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ORIGINAL PAPER

Understanding the swelling of poly (*N*-isopropyl acrylamide) gels through the study of free volume hole size distributions using positron annihilation spectroscopy

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Abstract Poly (*N*-isopropyl acrylamide) gels were prepared by UV polymerization with different degree of cross-linking in different solvents. Ethylene glycol dimethacrylate and penta-erythritol tetra-acrylate were used as cross-linkers, and methanol and dimethyl formamide (DMF) were used as solvents for gel preparation. The free volume fraction and hole size distribution in the dry gels were measured using positron annihilation lifetime spectroscopy. The equilibrium swelling of the samples in water was measured at room temperature. Both swelling properties of gels and the free volume distributions were seen to be sensitive to the amount, type, and functionality of cross-linkers as well as solvent medium used for synthesis. The gels prepared in DMF showed poor swelling properties than those prepared in methanol. The mean free volume hole size was higher while the variance of hole size distribution was smaller in the gels prepared in DMF medium compared to those prepared in methanol. The free volume fractions in the gels were found to be inversely correlated to the extent of equilibrium swelling for similar chemical compositions. The possible reasons are discussed.

Keywords Hydrogel · Free volume · Positron annihilation spectroscopy · Equilibrium swelling

Introduction

A polymer gel consists of an elastic cross-linked polymer network with fluid filling the interstitial space of network. Hydrogels, the polymer networks that swell in

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water, have received enormous attention due to their potential applications in biomedical use, drug delivery systems, separation sciences etc. Responsive gels are the systems those undergo abrupt changes during the gradual change in the state of the surroundings like pH and temperature [1]. *N*-isopropyl acrylamide (NIPA) is extensively studied starting material for thermo responsive hydrogels. NIPA has lower critical solution temperature (LCST) of about 32 °C. NIPA hydrogels shrink when the temperature is raised above LCST [2 and references there in].

The swelling dynamics of NIPA gels have been found to be very sensitive to purity of the raw material used in the preparation, the functionality or nature of cross-linkers used, preparation conditions, and the ionic strength of the solvents etc. [3]. A number of research works have been carried out to improve the swelling kinetics of these gels by altering the preparation procedures and introducing other copolymers into the gel network [3, 4].

The sensitivity of the swelling properties of the NIPA gel to the preparation conditions is well known. The NIPA gels prepared in mixed solvents of water and acetone showed faster kinetic in swelling and collapsing [4]. The gels prepared in water were found to swell less than the gels prepared in ethanol, acetone, and dimethyl formamide (DMF) [5]. Many studies have been carried out to understand the correlation between the physicochemical properties of the gels and their swelling dynamics using differential scanning calorimetry, electron paramagnetic resonance spectroscopy, nuclear magnetic resonance spectroscopy etc. [6–8]. However, the complete understanding about the role of the physico-chemical parameters to the phase transition as well as the swelling dynamics of the gel is still debatable [7].

The present work aims at understanding the role of the cross-linker and preparation conditions to the swelling properties of the NIPA gel. The different nature of the cross-linkers and the synthesis solvents causes the modification of the free volume hole size distribution in the polymer gel. Hence our focus is to understand the effect of free volume hole size distribution on the swelling of the NIPA gel. The free volume hole size distribution in the NIPA gel have been measured using positron annihilation lifetime spectroscopy (PALS). The PALS is known to be an extremely sensitive technique to measure the free volume hole size distribution in various polymeric materials [9, 10]. There are few reports on the positron annihilation lifetime studies on acrylamide based gels [11, 12]. However, systematic studies to understand the correlation between the free volume of the gels and their ability to swell are lacking [13]. In order to understand the correlation between these two, the NIPA gels with various amounts of cross-linker were prepared in methanol and DMF solvents using UV polymerization. Though both DMF and methanol are amphiphillic solvents, DMF is an aprotic and more polar than methanol [14, 15]. Ethylene glycol dimethacrylate (EGDM) and penta-erythritol tetra-acrylate (PETA) were used as cross-linkers. EGDM is glycol derivative and straight chain cross-linker with a four functionality, where as PETA is an erythritol derivative, hydrophobic in nature and branched cross-linker with an eight functionality. The equilibrium swelling ratio of the prepared gels has been determined by measuring the water uptake efficiency. The free volumes in the dry gels have been measured at room temperature using PALS.

