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Research Article

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Synthesis and Characterization of P (N-Isopropylacrylamide) Hydrogels with Tunable Swelling Behavior Using Different Crosslinkers

Farklı Çapraz Bağlayıcılar Kullanarak Şişme Davranışları Ayarlanabilen P (N-İzopropilakrilamid) Hidrojellerin Sentezi ve Karakterizasyonu

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ABSTRACT

In the present study, a set of hydrogels were synthesized using N-isopropylacrylamide with various cross linkers at various dosages via free radical polymerization. Thermal and structural properties of the synthesized hydrogels were characterized via thermogravimetric analyzer (TGA) and Fourier Transformation Infrared Radiation (FTIR) spectroscopy. The effect of crosslinkers such as N,N´-Methylenebisacrylamide, ethylene glycol dimethacrylate (EGDMA) polyethylene glycol dimethacrylate (p(EGDMA), and polyethylene glycol diacrylate (p(EGDA) (Mn: 258, Mn: 575, Mn: 700) were used in p(NIPAM) hydrogel preparation and their effect on swelling behavior was investigated. It was found that the swelling rate was increased as the molecular masses of the cross-linkers used decreased, whereas the hydrogel prepared using p(EGDA)-700 swelled more than the other p(EGDA) crosslinked p(NIPAM) hydrogels.

Key Words
Functional hydrogels, N-isopropylacrylamide, thermoresponsive hydrogels, swelling, crosslinker.

ÖZ

Bu çalışmada, bir dizi hidrojel, serbest radikal polimerizasyonu yoluyla çeşitli dozajlarda çeşitli çapraz bağlayıcılarla N-izopropilakrilamid kullanılarak sentezlendi. Sentezlenen hidrojellerin termal ve yapısal özellikleri, termogravimetrik analizör (TGA) ve Fourier Transformasyon Kızılötesi Radyasyon (FTKR) spektroskopisi ile karakterize edildi. N, N´-Metilenbisakrilamid, etilen glikol dimetakrilat (EGDMA) polietilen glikol dimetakrilat (p (EGDMA) ve polietilen glikol diakrilat (p (EGDA) (Mn: 258, Mn: 575, Mn: 700) gibi çapraz bağlayıcıların etkisi p (NIPAM) hidrojel preparasyonunda kullanıldı ve şişme davranışı üzerindeki etkileri araştırıldı. Kullanılan çapraz bağlayıcıların moleküler kütleleri azaldıkça şişme oranının arttığı, p (EGDA)-700 kullanılarak hazırlanan hidrojelin diğer p (EGDA) çapraz bağlı p (NIPAM) hidrojellerinden daha fazla şiştiği bulundu.

Anahtar Kelimeler
Fonksiyonel hidrojeller, N-izopropilakrilamid, ısı duyarlı hidrojeller, şişme, çapraz bağlayıcı.

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INTRODUCTION

Hydrogels are three-dimensional, cross-linked, water-swellable and hydrophilic polymeric flexible materials with a very special network structure [1]. As the highly swelling nature enable biocompatibility, the swelling rate and extent strongly govern by the hydrophilicity of functional on polymer chains as well as the amount and the types of the used crosslinkers [2]. Recently, various fields e.g., agriculture and horticulture, because of the high water retention capability and the functionality [3, 4], drug delivery systems [5], super absorbent [6], tissue engineering [7], waste water treatment [8], scaffold in bone repair and tissue membranes [9, 10], have been constantly employing and developing new hydrogels for multiple functions [11].

Unlike conventional hydrogels that just exhibit swelling behavior depending on the hydrophilicity of the functional groups on the polymer chains as well the crosslinker types and amount, the intelligent or stimulate sensitive hydrogels are further capable materials due to their sensing capabilities for the environmental stimuli such as temperature, pH, ionic strength electric, magnetic field etc. [11-14]. The behavior of smart hydrogel can be associated with environmental factors that promote the design and application in many useful bio and environmental system [15-17]. Even drug development systems also benefit from hydrogels [18], and many materials from organic and inorganic composites can employed in sensing of external stimuli [19]. Self-healing photosensitive polymers were reported [20] and smart inks have been obtained recently [21] employed organic and inorganic nano hybrid systems that can be used in the developed in memory systems [22]. Recently, a lot of data has been gathered in intelligent molecular switching methods using new metallopolymers sensitive to stimuli by exploiting their hydrophilic and hydrophobic properties [23-25]. Light photosensitive hydrogels and their applications are among the recent studies, new types of magnetic composite hydrogels are also being utilized [26, 27]. External stimuli in general e.g., mechanical pressure, temperature, pH, light, electric field, magnetic field are considered most effects stimuli to induce chemical, biological and physical change in hydrogels' color, durability, viscosity, mechanical durability, swelling ability and so on via changing the physical quantities of sensitive substances that provide the smart properties reversibly [28, 29]. The temperature-sensitive hydrogels have been reported [30, 31]. And their characteristic behavior such as the change in rheological properties i.e., deformation, restorage, swelling and shrinkage have been very well documented [32-34].

The objective of the current study is to prepare thermosensitive poly(N-isopropylacrylamide) (p(NIPAM)) using different crosslinkers, MBA, EGDA with three different molecular weights, EGDMA and p(EGDMA) and compare their effect on swelling and temperature responsiveness. Eight different p(NIPAM) based hydrogels were prepared having various cross-linkers and their water absorption behaviors were studied based on most commonly utilized kinetics models.

MATERIALS and METHODS

Materials

N-isopropylacrylamide (NIPAM, 97%, Alfa Aesar), and N,N´-Methylenebisacrylamide (MBA, 98%, Sigma-Aldrich), polyethylene glycol dimethacrylate (p(EGDMA, 98% Sigma-Aldrich), Ammonium persulfate (APS, 98%, Sigma-Aldrich), N,N,N′,N′-tetramethylethylenediamine (TEMED, 98% Sigma-Aldrich) were as received in p(NIPAM) hydrogel preparation. Also, the crosslinkers, ethylene glycol dimethacrylate (EGDMA, 98%, Sigma-Aldrich) and polyethylene glycol diacrylate (p(EGDA), Sigma-Aldrich, Mn:258, Mn:575, Mn:700) was used as received. All other reagents were of the highest grade available and used without additional purification. Distilled water was obtained from Millipore (DI, 18.2 MΩ cm; Millipore Direct-Q3UV).

