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Compressive Elastic Moduli of Poly(N-Isopropylacrylamide) Hydrogels Crosslinked with Poly(Dimethyl Siloxane)

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Hydrophobically modified and thermally reversible neutral and ionic copolymer hydrogels were prepared from N-isopropylacrylamide (NIPAAm), vinyl terminated poly (dimethylsiloxane) (VTPDMS) and itaconic acid (IA) by free radical solution polymerization, and their properties such as swelling ratio and compression modulus were studied at the 25°C. The incorporation of VTPDMS as a hydrophobic macrocrosslinker into the structures of neutral NIPAAm hydrogels increased their mechanical strength around 10 times than those of the ones crosslinked with conventional tetra functional monomer, i.e., N,N'-methylene bisacrylamide (BIS). Compression modulus decreased with an increase in IA content for ionic samples and increased with increasing molecular weight and content of VTPDMS for neutral samples. It was assumed that in the first case, electrostatic repulsive forces resulting from the ionized carboxyl groups of IA were responsible for decreasing mechanical strength, while in the second case, hydrophobic interactions between dimethylsiloxane units of VTPDMS chains enhanced the compression moduli. According to the results presented in this work, it can be said that the right balance of hydrophobic and hydrophilic constituents and adjustment of the number of ionized groups, as well as cross-linking degree, change the structure and physical properties of NIPAAm hydrogels.

Keywords poly(N-isopropylacrylamide), poly(itaconic acid), poly(dimethylsiloxane), mechanical strength, compression modulus

Introduction

Hydrogels containing sensor properties and designated as “smart” materials can undergo volume phase transition upon the changes in the environmental conditions such as composition, ionic strength and pH of the swelling medium, temperature, UV-light and electric field (1–6). Inverse temperature-sensitive hydrogels are made of hydrophobic polymer chains and used for biomedical applications such as selective membranes, enzyme activity controlling and drug delivery systems. Poly(N-isopropylacrylamide) (PNIPAAm) is the most widely used member of this type of polymer system because of its lower critical solution temperature (LCST) around 32°C, close to the body temperature (7–9).

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It is known that synthesis method and temperature, synthesis-solvent composition, type and concentration of initiator, monomer, comonomer crosslinker have important effects on both swelling and mechanical properties of NIPAAm hydrogels (10–19). Pure NIPAAm hydrogels crosslinked by using hydrophilic tetrafunctional N,N' -methylene bisacrylamide (BIS) and octafunctional glyoxal bis (diallyl acetal) (GLY) as crosslinker have low mechanical strength in the swollen state, i.e., below LCST (20). The combination of large swelling and high mechanical performance within the same gel structure is important for both industrial and biomechanical applications. The formation of hydrophobically modified copolymers, nanocomposite gels and double networks by incorporation of hydrophobic components into the hydrogel structure can be given as the main examples of the methods which are used to improve the mechanical properties (21–25).

In this study, hydrogels composed of NIPAAm, BIS, vinyl terminated poly(dimethyl siloxane) (VTPDMS) (commercial product) and itaconic acid (IA) as hydrophobic monomer, hydrophilic crosslinker, hydrophobic crosslinker and weakly ionizable comonomer, respectively, were prepared to investigate the effect of hydrophobic component, i.e., VTPDMS on the compression moduli of the samples attained equilibrium swollen state in distilled-deionized water at 25°C. For mechanical strength analysis, conventional rubber elasticity and swelling theories for networks formed in the presence of diluent were adopted. The second one deals with neutral polymer chains. From the swelling and compression measurements, effective crosslinking density ν_e , average molecular weight between crosslinks M_c and polymer-water interaction parameter χ , which can be used to characterize the structures of the hydrogels, were calculated.

Experimental

Materials

Hydrophobic monomer, N -isopropylacrylamide (NIPAAm; Aldrich); hydrophilic comonomer, itaconic acid (IA; Fluka); hydrophobic crosslinkers, α,ω -acryloxyorgano-functional poly(dimethylsiloxane) vinyl terminated PDMS (VTPDMS); Tegomer V-Si 2250 ($n \sim 20$, $5 < m < 10$) and Tegomer V-Si 2150 ($n \sim 10$, $5 < m < 10$), Goldschmidt AG); hydrophilic crosslinker, N,N' -methylenebisacrylamide (BIS; Merck) were used without any purification. The activator and initiator, tetramethylethylenediamine (TEMED) and potassium persulfate (KPS), were used as purchased from Merck A. G. Azobis(isobutyronitrile) (AIBN; Merck) was recrystallized from chloroform. 1,4-dioxane, methanol (Merck) and distilled-deionized water were used as solvents for polymerizations and swelling measurements.