Experimental

Materials

N-isopropyl acrylamide monomer (NIPAm), EGDM, PETA, and α,α-dimethoxy-α-phenylacetophenone (DMPAP) used in this study were of laboratory grade chemicals and used without any further purification. All other chemicals used were of AnalR grade purity. The distilled deionized water was used for swelling measurements.

Polymerization

The cross-linked network of NIPA was prepared by the free radical polymerization method. 1.0 g NIPA was dissolved in 1 ml of solvent (methanol or DMF as the case may be). 0.01 g of DMPAP (1 wt% with respect to the monomer) was added as photo initiator. The solution was sonicated and purged with nitrogen to remove residual oxygen. The desired amount of cross-linker (EGDM or PETA), as the case may be, was dissolved in another 1 ml of solvent. The solutions were mixed to make up the final volume to 2 ml and placed under the UV-irradiation chamber (HEBER multiphoto reactor, HEBER Scientific) for 20 min at wavelength 365 nm. The schematic of the synthesis of the gels is illustrated in Fig. 1. The gels were then immersed in excess distilled deionized water for 30 min to remove unreacted contents. The gels were alternately washed with deionized water and solvent used in synthesis and were dried in a vacuum oven at 50 °C until constant weight is obtained. These samples are referred in the further discussion as "dry gels." The polymer gels prepared are denoted by the number of moles of the cross-linker per 100 mol of NIPAm and the solvent used for synthesis. For example, 3% EGDM–DMF indicates 1 g NIPAm, 3 mol of EGDM per 100 mol of NIPAm, and DMF is used as solvent during synthesis.

PALS measurement and data analysis

The PALS measurements were carried out using a fast–fast coincidence system consisting of plastic scintillation detectors. The time resolution of the positron lifetime spectrometer measured for gamma-rays of ^{60}Co was 250 ps. ^{22}Na (15 μCi) deposited on 8 μm thick Kapton film was used as positron source. The positron source was sandwiched between two pieces of dried gel and wrapped in an aluminum foil. Total area under each lifetime spectra was about 10^6. All the measurements were performed at room temperature.

The positron lifetime spectra were fitted using PATFIT-88 [16]. The longest lived lifetime component corresponds to the o-Ps pick-off annihilation from the free volume holes. The free volume hole radii were calculated from o-Ps pick-off lifetime (τ_3) using the well known semi-empirical relation [17, 18], given as

