

Research Article

Investigation of the Effects of Different Hydrophilic and Hydrophobic Comonomers on the Volume Phase Transition Temperatures and Thermal Properties of N-Isopropylacrylamide-Based Hydrogels

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In this work, a series of thermally responsive terpolymers of N-isopropylacrylamide (NIPA) with three different comonomer contents was synthesized, and their swelling behaviour was studied as a function of composition and temperature. Temperature-sensitive, random cross-linked terpolymers of NIPA were prepared from methyl methacrylate (MMA), N-tert-butylacrylamide (NTBA), and acrylic acid (AA) using a free radical polymerization method. In the synthesis of terpolymer hydrogels, N,N-methylene bisacrylamide (BIS) was used as cross-linkers and ammonium persulfate (APS) as initiator. The NIPA content of the monomer feed varied from 80 to 50 mol %, and other comonomer feed varied from 40 to 5 mol %. The swelling equilibrium of these hydrogels was studied as a function of temperature and hydrophobic and hydrophilic comonomer contents. The swelling properties of the polymers were investigated in pure water at temperatures from 10 to 80°C. All of the synthesized gels were found to be sensitive to temperature. Glass transition temperature analyses and thermal analyses of the synthesized hydrogels were studied. The volume phase transition temperature and the swelling equilibrium (r) values of NIPA-based hydrogels synthesized in different feed ratios and in varying monomer contents were found in the range of 17–52°C and 14–51 g H₂O/g polymer, respectively. The glass temperature (T_g) of the NIPA/AA/(MMA or NTBA) hydrogels synthesized with feed ratios of 50/40/10 was found to be 133 or 142°C, respectively. The initial and the end degradation that were determined for hydrogels at high temperatures indicated the quite good thermal stability of hydrogels. When the mass loss of the synthesized hydrogels was 50%, the temperatures were measured between 247 and 258°C.

1. Introduction

This article is an attempt to develop terpolymer systems containing poly(N-isopropylacrylamide) (P(NIPA)). It is known that P(NIPA) gels are exposed to temperature-dependent phase transition due to their hydrophilic and hydrophobic groups in their structure [1, 2]. P(NIPA) belongs to a class of polymers which undergo a transition from the hydrophilic to hydrophobic state with increasing temperature and hence exhibit inverse temperature dependence of solubility [3, 4]. The pendant isopropyl group and the hydrocarbon backbone

in the structure of P(NIPA) are hydrophobic, and these hydrophobic groups form aggregates above the volume phase transition temperature [5]. Aqueous solutions of P(NIPA) exhibit a phase transition at temperatures called the lower critical solution temperature which occurs approximately at 32°C [6]. Below the volume phase transition temperature, the polymer chain is hydrated and adopts an extended coil conformation, while above it the polymer is dehydrated and adopts a globular conformation. Correspondingly, the cross-linked hydrogels obtained from these polymers swell under the volume phase transition temperature and shrink

above it [7–12]. It is known that all factors affecting hydrogel swelling can be controlled by monomer selection and polymerization conditions. The transition temperature can be altered by chemical interaction, e.g., via copolymerization, as the physical nature of the volume phase transition [13–16]. In copolymeric systems, the swelling process can be controlled by the introduction of the appropriate amount of a second monomer with hydrophobic and hydrophilic characters. If the amount of hydrophobic groups is reduced by further hydrophilic comonomers, the polymer hydrophilicity is increased due to the strong interaction between water and hydrophilic groups with the polymer [8, 17–19]. Incorporation of hydrophilic comonomer leads to an increase in the transition temperature, whereas incorporation of hydrophobic comonomer leads to a decrease [8, 15, 17–24]. The swelling ratios of hydrogels depend on the ratio of hydrophilic and hydrophobic structural units in the polymer, as well as on the network structures of the hydrogels [24, 25]. In addition to the hydrophobic and ionic interactions of monomers containing the amide and carboxylic acid groups, such systems exhibit hydrogen bonding due to the amide (proton acceptors) and carboxylic groups (proton donors) [26–28]. The balance between hydrophobic, ionic, and hydrogen bonding interactions controls the swelling behaviour of these gels. The precise control and tuning of the volume phase transition temperature are a requirement for different applications of polymeric materials [29]. The synthesis of copolymer gels whose swelling behaviour responds to different external stimuli provides a unique opportunity to tailoring multifunctional materials for specific applications. Stimuli-responsive polymers are polymers that can change their physical properties by responding to an external stimulant such as temperature, pH, illumination, and electric field [30, 31]. The ability of gels to respond strongly to slight changes in the external medium is possible with a sharp reduction in the specific volume of the macromolecule where a phase transition from the first order takes place. When polymers containing both hydrophilic and hydrophobic groups in their structures are cross-linked with suitable cross-linking agents, it results in the formation of hydrogels [32–35].

To date, many studies have been carried out to develop the phase transition temperature and to improve the physical properties by using a second comonomer in addition to NIPA. However, we did not see a literature report on studies using three different monomers in the same hydrogel. In this study, we obtained various terpolymers by inclusion of two different comonomers containing hydrophilic and hydrophobic groups in addition to NIPA.

In this context, this work is aimed at improving the weak physical properties of P(NIPA) and determining the phase transition temperature and swelling balance values for different applications. For this purpose, N-tert-butylacrylamide (NTBA), methyl methacrylate (MMA), and acrylic acid (AA) were used as comonomers in addition to NIPA. Eventually, various NIPA/MMA/(NTBA or AA) and NIPA/NTBA/AA terpolymer gels were synthesized. Furthermore, the effects of hydrophilic and hydrophobic comonomers on thermal properties of P(NIPA) hydrogels were investigated.

2. Materials and Methods

2.1. Materials. N-Isopropylacrylamide (NIPA), N-tert-butylacrylamide (NTBA), acrylic acid (AA), methyl methacrylate (MMA), ammonium persulfate (APS), N,N-methylenebisacrylamide (BIS), and methanol were all purchased from ACROS company and used as supplied. Water used in this experiment was double-distilled.

