

swelling properties. Generally, polyacrylamides, due to their solubility in water, are used particularly as thickening, suspending, flocculating, and coagulating agents in wastewater treatment and papermaking. Also, crosslinked polyacrylamides form highly swollen soft gels with applicability in a number of biomedical purposes. One of the advantages of polyacrylamides is that the swelling is independent of the pH, compared to that containing methacrylic acid salt. The polar nature of polyacrylamides and their compatibility with aqueous environments have led to their use as both solid supports for peptide and organic synthesis, antigen presentation for the generation of antibodies.³⁻¹¹ At the same time their use as a drug delivery vehicle is relatively underutilized.

In one of our study it was reported the synthesis of a copolymer based on 2-hydroxyethyl methacrylate and 3, 9-divinyl-2, 4, 8, 10-tetraoxaspiro (5.5) undecane (U) acquired through radical polymerization in the presence of 2, 2'-Azobis (2-methylpropionitrile) (AIBN).¹² Both comonomers offer special effects as for example network formation, biodegradability and biocompatibility, gel formation capacity, binding properties, amphiphilicity, good oxidative and thermal stability, good film forming, and acid pH sensitivity.

One particular monomer that recently received attention is *N,N*-dimethylacrylamide (DMA), owing to the highly hydrophilic and biocompatible hydrogels which can be prepared.¹³ Also, the dimethylamide group is known to be a powerful hydrogen bond acceptor. DMA can be copolymerized as well with hydrophobic monomers, when the glass transition temperature and water sorption and desorption kinetics of the hydrogel are modified by changing the structure, location, or concentration of the hydrophobic group. The hydrophobically-modified hydrogels are intended for temperature-sensitive applications where the hydrogels swell and shrink in response to the temperature change of the swelling medium. In this manner hydrophobically modified hydrogels can have "tuned" properties.¹⁴⁻¹⁷

Aqueous solutions of poly(*N,N*-dimethylacrylamide) (pDMA), having only two methyl groups and no hydrogen-bonding ability, do not show LCST's below 100°C.¹⁸ However, aqueous solutions of DMA copolymers containing hydrophobic comonomers that enhance polymer-polymer interactions are thermally responsive. Thus, DMA copolymers tend to undergo liquid-liquid phase transitions, with the phase transition

temperature depending on the amount of hydrophobic comonomer.¹⁹⁻²²

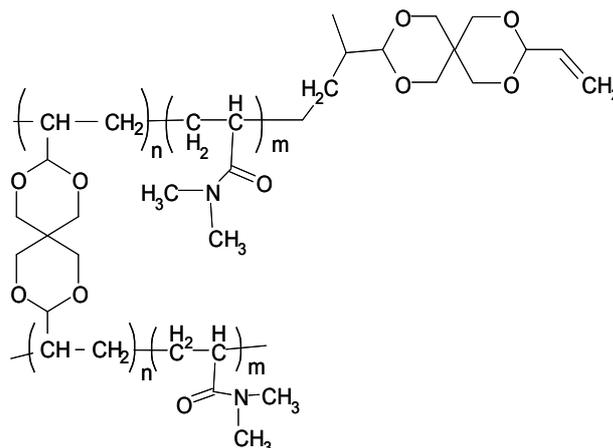
Thus, for example, the incorporation of spiroacetal groups in the polymers structures improves the solubility and the adhesive properties.²³⁻³³ More than that, these comonomers induce good oxidative and thermal stability. The polymers that include this structural unit are good fiber formers, and the films prepared from this kind of structures present good flexibility and tensile strength. These characteristics are attributed to the properties inherent into the spiroacetal ring: stiffness, which is higher than cycloaliphatic rings but lower than aromatic rings; interactions on ether oxygen such as hydrogen bonds or coordinate bonds with other functional groups, and bulkiness. The spiro systems are also unique in that the two core rings are arranged orthogonal about a tetrahedral atom common to both, making the compounds chiral in a similar way to an allene. In spiroacetals, the stereochemistry is predominantly driven by the number of anomeric effects contributing to the overall stability of the molecule. The spiroacetal ring system is taking as well conformation wherein the six-membered ring adopts a chair conformation with the O atom of the five-membered ring occupying an axial position thus gaining maximum stability from the anomeric effect.³⁴