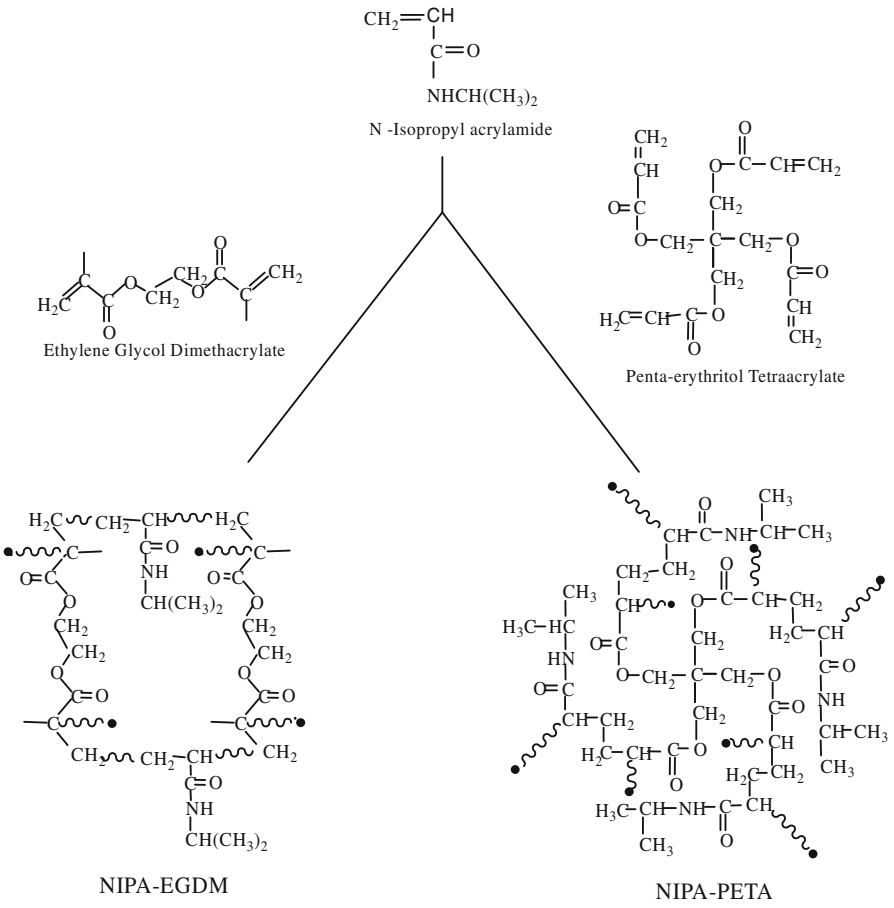

Fig. 1 Schematic of synthesis of NIPA gels

$$\frac{1}{\tau_3} = \lambda_3(\mathrm{ns}^{-1}) = 2 \times \left(1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi}\sin\left(\frac{2\pi R}{R + \Delta R}\right)\right), \tag{1}$$

where τ_3 is the o-Ps lifetime in nanoseconds (ns), R the mean radius of free volume holes in nanometer, and ΔR the fitted empirical electron layer thickness (0.166 nm). The product of the hole volume and the o-Ps intensity is proportional to the free volume fraction for chemically similar samples. The fractional free volume is calculated using the following relation

$$f_\mathrm{V} = C \cdot V_\mathrm{f} \cdot I_3, \tag{2}$$

where V_f is the volume of the holes calculated using radius R obtained from Eq. 1, I_3 the intensity (%) of the o-Ps pick-off lifetime component in the spectra, and C an empirical constant (0.018 nm^{-3}) [19].

The free volume hole size and hence the o-Ps lifetime, index of hole size, is expected to have a distribution. Therefore, the positron lifetime spectra were analyzed for continuous distribution of lifetimes using Laplace inversion technique, CONTIN [20] to obtain the decay profile ($\lambda\alpha(\lambda)$ versus λ). Using the relation between the o-Ps annihilation rate and the free volume hole radius (Eq. 1) and considering the difference in the o-Ps capture probability in different hole sizes [21], the free volume hole radius probability density $f(R)$ was calculated as:

$$f(R) = -2\Delta R\left[\cos\left(\frac{2\pi R}{R+\Delta R}\right) - 1\right].\frac{\alpha(\lambda)}{(R+\Delta R)^2(1+8R)}. \quad (3)$$

The free volume hole radius distribution was fitted to the Gaussian function and the relative widths of radius distribution in all the gel samples were calculated as:

$$\text{Relative width} = \frac{\text{FWHM}}{\text{Peak Position}} \times 100. \quad (4)$$

The positron annihilation lifetime spectrum of silicon single crystal was used as reference in analyzing the lifetime spectra.

Swelling studies

The dry gel samples of known weight were immersed in deionized water at desired temperature for 2 h to attain the equilibrium. From the initial studies on swelling kinetics, it was found that 2 h were sufficient to attain the equilibrium swelling. The samples were removed from water and weighed after the excess water was blotted with tissue paper. The percent equilibrium swelling (PES) was calculated as:

$$\text{PES} = \frac{W_w - W_d}{W_d} \times 100, \quad (5)$$

where W_w is the weight of the swollen gel and W_d is the weight of dry gel

Result and discussions

Positron annihilation studies

The NIPA gels were prepared with cross-linker amounts in the range of 3 to 10 mol.% with respect to the NIPAm. The positron annihilation lifetime spectra of all the dry gels could be successfully fitted to three lifetime components. The variance of the fit was close to 1. The shortest lived component (τ_1) of 125 ps corresponding to p-Ps lifetime was fixed. The second component (τ_2) was in the range of 300 to 340 ps corresponds to free positron annihilation in the samples. The longest lived component (τ_3), which is of our paramount interest, varied between 1.6 to 2.3 ns. The o-Ps lifetimes and intensities (τ_3 and I_3) are summarized in Table 1. Attempts to measure positron lifetime (and free volume) in swollen gels were not fruitful as all the samples yielded a constant τ_3 close to that of positronium lifetime