2.2. Synthesis of Poly(N-isopropylacrylamide) and of the P(NIPA)-Based Hydrogels. The hydrogels were synthesized by using free radical cross-linking terpolymerization in methanol at $50 \pm 1^\circ\text{C}$ in the presence of 0.1 mol % APS. The monomer concentration was fixed at 2 M. After preliminary experiments, it was found that this concentration of the solvent used the monomer in feed ratios was critical for obtaining both a homogeneous feed and high conversion. For the cross-linked terpolymers, the NIPA feed ratios varied from 80 to 50 mol %, and for other monomers, feed ratios varied from 40 to 5 mol % (Table 1). For the polymerization procedure, the details of a typical preparation of a terpolymer (NIPA60:MMA20:AA20), when other comonomers are equal and NIPA is 60%, are detailed below. A mixture of NIPA:MMA:AA (2.037 g:0.6 g:0.43 g) was dissolved in methanol (15 mL), and BIS (1.13 mol %, (2.03688 g)) was used along with monomers. The monomer solution was degassed for 15 min, and then, APS as the initiator 0.1 mol % (6.8×10^{-3} g) was introduced. After obtaining a homogeneous solution, it was transferred to glass tubes with dimensions of 15×150 mm by means of a funnel. The glass tubes were placed in a water bath and allowed to gel at 70°C . The gels formed after 45 minutes were removed from the tubes and washed with methanol to remove unreacted monomers. Following this process, gels were immediately cut at a thickness of 3 mm by means of a scalpel. The purified gels were then placed in a 15×55 mm Petri dish and were dried at 120°C in a vacuum oven to a constant weighing [36]. The P(NIPA) homopolymer was synthesized in a similar manner. The details of the comonomer feed ratios used in the terpolymerizations, as well as the conversion values of the resultant terpolymers, are shown in Table 1.

2.3. Swelling and Deswelling Measurements. Temperature-dependent measurements were examined in a thermostated water bath. The phase transition of P(NIPA), P(NIPA-co-NTBA-co-AA), P(NIPA-co-MMA-co-NTBA), and P(NIPA-co-MMA-co-AA) hydrogels was determined by measuring the swelling and deswelling as % (gravimetrically) at different temperatures. The dried hydrogel discs were swollen to equilibrium for a minimum period of 36 h over a range of temperatures on both heating and cooling. Temperature sensitivities of synthesized hydrogels were measured in the temperature range of 10 to 80°C , and their respective weights were noted at each temperature. After immersion in water at a specified temperature, each hydrogel was taken out of the water and blotted with Kimwipes to remove excess water on the surface of the hydrogel. Each hydrogel was weighed repeatedly over the day and reimmersed in water at a fixed temperature until the hydrated weight reached a constant value. It was then

TABLE 1: Conversion of the NIPA/MMA/(NTBA or AA) terpolymerizations.

Sample hydrogels	NIPA/MMA/(NTBA or AA) mole ratio (%)	NIPA (g)	MMA (g)	NTBA (g)	AA (g)	Conversion (%)
P(NIPA)	100	—	—	—	—	87.54 ± 0.13
NIPA/AA/NTBA	50/10/40	0.85	—	0.76	0.1	82.02 ± 0.16
NIPA/AA/NTBA	50/40/10	0.85	—	0.19	0.41	83.66 ± 0.17
NIPA/MMA/NTBA	50/10/40	0.85	0.16	0.76	—	80.34 ± 0.14
NIPA/MMA/AA	50/40/10	0.85	0.64	—	0.1	81.18 ± 0.15
NIPA/MMA/AA	50/10/40	0.85	0.16	—	0.41	81.87 ± 0.16
NIPA/MMA/NTBA	50/40/10	0.85	0.64	0.19	—	80.68 ± 0.14
NIPA/MMA/NTBA	60/30/10	1.018	0.48	0.19	—	81.51 ± 0.16
NIPA/MMA/NTBA	60/20/20	1.018	0.32	0.38	—	81.84 ± 0.15
NIPA/MMA/NTBA	60/10/30	1.018	0.16	0.57	—	82.35 ± 0.15
NIPA/MMA/AA	60/30/10	1.018	0.48	—	0.1	82.37 ± 0.15
NIPA/MMA/AA	60/20/20	1.018	0.32	—	0.21	82.58 ± 0.16
NIPA/MMA/AA	60/10/30	1.018	0.16	—	0.31	83.47 ± 0.17
NIPA/AA/NTBA	60/20/20	1.018	—	0.38	0.21	82.88 ± 0.16
NIPA/AA/NTBA	60/10/30	1.018	—	0.57	0.10	82.78 ± 0.16
NIPA/AA/NTBA	60/30/10	1.018	—	0.19	0.31	83.26 ± 0.17
NIPA/MMA/NTBA	80/5/15	1.36	0.08	0.29	—	83.01 ± 0.15
NIPA/MMA/AA	80/5/15	1.36	0.08	—	0.16	84.15 ± 0.18
NIPA/MMA/NTBA	80/15/5	1.36	0.24	0.10	—	83.64 ± 0.15
NIPA/MMA/AA	80/15/5	1.36	0.24	—	0.05	83.57 ± 0.15
NIPA/NTBA/AA	80/10/10	1.36	0.19	—	0.10	84.05 ± 0.17
NIPA/AA/MMA	80/10/10	1.36	0.16	—	0.10	83.82 ± 0.16
NIPA/NTBA/MMA	80/10/10	1.36	0.16	0.19	—	83.29 ± 0.15
NIPA/NTBA/AA	80/5/15	1.36	—	0.10	0.16	84.38 ± 0.18
NIPA/NTBA/AA	80/15/5	1.36	—	0.29	0.05	83.65 ± 0.16

rebalanced at another temperature. The hydrogels were then dried in a desiccator under a vacuum up to a dry weight. The equilibrium swelling ratio was calculated reading from the g H₂O/g polymer by (swollen hydrogel-dry hydrogel)/dry hydrogel formula [37]:

$$r = \frac{W_s - W_d}{W_d}, \quad (1)$$

where W_s is swollen hydrogel and W_d is dry hydrogel.

