

## Design and Properties of New Functional Water - Soluble Polymers of Citraconic Anhydride (CA) and Related Copolymers

Murat Barsbay, Hatice Kaplan Can(✉), Zakir M.O. Rzaev<sup>a</sup>, Ali Güner

Department of Chemistry, Faculty of Science, Hacettepe University, Beytepe, 06532 Ankara, Turkey

<sup>a</sup> Department of Chemical Engineering, Faculty of Engineering, Hacettepe University, Beytepe, 06532 Ankara, Turkey

E-mail: hkaplan@hacettepe.edu.tr, hkaplan@hacettepe.edu.tr; Fax: + 90 312 299 21 63

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### Summary

The binary and ternary copolymers are synthesized by free-radical initiated binary copolymerization of citraconic anhydride (CA) with acrylamide (AAm) and terpolymerization of acrylamide (AAm) - citraconic anhydride (CA) - vinyl acetate (VA) monomer system. Co- and terpolymerization were carried out in the presence of benzoyl peroxide (BPO) as an initiator at 70 °C in benzene under nitrogen atmosphere. Structure and monomer unit composition of the copolymers, obtained from a wide range of monomer feed were determined by elemental analysis. Structural peculiarities of synthesized PAAM, [poly (AAm-*alt*-CA)] and [poly(AAm-*co*-CA-*co*-VA)] were characterized by using Fourier Transform Infrared (FTIR), Uv-vis, <sup>1</sup>H-NMR, X-ray diffraction (XRD), elemental analysis, analytical methods (titration methods) and viscometric measurements.

### Introduction

Polymers containing epoxy, hydroxyl, amine, and carboxylic acid groups are widely used commercially in applications such as protective coatings, adhesives and composites. Functional groups can also be used to modify the properties of a polymer such as adhesion. Many of the functional groups currently in use have limitations in terms of reactivity or may have environmental or other hazards associated with them. Thus, the development of new functional groups for polymers is an active area of investigation in polymer science [1].

It is clear that for the synthesis of various functional polymers with given structure, composition and properties, the complex-radical copolymerization of donor-acceptor binary and ternary monomer systems is an effective polymerization method because, besides the easy manipulation, it is applicable to a great variety of monomers [2-5]. The radical-initiated copolymerization of *N*-isopropylacrylamide (NIPAM) with maleic anhydride (MA) and citraconic anhydride (CA) was studied as a way to obtain

new reactive amphiphilic water-soluble polymers potentially useful as carriers for gene delivery [6]. Synthesis and characterization of cationic stimuli-responsive acrylic acid-terminated poly(NIPAM) potentially useful as carrier for gene delivery, conjugates of poly(NIPAM) with amino acids as prodding, antitumor active binary and ternary copolymers of MA, vinyl acetate (VA) and acrylic acid have been reported [7-8]. Anhydride functional copolymers, usually prepared from maleic anhydride, styrene and acrylic monomers, are an increasingly important group of co-reactants for polyol and epoxide crosslinked coatings [9]. In the previous studies the reactivity and behavior of citraconic anhydride (CA) as an electron-accepting monomer in radical copolymerization were studied [10-14]. Acrylamide (AAM) and its derivatives can undergo alternating copolymerization with maleic anhydride (MA) under the given conditions [15-16]. These copolymers are potentially useful as flocculants, for purification of industrial wastewater, as coatings for microcapsule production and for paper dry-strength agents [17]. In the present study, the results of the complex-radical copolymerization of acceptor-donor-acceptor monomer system such as Citraconic Anhydride (CA)-Vinyl Acetate (VA) - Acrylamide (AAM) in low conversion conditions and some peculiarities of these novel polymers are described.