Synthesis of p(NIPAM) hydrogels

A library of Poly(N-isopropylacrylamide) (p(NIPAM)) based hydrogels were synthesized via free radical polymerization technique according to the formulation given in Table 1. The synthesized hydrogel codes were assigned to indicate the type of cross-linker used to prepare the hydrogel. All hydrogels were synthesized according to the method described in literature [35]. The amount of NIPAM monomer was kept constant, 0.175 g, initiator (APS) amount was 0.001 g, and the accelerator TEMED amounts (30 µL) were fixed in all reactions, and all hydrogels preparation reactions were terminated after 3 h. Briefly, 0.175 g of (NIPAM and MBA (2% mole ratio of NIPAM) were dissolved in 2.7 mL of DI water. Then 30 µL TEMED was added to the polymerization media. Finally, 0.3 mL of APS solution in 0.001 g/mL added to the reaction mixture as initiator. The mixture was vigorously mixed and transferred into plastic straw with 4 mm inner diameter and allow to polymerize and cross-

Table 1. Recipes for the preparation of thermo-sensitive hydrogels with various crosslinkers*.

Hydrogels	Cross-linker (g)						DI water (mL)
	MBA	P(EGDA)258	P(EGDA)575	P(EGDA)700	EGDMA	P(EGDMA)	
p(NIPAM)-1	0.0048	-	-	-	-	-	2
p(NIPAM)-2	0.0048	-	-	-	-	-	3
p(NIPAM)-3	0.0048	-	-	-	-	-	4
p(NIPAM)-258	-	0.008	-	-	-	-	3
p(NIPAM)-575	-	-	0.0177	-	-	-	3
p(NIPAM)-700	-	-	-	0.0216	-	-	3
p(NIPAM)-EGDMA	-	-	-	-	0.0061	-	3
p(NIPAM)-p(EGDMA)	-	-	-	-	-	0.0170	3

*All reactions were carried out at fixed monomer amount, 0.175 g NIPAM; initiator, 0.001 g APS; and accelerator, 30 µL. Reactions time: 3 h.

link for 3 hours at 20 °C. Then, synthesized hydrogels cylindrical shapes were removed from straw and cut approximately in 5 mm length cylinder. The obtained hydrogels pieces were immersed in DI water to remove unreacted monomers, initiators and cross-linkers for 15 hours for washing by substituting the was water every 3 hours. Finally, hydrogels were transferred to petri dishes and dried in an oven at 50 °C for 3 days prior to store for further uses.

Swelling of hydrogels

Swelling of p(NIPAM) hydrogels were carried out by measuring the ratio of the hydrogel mass submersed in DI water to the initial mass of hydrogel in various time intervals. The hydrogel swellings were determined in terms of percentage changes in mass of hydrogels with time using Eq. 1. Minimum three replicates were done for each p(NIPAM) hydrogel swellings and uncertainties were given in standard deviation for each measurement [36, 37].

$$\%S = \left(\frac{M_t - M_d}{M_d}\right) * 100 \quad (1)$$

where S% stands for

swelling percentage while M_t, M_d stand for mass at time t and dry hydrogel masses, respectively.

Characterizations of p(NIPAM) hydrogels

FTIR spectra of p(NIPAM) hydrogels prepared with different crosslinkers were recorded by an Attenuated Total Reflection (ATR) built-in Fourier Transform Infrared Spectroscopy (Thermo, model Nicolet iS10 FT-IR Spectrometer, USA). The spectral range was studied from 4000 to 650 cm^{-1} with resolution of 4 cm^{-1}.

Thermal analyses of p(NIPAM) hydrogels were studied by a Gravimetric Analyzer (TGA, SII, TG/DTA 6300). p(NIPAM) hydrogels by placing almost 30 mg sample in ceramic crucibles. Then, the samples were heated from 50 to 1000 °C at 10 °C min^{-1} heating rate under nitrogen atmosphere. The nitrogen gas flow rate in the analyzer was fixed at 100 mL min^{-1}.

Swelling kinetics

A pseudo-order kinetic model was applied in order to predict swelling kinetic as given in Eq (2):

$$\frac{dS}{dt} = k_{i,S}\,(S_e - S)^n \quad (2)$$

dS/dt in the equation is the swelling speed, S_e is the swelling value of the hydrogels at equilibrium (t_d), S is the swelling value at time t and k_s is the swelling speed constant. As a result of the mathematical arrangements made under the boundary conditions, at which $S = S_0$ at t = 0 and S = S at t = t;

$$S = \frac{t}{A + B\,t} \qquad (3)$$

equation is obtained (3).

In the equation;

$$A = \frac{1}{S_e^2 * k_s} \qquad (4)$$

equation 4 $B = \frac{1}{S_{max}}$ is the inverse of the starting speed ($1 / r_0$) and is the inverse of the maximum swelling value and k_s; swelling speed constant for.

Diffusion of water

The diffusion of the solvent to the synthesized hydrogels can be found by the following equation (5).

$$F = k_D t^n \qquad (5)$$

where *F* is the fractional uptake at time ***t***, k_D is a constant incorporating characteristic of the macromolecular network system and the penetrant, ***n*** is the diffusional exponent, which is indicative of the transport mechanism. Equation 4 is valid for the first 60% of the fractional uptake. Fickian diffusion and Case II transport are defined by n values of 0.5 and 1, respectively. Anomalous transport behavior (non-Fickian diffusion) is intermediate between Fickian and Case II. That is represented by n ranging between 1/2 and 1. The diffusion coefficients of the cylindrical p(NIPAM) hydrogels are calculated from the following relations:

$$D = \left(\frac{k_D}{4}\right)^2 \pi r^2 \qquad (6)$$

where D is in $cm^{-2}\ s^{-1}$, t is in sec and r is the radius of the cylindrical polymer sample [36-42].