2.4. Conversion. Following terpolymerization, a quantitative amount of inhibitor was introduced into the hydrogel and was cooled to room temperature for 2 h, then reheated to 60°C (above the volume phase transition temperature of hydrogels) to obtain the precipitates of the terpolymers. The precipitates were washed with water a few times for the removal of monomers and initiator and then dried in a vacuum oven at 50°C until the weight was constant. The conversion of the monomers was calculated as follows:

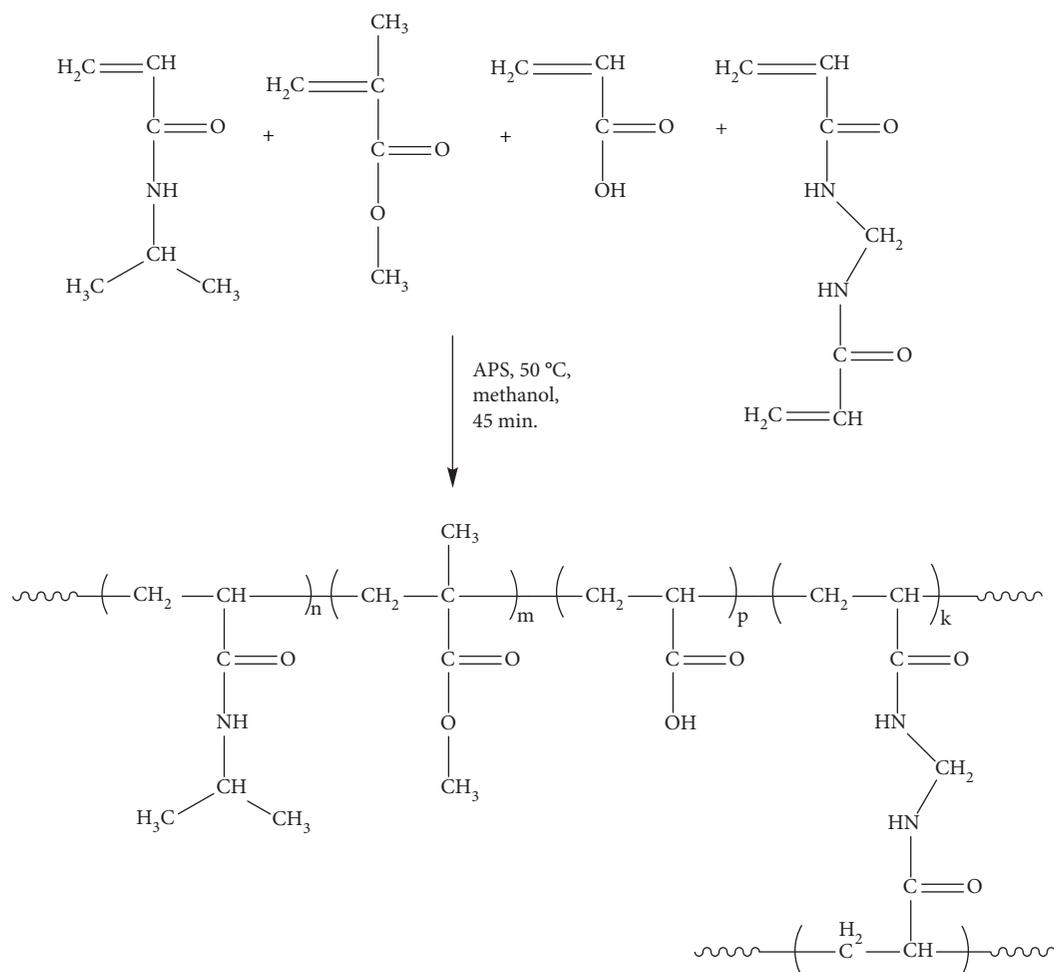
$$\text{Conversion} = \frac{P}{W \times M_o} \times 100\%, \quad (2)$$

where P is the weight of the dry hydrogel obtained from the sample, W is the weight of the sample taken out from the medium, and M_o is the weight fraction of monomers in feed [37].

2.5. Thermal Studies. TGA thermograms of the P(NIPA)-based hydrogels were recorded on a thermoanalyzer (Setaram TG 1750) under nitrogen atmosphere with a flow capacity of 20 mL/min from 50 to 650°C at a heating rate of 1.0°C/min. The starting decomposition temperature and weight loss values of the samples were evaluated by using the intersection point of tangents of TGA curves. The differential scanning calorimetry (DSC) studies were performed with a Setaram DSC 131. The samples were heated from 20 to 350°C, with a heating rate of 20°C/min under nitrogen atmosphere.

3. Results and Discussion

In our study, P(NIPA) and hydrogels of NIPA/MMA/(NTBA or AA) and NIPA/NTBA/AA were prepared by free radical cross-linking terpolymerization in methanol at 50 ± 1°C using 0.1 mol % APS and 1.13 mol BIS. The polymerization reaction of NIPA/MMA/AA hydrogels is presented in



SCHEME 1: The polymerization reactions of NIPA/MMA/AA hydrogel.

Scheme 1. The concentration of the monomers in synthesized P(NIPA)-based hydrogels was fixed at 2 M.

The effect of NIPA/MMA/(NTBA or AA) and NIPA/NTBA/AA mole ratio on the thermoresponsivities of the produced hydrogels was studied by changing this ratio from 80.0 to 50.0%/from 40.0 to 5.0%/from 40.0 to 5.0%, respectively. The quantities of the comonomers used in the synthesis of hydrogels and the hydrogel yields obtained from the synthesis are given in Table 1. The conversion data in Table 1 show that the increase of the NIPA weight ratio increased the conversion of copolymerization.

3.1. Swelling Behaviour of the Hydrogels. The volume phase transition is raised by a change between various types of interactions, in particular hydrogen bonding and hydrophobic interactions. Experimental results and theoretical considerations suggest that hydrophobic interactions play an important role in the swelling/deswelling process [38]. Furthermore, at the volume phase transition temperature, the hydrogen bonding between the polymer and water becomes unfavourable compared to the polymer-polymer and water-water interaction, and therefore, an abrupt transition occurs as the hydrated hydrophilic macromolecule quickly dehydrate and change to a more hydrophobic structure [39].

TABLE 2: The volume phase transition temperature (VPTT) and the swelling equilibrium values (r) of hydrogels containing 50% NIPA and P(NIPA).

Hydrogels	Monomer feed rates (%)	VPTT (°C)	Swelling ratio, r (g H ₂ O/g polymer)
P(NIPA)	—	24	38
NIPA/AA/NTBA	50/10/40	17	37
NIPA/AA/NTBA	50/40/10	39	51
NIPA/MMA/AA	50/10/40	52	27
NIPA/MMA/AA	50/40/10	30	14
NIPA/MMA/NTBA	50/10/40	24	20
NIPA/MMA/NTBA	50/40/10	23	14

For synthesized P(NIPA) hydrogel under polymerization conditions in which other hydrogels were synthesized, the lower critical solution temperature (LCST) value for P(NIPA) at the specified reaction conditions was 24°C. The swelling equilibrium (r) value of P(NIPA) synthesized under the determined reaction conditions was found to be 38 (g H₂O/g polymer) (Table 2). In many previous studies, for the P(NIPA) hydrogel obtained using a smaller amount of cross-linker, the phase transition temperatures were

TABLE 3: The volume phase transition temperature (VPTT) and the swelling equilibrium values (r) of hydrogels containing 60% NIPA.