## Experimental

### Materials

Initial monomers such as citraconic anhydride (CA), acrylamide (AAM), vinyl acetate (VA) supplied by Fluka, were distilled before use. They had following characteristics: Citraconic Anhydride (CA),  $C_5H_4O_3$ , b.p. 241 °C, m.p. 8 °C,  $d_4^{20} = 1.243 \text{ g/cm}^3$ , MW=112.08 g/mol. Acrylamide (AAM),  $C_3H_5NO$ , b.p. 87 °C (2.7 hPa), m.p. 84 °C,  $d_4^{20} = 1.127 \text{ g/cm}^3$ , MW=71.08 g/mol. Vinyl Acetate (VA),  $C_4H_6O_2$ , b.p. 73 °C, m.p. -100 °C,  $n_D^{20} = 1.3954$ ,  $d_4^{20} = 0.93 \text{ g/cm}^3$ , MW=86.09 g/mol. Benzoyl peroxide (BPO), initiator  $C_6H_5-COO-OOC-C_6H_5$ , as a Fluka product, was purified by recrystallizing twice from chloroform solution with methanol. It was dried under *vacuum*, m.p. 106°C. Solvents (MERC) such as p-dioxane, acetone, methyl ethyl ketone, chloroform, benzene, and toluene as well as methanol, ethanol, and n-hexane as precipitating agents (MERC) were purified before use by well-known distillation method.

### Copolymerization and Terpolymerization

Synthesis of CA, AAM binary copolymer and ternary AAM-CA-VA copolymers were carried out in degassed Pyrex glass in benzene with BPO as an initiator at 70°C under nitrogen atmosphere. After given amount of the monomers, initiator and solvent mixture has been placed into the glass tube and then degassed by three-fold freezing with subsequent melting under vacuum. The reaction system was blown off by purified nitrogen and the tube was sealed and placed a thermostat with glycerine bath. In order to determine the copolymer yield in the reaction mixture, hydroquinone was added as an inhibitor, and then this mixture was poured in a large amount of methanol to precipitate the copolymers. The powder-like product obtained was separated by filtration, and then purified by multiple washing in methanol and diethyl ether, and filtered one more. After allowing reaction to proceed for a given time ( $\leq 15\%$  for the low conversion and  $\geq 45\%$  for the high conversion), the reactive mixture was poured

into a large amount of methanol (solution/precipitor=1: 5) to precipitate the polymer and was separated by filtration. All polymers synthesized were converted to powder form in liquid nitrogen and the obtained product was dried under vacuum at 40°C to constant weight.

### *Measurements*

#### *FTIR Studies*

For the analysis of co- and terpolymer, Fourier transform infrared (FTIR) spectra of copolymer films with KBr pellet were recorded with FTIR Mattson 1000 spectrometer in the 4000-400 cm<sup>-1</sup> range, where 40 scans were taken at 16 cm<sup>-1</sup> resolution.

#### *Uv-vis Studies*

Jasco V-530 UV - visible double beams spectrophotometer was used for uv-vis studies of aqueous solutions of polymer samples (0.1 g/25 mL) at 20 ± 0.1°C.

#### *NMR Studies*

JEOL GX-400 NMR spectrometer with 400 MHz frequency was used for analyzing polymer solutions in deuterated DMSO-*d*<sub>6</sub> and CHCl<sub>3</sub>-*d*<sub>1</sub> chloroform as solvent and tetramethylsilane as an internal standard at 25 ± 0.1°C.

#### *X-ray Diffraction (XRD) Studies*

The powder diffraction patterns of synthesized samples were recorded using a Philips manual spectrogoniometer employing CuK<sub>α</sub> (λ = 1.54184 Å) radiation over the range 5° ≤ 2θ ≤ 50°. Crystallinity degrees of new products were determined by area ratio method

$$X_c = \int_0^\infty s^2 I_c(s) ds / \int_0^\infty s^2 I(s) ds$$

where *s* is the magnitude of the reciprocal-lattice vector and is given by  $s = (2\sin \theta) / \lambda$ .  $\theta$  is one-half the angle of deviation of the diffracted rays from the incident X-rays,  $\lambda$  is the wavelength, *I*(*s*) is the intensity of coherent X-ray scatter from a specimen (both crystalline and amorphous), *I*<sub>c</sub>(*s*) is the intensity of coherent x-ray scatter from the crystalline region. In this method, the areas of amorphous and crystalline parts of the patterns were calculated.