RESULT and DISCUSSION

Swelling behaviors of p(NIPAM) hydrogels prepared with different crosslikers

According to the recipes given in Table 1, eight different hydrogels were synthesized at the presences of various cross-linkers. In the preparation of thermo-responsive p(NIPAM) hydrogel, MBA, p(EGDA)258, p(EGDA)575 , p(EGDA)700, EGDMA and p(EGDMA) were used as crosslinkers, respectively to assess their effect on the swelling and temperature responsiveness. The p(NIPAM) hydrogels were alltocated into three groups in terms of the crosslinkers utilized. For example, MBA crosslinker used hydrogels were donated as p(NIPAM)-1, p(NIPAM)-2 and p(NIPAM)-3 at varied concentrations and p(EGDA) crosslinker used hydrogels were named as p(NIPAM)-258, p(NIPAM)-575 and p(NIPAM)-700 depending on MW of p(EGDA). Finally, hydrogels prepared by using EGDMA and p(EGDMA) crosslinkers were shown named as p(NIPAM)-EGDMA and p(NIPAM)-p(EGDMA), respectively. The swelling-equilibrium behaviors of these eight p(NIPAM) hydrogels were investigated in three different solutions and at two different temperatures 25 and 37°C. p(NIPAM) hydrogel preparation reactions were carried out at the fixed amount of NIPAM monomer, 0.175 g, APS initiator 0.001 g and catalyst, TEMED 30 µL, varying the content between 2-4 mL as shown in Table 1. As illustrated in Figure 1, the chemical structure of the crosslinkers were similar expect MBA. Figure 1 further shows the dry and DI water swollen p(NIPAM) hydrogels pictures prepared using different types of crosslinkers. It is clear that from the pictures that p(NIPAM)-EGDMA and p(NIPAM)-p(EGDMA9 hydrogels higher swelling ratios than the other p(NIPAM) hydrogels prepared using MBA and p(EGDA).

The swelling ratio of p(NIPAM)-1, p(NIPAM)-2 and p(NIPAM)-3 at 25°C and 37°C were illustrated in Figure 2 a and b, respectively. The swelling ratios of p(NIPA)-1, p(NIPAM)-2 and p(NIPAM)-3 were measured as about 870% ±12, 1390% ±12 and 2155% ± 36 at 25°C, respectively. On the other hand, as the temperature was increased to 37°C, the swelling ratios were sharply decreased to 31% ±2, 40% ±2 and 61% ±3, respectively. By comparing Figure 2a and b, p(NIPAM)-1, p(NIPAM)-2 and p(NIPAM)-3 hydrogels were swollen gradually reached to the equilibrium around 250 min. at 25°C, whereas their swelling behaviors were very fast at 37°C and it reached the equilibrium less than 2 min. showing very little water uptake due to the thermoresponsive behavior of p(NIPAM) chains. From Figure 2 a and b, it is obvious that the S% values were increased with the decrease in the concentration of MBA or by increasing the amount of DI water using the same amount of MBA as given in Table 1. So, the hydrogels swelling is inversely related to the crosslinker concentration as shown in Figure 2a.

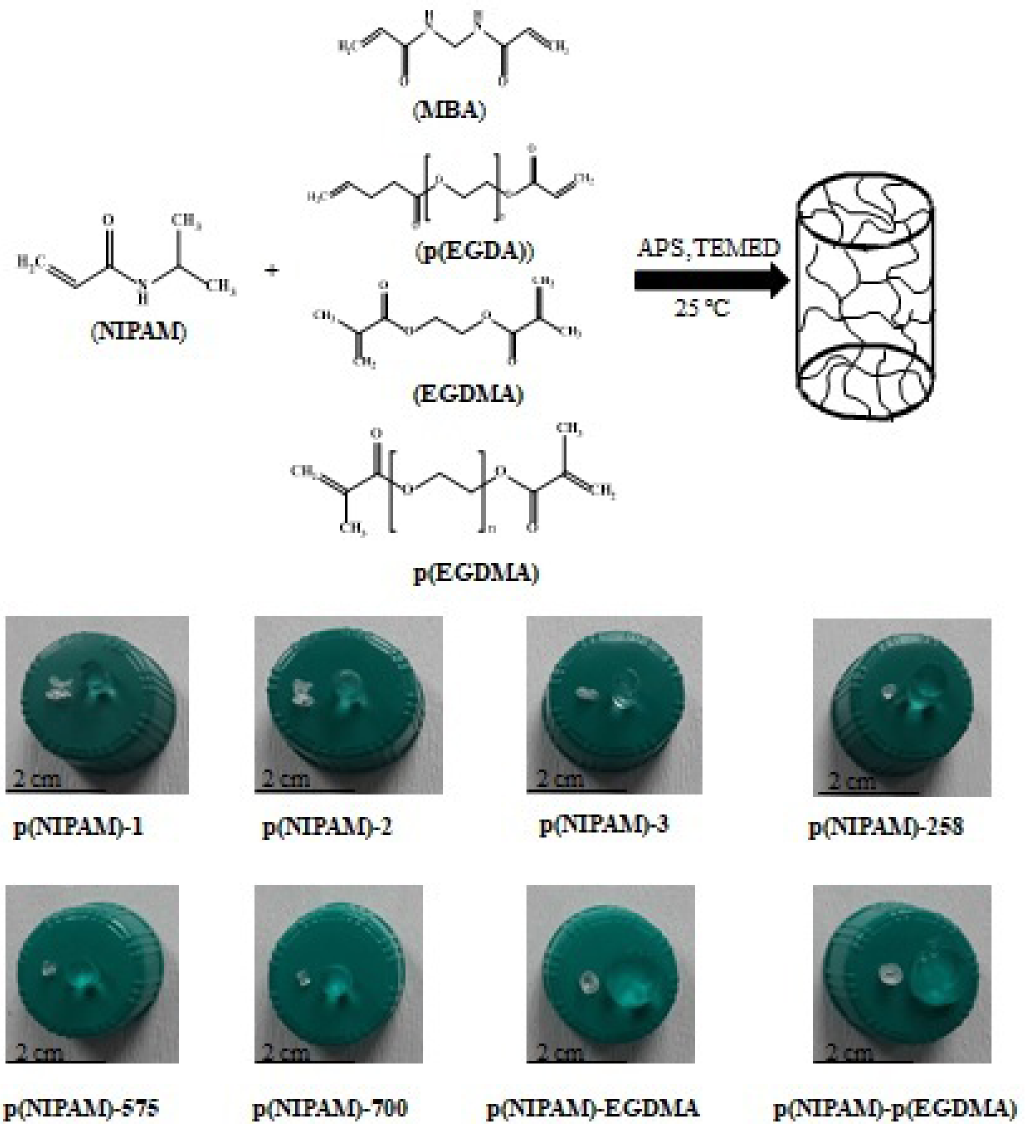


Figure 1. The chemical structures of the crosslinkers used in p(NIPAM) hydrogels their digital camera images comparing their dried and DI swollen pictures.

