Using Nonconventional Structures as Protective Colloids in the Dispersion Polymerization of 2 - Hydroxyethyl Methacrylate with a Comonomer with Spiroacetal Moiety

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***Abstract* – The study reports the synthesis of a copolymer based on 2-hydroxyethyl methacrylate and 3, 9-divinyl-2, 4, 8, 10-tetraoxaspiro (5.5) undecane acquired through radical polymerization in the presence of 2, 2'-Azobis (2-methylpropionitrile). The polymerization process was conducted in the presence of a classic ionic surfactant – sodium lauryl sulfate (SLS) – and comparatively using two variants of protective colloid: β cyclodextrin (CD) and poly(aspartic acid)(PAS) respectively. The polymers compositions were confirmed by FTIR spectra. SEM and AFM investigations of the polymer morphology are also presented. It was concluded on the proper critical micellar concentration for used tensioactive substances, respectively attributing a mixed mode of particle nucleation (micellar and homogeneous nucleation) in case of synthesis with SLS and an entropic mechanism of stabilization with CD and PAS as stabilizers. The mean particle size and size distribution, as well as zeta potential and conductivity determination on the prepared polymeric particles attest a relatively monodisperse distribution for the particle size; particles with negatively charged surfaces and copolymers conductivity prepared in the presence of PAS or CD increased by several orders against homopolymer.**

***Index Terms* – five key words or phrases arranged alphabetically and separated by commas.**

I. INTRODUCTION

The improvement of the p(HEMA) properties as for example the mechanical properties, permeability, temperature responsive characteristics, and degree of hydration or extent of hydrogel network swelling, for more favorable biological responses, it was taken into study. Thus, by synthesizing amphiphilic materials, combining HEMA with hydrophobic components, one can expect the improvement of the mechanical strength of the obtained materials, and in this context, the copolymerization is mainly used to improve mechanical properties of polyHEMA, the affinity for water, oxygen permeability etc. [1–4]

Bailey et al. [5] in 1976 described developments in the synthesis of alternating poly(ester–ether)s from spiroortho-esters. These are considered biodegradable and useful for biomedical applications. [6] In this context, spiroacetals are key structural elements in many bioactive polyketide natural products and related analogues. [7-11] The incorporation of spiroacetal groups in the polymers structures also, improves the solubility and the adhesive properties. [12] These polymers induce also good oxidative and thermal stability, are good fiber formers, and films with good flexibility and tensile strength. [12] These characteristics are owing to the spiroacetal ring presence.

The present study reports the synthesis of a copolymer based on HEMA and 3, 9-divinyl-2, 4, 8, 10-tetraoxaspiro (5.5) undecane (U) acquired through radical aqueous dispersion polymerization in the presence of AIBN. The attempt was to have a solid content as high as 10 wt.-percent and in this context the process was conducted in the presence of a classic ionic surfactant – sodium lauryl sulfate (SLS) – and comparatively using two variants of protective colloid: β cyclodextrin and poly(aspartic acid), respectively. AFM investigations of the polymer morphology are also presented. The poly(aspartic acid), belonging to the family of synthetic polypeptides, is a typical biocompatible, biodegradable with dispersing activity water-soluble polymer, which can be used as dispersant, antiscalant, or superabsorber, for home detergents, water treatment chemicals, and oil field treatment additives, for a variety of organic and inorganic solids and scales dispersal, in medicines, cosmetics, and food. It is considered to be a sustainable, environmentally compatible chemical product and its biodegradability makes it particularly valuable from the point of view of environmental acceptability and waste disposal. At the same time, no toxic or mutagenic effects have been reported for polyaspartic acid. Its derivatives starting from polysuccinimide are reported in the literature as carrier component in drug-polymer conjugates for non-steroidal, antineoplastic or other antiviral agents (acyclovir, zidovudine, paclitaxel, methotrexate, amphotericin B). [13] Also, a useful method for increasing the water solubility of organic compounds is to use cyclodextrin (CD) to form inclusion compounds with the guest hydrophobic species. [14, 15] In this context β-cyclodextrin was investigated in emulsion polymerization and the first successful application as protective colloid belongs to the group of Rimmer. [16]