#### *Elemental Analysis*

The Perkin-Elmer Model 240C Elemental Analyzer was used for determination of C, H, O and N contents in the synthesized polymers.

#### *The Acid Number (AN)*

The acid numbers (AN) of the anhydride-containing polymers were determined by non-aqueous titration method. Using-following equation:

$$AN \text{ (mg KOH)} = [56.1(V_1N_1 - V_2N_2) / m]$$

where *V*<sub>1</sub> is total content of KOH before added (ml); *N*<sub>1</sub> is normality of KOH (0.0909 N KOH); *V*<sub>2</sub> is content of HCl required to titrate the KOH abundance (ml); *N*<sub>2</sub> is

normality of HCl (0.096 *N* HCl); *m* is content of polymer sample (g). Thus, acid number (AN) is the number of milligrams of KOH required to neutralize 1 g of polymer sample.

#### Viscosity Studies

Intrinsic viscosities of synthesized polymers were determined in water at  $25 \pm 0.1^\circ\text{C}$  and in the concentration range of 0.1-1.0g/dL using an Ubbelohde viscometer. The values of  $[\eta]_{\text{in}}$  were determined from plot of  $\eta_{\text{sp}}/c$  vs. *c* concentration of polymers.

## Results and Discussion

#### Synthesis and Characterization of Co- and Terpolymers

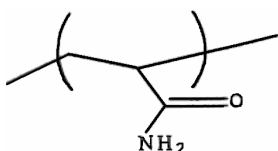
Anhydride containing alternating copolymers and terpolymers have received significant attention due to their unique properties and a wide range of applications as adhesives, photocrosslinkable and photostetting resin compositions, photographic films, electrophotographic recording and glass fiber coatings, reversible shear thinning gels, detergents, viscosity improvers, flocculants and cellular plastics as well as controlled-release coatings, medicinal tablet coatings [3]. Due to the nature of the conjugation between the double bonds and functional groups (C=O of amide and anhydride group), acrylamide and citraconic anhydride monomers can be considered as electron acceptors. However, this fact does not prevent the monomers from having sufficient activity in free-radical copolymerization of citraconic anhydride and acrylamide monomer pairs owing to the interaction between the functional groups of the monomers through the hydrogen bonding [6]. One of the important intra- and intermolecular structural characteristics of polyfunctional polymers is structural regularity and bond flexibility of their macromolecules. When the polar polymers show H-bonding capability, the most energetically favored crystal structures will tend to capitalize on these features. Synthesis of [poly (AAM-*alt*-CA)] and [poly (AAM-*co*-CA-*co*-VA)] polymers were carried out by the radical initiated solution copolymerization at different concentrations and various conditions (Table 1).

**Table 1.** Copolymerization of AAm ( $M_1$ ), CA ( $M_2$ ) and VA ( $M_3$ ) in benzene with BPO ( $2.1 \times 10^{-3}$  mol/L) at  $70^\circ\text{C}$ , reaction time 2 h, conversion >40%

Monomer Feed (mol %) [ $M_1$ ] [ $M_2$ ] [ $M_3$ ] AAm : CA : VA	Elemental Analysis (%)			Copolymers and terpolymer Composition		
	<i>C</i>	<i>H</i>	<i>N</i>	$m_1$	$m_2$	$m_3$
20 : 80 : 00	48.35	4.44	5.01	38.12	61.87	
40 : 60 : 00	49.6	4.92	5.46	37.68	62.32	
50 : 50 : 00	48.2	5.28	8.43	54.14	45.86	
60 : 40 : 00	47.72	6.72	10.92	66.25	33.75	
80 : 20 : 00	48.30	5.95	11.74	69.96	30.04	
25 : 50 : 25	49.80	5.65	8.15	12.01	58.32	29.66

