Linear Copolymer of N-isopropylacrylamide and 2-hydroxyethylacrylate: Synthesis, Characterization and Monomer Reactivity Ratios

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ABSTRACT

Ñopolymerization of N-isopropylacrylamide (NIPAAm) with 2-hydroxyethyl acrylate (2-HEA) carried out by solvent ethanol solution method, at 60⁰C, using Azoisobutyronitrile (AIBN) as an initiator. The hydrophilic copolymers were characterized by elemental analysis, DSC, TGA and turbidimetric method. The results showed thermal stability increase with increase of NIPAAm in the copolymers. It was found that copolymer solutions have lower critical solution temperature (by turbidimetric analysis). The reactivity ratios of monomers were determined using linear methods like Fineman-Ross and Kelen-Tudos. The reactivity ratios of r_1 and r_2 were found to be 0,86, 0,72 and 1,02, 1,04 respectively.

Keywords: NIPAAm, 2-HEA, LCST, Hydrophilic copolymers, Reactivity ratios.

INTRODUCTION

Among the synthetic polymers characterized by thermosensitive behavior the systems based on N-isopropylacrylamide (NIPAAm), whose homopolymer has a lower critical solution temperature (LCST) in water, are the most studied ones. Poly(N-isopropyl acrylamide) PNIPAAm dissolves at temperature below 32°C and precipitates at temperature above LCST[1, 2] due to the presence of the hydrophilic and hydrophobic groups in each monomer unit. Decrease in temperature below LCST is accompanied by the formation of hydrogen bonds between the amide groups of the polymer and water molecules, which significantly facilitates dissolution. At temperature above LCST hydrogen bonds begin to disintegrate. In contrast, hydrophobic interactions are enhanced; as a result the polymer precipitates[3].

Sol-gel transition of PNIPAAm is clearly visible to the naked eye. The results of recent studies using confocal laser microscopy scan have shown that the internal structure of PNIPAAm gel consists of continuous two-sphere structures with dense and sparse zones in the polymer network[4, 5].

Turbidimetry can be regarded as the more automated counterpart of the classical visual observation of macroscopic phase separation, although it may suffer complication arising from variation in precipitated aggregate sizes and settling of precipitates[6].

The determination of copolymer composition and reactivity ratios of the monomer is important in evaluation the specific application of the copolymer[7]. The monomer reactivity ratios determined by conventional linearization methods are not always accurate and several non-linear methods have been attempted to determine their value[8].

The present work aimed to study the preparation and characterization of poly [N-isopropylacrylamide (NIPAAm) –co– 2-hydroxy ethyl acrylate (2-HEA)] via DSC, TGA and CHN analysis. The phase transition temperature of NIPAAm-HEA copolymer aqueous solution were studied by turbidimetric analysis. Copolymer composition was obtained from CHN analysis data monomer reactivity ratios were determined by Fineman-Ros and Kelen – Tudos methods.

MATERIALS AND METHODS

N-Isopropylacrylamide (NIPAM) was purchased from TCI (Tokyo, Japan) and purified by recrystallization from n-hexane. 2-hydroxyethylacrylate (2-HEA) and Ammonium peroxodisulfate (APS) were purchased from Sigma (USA). Ethanol was purchased from Altey, Kazakhstan.

Synthesis and Characterization of Copolymers

NIPAAm is dissolved in ethanol. Then initiator is also dissolved in solution of NIPAAm ethanol under continuous stirring. 2-HEA is added to solution to form homogeneous blend. 2, 22 -Azoisobutironitrile (2.10^{-2}M) is used to initiate radical polymerization. The resulting mixture is poured into the glass ampoule and saturated by argon for 10 minutes to remove oxygen. Thus the copolymerization is performed in hermetically sealed glass ampoules at 60°C for 40 min. After that obtained copolymer is precipitated in the mixture of hexane and ethyl acetate (1:1) twice to remove unreacted monomers and dried at vacuum until it becomes powder. Copolymer of NIPAAm with 2-HEA with various ratios of hydrophilic chains (M1=30:70, M2= 40:60, M3=50:50, M4=60:40, M5=70:30 respectively) were synthesized by solution polymerization.