Hydrogel Preparation

Hydrogels were synthesized by free radical solution polymerizations of NIPAAm (0.7 and 2.0 mol/L) with a weakly ionizable comonomer, IA ($pK_1 = 3.85$ and $pK_2 = 5.45$) and two different crosslinking agents. Three types of NIPAAm gels were prepared: (1) The networks made of neutral NIPAAm chains and crosslinked with hydrophilic tetrafunctional constituent (BIS); (2) the neutral NIPAAm hydrogels containing hydrophobic and tetra functional macrocrosslinker (VTPDMS); (3) negatively ionizable hydrogels containing 1.0–7.5 mol% of IA with respect to total principal monomer, i.e., NIPAAm.

1. The gelation solutions containing NIPAAm (0.7 and 2.0 mol/L), BIS (1.25×10^{-2} and 2.50×10^{-2} mol/L) and KPS/TEMED (1.50×10^{-2} mol/L, for each constituent

of redox initiator pair) were prepared using a 40/60 mixture of distilled-deionized water/methanol (v/v%) as a polymerization solvent. The pre-gel solutions introduced into glass tubes of ~ 10 mm inner diameter were placed vertically in a large glass tube that was closed tightly with a rubber cap, then filled oxygen-free nitrogen by using a syringe, and placed in a thermostat at 25°C for 3 days.

2. The gels were prepared by free radical crosslinking polymerizations at 60°C under nitrogen atmosphere for 3 days. Monomer (2.0 mol/L), VTPDMS ($(1.25 \times 10^{-2}$ and 2.50×10^{-2} mol/L) and AIBN (5.8×10^{-3} mol/L) were dissolved in 1,4-dioxane. The polymerization mixtures loaded in test tubes with ~ 10 mm diameter were inserted into large glass tubes equipped with a rubber cap and a syringe.
3. IA (1.0, 2.5, 5.0 and 7.5 mol% of total NIPAAm concentration) was added into the pre-gel solutions of Type (1) and Type (2), and they were gelled in the same manner used for (1) and (2).

After the reaction periods needed to complete relation processes, each test tube was broken and the hydrogels were immersed in distilled-deionized water for Types (1) and (3), and in 1,4-dioxane for Types (2) and (3) to remove linear polymer chains and unreacted constituents. Type (1) and Type (2) include neutral NIPAAm hydrogels cross-linked with BIS (hydrophilic crosslinker) and VTPDMS (hydrophobic macrocrosslinker), respectively. However, Type (3) represent ionic NIPAAm hydrogels. The difference in the washing process of resulting gels is due to hydrophobic (VTPDMS) and hydrophilic (BIS) nature of the crosslinkers. For BIS-crosslinked samples (Samples 8–11, Type 3), ionic NIPAAm hydrogels were immersed in an excess amount of deionized water while for VTPDMS-crosslinked samples (Samples 12–18, Type 3), ionic NIPAAm hydrogels were extracted with 1,4-dioxane to remove uncrosslinked water insoluble compound, i.e., VTPDMS. A final wash of all samples was with deionized water for 1 week.

Hydrogel Characterization

The cylindrical gels, obtained as described before, were cut in pieces, 1.0 cm in height. Before the compression measurements, the gel samples were maintained in water at 25°C to achieve swelling equilibria. Hounsfield H5K-S model tensile testing machine, settled a crosshead speed of 1.0 cm/min and a load capacity of 5N was used to perform uniaxial compression experiments on the samples of each type of hydrogel. The compression modulus of each network was determined from the slope of the linear portions of compression stress-strain curves, using the following equation:

$$\tau = F/A_0 = S(\lambda - \lambda^{-2}) \quad (1)$$

where τ is the applied force per unit area of the sample, i.e., pressure in Pa to compress the undeformed swollen specimen to the required relative deformation, λ . The effective cross-linking density, ν_e was calculated from the compression modulus (S), i.e., slope of the linear portion using the equation (21, 22):

$$\nu_e = S/(RT\nu_{2s}^{1/3}\nu_{2r}^{2/3}) \quad (2)$$

where ν_{2s} and ν_{2r} are the polymer volume fractions in the equilibrium-swollen system and in the relaxed state, i.e., just after polymerization completed, but before swelling. The volume swelling ratio, defined as the reciprocal of polymer volume fraction was

calculated gravimetrically using the following equations:

$$1/v_{2s} = 1 + (w_1\rho_2/w_2\rho_1) \quad (3)$$

$$1/v_{2r} = 1 + (w_1\rho_2/w_2\rho_1) \quad (4)$$

where w_2 and w_1 are the weight of the dried gel sample and the solvent absorbed by the sample during the swelling (or gelation) processes, respectively. ρ_1 and ρ_2 signify the densities of the solvent used for swelling (or synthesis) experiments and the dried hydrogel, respectively. The densities of all dried polymers prepared in this work were taken as $1.1 \times 10^3 \text{ kg/m}^3$.