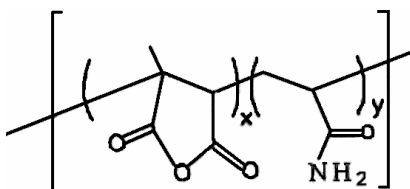
The synthesized copolymers and terpolymer by the use of 1: 1 and 1: 2: 1 molar ratio of initial monomers, respectively, had following characteristics:

*Poly (Acrylamide), PAAm*



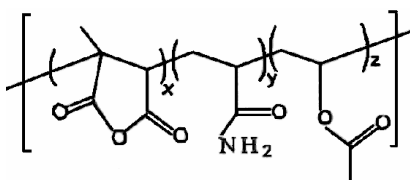
Yield 60 %, intrinsic viscosity  $[\eta]_{in} = 1.20$  dL/g in dioxane at 25 °C, acid number (AN) = 251 mg KOH/g.

*Poly (Acrylamide - Citraconic Anhydride) Poly (AAm-alt-CA)*



Yield 53 %, intrinsic viscosity  $[\eta]_{in} = 0.22$  dL/g in benzene at 25 °C, acid number (AN) = 244.4 mg KOH/g, monomer unit ratio in copolymer ( $m_1: m_2$ ) = 1.18: 1.

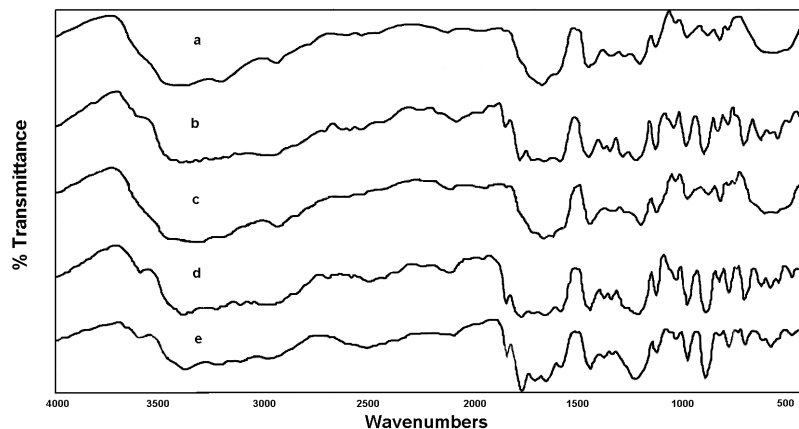
*Poly (Acrylamide-Citraconic Anhydride-Vinyl Acetate) Poly (AAm-co-CA-co-VA)*



Yield 30 %, intrinsic viscosity  $[\eta]_{in} = 0.11$  dL/g in dioxane at 25 °C, acid number (AN) = 308. 6 mg KOH/g, monomer unit ratio in copolymer ( $m_1: m_2: m_3$ ) = 1:2:1.

#### *Fourier Transform Infrared (FTIR) Studies*

Characterization of specific bands for synthesized copolymers was confirmed by FTIR spectral analysis (Figure 1). The analysis of the FTIR spectrum provides us valuable structural information about the novel macromolecules obtained via alternating copolymerization. FTIR spectra of copolymers at various ratios displayed strong absorption bands implying the presence of anhydride group of CA centered at 1850-1740  $\text{cm}^{-1}$ . At the higher concentrations of acrylamide, N-H stretching vibrations can be seen at 3500  $\text{cm}^{-1}$  with its characteristic adsorption bands.