Instrumentation

Glass transition temperature of samples were measured using differential scanning calorimetry (DSC), on a NETZSCH DSC200 PC,
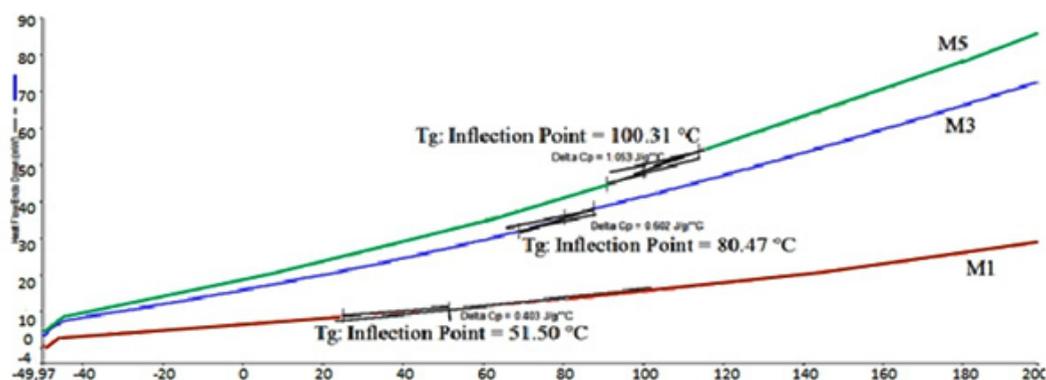
Fig. 1: DSC curves of NIPAAm-co-2-HEA
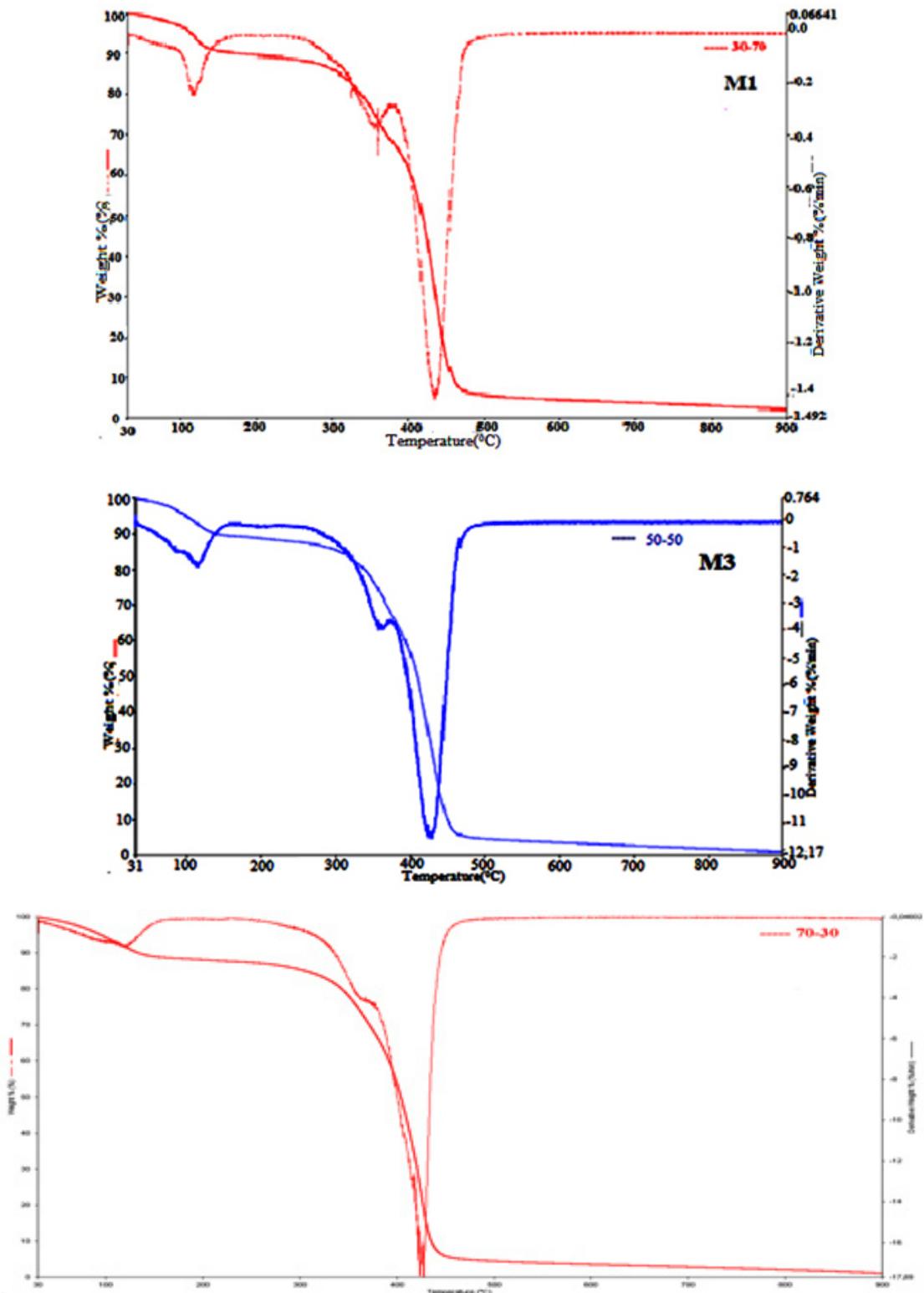
Fig. 2: TGA curves of NIPAAm-co-2-HEA