The gravimetric measurements are used to calculate the volumetric compositions of the hydrogels. Assuming that the gels swell isotropically and dividing Equation (3) into Equation (4):

$$V_s/V_r = v_{2r}/v_{2s} = (d/d_o)^3 \quad (5)$$

where V_s and V_r are the gel sample volumes after and before equilibrium swelling, respectively. d and d_o indicate the equilibrium and original diameters of the hydrogels. Cylindrical gel samples, with the same dimensions of the ones used in the compression experiments were swollen to equilibrium in distilled-deionized water at 25°C . The diameters of the gels were measured by a digital compass. From the values of v_e , v_{2r} , v_{2s} , and ρ_2 the polymer-solvent interaction parameter, χ and average molecular weight between crosslinking points, M_c can be calculated via Equations (6) and (7).

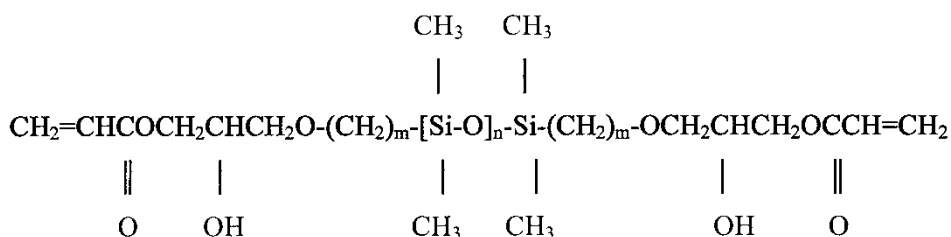
$$\chi = -[\ln(1 - v_{2s}) + v_{2s} + v_e V_1 v_{2r} \{(v_{2s}/v_{2r})^{1/3} - (v_{2s}/v_{2r})(1/2)\}] / v_{2s}^2 \quad (6)$$

$$M_c = \rho_2 / v_e \quad (7)$$

where V_1 is the molar volume of the solvent. These equations derived by using the phantom network model are valid for neutral networks in the highly swollen state (26–28).

Results and Discussion

In general, heterogeneous NIPAAm hydrogels are obtained by conventional method in water above the LCST. The inhomogeneity, being considered as a factor decreasing mechanical strength, may be optimized or removed by the choice of synthesis method, comonomer and crosslinker structure (10, 17, 23–25). In the present study, it has been observed that the mechanical performance of NIPAAm hydrogels could be improved by using hydrophobic macrocrosslinker, i.e., VTPDMS with two different molecular weights. Scheme 1 shows the chemical structure of Tegomer VSi. These commercial



Scheme 1. Chemical structure of hydrophobic macrocrosslinker

products were composed of soft and hydrophobic segments of dimethylsiloxane ($n \sim 10$ and $n \sim 20$ for VSi 2150 and 2250, respectively) and $-\text{CH}_2$ units ($5 < m < 10$).

Compression moduli of neutral and ionic NIPAAm hydrogels crosslinked with BIS and VTPDMS equilibrated in water at 25°C were determined by means of a Hounsfield H5K-S model tensile testing machine. Any loss of water and changing in temperature during the measurements was not observed because of the compression period being less than 1 min. Figures 1 and 2 show a comparison of the behaviors of neutral NIPAAm hydrogels crosslinked with BIS and VTPDMS, under uniaxial compression. Figures 3–5 show the measured force (F) for compressing samples (2–5), (6, 12–14), (7, 16–18) at 25°C , respectively. Forces (F) or loads corresponding to compressions (mm) were obtained from the original curves of uniaxial compression experiments. Figures 1(a) and 2(a) correspond to initial states, i.e., zero load and, Figures 1(b) and 2(b) point out the heights at 5N, i.e., final states of the $F(N)$ –compression (mm) curves of the samples 3 and 6 in Figures 3 and 4, respectively. Both the curves indicated