Hydrogels	Monomer feed rates (%)	VPTT (°C)	Swelling ratio, r (g H ₂ O/g polymer)
NIPA/AA/NTBA	60/10/30	23	37
NIPA/AA/NTBA	60/30/10	34	33
NIPA/AA/NTBA	60/20/20	25	46
NIPA/MMA/AA	60/30/10	27	16
NIPA/MMA/AA	60/10/30	27	29
NIPA/MMA/AA	60/20/20	25	23
NIPA/MMA/NTBA	60/30/10	23	14
NIPA/MMA/NTBA	60/10/30	23	15
NIPA/MMA/NTBA	60/20/20	22	17

determined at 32–34°C. When the amount of cross-linker was increased up to 1.13%, it was seen that this value decreased to 24°C (Table 2). The amount of cross-linker used in the polymerization appeared to affect and significantly reduce the phase transition temperature of the obtained hydrogel. Also, due to the decrease in the used NIPA ratio in synthesized hydrogels and the short polymerization time, there were difficulties in gelling, and this problem was overcome by increasing the polymerization medium temperature by 3°C and prolonging the polymerization time for 15 minutes. In particular, in the synthesis of 50% NIPA-based hydrogels containing more hydrophobic comonomers, the polymerization time and temperature were higher because of some difficulties in gelation. However, when one of the comonomers used in the polymerization was AA, no such problem was observed. This was due to the strong hydrophilic structure of AA comonomer and the increased hydrogen bond density in the medium. However, when one of the comonomers used in the polymerization was AA, no such problem was observed. This was due to the strong hydrophilic structure of AA comonomer and the increase hydrogen bond density in the medium. Strong polymer-polymer interactions and dense H-bonds in the environment were effective in facilitating hydrogel formation.

The phase transition temperatures of the hydrogels were determined by using the swelling equilibrium values obtained from the measurements. All obtained hydrogels were responsive to the stimulation with the effect of swelling-shrinkage in distilled water and were found to be sensitive to temperature in their temperature sensitivity measurements. By increasing the AA comonomer in the structure of the hydrogels, volume phase transition temperature and the swelling equilibrium values reached higher [37]. In general, in the volume phase transition temperature and in the swelling equilibrium values, a marked decrease was observed in comonomers containing hydrophobic groups in higher ratios [5, 40]. The volume phase transition temperature and the swelling equilibrium values of the hydrogels synthesized in our study are given in Tables 2–4.

The hydrogels containing 50% NIPA and comonomers in different ratios and the equilibrium swelling values against the temperature were shown in Table 2. NIPA/MMA/AA hydrogels containing 50% NIPA were synthesized in 50/10/

TABLE 4: The volume phase transition temperature (VPTT) and the swelling equilibrium values (r) of hydrogels containing 80% NIPA.

Hydrogels	Monomer feed rates (%)	VPTT (°C)	Swelling ratio, r (g H ₂ O/g polymer)
NIPA/NTBA/AA	80/15/5	25	29
NIPA/NTBA/AA	80/10/10	31	37
NIPA/NTBA/AA	80/5/15	30	35
NIPA/MMA/AA	80/15/5	27	34
NIPA/MMA/AA	80/10/10	45	36
NIPA/MMA/AA	80/5/15	42	33
NIPA/MMA/NTBA	80/15/5	24	21
NIPA/MMA/NTBA	80/10/10	20	30
NIPA/NTBA/MMA	80/5/15	20	26

40 ratios; the volume phase transition temperature and the swelling equilibrium values were determined as 52°C and as 27 g H₂O/g polymer, respectively. When the same hydrogel was synthesized at 50/40/10 ratios, the volume phase transition temperature of the obtained hydrogel was 30°C and the swelling equilibrium value was determined to be 14 g H₂O/g polymer (Table 2 and Supplementary data). In another hydrogel synthesis, when NIPA/AA/NTBA hydrogels containing 50% NIPA were synthesized in 50/10/40 ratios, the volume phase transition temperature and the swelling equilibrium values were 17°C and 37 g H₂O/g polymer, respectively. When the same hydrogel was run at 50/40/10 ratios, the volume phase transition temperature of the obtained hydrogel was 39°C and the swelling equilibrium value was 51 g H₂O/g polymer (Table 2 and Supplementary data).

In hydrogels containing 50% NIPA, when the amount of hydrophilic comonomer in the hydrogel decreased, there was a significant decrease in both the volume phase transition temperature and the swelling equilibrium values. The presence of hydrophilic AA comonomer in the structure of the hydrogel had a positive effect on the swelling equilibrium values and on the volume phase transition temperature values. However, sharp decreases were observed in the volume phase transition temperature and the swelling equilibrium values when hydrophobic MMA comonomer 40% mole was used instead of AA comonomer. In the presence of hydrophobic comonomer MMA in the structure of synthesized hydrogels, there was a decrease in both the volume phase transition temperature and the swelling equilibrium values [5, 40]. This decrease is sharper as the amount of MMA comonomer in the hydrogel was increased. The volume phase transition temperature and the swelling equilibrium values of NIPA/MMA/NTBA hydrogels were significantly lower than those of hydrogels containing AA comonomers (Table 2 and Supplementary data). The heterogeneity resulting from the random arrangement of monomers in the structure of the synthesized hydrogel and the hydrophobic nature of the MMA comonomer resulted in lower volume phase transition temperature and swelling equilibrium values compared to hydrogels containing AA comonomers. Also, the increase of NTBA comonomer in hydrogel negatively affected the swelling equilibrium value,

and the volume phase transition temperature significantly decreased [36]. Both the volume phase transition temperatures and the swelling equilibrium values were adversely affected by the increase in MMA comonomer in all synthesized hydrogels. It was seen that the use of MMA comonomer together with NTBA comonomer containing sterically hindered groups had a negative effect on the swelling equilibrium value. However, the NTBA comonomer also positively contributed to the swelling equilibrium value, when used together with the hydrophilic comonomer AA. Therefore, when the NTBA comonomer was used together with AA comonomer, the higher swelling equilibrium value was reached. In addition, in hydrogels containing hydrophobic MMA comonomers, the values of the swelling equilibrium were much lower than synthesized P(NIPA) hydrogels under the same working conditions, and also, the volume phase transition temperature values were close to those of P(NIPA) hydrogels.