using aluminum crimped pans under N$_2$ flow at 20 mL minute^{-1}. The measurements were carried out between -50°C and 200°C at a heating rate of 10°C Minute^{-1}. Thermograimetric analyzer (TGA) was recorded on TGA/SDTA851^e, METTLER TOLEDO.

The measurements were carried out between 30°C and 898°C at a heating rate of 10°C minute^{-1}. Spectro turbidimetric titration of polymer solutions was carried out at l = 400 nm using «UV-2401-PC Shimadzu» (Japan) spectrophotometer. Temperature
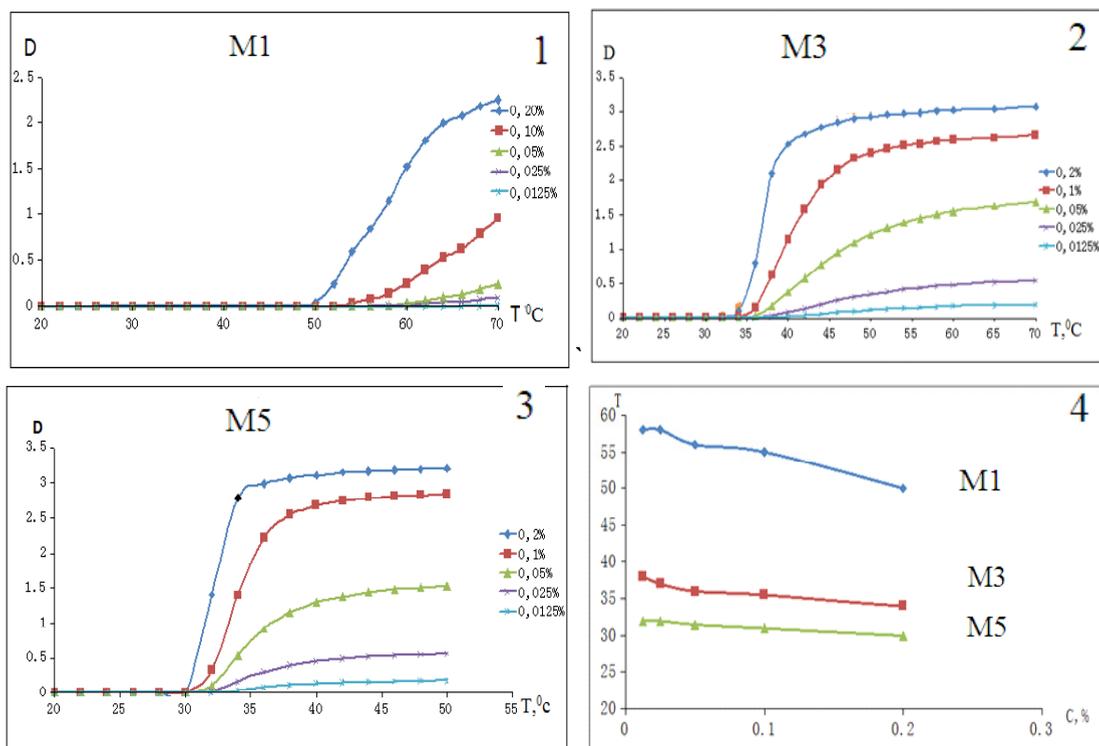
Fig. 3 : Dependence of turbidity of copolymer solutions on temperature (1, 2, 3) and Phase transition diagram of water soluble NIPAAm-2HEA copolymers (4)
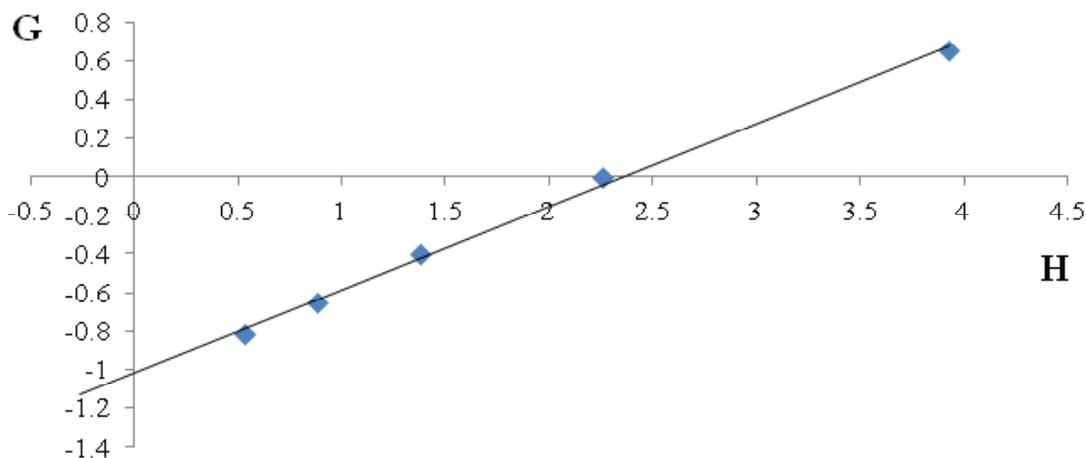
Fig. 4: Fineman-Ross plot of poly (NIPAAm-co-2-HEA)