The present study evidences the possibility for the preparation of the copolymer based on *N,N*-dimethylacrylamide and 3,9-divinyl-2,4,8,10-tetraoxaspiro (5.5) undecane (U) by the radical polymerization process in *N,N* - dimethyl acetamide solution and in the presence of dibenzoyl peroxide (BPO) as radical initiator. The new system is intended to be a "smart" polymer composition which brings pH sensitive response as well as is able to become intelligent gel offering a matrix which ensures intramolecular strategies for further coupling applications owing to the stereochemistry brought by the 3, 9-divinyl-2, 4, 8, 10-tetraoxaspiro (5.5) undecane comonomer for the new copolymer network.

RESULTS AND DISCUSSION

Kinetic evaluation

The new copolymer system has the idealized structure presented in Fig. 1:



Poly(N, N - dimethylacrylamide-co-3,9-divinyl-2,4,8,10-tetraoxaspiro[5.5]undecane)

Fig. 1 – The idealized copolymer structure.

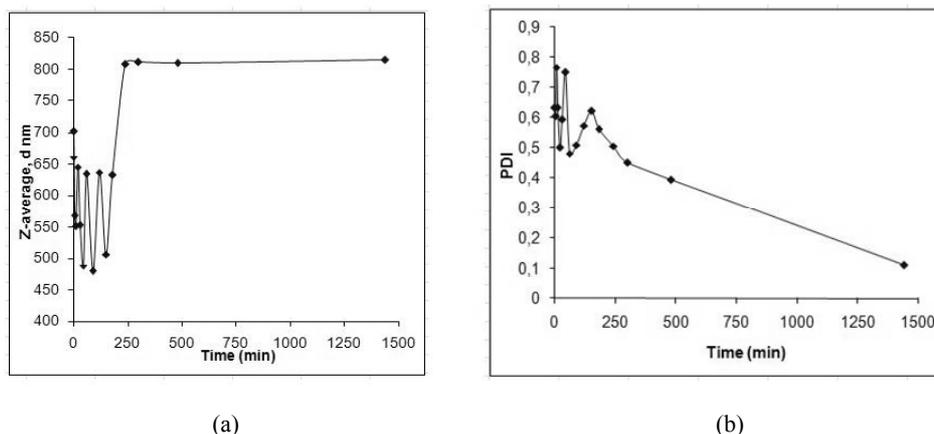


Fig. 2 – The development of the radical copolymerization process in relation with the evolution of (a) the hydrodynamic radius and (b) the polydispersity of the copolymer particles.

Fig. 2 presents the progress of the radical copolymerization process provided through the evolution of the hydrodynamic radius (a) and the polydispersity (b) of the copolymer particle dimension in the interdependence with the recipe and synthesis conditions.

From the evaluation of the copolymerization kinetic is evidenced the growth of the hydrodynamic radius of the copolymer nanoparticles followed by their decrease especially during the first 250 minutes. This behavior confirms the copolymerization process as well as the stereochemistry of the synthesized nanoparticles. As it is well known spiroacetal moiety offers specific conformational framework for the copolymers. In solution the electrostatic effects, as hard interactions, intervened during copolymerization process overwhelm the polarizability effect (the hyperconjugation: soft interactions).³⁵⁻³⁷

As it is well known to the acetals with vicinal oxy or other polar substituents, the attractive gauche effects³⁸⁻⁴² contribute to the difference in the stereoselectivity of the acetals conformers or/and their stereoisomers.^{43,44} To the spiroacetal moiety, with acid pH sensitivity and capability for interactions on ether oxygen such as hydrogen bonds or coordinate bonds with other functional groups, it is attributed the dynamic change of the stereochemistry through anomeric effect performed during copolymerization process. Thus, the spiroacetal moiety is getting an axial conformation, which may justify the increased dimension of the copolymer particles. The new conformation is at the same time more stable and has lower energy state as well as in this configuration the spiroacetal moiety is more able for specific future interactions.