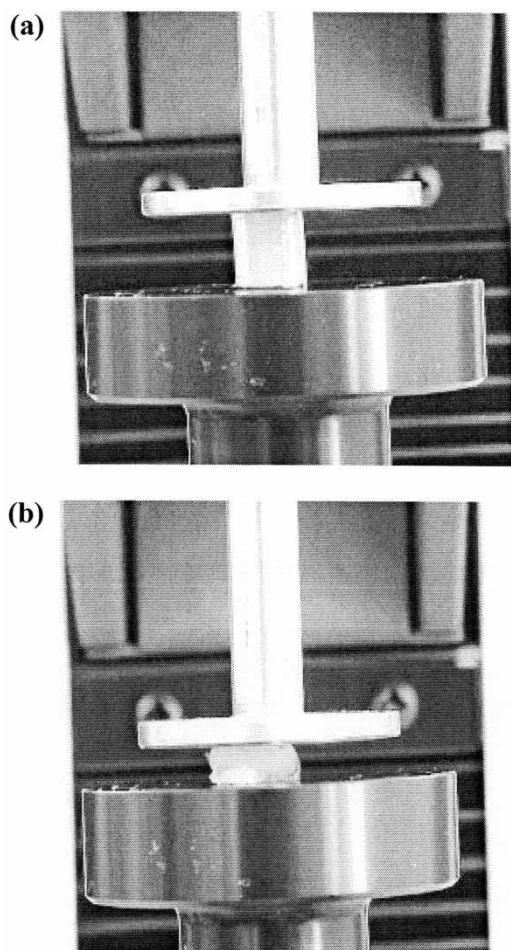


Figure 1. Compression process of Sample 3 in Table 1: (a) initial ($F = 0.0\text{ N}$) and (b) final states ($F = 5.0\text{ N}$).

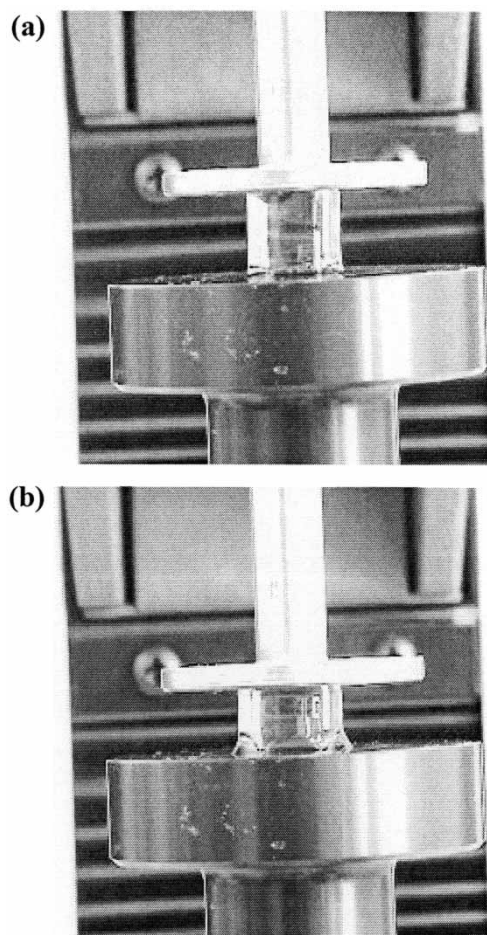


Figure 2. Compression process of Sample 6 in Table 3: (a) initial ($F = 0.0\text{ N}$) and (b) final states ($F = 5.0\text{ N}$).

above and the photographs corresponding to their behaviors during the compression processes show that the resistance to compression of the NIPAAm hydrogels crosslinked with VTPDMS is greater than the ones crosslinked with BIS in the range of $0.0\text{--}5.0\text{ N}$. Pressure (Pa) – linear deformation factor ($-(\lambda - \lambda^{-2})$) plots of all samples were drawn by using the data obtained from the linear portions of $F(\text{N})$ – compression curves (Figures 6–8). The slopes of these straight lines, i.e., compression moduli and Equation (2) were used to compute the effective network concentration, ν_e .

