THERMORESPONSIVE HYDROGELS OBTAINED BY GAMMA RADIATION: POLY(ALKYLENE GLYCOL) METHACRYLATES VS. POLY(N-ISOPROPYLACRYLAMIDE)

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Abstract

This study offers a comparative analysis of two most important types of thermoresponsive hydrogels: poly(N-isopropylacrylamide) (PNiPAM) and poly(alkylene glycol) methacrylates (PAGMA). The latter includes poly(oligo(ethylene glycol) methacrylate) (POEGMA), a moderately hydrophilic polymer, and poly(oligo(propylene glycol) methacrylate) (POPGMA), its more hydrophobic counterpart. The hydrogels were produced using gamma irradiation in three different solvent systems: demineralized water, a water/ethanol mixture, and pure ethanol. Gel fraction measurements were used to assess the effects of monomer type, irradiation dose, and solvent composition on crosslinking efficiency. Swelling behavior was examined over a wide temperature range, highlighting distinct thermoresponsive features and volume phase transition temperatures (VPTTs). Differential scanning calorimetry (DSC) confirmed the presence of temperature-dependent phase transitions, while structural and chemical changes caused by radiation-induced crosslinking were analyzed using Fourier-transform infrared (FTIR) spectroscopy. Results showed that effective hydrogel formation is achievable at relatively low radiation doses. The choice of synthesis medium significantly influenced the formation and the gelation efficiency of hydrogels. Particularly, PNiPAM hydrogels were successfully synthesized without the use of alcohol and still demonstrated excellent swelling capacity and VPTTs near physiological temperatures, making them suitable for biomedical applications. These findings provide valuable insights for designing advanced smart hydrogels for biomedical and environmental uses.

Keywords: *hydrogels, thermoresponsive, N-isopropylacrylamide, alkylene glycol methacrylate, gamma irradiation, DSC*

Introduction

Polymeric hydrogels based on short-chain (oligomeric) poly(alkylene glycols) monomethacrylate, such as oligo(propylene glycol) methacrylate (OPGMA) and oligo(ethylene glycol) methacrylate (OEGMA), along with hydrogels based on N-isopropylacrylamide (NiPAM), are recognized in the scientific literature as examples of smart temperature-sensitive synthetic hydrogels capable of undergoing a reversible volume change in response to temperature shifts. This behavior is governed by their volume phase transition temperature (VPTT), the critical point at which the hydrophilic-hydrophobic balance within the polymer network occurs, causing the hydrogel to swell or collapse [1].

Although both POPGMA and POEGMA hydrogels share methacrylate backbones, they differ markedly in structure and function. The methyl group on the methacrylate backbone increases hydrophobicity, enhancing the polymer's thermoresponsive behavior and supporting its widespread use in research [2]. The additional methyl group in each OPGMA monomer imparts greater hydrophobicity of POPGMA compared to POEGMA, influencing critical properties such as swelling behavior, volume phase transition temperature, and biocompatibility. POPGMA hydrogels exhibit VPTT below room temperature [3]. However, their limited water solubility and low VPTT limit their suitability for biomedical applications. To improve their biomedical applicability, particularly by tuning the VPTT toward physiological temperatures, copolymerization with more hydrophilic monomers has been investigated [3-4]. Poly(propylene glycol) (PPG) and its derivatives, including POPGMA and various block copolymers, have found use in pharmaceuticals and materials science due to their thermoresponsive nature [5-6]. Even so, publications considering POPGMA hydrogels remain significantly less studied than more established systems such as POEGMA and PNiPAM. Further systematic studies are needed to fully explore the potential of POPGMA-based hydrogels in biomedical and advanced material applications. POEGMA functions as a poly(ethylene glycol) (PEG) analog, offering advantages such as low cytotoxicity, biocompatibility, and strong resistance to protein adsorption [7]. Although various side chain lengths can be used in POEGMA synthesis, chains with 2–9 ethylene glycol repeat units are most common in biomedical applications. Compared to linear PEG, POEGMA exhibits thermoresponsive behavior (lower critical solution temperature, LCST, and VPPT) and lower immunogenicity while maintaining excellent anti-fouling properties [7].