FT-IR and ¹H-NMR spectra

The FT-IR spectrum (Fig. 3) confirms as well the achievement of the polymeric structure. The characteristic peaks of the copolymer resulted from

FT-IR spectra are presented in Table 1 and the structural analysis confirms the copolymer formation the absorption bands representing the presence of both co-monomers.

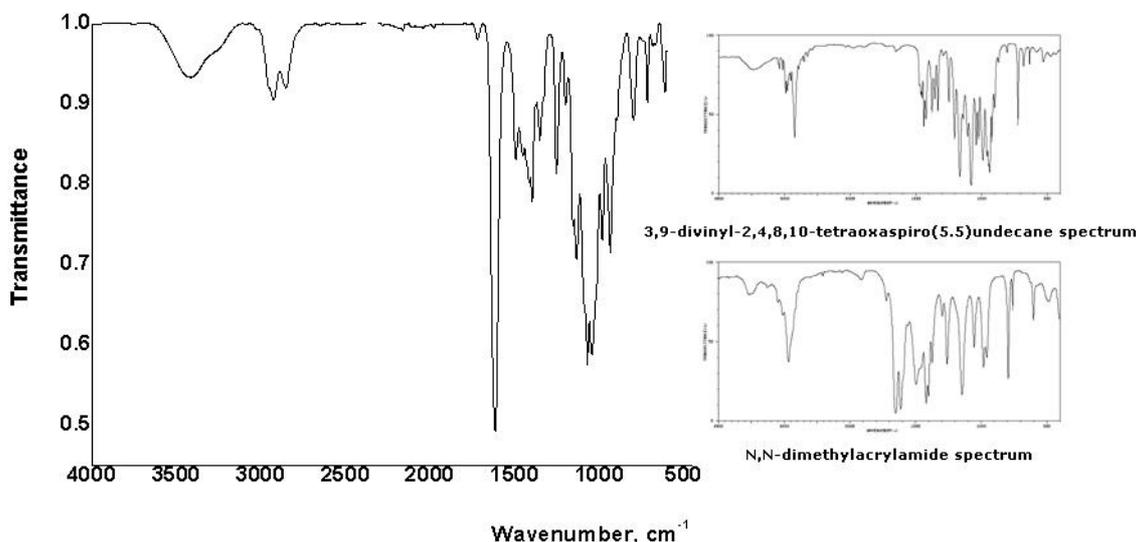


Fig. 3 – FTIR spectrum of the P(DMA-co-U) synthesized copolymer; insets show the details of the 3,9-divinyl-2,4,8,10-tetraoxaspiro(5.5)undecane and N,N-dimethylacrylamide spectra.

Table 1

The FT-IR characteristic peaks of the p(DMA-co-U) copolymer

Wavenumber, cm ⁻¹	Functional groups	Compound name
3600-3200	Hydrogen-bonded	N,N-dimethylacrylamide and 3, 9- Divinyl-2,4,8,10-tetraoxaspiro [5.5] undecane
2931 - 2855	C-H stretch ; CH ₂	N,N-dimethylacrylamide and 3, 9- Divinyl-2,4,8,10-tetraoxaspiro [5.5] undecane
1722	C=O carbonyl	N,N-dimethylacrylamide
1498-1380(v)	C-H scissoring and bending; CH ₂ bending vibrations; CH ₃ bending vibrations; CH ₃ umbrella deformation	N,N-dimethylacrylamide and 3, 9- Divinyl-2,4,8,10-tetraoxaspiro [5.5] undecane
1355	C-N stretch	N,N-dimethylacrylamide
1259	C-H and -CH ₃	N,N-dimethylacrylamide and 3, 9- Divinyl-2,4,8,10-tetraoxaspiro [5.5] undecane
1206	Ether C-O-C group	3, 9- Divinyl-2,4,8,10-tetraoxaspiro [5.5] undecane
1140 - 1077	C-N vibration	N,N-dimethylacrylamide
1049	C-O vibrations	3, 9- Divinyl-2,4,8,10-tetraoxaspiro [5.5] undecane
987 – 939	-CH=CH ₂	N,N-dimethylacrylamide and 3, 9- Divinyl-2,4,8,10-tetraoxaspiro [5.5] undecane
724	-CH=CH-	3, 9- Divinyl-2,4,8,10-tetraoxaspiro [5.5] undecane
619	δC=O carboxylic group	N,N-dimethylacrylamide