To understand the effect of structure, molecular weight, concentration of crosslinker, and monomer concentration on the mechanical performance and swelling properties of neutral NIPAAm hydrogels, the parameters ν_{2r} , ν_{2s} , ν_e , χ and M_c , which were used to describe the polymer-solvent systems, were calculated from Equations (1)–(7). Table 1 summarizes the synthesis conditions, swelling and mechanical properties of neutral NIPAAm hydrogels crosslinked with hydrophilic and hydrophobic tetrafunctional monomer and macromer, respectively. The data belonging to ionic NIPAAm hydrogels

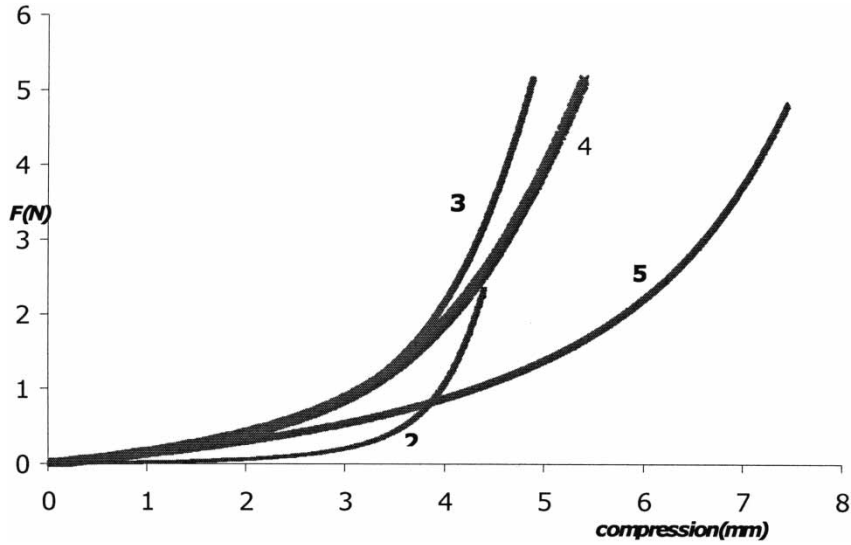


Figure 3. Measured force, F (N) as a function of compression (mm) for samples 2–5, given in Table 1.

prepared in the presence of two different concentration of BIS, Tegomer VSi 2250 and Tegomer VSi 2150 are listed in Tables 2 and 3.

As can be seen from Table 1, the much lower effective crosslinking densities and crosslinking efficiencies were obtained for the NIPPAm hydrogels crosslinked with BIS than for the ones crosslinked with VTPDMS. In another words, the compression

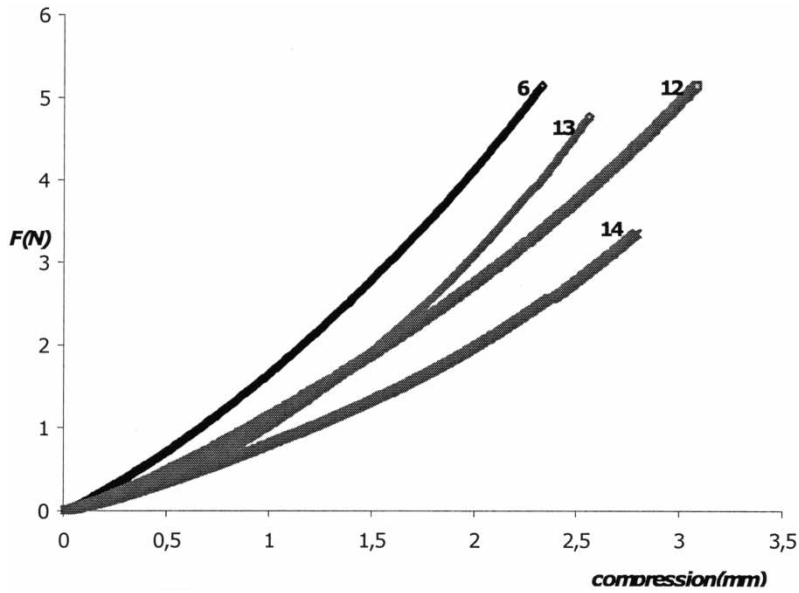


Figure 4. Measured force, F (N) as a function of compression (mm) for Samples 6, 12–14 given in Table 3.