Table 1 The o-Ps lifetimes and intensities in the dried NIPA gel samples

Cross-linker (mol.%)	τ_3 (ns)	I_3 (%)
EGDM–MeOH		
5	1.75 ± 0.01	20.8 ± 0.2
7	1.98 ± 0.01	16.7 ± 0.1
8.5	1.90 ± 0.01	23.7 ± 0.2
10	1.74 ± 0.01	16.8 ± 0.2
PETA–MeOH		
3	1.75 ± 0.01	22.9 ± 0.2
5	1.79 ± 0.01	23.1 ± 0.2
7	1.74 ± 0.01	20.2 ± 0.2
8.5	1.82 ± 0.01	22.1 ± 0.2
10	1.81 ± 0.01	20.5 ± 0.2
EGDM–DMF		
3	2.17 ± 0.01	20.6 ± 0.1
5	2.10 ± 0.01	20.4 ± 0.1
7	2.13 ± 0.01	21.4 ± 0.1
8.5	2.24 ± 0.01	19.7 ± 0.1
10	2.14 ± 0.01	20.2 ± 0.2
PETA–DMF		
3	2.14 ± 0.01	21.1 ± 0.1
5	2.03 ± 0.01	20.8 ± 0.1
7	2.08 ± 0.01	20.7 ± 0.1
8.5	2.07 ± 0.01	21.0 ± 0.1
10	2.04 ± 0.01	21.3 ± 0.1

in water [11, 22]. This shows that most of the positrons annihilate in water present inside the swollen gels. The free volume fractions in all the dry gel samples have been calculated from positronium pick-off annihilation parameters (using Eqs. 1 and 2), and its variation with amount of cross-linker is shown in Fig. 2. The free volume fraction did not change much with the amount of cross-linker. There was drastic difference in the fractional free volume between the gels prepared in DMF and methanol. The gels prepared in DMF showed very high fractional free volume in their dry state than the gels prepared in methanol. Among the gels prepared in DMF, the gels with PETA cross-linker showed lower free volume fraction than the EGDM cross-linker. However, the variation of fractional free volume with the type of cross-linker in the gels prepared in methanol was not very distinct.

In order to get better insight into the parameters influencing these free volume fractions, the free volume hole size distributions in these samples have been calculated from the o-Ps lifetime distributions. The free volume hole size distribution in the samples are shown in Fig. 3, which shows that the mean free volume hole size in the samples prepared in DMF is higher than the samples prepared in methanol. The hole size distribution is fitted to the Gaussian function and the relative widths (width × 100/mean) in all the samples are shown in Fig. 4. On an average, the relative widths of radius distributions are smaller in the samples prepared in DMF

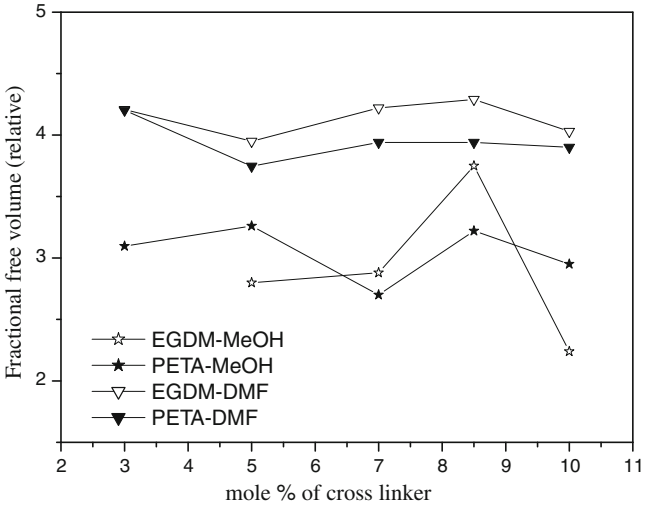

Fig. 2 Relative free volume fraction (f_V) of NIPA gels in dry state

than samples prepared in methanol. In both the samples, the gels with PETA cross-linker showed larger relative widths than the gels with EGDM as cross-linker.

The width of hole size distribution and free volume fractions are influenced by the cross-linker and the solvent. PETA is a branched cross-linker with octo-functionality, which causes faster gelation than that caused by linear EGDM cross-linker with tetra-functionality. The faster gelation leads to the non-uniformity in polymer chains, which, in turn, results in the broader distribution of free volume hole radius. This distinction is more evident in the samples prepared in DMF. However, DMF is a better solvent for the monomers and cross-linkers used. Consequently, it is better medium for polymerization reactions than the methanol [15]. Hence, the samples prepared in DMF are expected to be more uniformly cross-linked than the samples prepared in methanol. The packing of uniform sized molecular chains leads to larger free volume than the packing of chains with broader size distributions. Thus, the larger free volume fraction in the samples prepared in DMF shows that the polymer is more uniformly cross-linked. The narrower free volume hole size distribution (small relative width) also shows that the DMF helps in more uniform cross-linking than the methanol.