The new hydrogen bonds between N, N-dimethylacrylamide and 3, 9- Divinyl-2,4,8,10-tetraoxaspiro [5.5] undecane are observed in the 3600–3200 cm^{-1} range as broad absorptions, and a strong band between $\sim 2950\text{cm}^{-1}$ and $\sim 2850\text{cm}^{-1}$ indicated the $\nu(\text{C-H})$. Another strong band at $\sim 1720\text{cm}^{-1}$ is due to $\nu(\text{C=O})$ group; at $\sim 2930\text{cm}^{-1}$ to $\nu(\text{C-H})$ stretching of $-\text{CH}_3$, and also at $\sim 1270\text{cm}^{-1}$ to $\nu(\text{C-O})$ stretching vibration. The spiroacetal moieties presence is also confirmed by the new strong bands in the region of 1000 – 1200 cm^{-1} due to C-O-C stretching and at $\sim 1715\text{cm}^{-1}$ (due to C-O stretching of conjugated ether).

On $^1\text{H-NMR}$ spectra (Fig. 4) the presence of the N, N-dimethylacrylamide and 3, 9- divinyl-2, 4, 8, 10-tetraoxaspiro[5.5]undecane co-monomers and

N, N dimethylacetamide as reaction media is also confirmed. Thus, the proton peaks corresponding both to 3, 9-Divinyl-2, 4, 8, 10 tetraoxaspiro[5.5]undecane and N,N-dimethylacrylamide are refund: between 1 to 2 ppm the peaks of the protons corresponding to R- CH_3 , R- CH_2 , R-CH are evidenced; between 3.3 to 4 ppm the protons corresponding to H-C-O- ethers group of U; onto 7.26 ppm the CDCl_3 is registered; also, other peaks characteristics for U: 3.264 (CH_2O -), 4.663 ($-\text{CH}_2=\text{C}$), 5.662 ($=\text{CH}_2-\text{CH}$ -), 5.686 ($=\text{CH}$ -) –and for DMA characteristics are registered: 3.087 ($-\text{N-CH}_3$), 5.662 ($-\text{CH}_2-$), 6.320 ($=\text{CH}_2$) and 6.578 ($-\text{HC}=\text{}$).