II. EXPERIMENTAL PART

The continuous radical polymerization processes between 2 - hydroxyethyl methacrylate (HEMA) and 3, 9-divinyl-2, 4, 8, 10-tetraoxaspiro[5.5]undecane – (U) were initiated by 2, 2'-Azo bis(2-methylpropionitrile) (AIBN) and conducted under nitrogen atmosphere, at 70^0C, in a constant temperature bath, with a stirring rate of 250rpm, for 8h,

using sodium lauryl sulfate ($C_{12}H_{25}O_4SNa$) – (SLS) as tensioactive, or poly(aspartic acid) (PAS)(poly (a, b) -D, L aspartic acid sodium salt, M_w= 8100) or β cyclodextrin (M_w=1135) as protective colloid. The water used in all experiments was purified using an Ultra Clear TWF UV System. The attempt was to have a solid content as high as 10 wt.-percent and in this context the process was conducted in the presence of the classic ionic surfactant – sodium lauryl sulfate (SLS) – and comparatively using two variants of protective colloid: β cyclodextrin and poly(aspartic acid), respectively. After synthesis the polymeric particles were precipitated three times with methanol from water solution and finally freeze-dried by ***lyophilization during 24 h.***

The the zeta potential (ζ) and the conductivity were estimated by using a dynamic light scattering technique (Zetasizer model Nano ZS, with red laser 633 nm He/ Ne; Malvern Instruments, UK). The determinations were made on 2 ml sample of latexes without dilution. The sampling was done directly from the reaction vessel and was placed in the cell. All measurements were carried out at 25°C.

The mean particle size and size distribution of as-prepared latex polymer particles were also measured by laser diffraction. Mastersizer Hydro 2000 S (Malvern Instruments, UK with the whole measuring range from 0.02µm to 2000µm) was used to control the particles size in aqueous dispersion. Measurements of the particle size of the copolymers and homopolymer were performed with a pre-measurement treatment of 10 seconds at 1200 rpm in an ultrasonic bath built into the Malvern system for a better dispersion of the sample.

The thermal analysis of P(HEMA) and P(HEMA-co-U) copolymers has been carried in inert atmosphere at heating rate of 10^0C per minute up to 600 ^{0}C with a termobalance from Netzsch, Germany. Non-isothermal experiments were performed used an average sample weight to 7.5 mg and the nitrogen flow rate was 50 ml/min.

SEM studies were performed on samples fixed by means of colloidal copper supports. The samples were covered by sputtering with a thin layer of gold (EMITECH K 550x). The coated surface was examined by using an Environmental Scanning Electron Microscope (ESEM) type Quanta 200 operating at 30 kV with secondary electrons in high vacuum mode.

III. RESULTS AND DISCUSSIONS

The idealized reaction of the copolymerization process is illustrated in Figure 1.

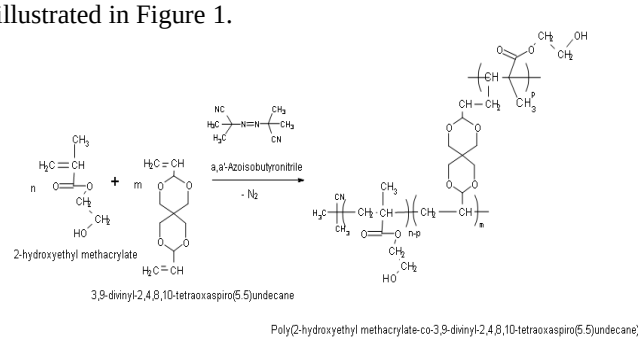

Fig. 1. Idealized copolymerization process

The structure of the new synthesized copolymers was confirmed by FT-IR spectra. Thus, the ν(O–H) stretching vibration in PHEMA was registered in the 3400–3500 cm^{-1} range as broad absorptions, and a strong band at ~ 2950cm^{-1} and ~ 2970cm^{-1} indicated the ν(C–H). Another strong band at ~1730cm^{-1} was attributed to ν (C=O) group; at ~2940 cm^{-1} to ν(C–H) stretching of -CH_3, and also at ~1270cm^{-1} to ν (C–O) stretching vibration. The spiroacetal moieties inclusion was also confirmed by the FTIR spectra. Thus, FTIR spectra of the copolymers presented some new strong bands in the region of 1000 – 1200cm^{-1} (due to esteric C-O-C stretching) and at ~1715cm $^{-1}$ (due to C=O stretching of conjugated ester). The relative thermal stability of the homopolymer and copolymers are illustrated in Figure 2. According the results the homopolymer and copolymers shows a high mass lost until 460^{0}C. By using thermal analysis (TG) it was found that the copolymerization process proceeds slowly decrease of thermal stability. Increasing the intermolecular space, induced by the copolymerization of 2-hydroxylethyl methacrylate with 3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5] undecane, leads to form a polymeric structure with a less thermal stability, modified slightly compared to homopolymer, where the polymeric chains are well wrapped through intramolecular attractive interactions especially hydrogen bonds.