POEGMA, POPGMA, and PNiPAM hydrogels all feature a vinyl group and amphiphilic nature, enabling unique interactions with water and other substances. PNiPAM also contains an amide group with a nitrogen atom, increasing its hydrophilicity and influencing its phase transition. Notably, PNiPAM is a widely studied thermo-responsive hydrogel, known for its sharp VPTT around 32 °C. Due to its transition occurring slightly below physiological temperature, many studies have focused on copolymerizing PNiPAM with other monomers to fine-tune its VPTT closer to physiological temperatures, making it highly suitable for biomedical applications [8].

Gamma irradiation is an efficient technique for synthesizing hydrogels, providing deep material penetration and precise control over the crosslinking process. Additionally, it allows for simultaneous sterilization, making it particularly advantageous for biomedical applications [9]. This method generates free radicals, which play a crucial role in the polymerization and crosslinking. Cobalt-60 is one of the most widely used gamma-ray sources for these processes [10]. In aqueous

environments, gamma radiation induces crosslinking reactions via a free radical mechanism, eliminating the need for external chemical initiators or activators. However, in some cases, the presence of a chemical crosslinking agent, such as EGDMA, is required to achieve the desired network structure and mechanical properties. Monomers involved in this process typically contain vinyl groups, which easily participate in radical-induced reactions, resulting in the formation of crosslinked polymer networks [11].

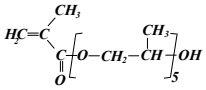
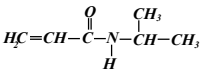
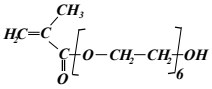
The novelty of this study lies in providing, for the first time, a detailed comparative analysis of hydrogels traditionally recognized as temperature-sensitive and evaluated for various applications, including biomedical use. In this study, we aimed to optimize the synthesis of three thermoresponsive homopolymeric networks: POPGMA, POEGMA, and PNiPAM, by investigating a range of parameters to identify the most favorable conditions. A primary objective was to determine the optimal solvent system and gamma radiation dose for forming hydrogels. Monomers were dissolved in different solvents: water, a 50/50 (v/v) water/ethanol mixture, and pure ethanol, to evaluate the effect of solvent composition on the outcome of the synthesis process. The most promising monomer/solvent combinations were then exposed to varying gamma radiation doses to assess their influence on gel content and to identify the dose that yields the highest gel content while maintaining desirable hydrogel properties for potential applications. Another key objective was to elucidate the respective advantages and limitations of PAGMAs and PNiPAM. Following gamma irradiation-induced polymerization, all samples, including monomers and xerogels, were characterized using FTIR spectroscopy, revealing the structural changes that occurred as a result of crosslinking. To assess thermal properties, DSC analysis was performed, along with swelling experiments conducted over a broad temperature range. These analyses proved the temperature-sensitive behavior of the hydrogels, highlighting their strengths, limitations, and suitability for future applications.

Experimental

Materials

The homopolymeric hydrogels were synthesized by radiation-induced polymerization using the following monomers: oligo(ethylene glycol) methacrylate, oligo(propylene glycol) methacrylate, and *N*-isopropylacrylamide (97% purity). The chemical structures, molecular weights, and labels of all monomers are provided in **tab. 1**.