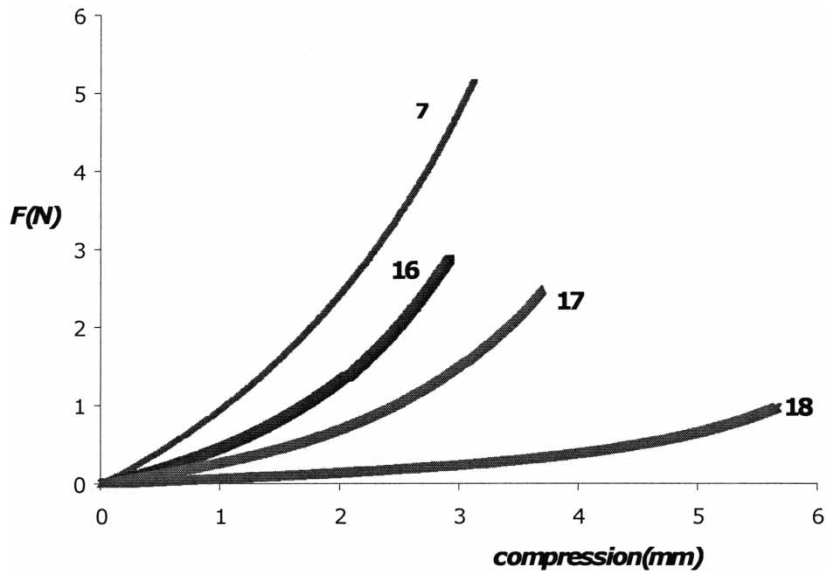


Figure 5. Measured force, F (N) as a function of compression (mm) for samples 7, 16–18 given in Table 3.

moduli of the latter samples were approximately seven times greater than those of the first ones. To be sure of this unexpected increase in mechanical strength, the syntheses of neutral NIPAAm hydrogels containing hydrophobic macromers as a crosslinker were repeated. Both of the tetrafunctional components were incorporated covalently into the gel structures by free radical solution copolymerization method. The effect of increasing monomer and crosslinkers content in reducing the swelling

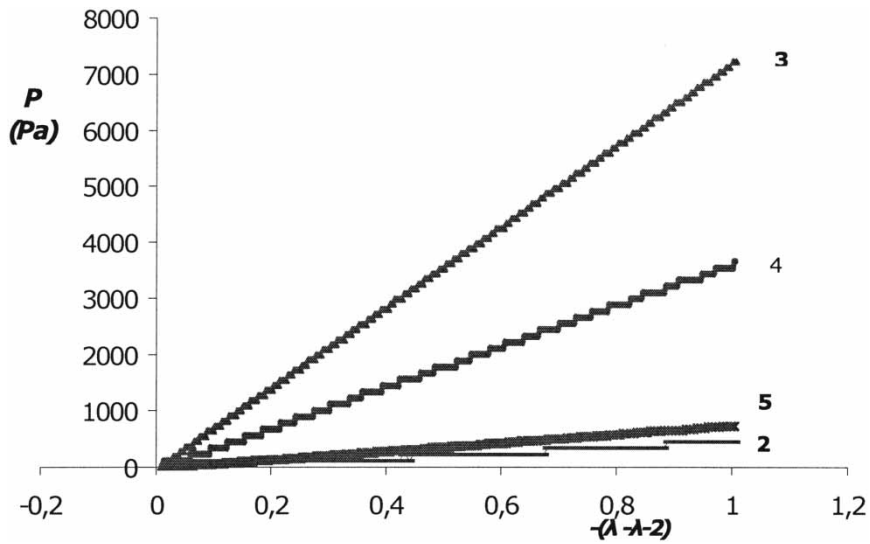


Figure 6. Compression stress-strain curves (pressure (Pa) vs. $-(\lambda - \lambda^{-2})$) for Samples 2–5 given in Table 1.