The equilibrium swelling values of the hydrogels containing 60% NIPA and comonomers in different ratios were shown against the temperature in Table 3. In the hydrogels containing 60% NIPA, changing the comonomer ratios used in the syntheses gave similar results as in the hydrogels containing 50% NIPA.

The effect of comonomer ratios was similar on the volume phase transition temperature and the swelling equilibrium values. As seen from Table 3, in hydrogels containing 60% NIPA, the volume phase transition temperature and the swelling equilibrium values were 22–27°C and 14–46 g H₂O/g polymer, respectively. In these hydrogels, the lowest volume phase transition temperature and swelling equilibrium values were observed in the NIPA (60)/MMA (30)/NTBA (10) hydrogel, and both values decreased when the AA comonomer was not used in the hydrogel. In synthesized hydrogels, higher swelling equilibrium values were reached when AA was used as a second comonomer in addition to NTBA. Similarly, the use of high amounts of AA comonomer again was seen to increase both the volume phase transition temperature and swelling equilibrium values. However, the higher MMA comonomer ratio decreased in both values (Table 3 and Supplementary data). This shows that the hydrophilic AA comonomer in the hydrogel had a stronger effect of H-bonds in the molecule than the effect of hydrophobic comonomers [38]. In general, relatively higher swelling equilibrium values were reached compared to hydrogels containing 50% NIPA (Tables 2 and 3). The high amount of NTBA in the synthesized hydrogels affected the volume phase transition temperature values slightly downwards. However, its effect on the swelling equilibrium values was more limited.

The equilibrium swelling values of the hydrogels containing 80% NIPA and comonomers in different ratios were shown against the temperature in Table 4. The volume phase transition temperature and the swelling equilibrium values of 80% NIPA-based hydrogels containing comonomers in different ratios were similar to that of 50% and 60% NIPA. When the NIPA ratio in NIPA-based hydrogels is 80%, and the amount of AA which is a hydrophilic comonomer in the hydrogel used a higher amount than the other comonomers,

the volume phase transition temperature value raised up to 45°C; also, the swelling equilibrium value raised up to 37 g H₂O/g polymer (Table 4). However, the increase in the amount of NTBA in the synthesized hydrogels, especially when MMA was used as comonomer, led to lower results compared to the other hydrogels in both the volume phase transition temperature and the swelling equilibrium values (Table 4). When the amount of hydrophobic MMA comonomer used in the synthesis of NIPA/NTBA/MMA hydrogel containing 80% NIPA was used in excess compared to NTBA, the volume phase transition temperature was measured at a lower temperature than that of synthesized P(NIPA) hydrogel in the same working conditions. Also, a decrease in the swelling equilibrium was observed for the same hydrogel. This reduction in the volume phase transition temperature and the swelling equilibrium values was due to the fact that both comonomers containing the sterically hindered group NTBA and the hydrophobic MMA were used in the same hydrogel [5, 40]. Increased network density may be considered to be effective on these values, and intense H-bond formation in the medium can be shown by causing both values to be lower than expected. If free volume in the hydrogel is too low, water may be unable to sink into the polymer matrix to initiate the swelling process. The free volume in the hydrogel was decreased due to the cross-link density in the medium and steric hindrances in the comonomers used. The high cross-linking density of the network could interfere with chain lengthening so that excess cross-linked polymers having a strong polymer structure swelled less.

If NIPA-based hydrogels is 80%, again similarly, the volume phase transition temperature and the swelling equilibrium values of the hydrogels have increased with increasing the amount of the hydrophilic comonomer AA. The increase in the amount of MMA, which is a hydrophobic comonomer, led to the decrease in the volume phase transition temperature and the swelling equilibrium values. The volume phase transition temperature and the swelling equilibrium values decreased slightly with the increase in the amount of NTBA containing steric groups.

When the Supplementary Figures S4-S13 (Supplementary data) related to the swelling values of hydrogels are examined, it was seen that there was an increase in swelling ratios of hydrogels at temperatures 5–20°C, under the volume phase transition temperature. It was thought that the increase in swelling equilibrium values of hydrogels was due to the intermolecular interactions in this temperature range.

All of the gels obtained were responsive to the stimulation with the effect of swelling-shrinkage in distilled water. In parallel with the increase of AA comonomer in the structure of hydrogels, hydrogel had reached high temperature and high swelling equilibrium values [42]. In the case of hydrophobic groups predominantly, the volume phase transition temperature and the swelling equilibrium values significantly decreased [5, 40]. The hydrophilicity or hydrophobicity of used comonomers in the hydrogel synthesis changed the volume phase transition temperature and the swelling equilibrium values depending on the

increasing amounts in the hydrogel, in accordance with literatures [5, 36, 38, 40]. The steric hindrance resulting from the structure of the NTBA comonomer led to lower measurements compared to P(NIPA) for the swelling equilibrium value [36]. When comonomers with steric hindrance and hydrophobic structure were used in hydrogel syntheses, the volume phase transition temperature and swelling balance values were lower. As expected, the swelling behaviour of the hydrogel obtained with a higher amount of NIPA content had more similarity to that of the P(NIPA) hydrogels. However, the comonomers added to the hydrogel had a significant effect on the volume phase transition temperature and the swelling equilibrium values.

3.2. Thermal Analysis. In this study, we also report a thermal analysis study of hydrogels NIPA/MMA/(NTBA or AA) and NIPA/NTBA/AA. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were used for synthesized hydrogels. The glass transition temperatures (T_g) of the hydrogels were determined, as well as their degradation temperatures (TG) [41, 42]. The thermal stability of the hydrogels was analyzed, and all the results are discussed in terms of the changes in the hydrogels' structure as a consequence of different polymer-polymer interactions due to the presence of comonomers in varying compositions.

