

Thermodynamics of swelling of poly (NIPAM-co-NTBA-co-MAAm) hydrogels

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Abstract : In the present study, the swelling properties of poly (NIPAM-co-NTBA-co-MAAm) hydrogels have been discussed. The enthalpy change of mixing " H_{mix} ", entropy change of mixing " S_{mix} ", free energy change of mixing " G_{mix} " were determined for swelling of hydrogels at 25°C. The values of " H_{mix} " and " S_{mix} " increase and " G_{mix} " decrease with increasing amount of crosslinker MBA from 0.03 to 0.12 molar concentrations which further decreased and increased, respectively beyond 0.12 to 0.2 molar concentration of MBA. The values of " G_{cla} " are found to be increased with increasing the crosslinking ratio followed by decrease in swelling percentage. At all temperatures the equilibrium swelling percentage of the hydrogels are found to be increased with decreasing the crosslinking ratio.

(Keywords : NIPAM, swelling percentage, thermodynamic properties)

Introduction

Poly N-isopropylacrylamide (PNIPAM) based thermoresponsive hydrogels are of interest in various fields of biotechnology, biomedical and drug delivery owing to their ability to change their physiological properties in response to temperature¹⁻³. Swelling behaviour across the ambient temperature of these hydrogels play a vital role for concerned applications which need the fundamental understanding of swelling behavior of the hydrogels with water.⁴ Swelling behaviour may be affected by the environmental temperature, network structure and thermodynamics of diffusion mechanism of water into hydrogels.^{5,6} Flory and Rehner kept the foot print and given basic thermodynamic framework for analyzing the

swelling of hydrogel⁷⁻⁹ which was further modified by Tanaka and workers¹⁰. Zhang et al. extended the previous thermodynamic models to include the effects of salts and fixed charge on polymer¹¹. Most applications of these thermodynamic models focused on the gel swelling behaviour of the hydrogels. Some experimental observations look forward to explanations and demand deeper understanding of water diffusion characteristics into hydrogels from thermodynamics perspective.

The main aim of current research work was to gain insight into the thermodynamics of swelling poly(NIPAM-co-NTBA-co-MAAm) terpolymeric hydrogels. Attempts have been made to synthesize the poly(NIPAM-co-NTBA-co-MAAm) hydrogels by free radical polymerization keeping constant molar ratio of NIPAM, NTBA and MAAm and varying the molar concentration of crosslinking agent methylene-bis-acrylamide (MBA). The thermodynamics of swelling behaviour of poly(NIPAM-co-NTBA-co-MAAm) hydrogels were discussed using Flory-Rehner theory. Also, effects of temperatures on the swelling of hydrogels were studied.

2. Experimental

2.1 Materials

NIPAM, NTBA and MAAm monomer was purchased from TCI, USA. The other chemicals N,N-methylene-bisacrylamide (MBA), Ammonium persulfate (APS) and N,N,N,N-tetramethylene-diamine (TEMED) from Central Drug House Ltd. Co., India were used as cross-linking agent, initiator and accelerator, respectively. 1,4-

Dioxane was also obtained from Central Drug House Ltd. Co., India. All other reagents were of AR grade and double distilled water was used for swelling and deswelling studies.

2.2 Hydrogel Preparation

NIPAM, NTBA, and MAAm random copolymers with different compositions were prepared by free radical polymerization (12). In the copolymerization process NIPAM, NTBA and MAAm were dissolved in a mixture of doubly distilled water and 1, 4-dioxane (1:2 vol). After dissolution crosslinking agent MBA and initiator APS (1 mole % in terms of monomer) was added consequently and stirred for dissolution. After few minutes the accelerator TEMED (0.25 ml

solution (0.3 ml in 1.5 ml water)) was mixed. After completion of the reaction (24 hours) the hydrogel was removed washed 8-10 times with distilled water followed by SOXHLET extraction for 10-12 cycles with 1-4 dioxane to remove the unreacted monomer, linear homopolymer and physically entrapped chemicals within the gel. After washing the prepared gels were dried at room temperature for 2-4 days. Subsequently they were dried in vacuum oven for 48 hrs at about 80 °C until constant weight.

The compositions for the production of poly (NIPAM-co-NTBA-co-MAAm) copolymers are summarized in the following Table 1:

Table 1:

The different proportions of monomers and reagents in copolymer composition

NIPAM/NTBA/MAAm (Molar ratio)	MBA (moles) $\times 10^{-8}$	APS (moles) $\times 10^{-4}$	TEMED (20 vol %)	Nomenclature
25/37.5/37.5	0.03	1.85	0.25	NTM1
25/37.5/37.5	0.06	1.85	0.25	NTM2
25/37.5/37.5	0.12	1.85	0.25	NTM3
25/37.5/37.5	0.15	1.85	0.25	NTM4
25/37.5/37.5	0.20	1.85	0.25	NTM5

2.3 Characterizations

2.3.1 Swelling and deswelling behaviour

Swelling measurement was carried out in constant temperature water bath and the swelling percentages were calculated by using following equation (1),

$$\%Swelling = \frac{m_t - m_d}{m_d} \times 100 \quad (1)$$

Where m_d is the dry weight of hydrogel and m_t is the weight of swollen hydrogel at different time intervals.