The swelling behavior of p(NIPAM) hydrogels prepared by using p(EGDA) crosslinker with three different molecular weights, p(NIPAM)-258, p(NIPAM)-575 and p(NIPAM)-700 was also investigated at 25°C and 37°C, and the corresponding graphs is shown in Figure 3a and b, respectively. As shown in Figure 3a, the equilibrium or maximum swelling ratio of p(NIPAM)-258 was found to the highest in comparison to p(NIPAM)-575 and p(NIPAM)-700 hydrogels. The maximum swelling ratios at 25°C were determined for p(NIPAM)-258, p(NIPAM)-575 and p(NIPAM)-700 as follows 4500%±50, 1865%±20 and 2140%±20, respectively and reached in 250 min. The swelling behavior of the same hydrogels at 37°C also revealed very similar results. As shown in Figure 3b, the equilibriums swelling values of these p(NIPAM) hydrogels were achieved in 4 min with the maximum swelling % values of 52,789% ±, 32,587% ±20 and 34,378% ±20. while the swelling ratios observed for p(NIPAM)-258, p(NIPAM)-575 and p(NIPAM)-700, respectively. The reason for the values of the maximum swellings of p(NIPAM)-575 and p(NIPAM)-700 hydrogel are very close to each could be due to the hydrophilicity of the repeating unit of crosslinker is less than the hydrophilicity of NIPAM unit as the same numbers of moles the crosslinker, the higher amounts of p(EGDA) with higher MW is required.

Also, to evaluate the impact of EGDMA and p(EGDMA) cross-linkers used on swelling behavior of p(NIPAM) at two different temperature. Figure 4a and b show the swelling behavior of p(NIPAM)-EGDMA and p(NIPAM)-p(EGDMA) at 25°C and 37°C. As shown in Figure 4a, swelling ratios of p(NIPAM)-EGDMA were found about 7400% at 25°C and 2800% at 37°C. Similar results were obtained for p(NIPAM)-p(EGDMA), about 2700% at

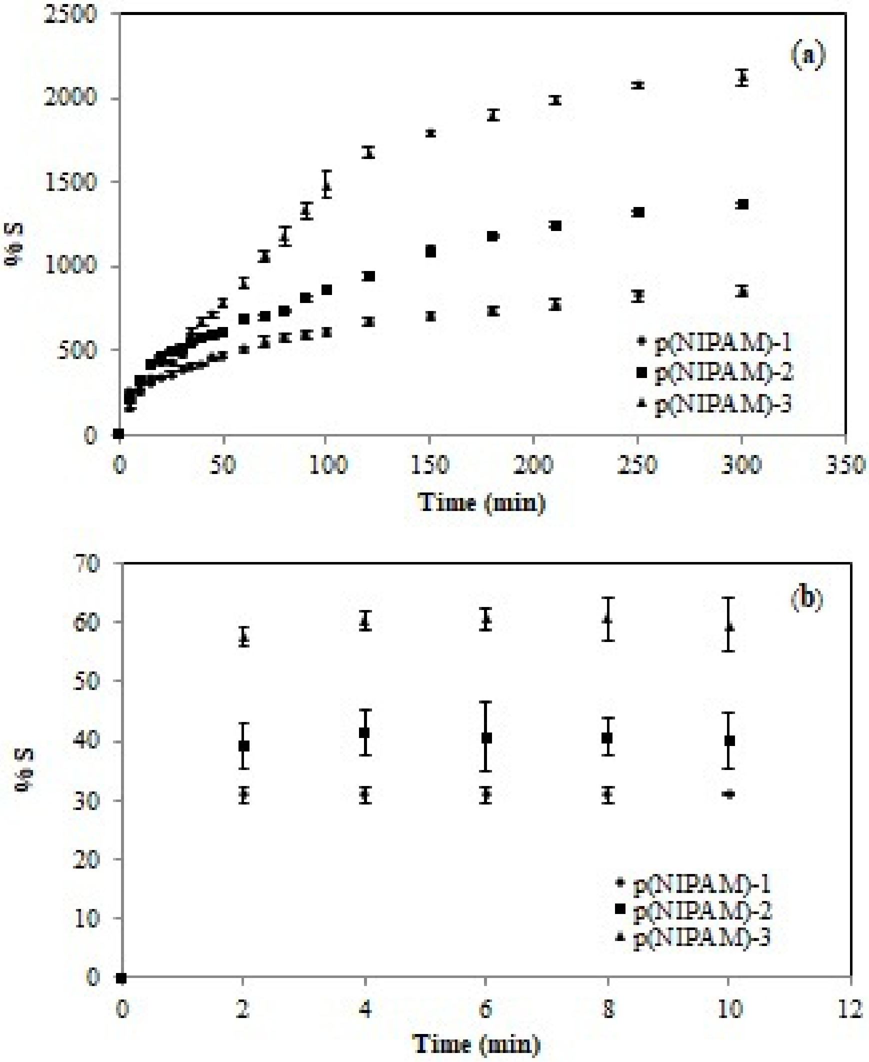


Figure 2. Swelling behaviors of p(NIPAM)-1, p(NIPAM)-2, p(NIPAM) at (a) 25°C and (b) 37°C.