According to the resulting DSC results obtained at 20 to 350°C for NIPA hydrogel, the glass transition temperature of the NIPA hydrogel was 110°C (Supplementary data). In the same temperature range, the glass transition temperatures for NIPA/MMA/(NTBA or AA) and NIPA/NTBA/AA hydrogels were determined. It was observed that the T_g of the synthesized NIPA-based hydrogels were higher than that of P(NIPA). The glass transition temperatures obtained from DSC studies are given in Table 5 and Supplementary data. In all the samples studied, a single glass transition temperature was observed. The T_g varied with the composition of the hydrogels. In the hydrogels containing AA and NTBA comonomers, higher glass transition temperature values were observed. In particular, in the hydrogels containing AA comonomer and forming strong hydrogen bonds, H-bonds reduced mobility of the polymer chain. With the increase in AA comonomer content, the transition was observed to shift to higher values, indicating a nearly random distribution of NTBA and AA comonomers in hydrogel segments. Due to the random sequence of the comonomers in the obtained hydrogels and the differences between the structures of the comonomers used in the synthesis of the hydrogels, heterogeneity in the molecular chain occurred in excess.

The glass transition temperatures of P(NIPA) hydrogel and hydrogels containing 80% NIPA were measured lower than the hydrogels containing 50% NIPA. It is clear that the comonomers used in the synthesis affected the thermal stability of P(NIPA). When the NIPA/MMA/NTBA hydrogel was studied in feed rates 80/15/5 and the third comonomer NTBA was taken as 5 mol % according to the total mol, the T_g temperature was determined as 121°C. While the absence of AA comonomer in hydrogel negatively affected the T_g , it was seen that the NTBA comonomer used

TABLE 5: Weight loss and the glass transition temperature and corresponding degradation temperatures for the hydrogels.

Hydrogel sample (%)	T_g	T_i	T_m	T_f	Residual value at 500°C (%)
	(°C)				
P(NIPA)	110	315	352	381	9.1
NIPA/MMA/NTBA (80/15/5)	121	326	368	404	7.4
NIPA/MMA/AA (80/15/5)	127	328	373	405	8.8
NIPA/AA/NTBA (80/5/15)	129	325	371	406	9.6
NIPA/AA/MMA (50/40/10)	133	329	374	409	10.1
NIPA/AA/NTBA (50/40/10)	142	332	376	412	10.4

T_g : glass transition temperature; T_i : temperature at which degradation starts; T_m : temperature at which the degradation rate is at maximum temperature; T_f : temperature at which degradation ends.

in a small amount had a positive effect on T_g . When the NIPA/MMA/AA hydrogel was studied in feed rates 80/15/5 and the third comonomer AA was taken as 5 mol % according to the total mol, the T_g temperature of the hydrogel was determined as 127°C. At the same rate, when studying with NTBA as the third comonomer instead of MMA, this time, the T_g temperature of the hydrogel was 129°C. The increase in the amount of NIPA in the synthesized hydrogels slightly decreased the glass transition temperature. When the NIPA/AA/(MMA or NTBA) hydrogel was studied in feed rates 50/40/10 and the third comonomer MMA comonomer was taken as 10 mol % according to the total mol, the T_g temperature was determined as 133°C. At the same rate, when studying with NTBA as the third comonomer instead of MAA, this time, the T_g temperature of the hydrogel was 142°C (Table 5 and Supplementary data).

The use of AA comonomer in hydrogel synthesis and the use of NTBA as the third comonomer resulted in a high glass transition temperature. It is seen that tert-butyl groups in the structure of the NTBA comonomer in the hydrogel made it difficult to rotate around the bonds and this increased T_g temperature of the hydrogel. This result shows that the intense hydrogen bonds formed in the hydrogel increase the interaction between the polymer chains in the hydrogel and give the polymer more stability. It is thought that the NTBA comonomer had polymer-polymer interactions in the molecule as well as intramolecular H-bonds and the free volume ratio around the chain in the molecular structure hence increased T_g . The presence of AA comonomer in the same hydrogel helped to reveal this situation. In addition, the high T_g temperature in obtained hydrogels using the NTBA comonomer may also be attributed to the lack of regular cross-linking density due to heterogeneity in the hydrogel [42]. In the high ratio use of AA comonomer in hydrogel, even in the case in which MMA was used as the third comonomer, the glass transition temperature was measured at a high value. When the high amount of AA comonomer (40%) was used as joint comonomer in hydrogels, T_g temperature of hydrogels was observed to increase highly. However, the T_g temperature of obtained hydrogels by using

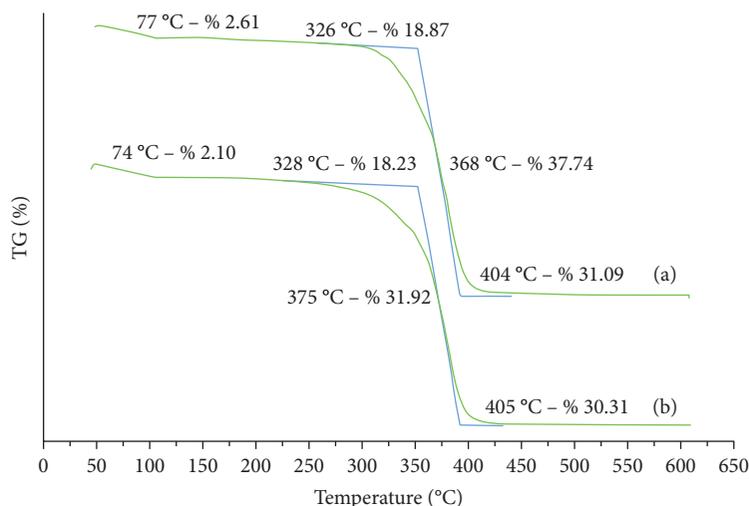


FIGURE 1: TGA thermograms of (a) NIPAAm%80/MMA%15/NTBA%5 and (b) NIPA%80/MMA%15/AA%5 hydrogels. Scan was run at 10°C/min under nitrogen atmosphere.