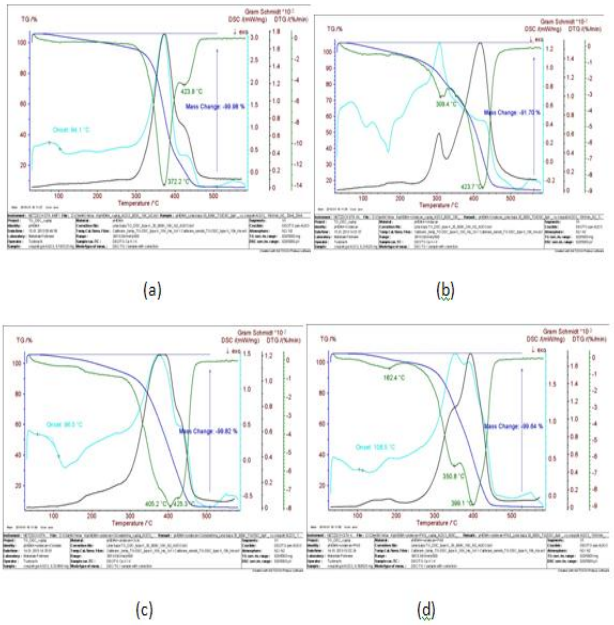

Fig. 2. The behavior during thermal decomposition for the studied polymeric samples: (a) P(HEMA), (b) P(HEMA–co–U)$_{DBS}$, (c) P(HEMA–co–U)$_C$, (d) P(HEMA–co–U)$_{PAS}$

The inclusion of the oligosaccharides in the synthesis, like β–cyclodextrin also, leads to decrease the initial decomposition temperature, owing to the hydroxyl groups that are border outside of the ring. The same behavior is experienced for the copolymer synthesized in the presence of PAS as protective colloid. This slight decrease in the thermal stability did not significant affect system stability, offset by the other improved properties conferred by achieving a network structure for example. At the same time, based on the maximum temperature decomposition, the copolymers show an increase of the thermal stability with 30^{0}C until 50 ^{0}C (Table 1). Figure 1 shows that each DTG curve of homopolymer and copolymers has two or three peaks which is usually interpreted as the decomposition of the sample in the first step and for the second one is due to a less stable intermediate product. It can be concluded that the presence of the comonomer positively affects the thermal behavior of the copolymer as it can be observed from the DTG curves.

TABLE I. DATA RESULTED FROM TG AND DTG CURVES OF THE STUDIED POLYMERS

Sample	W	T_{onset}	T_{peak},	T_{endset},	T_{10}
P(HEMA)	94.5	282	372	472	333
$P(HEMA–co–U)_{DBS}$	94.6	279	423.7	484	326
$P(HEMA–co–U)_{C}$	94	279	405	482	315
$P(HEMA–co–U)_{PAS}$	94	235	399	468	317
W - %; T - ^{0}C;					

Compared data concerning the dispersion dimensions and their zeta potential were also obtained onto the lyophilized particles (Figure 3 and Table 2). From the size distribution results (Figure 3) it is obviously the influence of the stabilizer type used in the synthesis. Even strange, it results the better performance of PAS and CD as stabilizer then that of the classical one SLS. Thus, the broadness of the resultant particle size distribution in decreasing order is : $P(HEMA\text{-}co\text{-}U)_{DBS}$ 〉 P(HEMA) 〉 $P(HEMA\text{-}co\text{-}U)_{CD}$ 〉 $P(HEMA\text{-}co\text{-}U)_{PAS}$.