Table 1. Chemical structures, molecular weights, and short labels of the monomers used in this study

Full monomer name	Monomer structure	Monomer label	M_w (g/mol)
oligo(propylene glycol) methacrylate		**OPGMA**	375
N-isopropylacryl amide		**NiPAM**	113
oligo(ethylene glycol) methacrylate		**OEGMA**	360

Ethylene glycol dimethacrylate (EGDMA, Mw = 198 g/mol) was employed as the crosslinking agent. All monomers and the crosslinker were purchased from Sigma-Aldrich and used as received. Demineralized water (Milli-Q purification system) and absolute ethanol (C_2H_5OH; Fluka, 99.8% purity) were used as solvents, either pure or as a 50/50 (v/v) mixture, for dissolving the monomers before irradiation. Buffer solution was prepared at pH 7.4 with a constant ionic strength of 0.1 mol·dm^{-}3 using potassium chloride and a phosphate buffer system comprising potassium dihydrogen phosphate and dipotassium hydrogen phosphate (Fluka). All chemicals were of analytical grade or higher and were used as received without further purification. Argon gas (Messer Tehnogas, 99.5% purity) was employed to degas the reaction mixtures prior to irradiation.

Preparation

A total of nine homopolymeric hydrogels, POEGMA, POPGMA, and PNiPAM, were synthesized via gamma radiation-induced polymerization and crosslinking, using varying radiation doses and monomer–solvent systems. Each monomer was dissolved separately in three different solvent systems: demineralized water, absolute ethanol, and a 50/50 (v/v) water/ethanol mixture. The dissolution was carried out by stirring at room temperature for 15 minutes. The monomer concentration in all formulations was maintained at 10 wt%. Ethylene glycol dimethacrylate (EGDMA) was added as a crosslinker to promote network formation [12].

To remove dissolved oxygen prior to γ-irradiation, the prepared solutions were purged with argon gas for 20 minutes and then sealed in molds constructed from two glass plates separated by a 4 mm-thick rubber spacer. The polymerization process was initiated using a cobalt-60 gamma source under ambient conditions at the Vinca Institute of Nuclear Sciences. Alanine pellets (Aerial) were used to determine the absorbed doses delivered to the samples. To reduce the uncertainty in determining the total absorbed doses, an interlaboratory comparison of the dosimetry (together with Aerial and IAEA Collaboration Centre) was performed. Irradiation was conducted at a dose rate of 0.5 kGy/h across six absorbed doses: 5, 10, 15, 25, 37, and 50 kGy. After irradiation, the hydrogels were annealed at 30 °C for 24 hours, then sectioned into discs (10 mm in diameter and 4 mm in thickness), and dried at room temperature to a constant weight, producing xerogels. Each gel formulation was prepared in triplicate to ensure reproducibility.

Sol-gel conversion

To eliminate any unreacted monomers or soluble components, all xerogels obtained after synthesis and drying were subjected to an extraction process in a sealed system under controlled temperature conditions (40 °C) for 48 hours. Following extraction, the samples were further purified by immersion in demineralized water for 5 days, then dried in a vacuum oven at 40 °C until a constant mass was achieved. The gel fraction was determined gravimetrically according to the following equation [13]:

$$\text{Gel content (\%)} = (W_e/W_0) \times 100 \quad (1)$$

where W_0 represents the initial xerogel weight and W_e is the xerogel weight after extraction.

Gel content was determined for the three homopolymeric hydrogels synthesized at 25 kGy in water, water/ethanol, and ethanol, as 25 kGy is recommended for medical sterilization [14]. Furthermore, the gel content was determined for POPGMA and POEGMA synthesized in water/ethanol and PNiPAM synthesized in pure water as a function of different absorbed radiation doses.

FTIR spectroscopy

ATR-FTIR spectra were recorded at room temperature using a Nicolet IS-50 (4000–400 cm^{-1}, 4 cm^{-1} resolution) to analyze structural changes in xerogels compared to the FTIR spectra of their monomers (OEGMA, OPGMA, and NiPAM).

Swelling measurement

The swelling behavior of the hydrogels was evaluated over a temperature range of 5–80 °C (i.e., to 85 °C in the case of POEGMA, to observe the volume phase transition occurring at elevated temperatures) in a pH 7.4 buffer solution, to assess temperature responsiveness. The equilibrium swelling degree (Q_e) was determined gravimetrically using the following equation:

$$Q_e = (W_e - W_0) / W_0 \quad (2)$$

where W_e denotes the mass of the hydrogel after reaching swelling equilibrium at a given temperature, and W_0 is the mass of the corresponding xerogel.