control was executed by thermoelectronic controller of curettes «CPS-240A Shimadzu» (Japan). Perkin Elmer CHN-2400 was used for elemental analysis.

RESULT AND DISCUSSIONS

Differential Scanning Calorimeter (DSC)

Glass transition temperature (T_g) which is an important property for a polymer was determined by Differential Scanning Calorimetry (DSC). DSC thermograms obtained for NIPAAm-co-2-HEA copolymers with composition ratio was M1, M3 and M5 in the temperature range -50-200°C is showed in Figure 1 and respectively, as well as table 1. According to available literature the glass transition temperature of poly(N-isopropylacrylamide) homopolymer has between 85 and 135°C maybe depending on molecular weight while poly 2-HEA has a Tg at -15°C[9-12]. The poly(NIPAAm-co-2-HEA) hydrogels would exhibit a single transition between Tg of the two homopolymers. The glass transition temperature of M1 may be due to poly (2-HEA), and Tg of M3, M5 due to poly NIPAAm.

Thermogravimetric Analyses (TGA)

Figure 2 and table 1 summarize the TGA results of poly(NIPAAm-co-2-HEA) with composition ratio was M1, M3 and M5. These TGA's were performed 30°C to 900°C at 10°C/min and using N_2 gas as inert atmosphere. The typical TGA thermograms show there were two decomposition stages. The first weight loss of 10.4 wt.% between
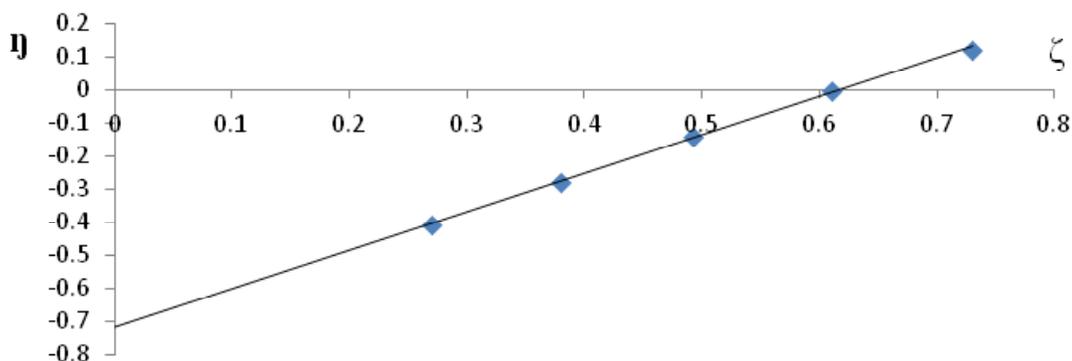
Fig. 5: Kelen-Tudos plot of poly (NIPAAm-co-2-HEA)
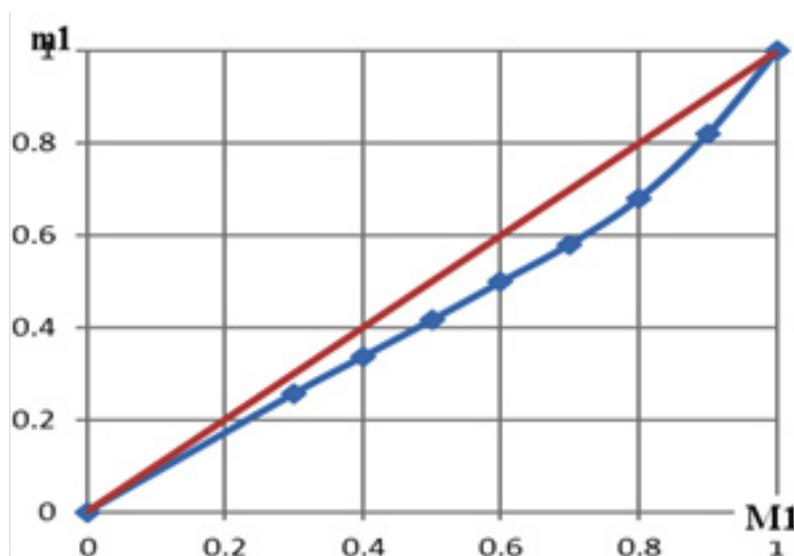
Fig. 6: Composition of NIPAAm and HEA