Swelling studies

The PES of all the samples at room temperature is shown in Fig. 5. It is seen that, the gels formed in DMF and methanol solvents exhibited different swelling behavior. Also, even in the same solvent, the gels formed using different cross-linkers (PETA and EGDM) showed different swelling properties. It is generally expected that higher free volume fraction should facilitate the water uptake and results in higher PES. Conversely, the gels having high entanglement of molecular chains with smaller free volume fraction should exhibit poor swelling. Based on the

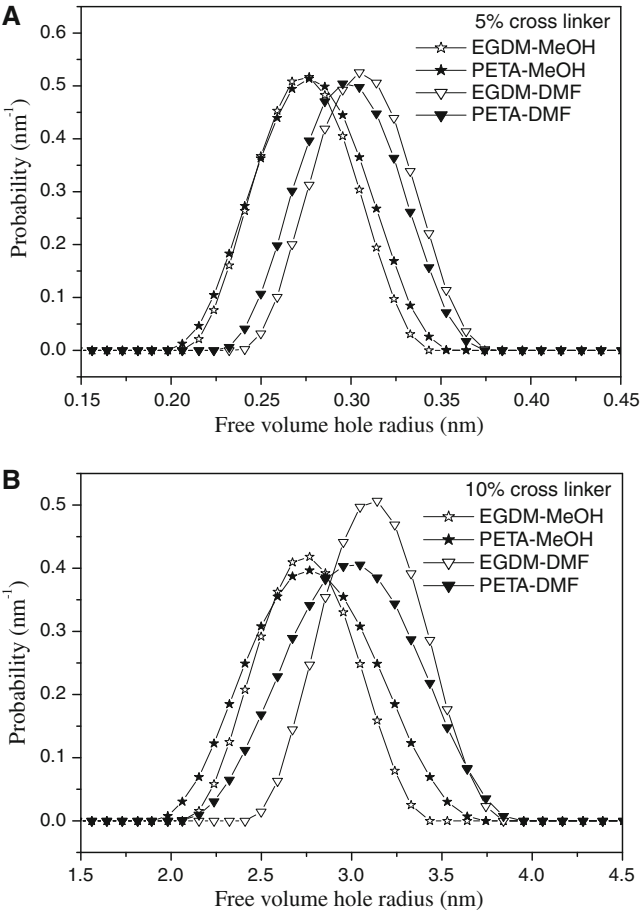

Fig. 3 Typical free volume hole radius distribution in NIPA gels. The concentration of cross-linker is **A** 5 mol.% and **B** 10 mol.% with respect to monomer

above expectation, the gels prepared in DMF should show more swelling than the gels prepared in methanol; on the other hand, the EGDM cross-linked gels should show more swelling than PETA cross-linked gels. Besides the free volume effect, it is also reported that the higher functionality of the cross-linker favors the swelling of the gels. This may be due to the presence of the dangling chains or network chains having one end attached at the cross-link point and other unattached to the network. These dangling chains contribute to the swelling of the polymer by the solvent. Based on this argument, PETA cross-linked gels should have better swelling over EGDM [23].

However, it is seen in Fig. 5 that the gels prepared in methanol with smaller free volume fractions show higher swelling as compared to the gels prepared in DMF having larger free volume fractions. Nevertheless, the swelling of the EGDM cross-linked gels is seen to be higher than that of the PETA cross-linked gels, which is in