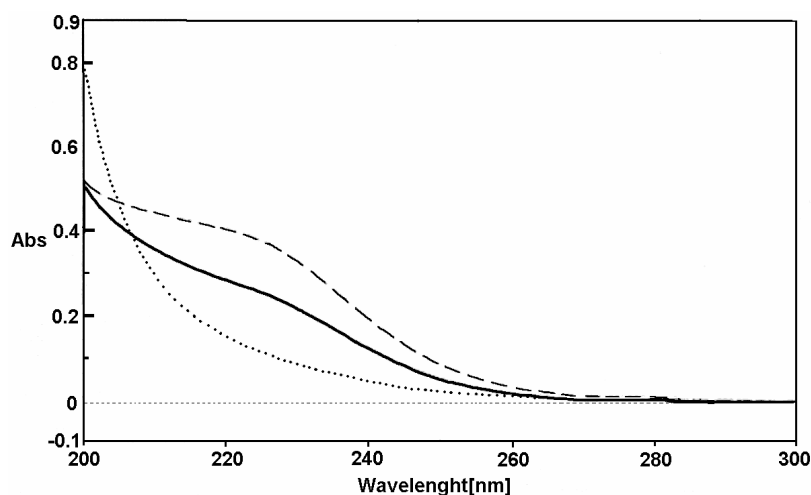


**Figure 1.** FTIR spectra of poly(AAm-*alt*-CA) copolymers with different composition (a) % 20 AAm, (b) % 40 AAm, (c) % 50 AAm, (d) % 60 AAm and (e) % 80 AAm

The intensity of anhydride band at  $1730\text{ cm}^{-1}$  increases because of the intra- H bonding between anhydride  $\text{-C=O}$  and acrylamide groups. Appearance of the new peak of  $\text{COOH}$  at  $3425\text{ cm}^{-1}$  can be observed in the spectra due to the inter- H bonding between anhydride  $\text{-C=O}$  groups and the amide groups (spectrum e). At high concentrations of acrylamide (spectrum e), N-H bending and C-N stretching bands can be seen at  $1650$  and  $1250\text{ cm}^{-1}$  [11].

#### *Uv-vis Studies*

AAM and CA have a large tendency to form alternating copolymers [11]. In order to examine whether such a charge transfer complex (system is realized according to complex-radical mechanism in the stage of binary copolymerization of CA...VA and

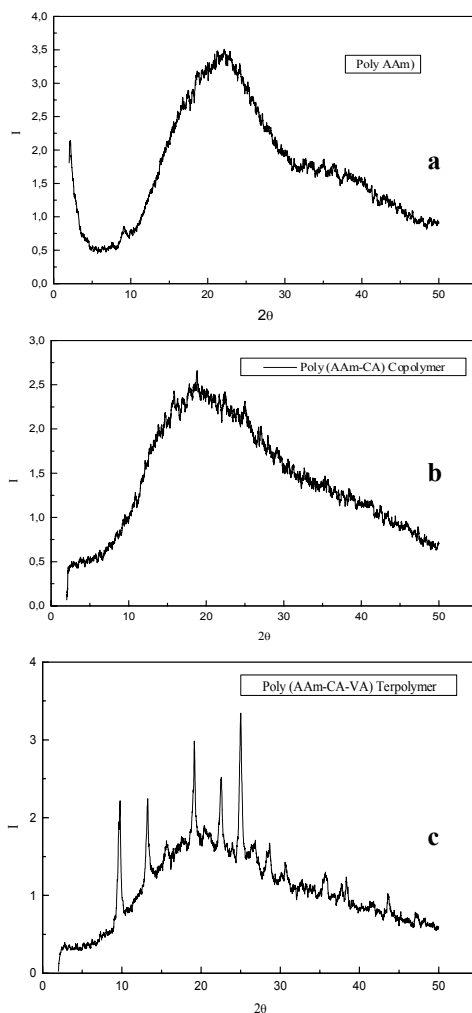


**Figure 2.** Uv-vis spectra of PAAm (....), [poly (AAm-*alt*-CA)] (-) and [poly(AAm-*co*-CA-*co*-VA)] (- -).aqueous solutions  $[\text{M}]=9.10 \times 10^{-6}\text{ g/mL}$

AAm...VA charge transfer complex with free AAm monomers) exists in [poly (AAm-*alt*-CA)] and [poly(AAm-*co*-CA-*co*-VA)] systems the uv-vis spectroscopic studies were carried out and uv-vis absorption spectra of PAAm, poly (AAm-*alt*-CA) and [poly (AAm-*co*-CA-*co*-VA)] are shown in Figure 2. Aqueous solutions of PAAm, [poly (AAm-*alt*-CA)] and [poly(AAm-*co*-CA-*co*-VA)] gave increasing intensity in absorption bands, respectively. This region has been characteristic of charge-transfer complex absorption [12].