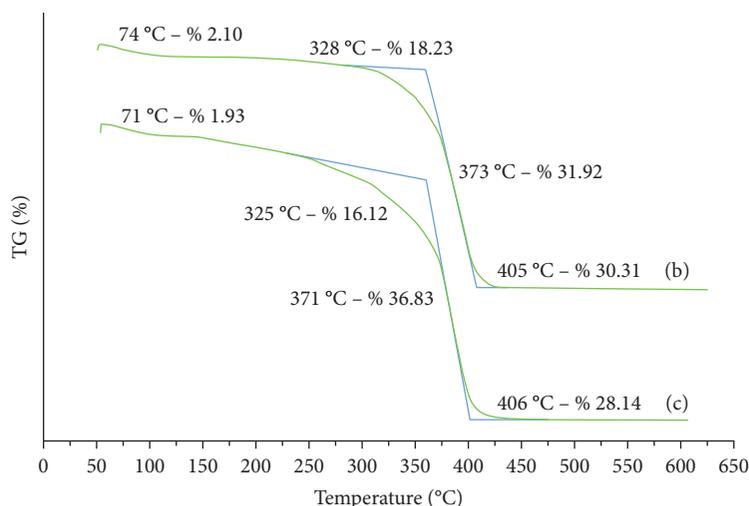


FIGURE 2: TGA thermograms of (b) NIPA%80/MMA%15/AA%5 and (c) NIPA%80/AA%5/NTBA%15 hydrogels. Scan was run at 10°C/min under nitrogen atmosphere.

hydrophobic comonomer MMA was determined to be smaller than those of hydrogels having hydrophilic AA comonomer. In addition, also, the high proportion of cross-link density in all synthesized hydrogels increased the T_g value.

Degradation temperatures were determined by derivative (DTG) of the obtained TG curve (Supplementary data). It is understood from the DTG curve that hydrogels were degraded in a single step. It is also thought that large and small peaks at low temperatures came from solvent (methanol) trapped in the polymer structure. In hydrogels, the weight loss in the thermal degradation process began at about 300°C by the disintegration of the hydrogel chains and side groups and ended at about 425°C after a complete breakage of the hydrogel chains. The relative thermal stability of samples was evaluated by comparing the dedegradation temperature and residual weight percent at 500°C. The TGA results are summarized in Table 5. It is clear that

NIPA/MMA/NTBA (80/15/5), NIPA/AA/MMA (50/40/10), NIPA/AA/NTBA (50/40/10), NIPA/MMA/AA (80/15/5), and NIPA/AA/NTBA (80/5/15) showed a residual mass percent of 7.4 wt%, 8.8 wt%, 9.6 wt%, 10.1 wt%, 10.4 wt%, and 10.9 wt% at 500°C, respectively.

When the NIPA/MMA/(NTBA or AA) hydrogel at 80/15/5 feed rates was examined and the third comonomer AA and NTBA were taken as 5 mol % over total mol, the AA comonomer had much more intermolecular interaction (H-linkage, polymer-polymer) within the hydrogels. Because of that, the degradation temperatures of NIPA/MMA/AA hydrogel occurred at a bit higher temperature than the NIPA/MMA/NTBA hydrogels. It is seen that the thermal stability of the hydrogel containing AA comonomer was better than that of NTBA and the mass losses took place at higher temperature. As shown in Table 5 and Figures 1 and 2, when NIPA/AA/(MMA or NTBA) hydrogels was studied in feed rates 80/5/15, it is seen that the values were very close

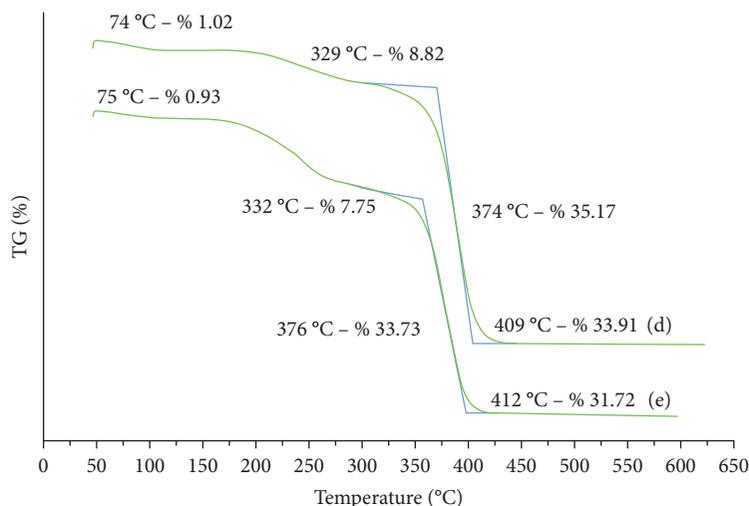


FIGURE 3: TGA thermograms of (d) NIPAAm%50/AA%40/MMA%10 and (e) NIPAAm%50/AA%40/NTBA%10 hydrogels. Scan was run at 10°C/min under nitrogen atmosphere.

to each other and both hydrogels showed similar degradation with increasing temperature. As it is understood from these results, it was seen that hydrophobic comonomer varieties did not significantly affect the degradation temperatures and mass losses of hydrogels. However, it is seen that the excessive use of MMA comonomer adversely affected TG compared to other comonomers.

When the thermal properties of NIPA/AA/MMA and NIPA/AA/NTBA hydrogels synthesized at 50/40/10 feed rates are examined, it is seen that the results are slightly better when NTBA comonomer is used instead of MMA comonomer (Table 5, Figure 3). However, the results are very close to each other, and their thermal stability was better compared to P(NIPA) (Table 5). In parallel with the increase in the ratio of the AA comonomer in the hydrogel, an increase in the temperature of the degradation was observed. It can be concluded that AA comonomer content of the hydrogel led to strong H-bonds inside the hydrogel and this increased the thermal stability of the hydrogel. It is seen that the thermal stability of the hydrogel containing AA comonomer was better than that of NTBA comonomer and the mass losses occurred at higher temperature. Using more amounts of AA comonomer in the synthesis gave the hydrogels a thermal stability, and consequently, the % mass loss remained lower.

When the 10% mol rate NTBA comonomer was used as the third monomer, the total mass loss was 50% and temperature was measured at 258°C. When working in the NIPA/NTBA/AA hydrogels with 50/10/40 feed supply, the polymer-polymer interaction in the hydrogel increased, and the number of intramolecular H-bonds increased as well. The AA comonomer in the hydrogel structure made the hydrogels thermally more stable by forming intensive H-bonds with the NIPA, which was used in particular by 50%. Therefore, it can be assumed that the mass loss of 10% at 258°C was the NTBA comonomer parts of the hydrogel. When the NIPA/MMA/AA hydrogel was examined at 50/10/40 feed rates, this time mass loss occurred at 247°C. This temperature was lower than that of the hydrogel that used NTBA comonomer. This may be attributed to the

expansion of the volume around the chain and to the increase in chain flexibility due to the effect of the branching of the tert-butyl groups in the structure of the NTBA comonomer.