25°C and 175% at 37°C as shown in Figure 4b. It is obvious that the low swelling values of p(NIPAM) at higher temperatures e.g., 37 vs 25°C is due to thermoresponsive nature of p(NIPAM) chains. On the other hand, although the same mole number of crosslinkers are used for p(NIPAM)-EGDMA versus p(NIPAM)-p(EGDMA) with the swelling values of 7400% versus 2700% also further corroborates the higher degree of hydrophilicity of NIPAM units then that of EGDMA units as more numbers of p(EGDMA) crosslinker is required in comparison to EGDMA crosslinker to obtained the same mole ratio of crosslinked p(NIPAM) hydrogel.

The swelling behavior of all p(NIPAM) hydrogels prepared with different cross-linkers i.e., BMA, EGDA-258, EGDA-575, EGDA-700, EGDMA, p(EGDMA) show that regardless of the used crosslinker all p(NIPAM) hydrogels swell to a higher swelling degree at 25°C then at

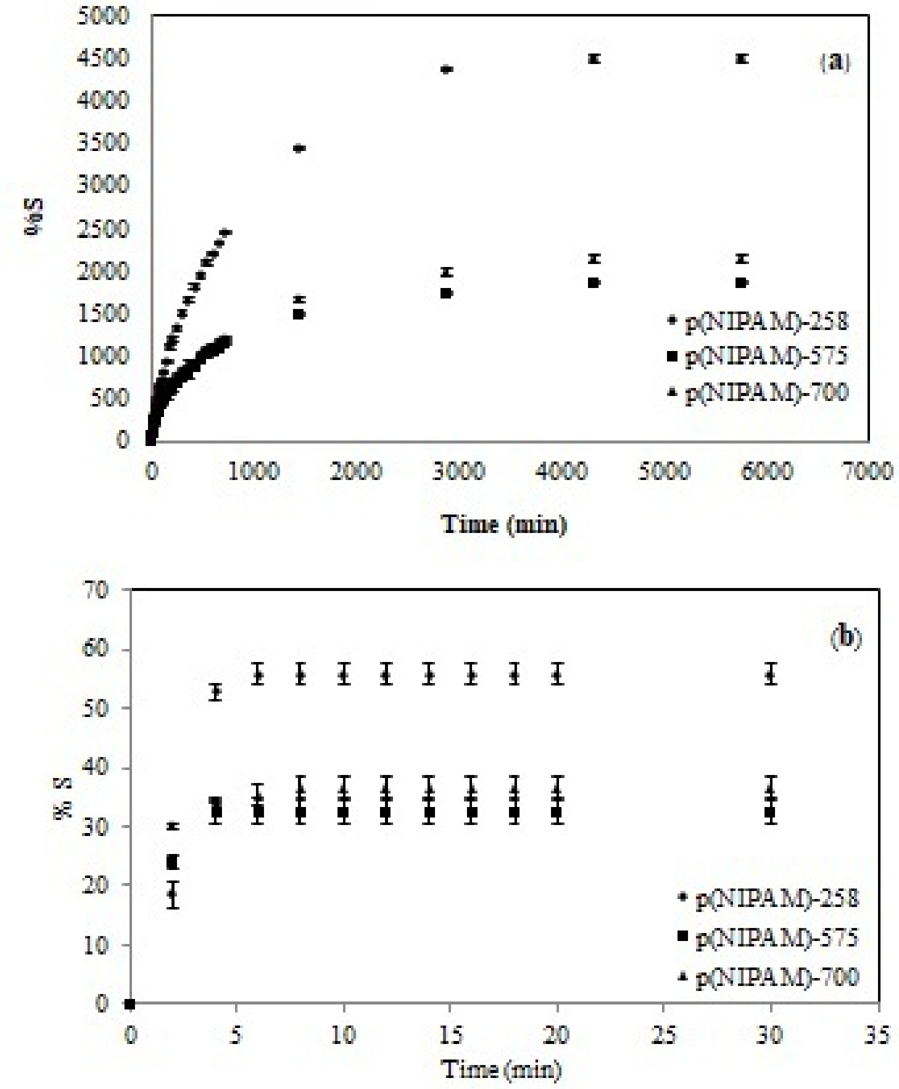


Figure 3. Swelling behaviors of p(NIPAM)-258, p(NIPAM)-575 and p(NIPAM)-700 at (**a**) 25°C and (**b**) 37°C.