Each xerogel specimen was initially immersed in an excess of a pH 7.4 buffer solution at 5 °C until equilibrium swelling was achieved, after which the sample was weighed. The temperature was then increased in 2.5 °C increments every 24 hours, allowing sufficient time for equilibration at each step, following the procedure described in the literature [15]. Finally, the swelling measurements were taken at each temperature increment up to the designated temperatures.

The VPTT was determined from the Q_e versus temperature curve as the point where a notable change in slope occurred. Reported VPTT values for POPGMA, PNiPAM, and POEGMA homopolymeric hydrogels represent the average of three independently prepared samples.

Differential scanning calorimetry

DSC analyses were performed on about 5 mg xerogel samples using a TA Q2000 calorimeter (3–90 °C, 1 °C/min) under nitrogen. Samples were pre-swollen in a pH 7.4 buffer and sealed in aluminum pans, with the same buffer used as a reference. The experiments were carried out in a nitrogen atmosphere to ensure stable conditions. The onset temperature of the endothermic peak was taken as the VPTT, which corresponds to the point where polymer-water interactions, such as hydrogen bonds, begin to break. This disruption requires energy input, marking the transition from a

swollen to a collapsed polymer state and resulting in an endothermic process. The heat absorbed during this phase reflects the breaking of these hydrogen bonds between the polymer chains and the surrounding water molecules [8].

Results and discussion

To investigate suitable conditions for hydrogel synthesis, we first focused on identifying an appropriate solvent system for the monomers. Hydrogels based solely on OPGMA, NiPAM, and OEGMA were each synthesized in three different solvents: water, a 50/50 (v/v) water/ethanol mixture, and pure ethanol. The polymerization and crosslinking were initiated by gamma irradiation at an absorbed dose of 25 kGy, using a monomer concentration of 10 wt% relative to the solvent. The results of these syntheses are summarized in a **tab. 2**. Due to the poor solubility of OPGMA in water, POPGMA was the only monomer that failed to form a hydrogel under these conditions. The results suggest that the presence of alcohol is essential for the successful synthesis of POPGMA hydrogel, whereas this is not the case for PNiPAM. Although PNiPAM hydrogels were obtained in all solvent systems, those synthesized in alcohol-containing media exhibited notable limitations: hydrogels formed in the water/ethanol mixture showed poor mechanical integrity, while those prepared in pure ethanol demonstrated significantly reduced yields compared to the initial amount of monomer, suggesting that aqueous conditions are more favorable for efficient polymerization and network formation.

Table 2. Hydrogel formation from monomers in various solvents obtained via gamma radiation-induced polymerization and crosslinking

Solvent	Monomers		
	OPGMA	**NiPAM**	**OEGMA**
Water	-	+	+
Water/Ethanol (v/v)	+	+	+
Ethanol	+	+	+

*All results are obtained for 25 kGy and 10 wt% of monomers at room temperature.

The gel content refers to the fraction of the polymer network that remains after the removal of unreacted components. Based on the results obtained from syntheses performed in different solvents, gel contents were calculated for all synthesized hydrogels at a radiation dose of 25 kGy, as shown in **fig. 1**. The data illustrate the influence of solvent composition on the crosslinking efficiency and network formation in each hydrogel system**.** Excluding water as a solvent, the monomer OPGMA was found to be soluble in both a water/ethanol mixture and pure ethanol, yielding high gel contents of 94.5% and 78.4%, respectively. A similar trend was observed for OEGMA, which could be synthesized in all the mentioned solvents, with gel contents of 82.5% in water, 87.5% in a

water/ethanol mixture, and 74.1% in ethanol. PNiPAM hydrogels had 99.5% gel content in water, significantly dropping to 17.2% in water/ethanol and 39.2% in pure ethanol.