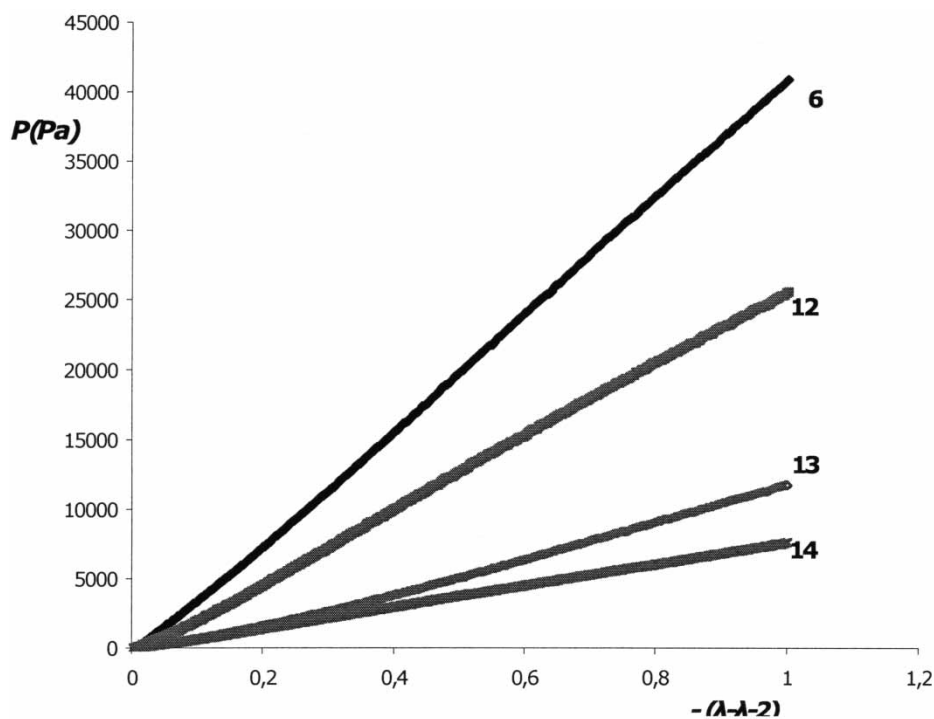


Figure 7. Compression stress-strain curves (Pressure (Pa) vs. vs. $-(\lambda - \lambda^{-2})$) for Samples 6, 12–14 given in Table 3.

and in increasing the compression modulus was an expected result for the conventional crosslinking agents, i.e., for BIS-crosslinked gels. However, the effective crosslinking densities of NIPAAm hydrogels containing VTPDMS (Tegomer VSi 2250) chains were nearly seven times greater than the theoretical ones calculated from the feed composition. The reason for high crosslinking efficiency for VTPDMS-crosslinked gels can be the strong hydrophobic interactions between the methyl groups on the siloxane portions of macromer (Scheme 1). In another words, the unusual value of effective crosslinking for the VTPDMS-crosslinked NIPAAm hydrogels arise from the contribution of physical crosslinks to the crosslinking efficiencies. Furthermore, the increases in ν_{2s} and χ produced by increasing molecular weight of VTPDMS showed that the hydrophobicity of neutral NIPAAm hydrogels increase with increasing length of siloxane portions, as expected. The inverse relation between the number of dimethylsiloxane units and the crosslinking efficiencies of Tegomer VSi 2250 and 2150 supports the interpretation based on mainly hydrophobic interactions (Samples 6 and 7 in Table 1).

Tables 2 and 3 summarize the physical parameters such as S , ν_c and M_c , defining the mechanical properties of ionic NIPAAm hydrogels crosslinked with BIS and VTPDMS. From the comparison of the data in these Tables with the ones in Table 1 and Figures 6–8, it was seen that the ionic NIPAAms containing 2.50 mol% of IA in the feed and crosslinked with BIS (Samples 8, 11) exhibited higher compression moduli than those of the neutral ones (2, 3), whereas all of the ionic NIPAAm hydrogels crosslinked with VTPDMS tetramers (Samples 12–15 for Tegomer VSi 2250; Samples

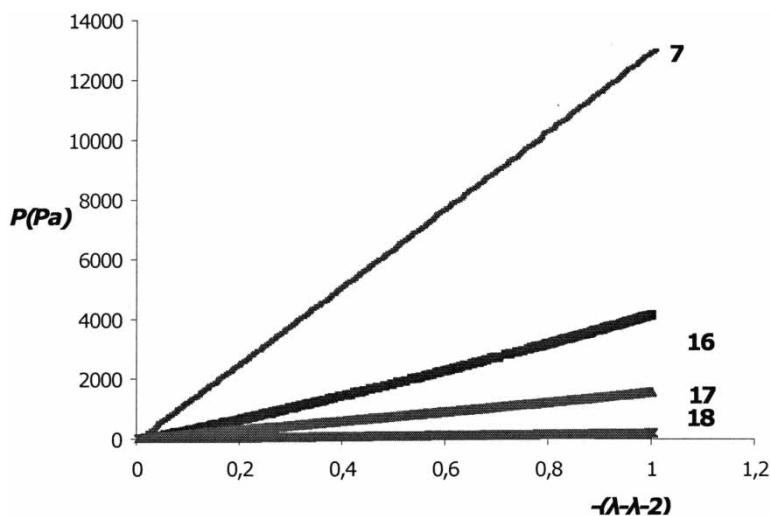


Figure 8. Compression stress-strain curves (Pressure (Pa) vs. $-(\lambda - \lambda^{-2})$) for Samples 7, 16-18 given in Table 3.