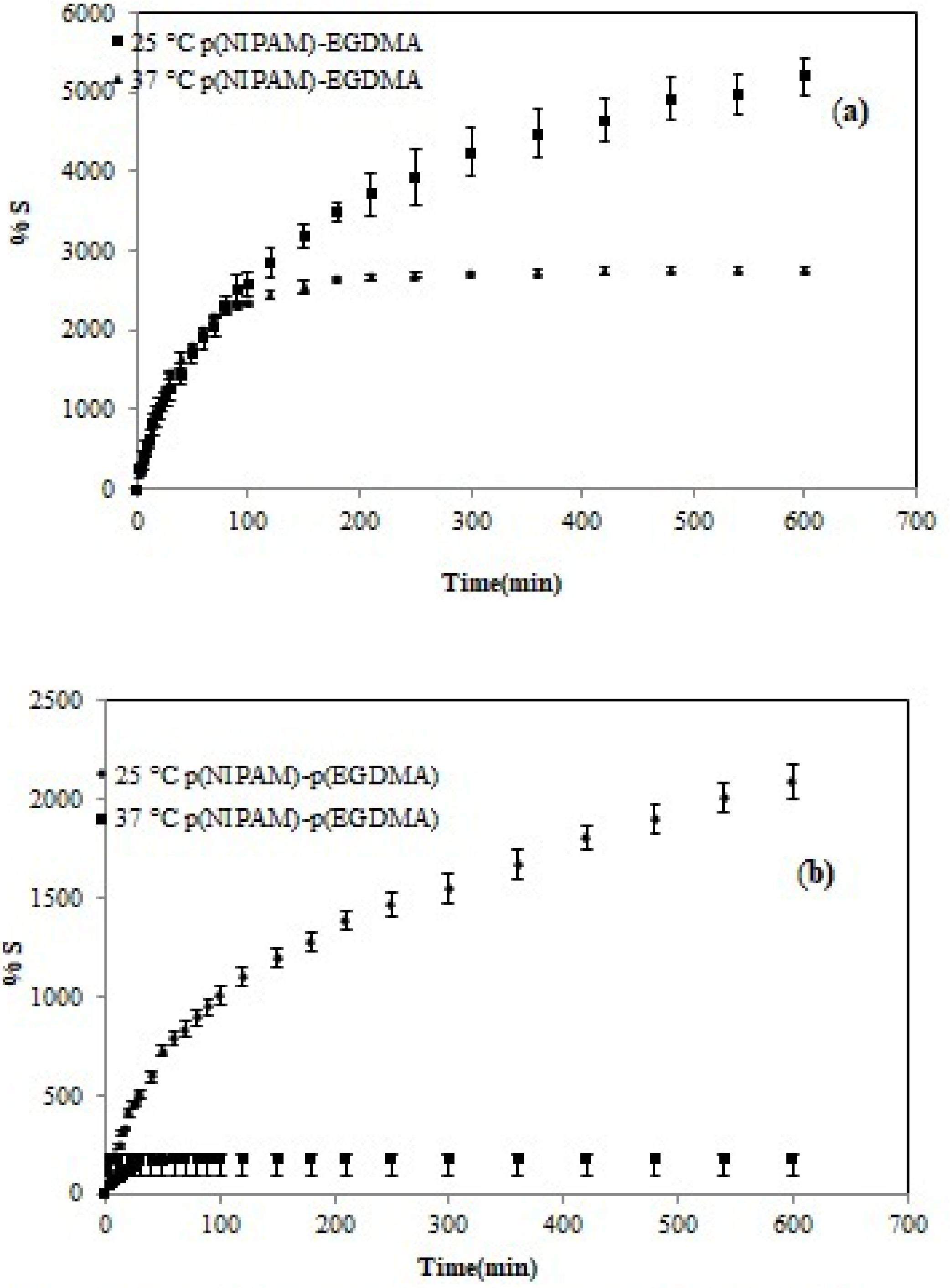


Figure 4. Swelling behaviors of p(NIPAM)-EGDMA at (a) 25°C and (b) 37°C.

37°C. It is very well known that Low Critical Solution Temperature (LCST) of 32°C plays significant role about the swelling ratio of p(NIPAM) hydrogels. However, the swelling ratios of the prepared polymers at different temperatures also depend on the utilized crosslinkers used. The hydrophilicity and/or chemical structure of crosslinker also significantly effect the equilibrium swelling values of p(NIPAM) hydrogels. For example, p(NIPAM) hydrogels prepared with EGDMA crosslinker has the equilibrium swelling values of about 2100% at 37^{o}C whereas p(EGDMA) crosslinked p(NIPAM) hydrogel has the equilibrium swelling values of about 170%, and about 32-55% for p(EGDA) crosslinked of p(NIPAM) hydrogels (with different mole ratio) at 37^{o}C. Therefore, it is possible to design p(NIPAM) hydroges with tunable swelling values at different temperature by the choice of suitable crosslinkers. Among the prepared polymers structures p(NIPAM)-EGDMA showed the highest equilibrium swelling values even at above LCST of p(NIPAM) hydrogels.

Kinetic of the swelling of p(NIPAM)hydrogels

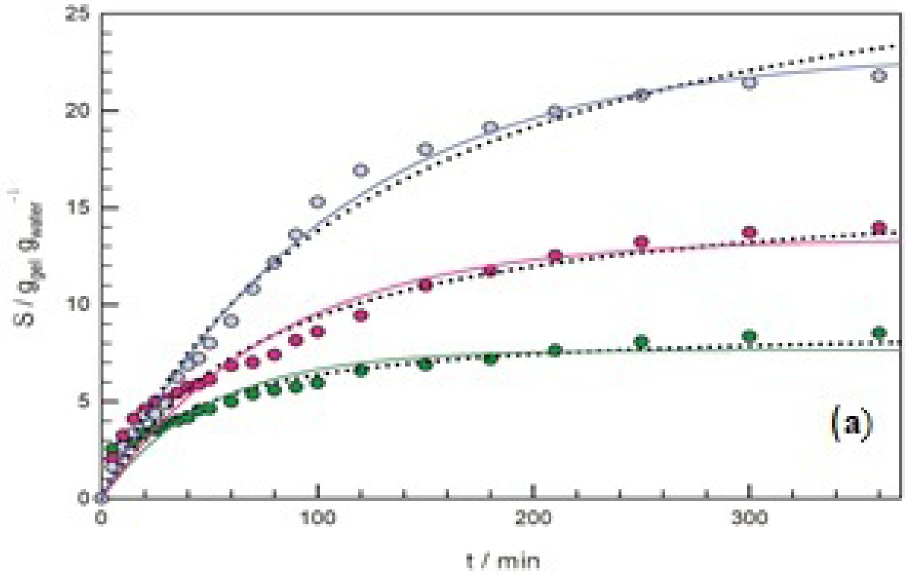
Diffusion properties of the synthesized polymers were studied based on the common diffusion models presented in the literature [43]. For pseudo-first-order kinetics, the ratio of power parameter (S_e) to the rate parameter gives the swelling rate (SR, g g^{-1} min^{-1}) at time τ, while the inverse of the rate parameter gives the rate constant (k_1,S, min^{-1}). The rate parameter value is a measure of the SR (i.e., the lower the τ value, the higher the rate of swelling) this studies showed Figure 5 (a) The rate parameters are found to be 49, 80 and 105 min for the respectively p(NIPAM)-1, p(NIPAM)-2, p(NIPAM)-3 hydrogels, Table 2. It means that according to the model (Eq. 2), these samples absorb approximately 63% of their maximum absorption capacity during 49−105 min.