The reduced gel content of PNiPAM synthesized in water/ethanol mixtures is probably due to the cononsolvency effect [16], where the combination of two good solvents, water and ethanol, reduces polymer solubility more than either solvent alone [17]. On the other hand, some monomers and polymers that are normally insoluble in either water or ethanol on their own can become soluble when the two solvents are mixed [18]. This phenomenon, known as cosolvency, is thought to arise from alterations in how water and ethanol molecules arrange themselves around the solute [19]. In the case of PAGMA hydrogels, it is evident that the OPGMA monomer requires ethanol for dissolution, whereas OEGMA is readily soluble in both pure water and pure ethanol. Notably, both monomers show improved solubility in a 50/50 (v/v) water/ethanol mixture. This enhanced solubility correlates with higher gel content observed in both PAGMA hydrogels when prepared in the mixed solvent system, supporting the idea that the cosolvency effect plays a key role in optimizing gel formation. In other words, based on the gel phase data and some of our previous results [6], it can be confirmed that the optimal solvent for OPGMA and OEGMA is the 50/50 (v/v) water/alcohol mixture, whereas for NiPAM, water is the most suitable solvent.

The relationship between radiation dose and gel content, indicating the degree of polymerization under varying irradiation doses, is shown in **fig. 2a**. To investigate the effect of radiation dose on the degree of crosslinking and the structural integrity of the resulting hydrogels, aqueous solutions of NiPAM and water/ethanol solutions of OEGMA and OPGMA were irradiated at doses of 5, 10, 15, 25, 37, and 50 kGy. High gel content values, exceeding 70%, were obtained for all tested monomer solutions, even at the lowest dose of 5 kGy. With increasing radiation dose, a gradual rise in gel content was observed, reaching a saturation point around 25 kGy. The maximum gel content values achieved were 95% for POPGMA, 99.8% for PNiPAM, and 88% for POEGMA.

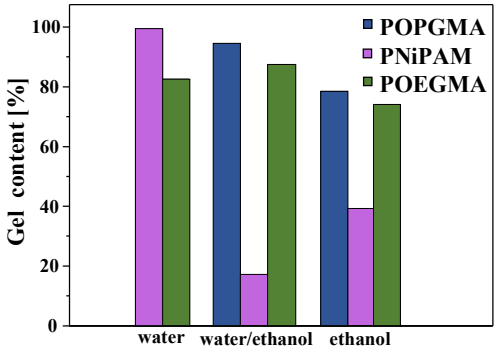


Figure 1. Gel content of three homopolymeric hydrogels (POPGMA, PNiPAM, and POEGMA) synthesized via gamma radiation (25 kGy) in different solvents: water, water/ethanol, and pure ethanol.

This study focuses on temperature-sensitive hydrogels, evaluating their swelling behavior over a wide temperature range. **Fig. 2b** presents both the swelling data and the DSC thermograms, which together provide complementary insights to identify and confirm the phase transition temperatures. Swelling studies were conducted with a very gradual 2.5 °C increase over 24 hours, allowing the hydrogels to equilibrate at each temperature step. On the other hand, DSC analyses were performed at a heating rate of 1 °C/min, which may not entirely mitigate kinetic interference. Slower heating rates are generally more effective in minimizing such effects [20]. The discrepancy in heating rates likely

accounts for the closer alignment between the inflection points of the swelling profiles, which are 13.4, 31.5, and 70.3 °C for hydrogels POPGMA, PNiPAM, and POEGMA respectively, and the onset temperatures of the thermal transitions recorded by DSC, measured at 13.7, 32.9, and 72.1 °C for the respective hydrogels. In this study, the VPTT is defined as the onset of the endothermic peak in the DSC thermograms, corresponding to the initial collapse and dehydration of the hydrogel network [8, 21]. While the peak or end temperatures of the thermal transition are also occasionally used to estimate the VPTT, they tend to show slight variation [21-23].

To investigate the molecular interactions and chemical modifications in greater detail during the hydrogel synthesis process, FTIR spectroscopy was employed. This spectroscopic analysis was conducted on the initial monomers, OPGMA, NiPAM, and OEGMA, as well as on the POPGMA, PNiPAM, and POEGMA xerogels, synthesized from the corresponding monomers (**fig. 2c**).