30 and 198°C for M1, 10,95 wt.% between 30 and 227°C and 10.2 wt.% between for M3 and 12,81 wt.% 30 and 221°C for M5 are attributed to the desorption of physically adsorbed water and organic molecules such as residual and impurities from solvents and moisture. TGA showed that copolymers have relatively good thermal stability up to 198°C then the degradation starts till maximum at about 300°C. Of course the temperature for maximum degradation

depends on the polymer structure whether the polymer is linear or hyperbranched[13, 14]. The second weight loss occurs between 198 and 900°C. These weight loss could be attributed to the exothermic decomposition of N group and decomposition of other parts of 2-HEA. However, the initial weight loss increased and second weight loss decreased with increasing the ratio of 2-HEA in copolymer.

Table1: Thermal properties of NIPAAm and 2-HEA

Copolymer	T_g, (°C)[a]	Temperature decomposition(°C) [b]	Weight loss (%)[b]	Residual (%)[b]	PDT_{max} (°C)[b]	LCST (°C)[c]
M1	52,51	31,24-198198-900	10,487,61	89,601,98	450	33
M3	80,47	31,24-227227-900	10,9587,06	89,051,98	439	37
M5	100,31	31,12-221221-858	12,8187,17	87,170	420	57

a: Determined from DSC Curves
b: Determined from TGA Curves
c: Determined from turbidimetric Curves

Table 2: Elemental analysis, mole fraction of monomer in feed

Mole fraction of NIPAAm in feed, (M_1)	Mole fraction of 2-HEA in feed, (M_2)	Mole fraction of NIPAAm in copolymers, (m_1)	Mole fraction of 2-HEA in copolymer,(m_2)	$F=M_1/M_2$	$f= m_1/m_2$	$G=F(f-1)/f$	$H=F^2/f$	$\eta=G/(\alpha+H)$	$\xi=H/(\alpha+H)$
30	70	25,68	74,32	0,43	0,3455	-0,8146	0,5352	-0,4108	0,2699
40	60	33,67	66,33	0,67	0,5076	-0,6499	0,8844	-0,2787	0,3792
50	50	41,64	58,36	1	0,7135	-0,4015	1,4015	0,1409	0,4919
60	40	49,89	50,11	1,5	0,9956	-0,0066	2,2599	-0,0018	0,6096
70	30	58,11	41,89	2,33	1,3872	0,65	3,9136	0,1212	0,73

$\alpha= (H_{max} H_{min})^{1/2} =1,4473$

Table 3: Fineman-Ross and Kelen-Tudos parameters for the copolymer

	Mole fraction of NIPAAm monomer in feed NIPAAm (M_1)	Elemental analysis			Mole fraction of NIPAAm in * copolymers NIPAAm (m_1)
		C, %	H, %	N, %	
1	30	51,19	8,12	3,12	25
2	40	51,98	8,61	4,1	34
3	50	52,93	9,09	5,08	42
4	60	53,3	9,36	6,1	50
5	70	53,82	9,63	7,12	58