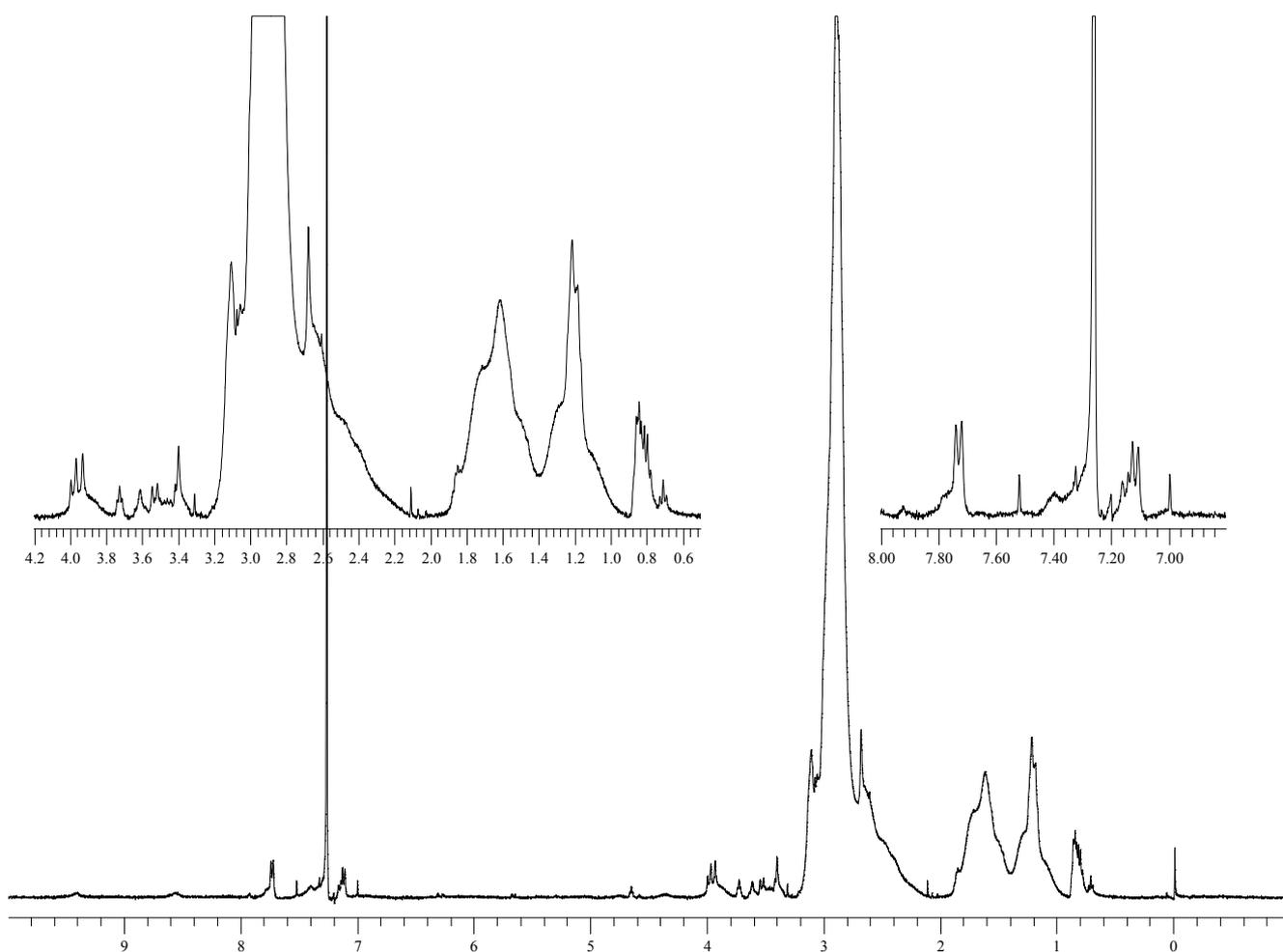


Fig. 4 – $^1\text{H-NMR}$ spectra for poly(DMA-co-U) copolymer synthesized in N,N dimethylacetamide as reaction media.

Thermal analysis

The data concerning the thermogravimetric analysis of poly(DMA-co-U) copolymer are

depicted in Fig. 5 and Table 2. The weight loss and the thermogravimetric curves recorded on the polymeric sample versus the temperature are presented in Fig. 5. It can be seen that in nitrogen

atmosphere the copolymer has a first domain of losing weight which starts from 90°C and has the maximum around of 172°C, area corresponding to losing the N, N dimethyl acetamide solvent. The second process comprised between 380°C and 460°C attests the good thermal stability of the p(DMA-co-U) polymeric compound as well as the improvement of the thermal degradation in interdependence with its composition, respectively the presence of the 3, 9-divinyl-2, 4, 8, 10-tetraoxaspiro (5.5) undecane as comonomer. The data are in good agreement with other literature results.⁴⁵

As it is well known the substitution of the hydrogens in the amide group by alkyl substituents leads to the weakening of the hydrogen interactions. In case of poly(DMA-co-U) copolymer new intramolecular hydrogen bonds intervene, making the copolymer more stable from the thermal viewpoint. The specific conformational framework resulted from the spiroacetal moiety presence can be this time considered as steric hindrance that makes the

intramolecular interactions preformed (see as well the particle size dimension) with benefit effect upon the thermal stability of the copolymer.