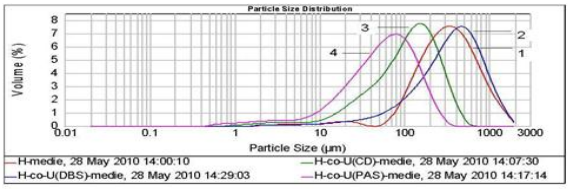

Figure 3. The particles size distribution after the volume distribution for P(HEMA) (1), $P(HEMA\text{-}co\text{-}U)_{DBS}$ (2), $P(HEMA\text{-}co\text{-}U)_{CD}$ (3), $P(HEMA\text{-}co\text{-}U)_{PAS}$ (4)

TABLE 2. THE ZETA POTENTIAL AND CONDUCTIVITY OF THE SYNTHESIZED POLYMERIC PARTICLES

Sample name	ζ, mV	Conductivity, mS/m
P(HEMA)	-0.295 ± 0.01	0.353 ± 0.002
$P(HEMA\text{-}co\text{-}U)_{DBS}$	-7.6 ± 1.04	0.207 ± 0.003
$P(HEMA\text{-}co\text{-}U)_{PAS}$	-1.923 ± 0.41	0.970 ± 0.01
$P(HEMA\text{-}co\text{-}U)_{CD}$	-0.39 ± 0.24	0.573 ± 0.001

From the determinations it results all particle surfaces were negatively charged, and also the surfactant nature significantly influences the surface charges, due to the functional groups. The zeta potential results indicate a low surface charge for the homopolymer, followed by the $P(HEMA\text{-}co\text{-}U)_{CD}$ 〉 $P(HEMA\text{-}co\text{-}U)_{PAS}$ and finally $P(HEMA\text{-}co\text{-}U)_{DBS}$. The conductivity of the copolymers prepared in the presence of PAS or CD was found to be increased by several orders against homopolymer.

Morphological information concerning the studied polymeric compounds utilizing SEM is presented in Figures 4 a – d. The structural and compositional characteristics of the surfaces are evidenced and differences between the synthesized homopolymer (Figure 4a) and the copolymers (Figures 4b-d) are proof. SEM micrographs show that the polymers prepared with different stabilizers possess a distinct structure. The homopolymer seems to have more homogeneous structure instead of the copolymers that appear with an internal lamellar structure in case of using CD as protective colloid, like a lace when PAS is the stabilizer, and a little bit inhomogeneous structure in case of SLS.

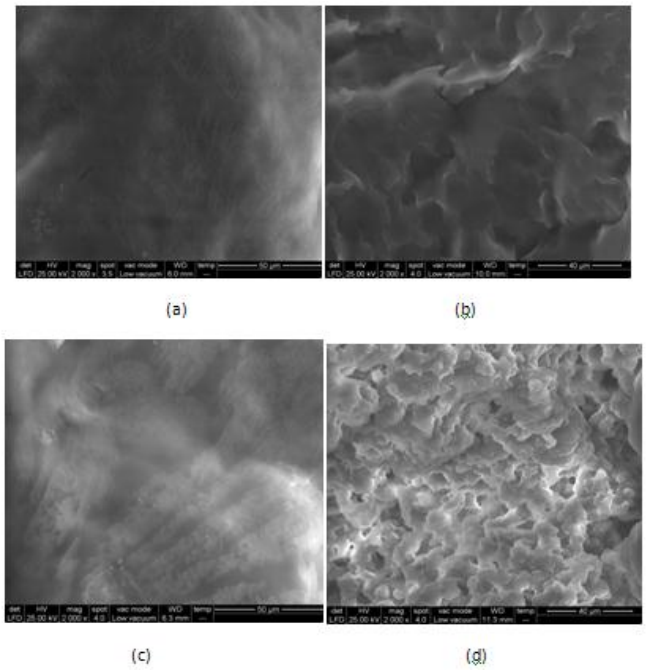

Figure 4. SEM micrographs of the studied polymers PHEMA (a),$P(HEMA–co–U)_{DBS}$ (b), $P(HEMA–co–U)_{CD}$ (c), $P(HEMA–co–U)_{PAS}$ (d)

IV. CONCLUSION

Taking into account the special effects which may be generated by both comonomers – network formation, biodegradability and biocompatibility, gel formation capacity, binding properties, amphilicity, good oxidative and thermal stability, good films formers, acid pH sensitivity – the interest in the development of these new polymeric structures with emphasis on theoretical aspects is thoroughly justified. In this context further investigation are in course.

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