Diffusion of water into p(NIPAM) hydrogels

The number to determine the type of diffusion ***(n)*** is found to be below 0.50 for P(NIPAM)-1, P(NIPAM)-2, and over 0.50 for P(NIPAM)-3. The diffusion of penetrant into the P(NIPAM)-1, P(NIPAM)-2 hydrogel has taken a ***Fickian*** character while the diffusion of penetrant into the P(NIPAM)-3 hydrogel has taken a non-*Fickian* character , this studies showed Figure 5 (b) [44]. The values of the diffusion coefficients of the hydrogels are calculated and summarized in Table 3. As can be seen the amount of water is increased from 2 mL to 4 mL for the p(NIPAM) hydrogel prepared via MBA crosslinker, the n exponent increased significantly e.g., from 0.223 to 0.6697 in parallel to the maximum swelling ratio values. On the other hand, diffusion coefficient also significantly reduced by increased amount water used during p(NIPAM) hydrogels preparation due to increase in the porosity and hydrophilicity of the prepared hydrogel network.

Table 2. Swelling kinetic parameters of thermo-sensitive hydrogels with various crosslinkers.

Hydrogel	p(NIPAM)	p(NIPAM)	p(NIPAM)
parameters	1	3	4
Experimental equilibrium swelling (Seq gg^{-1})	8,529529	13,96838	21,79486
Pseudo-first order			
Power parameter (p gg^{-1})	7,665	13,406	23,082
Rate parameter (τ/ min)	49.02	80.00	105.26
Swelling rate (SR gg-1min^{-1})	0.1564	0.1676	0.2193
Rate constant (k_1,S min^{-1})	0.0204	0.0125	0.0095
Correlation coefficient (r)	0.9438	0.9691	0.9965
Correlation coefficient (r^2)	0.8908	0.9392	0.9930
Pseudo-second order			
maximum swelling (Seq gg^{-1})	8.9127	16.6389	31.44654
Initial rate (r_o, $(dS/dt)_o$ gg-1min^{-1})	0.2234	0.2141	0.2484
Rate constant (k_2, S g^{-1}g min^{-1})	0.00281	0.00077	0.00025
Correlation coefficient (r)	0,9713	0,981	0,9932
Correlation coefficient (r^2)	0.9434	0.9623	0.9865



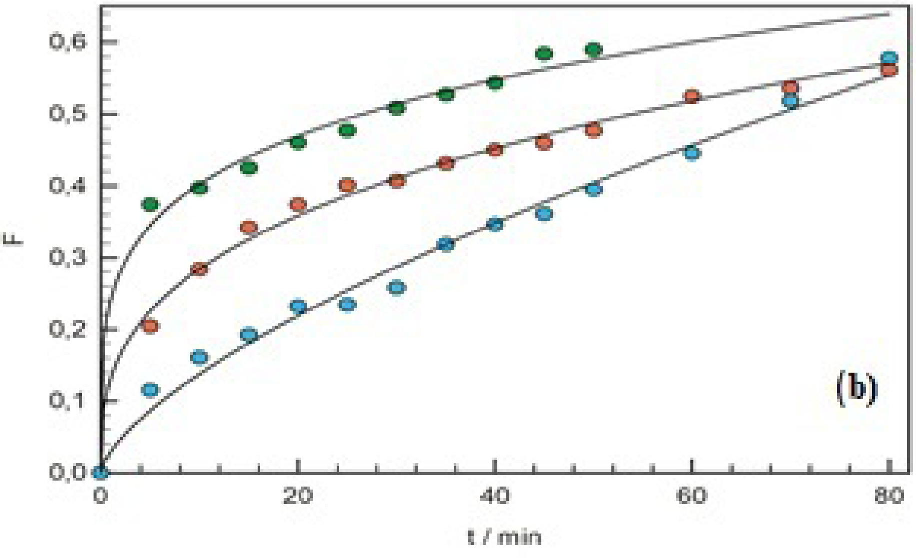


Figure 5. Pseudo-first-order kinetics (dashed line) and pseudo-second order kinetic (solid line) **a)** p(NIPAM)-2(Green), p(NIPAM)-3(Red), p(NIPAM)-4(Blue) **b)** p(NIPAM)(Green), 3 mL p(NIPAM)(Red), 4 mL p(NIPAM)(Blue)

Characterization

FTIR studies were conducted on p(NIPAM) hydrogels synthesized with different crosslikers. As illustrated in Figure 6a, b and c, the FTIR spectra of p(NIPAM) hydrogels have the common peaks observed at 1732 and 1633 cm^{-1} belong to C=O as C—HN stretching peaks and also the peak at 1529 cm^{-1} for C—H groups and at 1456 cm^{-1} for N—H binding was observed were in agreement of literature [45]. Also, depending on the used crosslinker, mostly the ether bond stretching in p(NIPAM) hydrogels prepared using p(EGDA) and p(EGDMA) at about 1104 cm^{-1} is significantly observable.

Figure 6d, e and f illustrate thermograms of p(NIPAM) based hydrogels. A total of 72.2% of p(NIPAM)-1 was degraded between 330-420°C, while 99.5% of total weight was lost around 620°C as shown in Figure 6d. The thermal degradation of p(NIPAM)-2 shows that 66.3% of total weight was lost between 310-420°C whereas 97.5% was lost around 620°C. Additionally, thermal degradation of p(NIPAM)-3 shows that 74.3% of total weight was lost between 310-420°C and 99.2% was lost at around 630°C. Almost all the MBA crosslinked of p(NIPAM) hydrogel thermally degraded as temperature was increased up to 1000°C as shown in Figure 6d. The thermal degradation of p(NIPAM)-258, p(NIPAM)-575 and p(NIPAM)-700 were also studied and the weight losses of 77.5%, 80.1%, 80.2% between 330-425°C, were observed respectively. At the higher temperatures between 600-1000°C, these hydrogels showed similar degradation amounts which is about 97% as shown in Figure 6d. Thermal degradation of p(NIPAM)-EGDMA and p(NIPAM)-p(EGDMA) is shown in Figure 6e. revealed that 70.9% between 260-420°C, 84.4% between 425-523°C, 95.4% between 570-600°C and 96.9% at 1000 °C were seen. Moreover, the thermal degradation of p(NIPAM)-p(EGDMA) was also 79.4% between 320-420°C, 98.3% at 610°C and 98.4% at 1000°C. Therefore, it is obvious that depending on the used amount and the type of crosslinker, the prepared p(NIPAM) hydrogels show different thermal degradation profile.