As it was mentioned before, the polymers having spiroacetal are considered multi-functional and useful as heat-resistant materials. The results from thermal analysis of the copolymer sustain our previous data.⁴⁶

SEM studies

The morphological information concerning the studied polymeric compound utilizing SEM is presented in Fig. 6. The structural and compositional characteristics of the surface are evidenced. SEM micrograph shows the morphology of an open homogeneous and dense network structure with the polymer in the form of strings of particles.

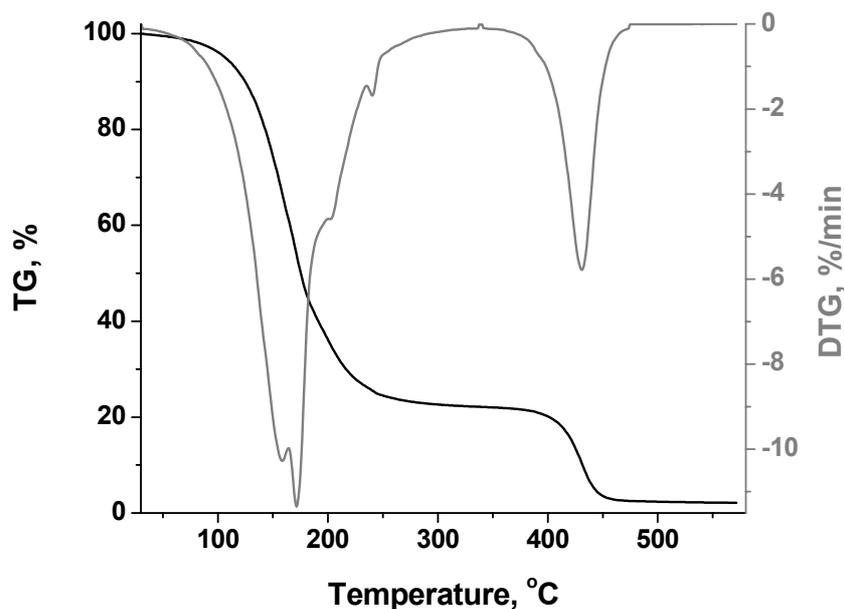


Fig. 5 – TG (a) and DTG (b) curves for the poly(DMA-co-U) copolymer.

Table 2

Data obtained from TG and DTG curves

	Mass Change, %	T _{onset} , °C	T _{max} , °C	T _{endset} , °C
Process I	77.7	90	172	246
Process II	20.2	380	431	460
Residual mass: 2.1% at 573 °C				

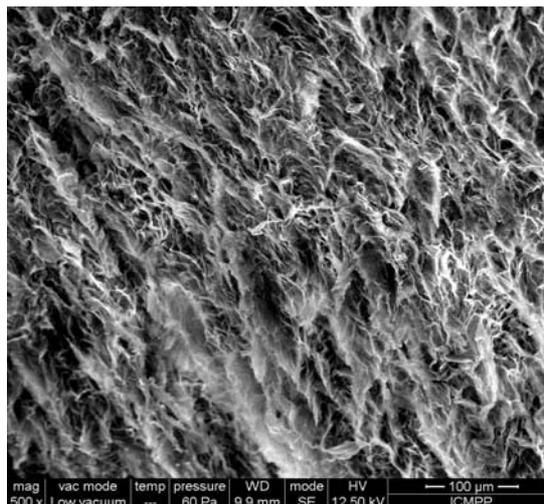


Fig. 6 – SEM micrograph of the studied polymers P(DMA-co-U).

