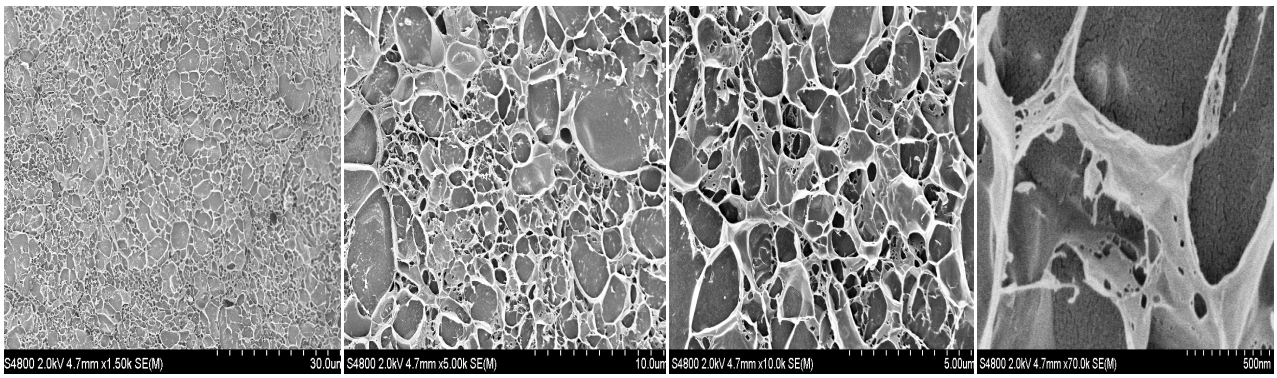


Figure 1 – Schematic diagram of cryotracks gellification
1 – polymeric gelling agent (PAA); 2 – low-molecular substances (NaOH); 3 – solvent (water);
4 – initiator (ammonium persulphate and sodium metabisulphite); 5 – polycrystals of the frozen solvent;
6 – unfrozen liquid microphase; 7 – polymeric grid of a gel phase of heterophase cryogel; 8 –macropore.



(a) (b) (c) (d)

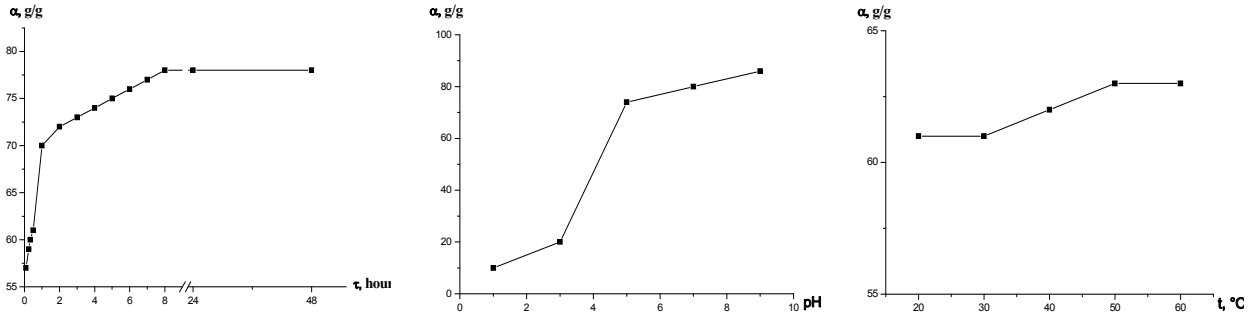
30 μm (a); 10 μm (b); 5 μm (c); 500 nm (d) the reduced figures

Figure 2 – Photographs obtained by the scanning electronic microscope

One of the important properties of cryogel – equilibrium swelling degree was investigated (Fig.3.) [6]. Equilibrium swelling kinetic of cryogel based on PAA was determined approximately in one day (Fig.3 (a)).

We checked influence of external factors on swelling of 10% PAA cryogel [7]. Swelling dependence on pH and temperature during 30 minutes is shown (Fig.3.). We can notice sharp increasing of swelling when turning from acid to alkaline environment and it also increases with increasing of temperature. On dependence of pH shows good dissociation at turning from acid to alkaline environment and ionic strength increase. Such regulations can be easily explained by interaction nature of polymeric components. PAA is polyanionic polymer. Due to what at pH increasing by mutual repulsion of the same charged particles it is proceed the volume increasing of polymer grid. And in the case of temperature increasing it is necessary to notice big investment of hydrogen bonds into polymer interaction in gels. As it is known, extension of temperature allows hydrogen bonds breaking and leads to weakening of polymeric framework. That is why for PAA cryogels it is observed some increasing of volume of polymeric grid at temperature 60^0C.

One of the most important properties of composition gels is sorption [8-10]. Recently, the researches of cryogels in direction of polymer composition materials (PCM) have shown the importance of using cryogels to purify production sewage. Heavy metals that are in deep waters have a technological action; it describes basic geochemical action of water of area. Sorption is an important method at sewage purification. Due to it, at the last time, the PCM with more involved sorption, physico-chemical, mechanical properties of compliance of organic and inorganic polymers are highly developed.