Conclusion

Here, it was shown that thermoresponsive p(NIPAM) hydrogels can be prepared readily via redox polymerization and simultaneous crosslinking method using various cross likers such as MBA, EGDA with variant MW (258, 575, 700 g/mol), and EGDMA and p(EGDMA) cross-linkers. These p(NIPAM) hydrogels were all prepared at 20°C. Also, swelling behaviors of the prepared hydrogels were studied at 25 and 37°C showing that the crosslinking type plays significant role on the thermoresponsive behavior of p(NIPAM) hydrogels and effect their equilibrium swelling ratios. Furthermore, the diffusion properties of prepared hydrogels were investigated and kinetic models for water diffusion into p(NIPAM) hydrogels were evaluated and found again that diffusion types e.g., Fickian or non-Fickian can tuned by the concentration of MBA and its content (e.g., increasing or decreasing water content). Therefore, p(NIPAM) hydrogels' swelling ratio, water diffusion types, thermoresponsiveness can be readily tuned with used types and extent of the crosslinker and the total water content hydrogel precursors.

Table 3. Diffusion parameters of thermo-sensitive hydrogels with various crosslinkers.

Hydrogel	p(NIPAM)	p(NIPAM)	p(NIPAM)
parameters	1	2	3
Diffusion constants (kD)	0.2406	0.1311	0.0294
Diffusion exponent (nD)	0.223	0.3356	0.6697
Diffusion mechanism type	Fickian	Fickian	non-Fickian
Correlation coefficient (r)	0.9960	0.99871	0.9938
Correlation coefficient, (r2)	0.9919	0.9942	0.9865
	875.24×10^{-6}	284.60×10^{-6}	21.38×10^{-6}

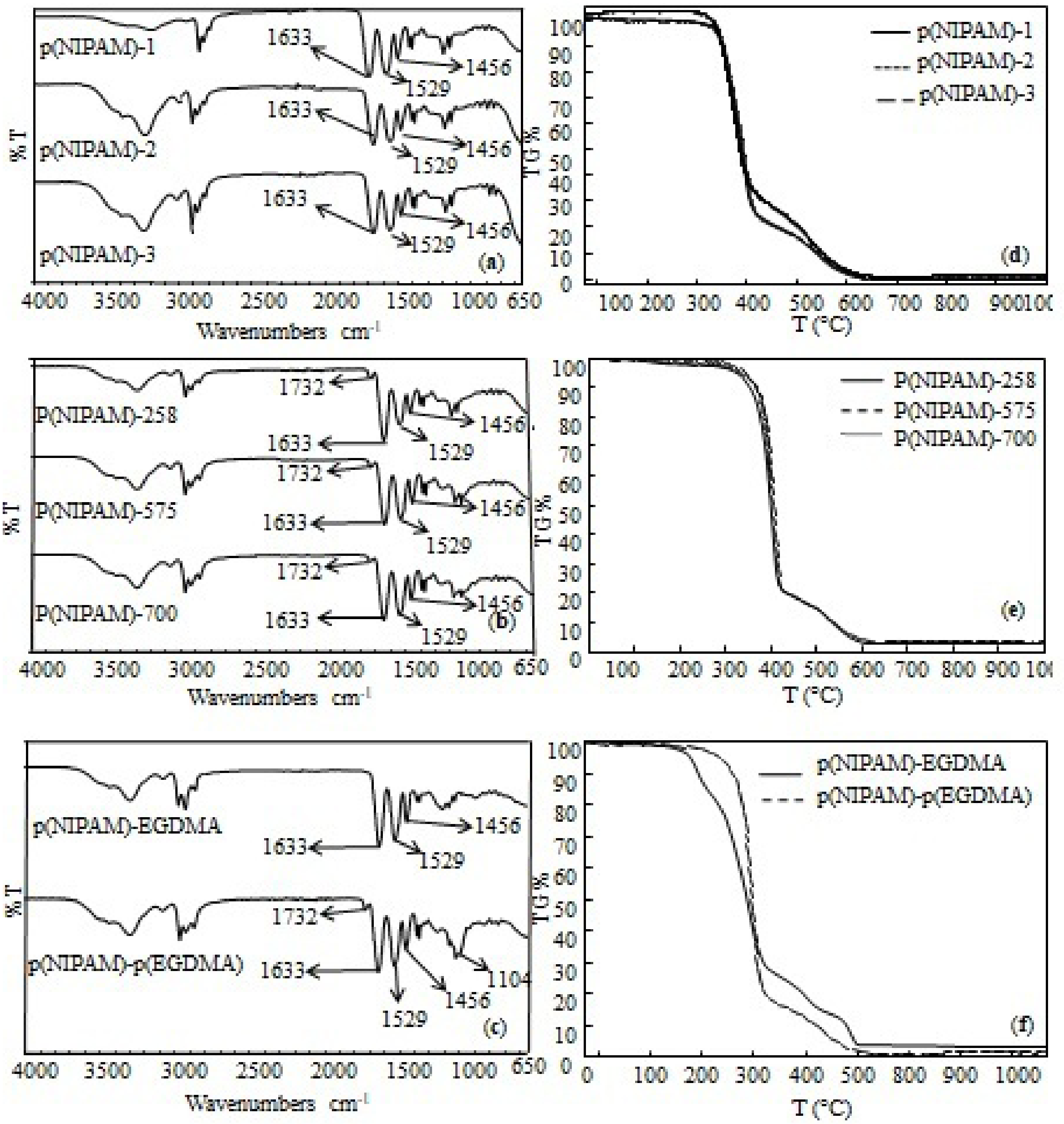


Figure 6. FT-IR spectra of **a)** p(NIPAM)-1, p(NIPAM)-2, p(NIPAM)-3, **b)** p(NIPAM)-258, p(NIPAM)-575, p(NIPAM)-700, and **c)** p(NIPAM)-EGDMA and p(NIPAM)-p(EGDMA), and TGA thermograms of **d)** p(NIPAM)-1, p(NIPAM)-2, p(NIPAM)-3, **e)** p(NIPAM)-258, p(NIPAM)-575, p(NIPAM)-700, and **f)** p(NIPAM)-EGDMA and p(NIPAM)-p(EGDMA)

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