In OEGMA and OPGMA monomer, as well as the POEGMA and POPGMA xerogel samples, the broad, low-intensity band observed around 3400 cm^{-1} corresponds to the stretching vibrations of hydrogen-bonded hydroxyl (–OH) groups. In the single-bond region, absorption bands between 3000 and 2800 cm^{-1} are attributed to the stretching vibrations of saturated aliphatic C–H bonds from CH, CH_2, and CH_3 groups. Specifically, the band at 2970 cm^{-1} is associated with the asymmetric stretching of CH_3 groups, the band at 2930 cm^{-1} corresponds to asymmetric stretching of CH_2 groups, while the band at 2870 cm^{-1} represents the symmetric stretching of both CH_3 and CH_2 groups. Two absorption bands are expected for (P)OPGMA, one of which is at 2970 cm^{-1}, corresponding to the asymmetric stretching of CH_3 groups, that gradually diminishes toward (P)OEGMA. This behavior is attributed to the presence of an additional methyl group in each OPGMA monomer, which distinguishes it from ethylene glycol-based structures. In the region of double bonds, a characteristic absorption band of the carbonyl group (C=O) is observed between 1710 and 1730 cm^{-1}. Carbonyl bonds are highly polar, and their vibrational responses exhibit strong intensity, typically appearing as a distinct band at a well-defined wavenumber. A comparison between the spectra of the monomers and the corresponding xerogels reveals a noticeable shift in the C=O absorption peak.

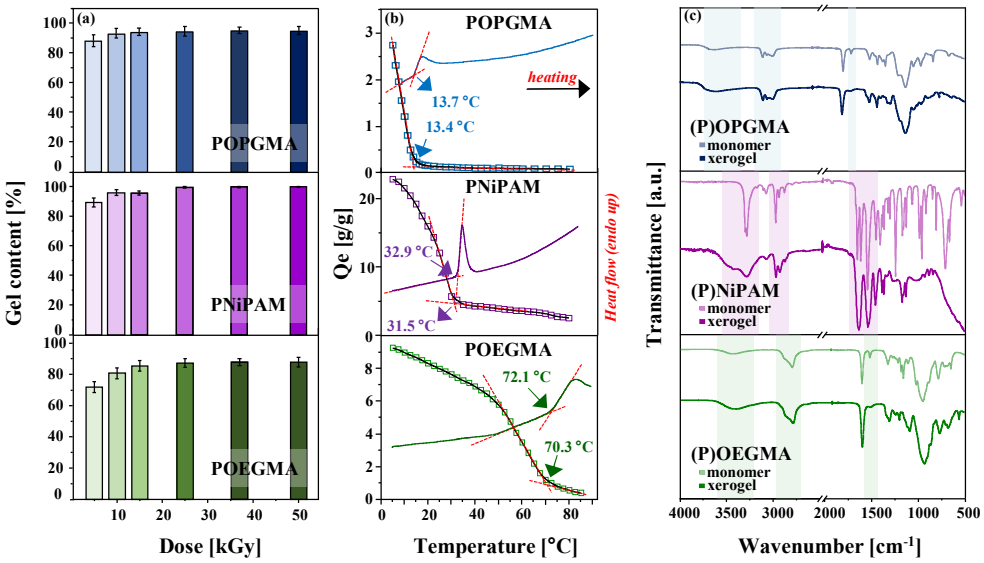


Figure 2. Physicochemical characterization of POPGMA, PNiPAM, and POEGMA hydrogels: (a) Gel content as a function of absorbed radiation dose, (b) Equilibrium swelling and DSC heating scans in pH 7.4 buffer (5–90 °C), (c) FTIR spectra of xerogels and their corresponding monomers.

The monomers contain carbonyl (C=O) groups conjugated with adjacent carbon–carbon double bonds (C=C), typically observed at around 1640 cm^{-1}. During polymerization, the alkene functionality is converted into an alkane, disrupting the conjugation with the carbonyl group. This structural change leads to a shift in the corresponding absorption peak [24]. The absence of the absorption band around 1640 cm^{-1} in the FTIR spectra of POPGMA and POEGMA xerogels indicates the consumption of C=C bonds, demonstrating effective gamma-induced crosslinking.