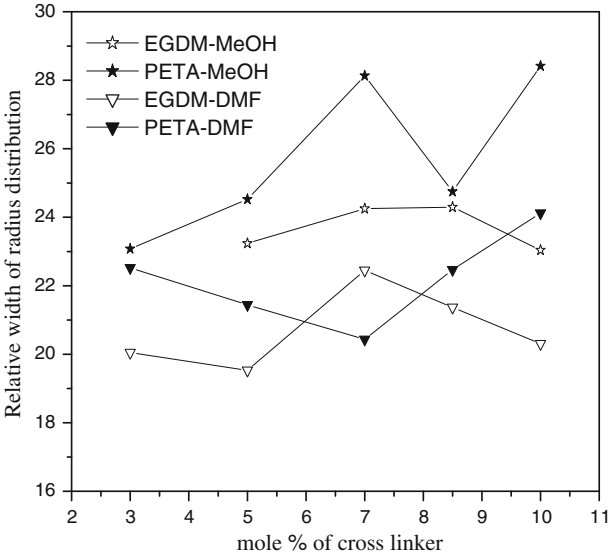

Fig. 4 Relative width of radius distribution in the NIPA gels

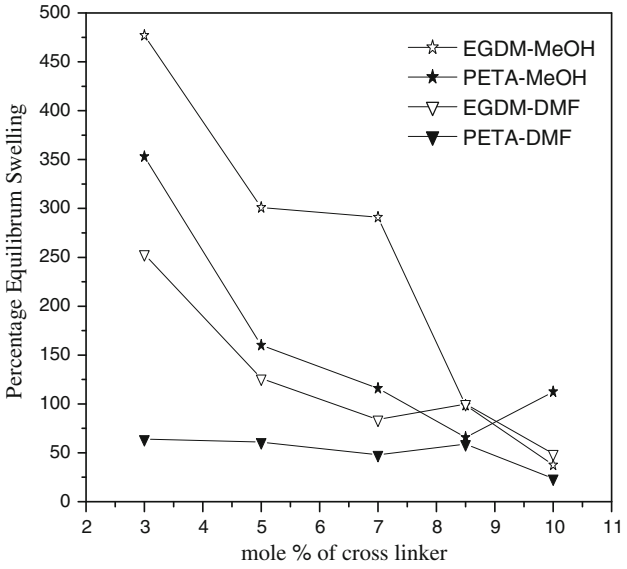

Fig. 5 Percentage equilibrium swelling of NIPA gels in water at 25 °C

line with expectations based on free volumes as the linear EGDM causes less rigid cross-linking with larger free volume than the branched PETA. Also, it is seen that the equilibrium swelling ratio decreases with the increase in the mole fraction of cross-linker. As the amount of cross-linker increases, the polymer becomes more rigid due to the increase in cross-link density, which results in decrease in the

swelling [3]. However, the unusual swelling behavior of the gels formed in DMF and methanol solvents may depend on the free volume hole size distribution. The relative widths of free volume distribution of gels prepared in methanol are higher. This shows non-uniform cross-linking as the packing of molecular chains of non-uniform size is leading to smaller free volume fraction but broader hole size distribution. Whereas, the more uniform cross-linking in DMF leads to large free volume fractions with narrower hole size distribution. This suggests that non-uniform cross-linking may favor the water uptake by the gels. The larger swelling in the gels prepared by electron beam irradiation than the gels prepared in γ-irradiation also points toward this [11].

The PETA cross-linked gels showed poor swelling even with broad free volume hole size distribution and higher functionality. Even with the faster gelation and non-uniform cross-linking, the higher functionality in PETA also results into the high cross-link density in the gel samples. The higher cross-link density along with more hydrophobic nature (as it is erythritol derivative) might be responsible for the poor swelling of PETA cross-linked gels.

The results suggest that, if the nature of the cross-linker is same, the larger free volume hole size distributions may favor the swelling as shown by the gels prepared in different solvents. However, the larger cross-link densities make the gels more rigid and reduce the swelling drastically.

Conclusion

The NIPA gels prepared in DMF solvent showed low swelling in water, although it has large free volume fractions in dry state as compared to gels prepared in methanol solvent. However, the relative width of free volume hole radius distribution is higher for the gels prepared in methanol. As DMF is aprotic solvent, it is suitable for polymerization and leads to homogenous cross-linking with high rigidity making both swelling and collapsing difficult. On the other hand, methanol forms inhomogeneous cross-linking with low rigid structure, which easily swells and collapses (shrinks). The inhomogeneous cross-linking or cluster formation results in broader free volume hole size distribution. Contrary to this observation, all PETA cross-linked hydrogels with broader distribution of free volume hole size showed lower swelling than EGDM cross-linked gels. This shows that the functionality of cross-linker. The hydrophobic nature and the rigidity of chains caused by cross-linker also plays an important role along with the free volume hole size distribution in determining the swelling behavior.

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