3. Results and Discussion

3.1 Thermodynamics of swelling

The swelling of polymeric networks can be explained by Flory and Rehner mathematical model which demonstrates that the equilibrium swelling of hydrogel are attained by balancing the mixing and elastic contributions to the osmotic

pressure^{7-9, 13}. The free energy change can be given as sum of free energy of mixing (ΔG_M) and the elastic free energy (ΔG_{el}) can be expressed as follows⁷⁻⁹,

$$\Delta G = \Delta G_M + \Delta G_{el} \quad (2)$$

$$\Delta G_M = \Delta H_M - T\Delta S_M^* = RT[(n_1 \ln f_1) + \chi n_1 \phi] \quad (3)$$

$$\Delta G_{el} = -\frac{RT n_e}{2} \left(3 \left(\frac{V}{V_0} \right)^{2/3} - 3 - \ln \left(\frac{V}{V_0} \right) \right) \quad (4)$$

Putting the value of equation 3 and 4 we can write

$$\Delta G = RT[(n_1 \ln f_1) + \chi n_1 \phi] + \left[\frac{RT n_e}{2} \left(3 \left(\frac{V}{V_0} \right)^{2/3} - 3 - \ln \left(\frac{V}{V_0} \right) \right) \right] \quad (5)$$

ΔG is the total change in the Gibbs free energy for isotropic swelling. n_1 is the no of moles of solvent and f_1 and ϕ represent the volume frac-

tion of the solvent and polymer, respectively. The increase in configurational entropy (S_M^*) representing the total entropy change due to mixing (S_M^*) and χ represents the flory-Huggins polymer-solvent interaction parameter signifying the nature of mixing (>0 signifies the mixing as endothermic and as exothermic). Generally, poly-

mer solvent mixing belongs to >0 . $n_c = v_c / N_A$ and R the universal gas constant, v_1 is molar volume of the solvent. To evaluate the above parameters, five hydrogel samples, with varying crosslinking ratio were allowed to swell in distilled water at 25°C and their mass measurement has been done at different time intervals till attainment of equilibrium swelling.

Table - 2
Thermodynamic parameters of hydrogels with varying crosslinking ratio

Samples	ΔS_{mix}	ΔH_{mix}	ΔG_{mix}	$\Delta G_{elastic}$	Total free energy ($\Delta G_{mix} + \Delta G_{el}$)
NTM 1	0.349541	52.82746	-51.3359	0.038756	-51.2971
NTM 2	0.57554	87.11066	-84.4004	0.033482	-84.3669
NTM 3	0.763959	113.1451	-114.515	0.048048	-114.466
NTM 4	0.63615	81.60474	-107.968	0.084382	-107.884
NTM 5	0.551318	68.55813	-95.7347	0.336109	-95.3986

The results of H_{mix} , S_{mix} and G_{mix} are displayed in Table 1. It is seen that the negative signs of total free energy ($G_{mix} + G_{el}$) are indicate that the NTM hydrogels studied in the present work have LCST's. Moreover, the values of H_{mix} and S_{mix} increase and G_{mix} decrease with increasing amount of crosslinker MBA from 0.03 to 0.12 molar concentrations indicating that the thermoresponsive properties of the hydrogels increase with increasing crosslinking ratio [14]. After 0.12 to 0.2 molar concentration of MBA the value of H_{mix} and S_{mix} decrease and G_{mix} increase which shows the decreasing thermosensitivity of the hydrogels. The value of G_{ela} are found to be increased with increasing the crosslinking ratio followed by decrease in swelling percentage. The increase in G_{ela} may be attributed to hydrophobic interaction showing their thermoresponsive behaviour.

3.2 Effect of temperature on swelling

The temperature dependence swelling ratio of poly (NIPAM-co-NTBA-co-MAAm) was examined to evaluate the effect of temperature on

copolymer gel. The copolymers were prepared for different concentration of MBA and their swelling study was observed gravimetrically. As evident from Table 2, the equilibrium swelling percentage of poly (NIPAM-co-NTBA-co-MAAm) is decreased with increasing the temperature. As the MBA proportion in the copolymer increases the swelling percentage decreases. All the hydrogels are showing thermosensitivity in the broader temperature range.

3.9 Conclusions

Poly(NIPAM-co-NTBA-co-MAAm) hydrogels synthesized varying the relative amount of the MBA as a crosslinker could be used as an alternative of PNIPAM in the various applications. Thermodynamics of swelling revealed that the NTM having different MBA concentration can also be used in agriculture field for water absorption, sanitary napkins, concentration of sludge, etc. This study may represent the first step towards a full understanding of the correlation between swelling and thermodynamic properties for Poly (NIPAM-co-NTBA-co-MAAm) hydrogels .

Table 2 Equilibrium swelling percentage of hydrogels at 5, 10, 15, 25, 40, 50 and 60°C

Temperature (°C)	Equilibrium Swelling percentage				
	NTA1	NTA2	NTA3	NTA4	NTA5
5	2800	2260	1295	605	501
10	2132	1896	885	315	215
15	1623	1536	501	205	142
25	1185	785	412	149	132
40	65	59	46	41	34
50	50	48	38	30	21

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