*Calculated from nitrogen results in copolymers

Table 4: Copolymerization parameter for the NIPAAm (r_1) and 2-HEA (r_2)

Methods	r_1	r_2	$r_1 \cdot r_2$
Fineman –Ross (FR)	0,86	1,02	0,88
Kelen-Tudos (KT)	0,72	1,04	0,75

The maximum polymer degradation temperature (PDT_{max}) corresponds to the temperature at which the maximum rate of weight loss occurred and appeared at 450,439 and 420°C for M1, M3 and M5. The PDT_{max} increases as the ratio of 2-HEA with in copolymer structure increases.

Turbidometric method

It should be note HEA homopolymer is high hydrophilic and aqueous solution of there homopolymer do not show LCST[15].

Hydrophobic and hydrophilic groups providing water solubility are part and parcel of thermosensitive polymer macromolecules. Hydrophobic interactions strengthen with temperature rise, as a result, separation into two phases occurs in linear macromolecules. The phase transition of obtained NIPAAm-2HEA copolymers (M1, M2 and M3) aqueous solutions at different temperatures was investigated by turbidimetric method. It can be seen from figure 3 (1,2,3) that the increase in the temperature leads to the rise in solution turbidity, i.e. due to temperature change initial homogeneous system separates into two phases. One of these phases is enriched with polymer, another one is depleted. This is due to the destruction of hydrogen bonds between water and copolymer molecules and the enhancement in hydrophobic interactions. At low temperature hydrophobic interactions are sufficiently strong, i.e. they enable macromolecules to be unassociated in aqueous solutions. However, as temperature rises hydrogen bonds are no longer stable and hydrophobic interactions intensify, which results in phase separation.

According to turbidimetric data, phase transition diagram in figure 3 (4) was plotted for water soluble NIPAAm-2HEA copolymers. It was revealed that the temperature at which phase transition occurs is dependent on feed composition of poly(NIPAAm-co-2HEA). The increase in NIPAAm units in the copolymer brings about the shift in LCST to lower values. Thus, it was proved that LCST is inherent to obtained linear copolymers based on NIPAAm-2HEA and the dependence of copolymer composition and its concentration on turbidity growth was investigated.

Reactivity ratio

Table 2 show the influence of the molar fraction of NIPAAm in the copolymer (m_1), mole 'fraction of NIPAAm monomer in feed (M_1) and nitrogen results of elemental analysis of NIPAAm and 2-HEA comonomers depending on the copolymer composition in free radical copolymerization. The reactivity ratio was calculated using Fineman-Ross (FR) and Kelen-Tudos (KT) method. The signification parameters of FR and KT equation are presented in table 3. The reactivity ratio for NIPAAm (r_1) and 2-HEA (r_2) from the FR plot (Figure 4) and FT

(Figure 5) plot are given in table 3. The value of r_1 is less than 1 and r_2 is greater than 1. r_1 show that NIPAAm favors cross-propagation as opposed to homopropagation and r_2 show that 2-HEA favors homopropagation over cross-propagation. r_1 and r_2 together show that HEA exhibits significantly higher activity in radical copolymerization compared with NIPAAm. The copolymer composition was determined elemental analysis of the copolymer. The kinetic behavior was determined by plotting the mole fraction of NIPAAm in the feed against that in the copolymer (Figure 6)

CONCLUSION

Linear copolymers based on N-isopropylacrylamide (NIPAAm) and 2-hydroxyethylacrylate (HEA) having different ratio were syntheside in ethanol by free radical polymerization.

It was observed that for obtained novel linear NIPAAm-HEA copolymers exhibit lower critical solution temperature (LCST). Moreover, the cloud point of NIPAAm-HEA copolymers compared with poly-NIPAAm depends on copolymer composition and their concentration in solution. By varying these parameters, it is possible to synthesize copolymers with desired LCST, which suitable for certain applications. Tg of the copolymer increases with increasing of the ratio of NIPAAm in the copolymer. Furthermore, it was found that Tg of the copolymer increases with increasing molecular weight of the copolymer. TGA showed that copolymers have good thermal stability, especially with increasing NIPAAm. The copolymer composition wrer determined from CHN analysis data. The reactivity ratios of monomers were determined by linear methods like Fineman-Ross (r_1= 0,86, r_2= 1,02) and Kelen – Tudos (r_1= 0,72, r_2=1,04).

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