In the FTIR spectrum of the NiPAM monomer, a prominent absorption band appears at 3280 cm^{-1}, attributed to the stretching vibrations of the N–H bond, ν(N–H). Near 3000 cm^{-1}, additional peaks are present at 2971 and 2878 cm^{-1}, which are assigned to the asymmetric and symmetric stretching vibrations of C–H bonds in methyl groups. The presence of the isopropyl group is confirmed by absorption bands: asymmetric C–H stretching at 2935 cm^{-1}, ν_{as}(C–H), and in-plane deformation at 1369 and 1170 cm^{-1}, δ(C–H). The amide functionalities of NiPAM molecules are identified by the characteristic amide I and amide II bands at 1659 and 1550 cm^{-1}, respectively. The amide I band mainly results from the stretching of the carbonyl (C=O) group, while the amide II band involves a combination of in-plane bending vibrations of the N–H bond, δ(N–H), and stretching vibrations of the C–N bond, ν(C–N). A strong absorption band at 1620 cm^{-1} is attributed to the stretching vibration of the carbon–carbon double bond, ν(C=C). The vinyl group exhibits characteristic FTIR absorption bands of asymmetric C–H stretching at 3074 cm^{-1}, in-plane deformation at 1427 and 1458 cm^{-1}, and out-of-plane bending at 990 and 917 cm^{-1} [25].

The FTIR spectrum of the crosslinked PNiPAM hydrogel shows a reduced number of absorption bands. Compared to the NiPAM monomer, the PNiPAM spectrum contains pronounced bands associated with water, indicating high hydration and strong interactions between water and the functional groups of the gel. Significantly, the FTIR analysis was performed on the xerogel, revealing

that molecularly bound water persists within the material despite thorough drying. This retention of water is attributed to hydrogen bonding between water molecules and the PNiPAM polymer network, even when the free water is no longer present [26]. The absorption bands above and near 3000 cm^{-1} exhibit negligible shifts compared to the corresponding bands in the monomer spectrum. Comparative analysis of the spectral data reveals the disappearance of the band at 1620 cm^{-1}, attributed to the stretching vibration of the carbon–carbon double bond, ν(C=C), indicating its consumption during the crosslinking process. Following the consumption of the C=C bonds, the peaks corresponding to amide functional groups exhibit slight shifts and a noticeable broadening of their absorption bands, which can be attributed to hydrogen bonding interactions between the polymer chains and residual water molecules. Absorption bands in the IR spectrum below 1500 cm^{-1} can be attributed to vibrational modes of isopropyl and methyl functional groups, similar to the characteristic signals observed in the monomer spectrum. Their slight shifts and broadening of the spectral range can be interpreted as a consequence of crosslinking and the presence of bound water within the xerogel structure.

A digital photograph depicting the POPGMA, PNiPAM, and POEGMA xerogels and hydrogels after reaching equilibrium swelling in a pH 7.4 buffer at 5, 25, and 37 °C is presented in **tab. 3**. The visual differences in transparency clearly illustrate the thermoresponsive nature of the hydrogels and align well with the quantitative swelling data. All xerogels appear as transparent discs with an average diameter of 0.04 ± 0.01 cm. While only changes in diameter are evident in the images, it is noteworthy that temperature variations also affect the height (thickness), and thus the overall volume of hydrogels.