EXPERIMENTAL

Materials

The monomers *N, N*-dimethylacrylamide (DMA) and 3, 9-Divinyl-2, 4, 8, 10-tetraoxaspiro[5.5]undecane – (U) were supplied by Aldrich Chemical Co. and were used without further purification as well as the used solvent *N, N* dimethyl acetamide (from Sigma-Aldrich). Dibenzoyl peroxide (BPO) was dissolved in chloroform and then precipitated for recrystallization with methanol. The water used in all experiments was purified using an Ultra Clear TWF UV System.

Polymerization Process

The copolymer P(DMA-co-U) was prepared by radical polymerization process using BPO as initiator, *N, N* – dimethyl acetamide as solvent, under nitrogen atmosphere, at 75°C for 6 h, and at 80°C for other 2 hours as thermal treatment; the reaction was performed in a constant temperature bath, with a stirring rate of 250 rpm. The reaction recipe is presented in Table 3.

After synthesis the copolymer was dried in a vacuum oven and finally freeze-dried by lyophilization for 24h.

The reaction kinetic during copolymer synthesis was evaluated by the mean particle size and size distribution of the copolymer nanoparticles using 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 the copolymer solution 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.

Copolymer characterization

The p(DMA-co-U) FTIR spectrum was recorded on a Vertex Bruker Spectrometer in an absorption mode ranging from 400 cm⁻¹ to 4000 cm⁻¹ and acquired at 4 cm⁻¹ resolution as an average of 64 scans. The polymer sample was grounded with potassium bromide (KBr) powder and compressed into a disc to analysis.

¹H-NMR experiments were performed with a Bruker Avance DRX 400 spectrometer equipped with a 5 mm broad band probe. ¹H NMR spectra were recorded at a frequency of 400 MHz in CDCl₃.

Thermal analysis of polymer solution was performed using a STA 449F1 Jupiter model (Netzsch-Germany) system. The system is equipped with an apparatus of simultaneous thermogravimetric and differential scanning calorimetry analyses. Samples ranging between 7.4-7.6 ml were heated from 30°C to 580°C, at heating rate of 10°C/min. As carrier gas was used the nitrogen (99.95 % purity) with the flow rate of 50 ml/min. The sample was heated in an open Al₂O₃ crucible with Al₂O₃ as reference material.

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.

Table 3

The recipe for 100 ml copolymer solution preparation

Components	Quantities in M/100 ml copolymer solution
<i>N, N</i> -dimethylacrylamide (DMA)	0.2825 M
3, 9-Divinyl-2, 4, 8, 10-tetraoxaspiro[5.5]undecane – (U)	0.1319 M
Dibenzoyl peroxide (BPO)	0.0005 M
<i>N, N</i> dimethyl acetamide (DMAc)	1.076 M

CONCLUSIONS

The study presents the preparation of the copolymer based on *N,N*-dimethylacrylamide and 3, 9-divinyl-2, 4, 8, 10-tetraoxaspiro (5.5) undecane (U) by the radical polymerization process in *N,N*-dimethyl acetamide solution and in the presence of peroxide benzoil (PBO) as radical initiator. The copolymerization kinetic was evidenced by the growth of the hydrodynamic radius of the copolymer nanoparticles during reaction and the stabilization of the particle size after 250 minutes reaction time. The FT-IR and ¹H-NMR spectra also confirm the achievement of the polymeric structure. The advantage brought by the U comonomer is concretized by the thermal stability of the copolymer. The new system can be included into the “smart” polymer class owing to the gel formation capacity, binding properties, amphiphilicity, good oxidative and thermal stability, biocompatibility, good films formers, pH sensitive response which is able for. The stereochemistry of the copolymer network ensures as well intramolecular strategies for further coupling processes of various molecular compounds as the polymer matrix to become for example a multi-sensitive structure or a drug delivery system.

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