#### *X-ray Diffraction (XRD) Studies*

X-ray diffraction (XRD) patterns of PAAm (a), [poly (AAm-*alt*-CA)] (b) and [poly (AAm-*co*-CA-*co*-VA)] (c) are represented in Figure 3. Using integrated areas of total

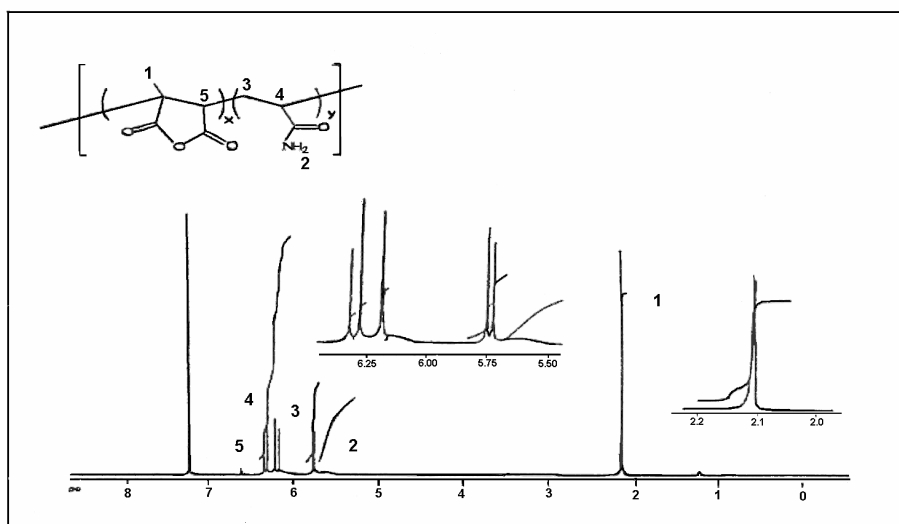


**Figure 3.** XRD patterns of PAAm (a), [poly (AAm-*alt*-CA)] (b) and [poly (AAm-*co*-CA-*co*-VA)] (c)

and crystalline regions the degrees of crystallinity of samples were calculated. The calculated crystallinity degrees of PAAm, [poly (AAm-*alt*-CA)] and [poly (AAm-*co*-CA-*co*-VA)] are given in Table 2. According to the degrees of crystallinity of PAAm and [poly (AAm-*alt*-CA)] polymer samples, it is easily seen that they have nearly amorphous character because of the highly H-bonded structure in the polymer, giving the polymer an irregular character. With the addition of VA monomer to the terpolymer, the degree of crystallinity of [poly (AAm-*co*-CA-*co*-VA)] increases. VA monomer gives regularity to polymer segments in the chain [18].