At 5 °C, well below the VPTT of the studied hydrogels, a significant increase in volume was observed, indicating enhanced water absorption. Upon heating to 25 °C, the most notable changes occurred in hydrogels POPGMA and PNiPAM, with their Q_e decreasing by about 96 and 47%, respectively. The considerable drop in Q_e for hydrogel POPGMA suggests a near-complete collapse of the polymer network in response to thermal stimuli. This transition was accompanied by a visible loss of transparency, likely because the measurement temperature greatly exceeded the VPTT of POPGMA. In contrast, raising the temperature to 25 °C did not cause significant changes in either transparency or Q_e of the POEGMA hydrogel. At 37 °C, the POPGMA hydrogel remained unchanged in both appearance and volume, maintaining its white, opaque state. Similarly, the POEGMA hydrogel showed minimal volume change and kept its transparent appearance. The PNiPAM hydrogel, however, displayed behavior suggestive of nearing its VPTT, with a decrease in Q_e and a temporary visual shift from white to transparent during photography, although this was not quantitatively documented. This likely results from a sharp thermal transition that occurred between the sample thermostating process and room temperature conditions.

Table 3. Digital optical images of POPGMA, PNiPAM, and POEGMA xerogels and hydrogels at 5, 25, and 37 °C with their corresponding equilibrium swelling degrees.

		POPGMA	PNiPAM	POEGMA
Xerogel				
Hydrogel	T = 5 °C	 Q_e = 2.7 g/g	 Q_e = 22.8 g/g	 Q_e = 9.3 g/g
	T = 25 °C	 Q_e = 0.1 g/g	 Q_e = 12.1 g/g	 Q_e = 8.0 g/g
	T = 37 °C	 Q_e = 0.1 g/g	 Q_e = 4.2 g/g	 Q_e = 7.2 g/g

The temperature-dependent changes in size and optical properties closely align with equilibrium swelling data, confirming the hydrogels' thermoresponsive behavior and indicating that the VPTTs of hydrogels POPGMA, PNiPAM, and POEGMA lie between 5 and 25 °C, near 37 °C, and above the studied temperature range, respectively.

Conclusion

In this study, methacrylate-based hydrogels containing ethylene glycol (EG) and propylene glycol (PG) pendant chains were investigated as potential alternatives to PNiPAM hydrogels. In comparison to POEGMA hydrogel, POPGMA hydrogel exhibited a markedly lower volume phase transition temperature, which is attributed to the reduced hydrophilicity and increased hydrophobic character of the propylene glycol side chains. Additionally, both PAGMA hydrogels exhibited VPTTs that deviated significantly from physiological conditions, whereas PNiPAM demonstrated a transition temperature close to physiological temperatures, highlighting its suitability for biomedical applications.

Gel content measurements confirmed efficient crosslinking, with values exceeding 80% at a 10 kGy dose for all hydrogels. No significant increase was observed beyond 25 kGy, indicating saturation. This dose, also recommended for medical product sterilization, was selected as optimal for synthesis and further characterization. According to gel content measurements obtained for hydrogels in different solvents, ethanol was found essential for the successful synthesis of poly(alkylene glycol) methacrylate (PAGMA) hydrogels, enhancing polymerization and crosslinking efficiency by promoting solvated coil states of the monomers. In contrast, ethanol negatively affected PNiPAM synthesis, likely due to cononsolvency effects, reducing gelation efficiency. Consequently, PNiPAM hydrogels were best synthesized in pure water, while a 50/50 (v/v) water/ethanol mixture was optimal for PAGMA hydrogels. FTIR analysis and gel content data confirmed successful polymerization and

crosslinking, while swelling behavior and DSC measurements verified the hydrogels' thermoresponsive nature, emphasizing the influence of monomer hydrophilicity on VPTT.

In summary, the optimal conditions for PAGMA hydrogel synthesis were established at a radiation dose of 25 kGy and a 50/50 (v/v) water/ethanol solvent mixture. While limitations such as modest swelling capacity, VPTTs outside the physiological range, and the requirement for alcohol reduce its suitability for certain biomedical uses, PAGMA-based hydrogels are still employed in various practical applications. On the other hand, PNiPAM hydrogels demonstrated distinct advantages, including ethanol-free synthesis, which not only simplifies processing but also lowers production costs. Combined with their high swelling capacity, physiological VPTT, and excellent gel content at low radiation doses, PNiPAM systems are particularly well-suited for green and biomedical applications.

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