(a) dependence of extent of swelling on time

(b) dependence of extent of swelling on pH

(c) dependence of extent of swelling on temperature

Figure 3 – Dependence of swelling of cryogel 10 % PAA

In order to prove binding of cryogel with ions of metal we observed sorptioned sample in lead nitrate solution by optical and atomic force microscopes (Fig.4). By optical microscopy, it was noticed that heavy metal – lead ions sit on cryogel surface. Atomic force microscope shows that metal ions go to porous internal structure and sorptioned.

It is important to know numerical values of sorption at entering of metal ions into composite materials. Figure 5 shows percentage value of metal ions sorption into cryogel based on PAA. Also here is shown swelling kinetics of cryogel on the basis of PAA in water and Pb^{2+} solutions, swelling in lead salt solution is lower due to negative charge of PAA, it is electrostatically linked with metal solution. It is good index of sorption ability. Thus, due to research of lead nitrate sorption results, at room temperature during 6 hours sorption value reached 90 %. As seen, swelling and sorption are closely connected with each other. If swelling increases by time, the sorption increases too.

Figures by an optical microscopy

Figures by atomic-force microscopy

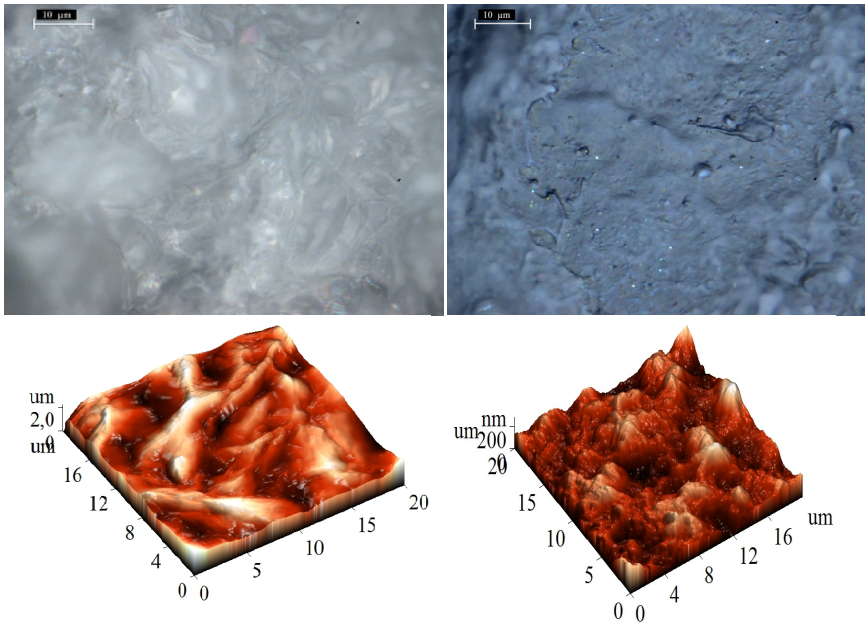
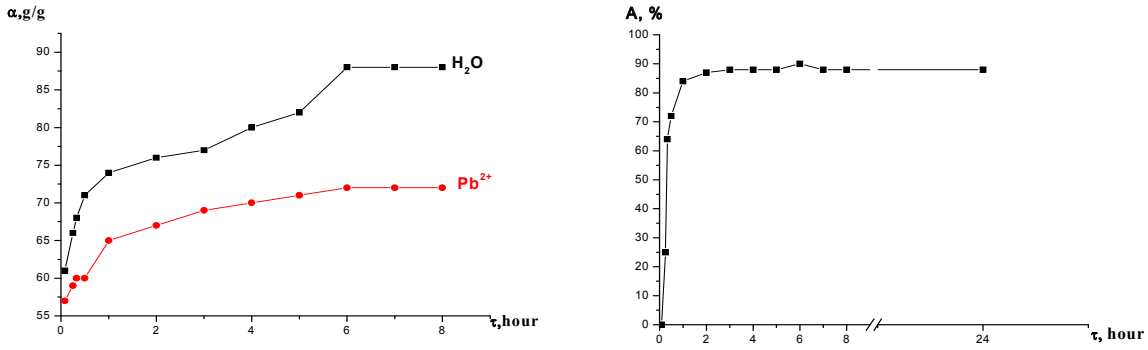


Figure 4 – Sorption figures in polyacrylic acid and in solution Pb^{2+}



(а) swelling of PAA cryogel in solution Pb^{2+}

(б) sorption of PAA cryogel in solution Pb^{2+}

Figure 5 – Sorption and swelling of PAA cryogel in solution Pb^{2+}

Conclusion

In conclusion, cryogel based on polyacrylic acid was obtained. Equilibrium swelling degrees and density were determined, pictures on atomic–force microscope, scanning electron and optical microscopes were obtained. Structure of PAA based cryogel is porous, that is why its swelling degree is high. Also we studied sorption ability of PAA 10 % cryogel, and proved its high value – 90 %. According to conducted research, cryogel based on PAA can be used to purify sewage from heavy ions.

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