In hydrogels containing AA comonomer, the degradation also occurred at a high temperature due to the presence of intensive hydrogen bonds. The increase in the content of the AA comonomer in the hydrogel structure generally increased the thermal stability of the hydrogels and accordingly increased the temperatures of degradation. Thermal analysis results showed that hydrogels had a high degradation temperature and their thermal stability was quite good, and synthesized P(NIPA)-based hydrogels were more compact. In hydrogels containing NTBA comonomer, the degradation occurred also at a high temperature. The substitution of amide-H with the tert-butyl group increased the steric hindrance and hence made it more difficult for the adjacent amino group to interact. Amide groups in NTBA comonomer led to strong hydrogen bonding and hence reduced mobility of the polymer chain. MMA comonomer containing hydrogels, although slightly lower than other hydrogels, had a high degradation temperature. However, when the total weight loss in hydrogels is compared at 500°C, there was no significant difference in thermal stability. Due to small differences, we cannot draw any conclusive inferences.

The degradation at high temperatures showed that the thermal stability of hydrogels was quite good. The use of a high amount of cross-linker in syntheses can also be considered to be effective on the thermal stability of the hydrogels. As seen from the TG and DTG thermograms, almost all of the gels degraded in the same temperature range and in almost the same amounts. The differences in the amount of the comonomer in the hydrogels did not affect the degradation much. However, when the AA and NTBA comonomers in the hydrogel structure were in a high amount, these increased the thermal stability of the hydrogel and the likelihood of H-bonding in the medium. This also led to low mass losses along with the high degradation temperatures.

4. Conclusion

Hydrogels have found a wide range of application areas due to their specific structure and swelling properties. Accordingly, hydrogels are used in many fields such as contact lenses, hygiene products, wound dressings, pH sensors, biosensors, drug delivery, tissue engineering, water treatment, heavy metal ion removal, and electronic conductive material production. Each passing day, their importance increases. Based on this, in this work, NIPA-based temperature-sensitive hydrogels were synthesized using various hydrophilic and hydrophobic comonomers. As a result, NIPA-based hydrogels were obtained which can be used in different application areas and different volume phase transition temperatures and swelling equilibrium values close to or higher than P(NIPA). In NIPA-based hydrogels, it was proved that the desired volume phase transition temperature and the swelling equilibrium values can be reached by varying hydrophilic and hydrophobic comonomer contents. Thermal characterizations of these hydrogels were also studied. The thermal stability of synthesized hydrogels was found to be high. Because of the use of different comonomers in the production of P(NIPA) hydrogels and the increased interaction between the polymer chains, P(NIPA) hydrogels were more compact, which resulted in high mechanical strength in the hydrogels. These results showed that the use of temperature-sensitive hydrogels can be further increased.

Data Availability

The research article we submitted was prepared by Ahmet Okudan, Abdullah Altay's master's study advisor. This study was supported by Selçuk University Scientific Research Projects. The data used in the project were taken from this thesis project. The data can be seen and examined according to the mentioned master thesis.

Conflicts of Interest

The authors declare no conflict of interest. The data in this manuscript were taken from the master thesis done by Abdullah Altay, whose thesis advisor was Ahmet Okudan.

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Supplementary Materials

S1: the NIPA/AA/NTBA hydrogel. S2: the NIPA/MMA/NTBA hydrogel. S3: the NIPA/MMA/AA hydrogel. S4: dependence of the swelling ratio on temperature in pure water for P(NIPA) hydrogel. S5: dependence of swelling ratio on temperature in pure water for NIPA(50)/MMA(40)/AA(10), NIPA(50)/AA(40)/NTBA(10), and NIPA(50)/MMA(10)/NTBA(40) hydrogels. S6: dependence of the swelling ratio on temperature in pure water for NIPA(50)/MMA(10)/AA(40), NIPA(50)/AA(40)/NTBA(10), and NIPA(50)/MMA(10)/NTBA(40) hydrogels. S7: dependence of the swelling

ratio on temperature in pure water for NIPA(60)/AA(20)/NTBA(20), NIPA(60)/MMA(20)/AA(20), and NIPA(60)/MMA(20)/NTBA(20) hydrogels. S8: dependence of the swelling ratio on temperature in pure water for NIPA(60)/MMA(10)/AA(30), NIPA(60)/AA(30)/NTBA(10), and NIPA(60)/MMA(10)/NTBA(30) hydrogels. S9: dependence of the swelling ratio on temperature in pure water for NIPA(60)/MMA(30)/AA(10), NIPA(60)/MMA(30)/NTBA(10), and NIPA(60)/AA(10)/NTBA(30) hydrogels. S10: dependence of the swelling ratio on temperature in pure water for NIPA(80)/AA(10)/NTBA(10), NIPA(80)/MMA(10)/AA(10), and NIPA(80)/MMA(10)/NTBA(40) hydrogels. S11: dependence of the swelling ratio on temperature in pure water for NIPA(80)/MMA(5)/NTBA(15) and NIPA(80)/MMA(5)/AA(15) hydrogels. S12: dependence of the swelling ratio on temperature in pure water for NIPA(80)/MMA(15)/AA(5), and NIPA(80)/MMA(15)/NTBA(5) hydrogels. S13: dependence of the swelling ratio on temperature in pure water for NIPA(80)/AA(5)/NTBA(15) and NIPA(80)/AA(15)/NTBA(5) hydrogels. S14: DSC thermogram of P(NIPA) hydrogel. S15: DSC thermograms of a: (NIPAAm%80/MMA%15/NTBA%5), b: (NIPAAm%80/NTBA%15/AA%5)P(NIPA), and c: (NIPAAm%80/AA%5/NTBA%15) hydrogels. S16: DSC thermograms of d: (NIPAAm%50/AA%40/MMA%10) and e: (NIPAAm%50/AA%40/NTBA%10) hydrogels. S17: DTG thermograms of the (NIPA%80/MMA%15/NTBA%5) and b: (NIPA%80/MMA%15/AA%5) hydrogels. Scan was run at 10°C/min under nitrogen atmosphere. S18: DTG thermograms of the b: (NIPA%80/MMA%15/AA%5) and c: (NIPA%80/AA%5/NTBA%15) hydrogels. Scan was run at 10°C/min under nitrogen atmosphere. S19: DTG thermograms of the d: (NIPA%50AA%40/MMA%10/) and e: (NIPA%50/AA%40/NTBA%10) hydrogels. Scan was run at 10°C/min under nitrogen atmosphere. (*Supplementary Materials*)

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