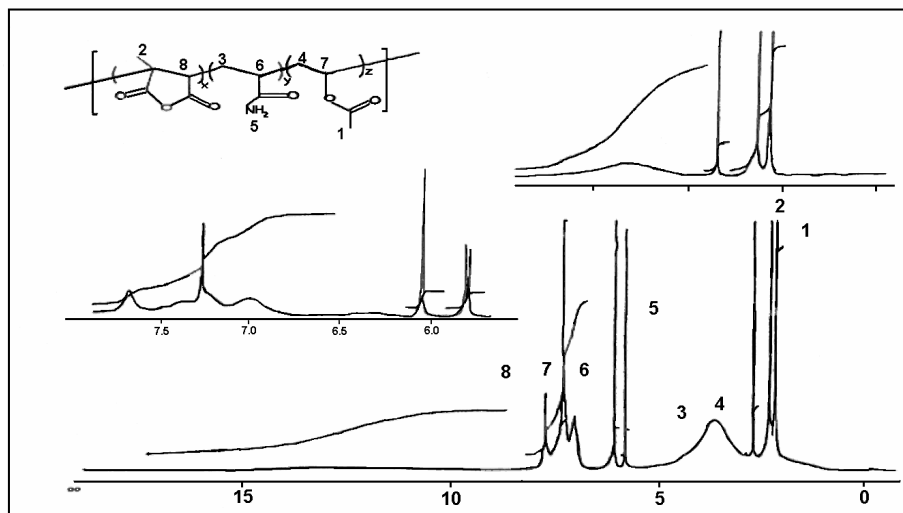
#### Nuclear Magnetic Resonance (NMR) Studies

In order to confirm acceptor-donor interaction and characterize the synthesized novel [poly (AAm-*alt*-CA)] (50:50) and [poly (AAm-*co*-CA-*co*-VA)] (25:50:25) polymers  $^1\text{H}$  NMR method was employed and spectra of polymers are shown in Figures 4, 5. Expected specific chemical shifts for [poly (AAm-*alt*-CA)] (50:50) copolymer can be seen from the  $^1\text{H}$  NMR spectra in Figure 4. According to Figure 4: at  $\delta=2.1$  ppm monosubstituted methyl of CA and at  $\delta=6-6.3$  ppm  $-\text{CH}_2$  and  $-\text{CH}$  protons appear; at  $\delta=5.75$  ppm  $-\text{NH}_2$  protons of AAm appear and solvent- $\text{CHCl}_3-d_1$  occurs at  $\delta=7.25$  ppm. Expected specific chemical shifts were detected in NMR spectra of poly (AAm-*co*-CA-*co*-VA) as can be seen from Figure 5: at  $\delta=2.1-2.4$  ppm monosubstituted methyl of CA and VA methyl group; at  $\delta=2.5$  ppm solvent-DMSO- $d_6$ ; at  $\delta=3-4$  ppm protons of  $-\text{NHC}=\text{O}$  and protons of  $-\text{OC}=\text{OCH}_3$ ; at  $\delta=5.75$  ppm  $-\text{NH}_2$  protons of AAm; at  $\delta=6-6.3$  ppm and  $7-7.8$  ppm  $-\text{CH}$  protons of three different  $-\text{CH}$  groups of terpolymer were detected ( $-\text{CH}$  groups of AAm, CA and VA).



**Figure 4.**  $^1\text{H}$ -NMR spectra of [poly (AAm-*alt*-CA)] (50:50) solvent- $\text{CHCl}_3-d_1$ , internal standard-tetramethylsilane (TMS),  $25 \pm 0.1^\circ\text{C}$





**Figure 5.**  $^1\text{H-NMR}$  spectra of [poly (AAM-co-CA-co-VA)] (25:50:25) solvent-DMSO- $d_6$ , internal standard-tetramethylsilane (TMS),  $25 \pm 0.1^\circ\text{C}$

## Conclusion

New functional [poly (AAM-*alt*-CA)] and [poly (AAM-co-CA-co-VA)] water-soluble polymers were synthesized by complex-radical terpolymerization using BPO as an initiator and benzene as the solvent under nitrogen atmosphere at  $70^\circ\text{C}$ . All synthesized binary and ternary polymers were characterized by chemical (titration of anhydride units), elemental (contents of  $N$  for acrylamide units), FTIR, Uv-vis, XRD,  $^1\text{H-NMR}$  and viscometric methods. Generally, new polymers will be designed allowing us to design new macromolecular architectures with given hyperbranched network structure and synthesis novel types of gels systems with unique properties [19]. These will be the focus of our future studies.

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