16–18 for Tegomer VSi 2150) showed higher swelling degrees and lower compression moduli than the corresponding neutral ones (Samples 6 and 7 for Tegomer VSi 2250 and VSi 2150, respectively). In the case of NIPAAm hydrogels containing 2.50 mol% of IA as acidic comonomer with two carboxyl groups and BIS as hydrophilic crosslinker, the presence of nonionized carboxyl groups in the structures of weakly ionized IA molecules in addition to $-NHR$ and $C=O$ groups in the molecular structures of BIS and NIPAAm units increase the strength of noncovalent intramolecular hydrophilic interactions, i.e., the number of hydrogen bondings between the NIPAAm chains. The lower compression modulus of NIPAAm hydrogel having 5.00 mol% of IA in the pregel solutions (Sample 9) indicates that increasing number of carboxylate groups with increase in the mole content of IA causes to rise the electrostatic repulsive forces between the same type ions. It means that the increasing numbers of the intermolecular hydrogen bonds between the $-COOH$ groups with negative charged, i.e., $-COO^-$ groups and water molecules decrease the strength of the physical crosslinks between the $-COOH$ groups and amide groups, resulting from the intramolecular interactions, and thus the strength of the mechanical performance.

The mechanical behaviors of neutral and ionic NIPAAm hydrogels crosslinked with hydrophobic macromers, Tegomer VSi 2250 and 2150 are similar to those of the ones crosslinked with hydrophilic monomer, i.e., BIS. The main difference results from the nature of secondary forces, being highly effected on the degree of physical crosslinkings. In the case of the NIPAAm hydrogels containing vinyl terminated poly(dimethylsiloxane) as a macro crosslinker, hydrophobic interactions between Tegomer molecules incorporated covalently into the gel structures were mainly responsible for their high compression moduli and crosslinking efficiencies. The lower mechanical responses of the hydrogels composed of temperature-sensitive NIPAAm molecules and less hydrophobic macrocrosslinker, i.e., Tegomer VSi 2150, containing half of the dimethylsiloxane units in the molecular structure of Tegomer VSi 2250 also supported this interpretation. For both Tegomer VSi 2250 and Tegomer VSi 2150, crosslinking

Table 1

Polymerization conditions, polymer volume fractions (v_{2r} , v_{2s}), compression moduli (S) and polymer-water interaction parameters (χ) at swelling equilibria at 25°C for neutral PNIPAAm hydrogels prepared in the presence of two different crosslinker

Sample no.	NIPAAm (mol/L)	Crosslinker ($\times 10^{-1}$ mol/L)	v_{2s}	v_{2r}	S(Pa)	v_e (mol/m ⁻³)	C.E	χ	M_c (kg/mol)
1	0.7	BIS, 1.25	0.0221	0.0818	101	0.77	0.06	0.506	1429
2	0.7	BIS, 2.50	0.0361	0.0716	422	2.99	0.12	0.511	363
3	2.0	BIS, 2.50	0.0646	0.1729	7132	23.12	0.92	0.513	47.6
4	2.0	BIS, 1.25	0.0487	0.3102	3558	8.57	0.69	0.508	128.4
5	2.0	BIS, 1.25	0.0289	0.2532	755	2.48	0.19	0.504	444.3
6 ₁ ^a	2.0	VTPDMS, 1.25	0.1935	0.2158	40115	77.77	6.22	0.571	14.1
6 ₂ ^a	2.0	VTPDMS, 1.25	0.1732	0.2185	44642	89.05	7.12	0.560	12.4
7 ₁ ^b	2.0	VTPDMS, 1.25	0.1149	0.1976	12879	31.50	2.52	0.537	34.9
7 ₂ ^b	2.0	VTPDMS, 1.25	0.0898	0.2110	12418	31.56	2.52	0.524	34.9

C.E = Crosslinking efficiency ($v_e/v_{e,i}$). $v_{e,i}$ is taken as initial concentration of crosslinker (column 2).

^aTegomer VSi 2250; M.W = 2000 g/mol.

^bTegomer VSi 2150; M.W = 1000 g/mol.

(Subscripts 1 and 2 indicate the results of two different synthesizes carried out with the same experimental procedure; Samples 1–4 were the ones initiated with KPS/TEMED redox pair in water/methanol mixture while for the others synthesized in 1,4-dioxane AIBN was used as free radical initiator).

Table 2

Polymer volume fractions (v_{2r} , v_{2s}) compression moduli (S) and polymer-water interaction parameters (χ) at swelling equilibria at 25°C for ionic PNIPAAm hydrogels prepared in the presence of BIS

Sample no.	NIPAAm (mol/L)	Crosslinker ($\times 10^{-2}$ mol/L)	Comonomer (mol%)	v_{2s}	v_{2r}	S(Pa)	v_e (mol/m ⁻³)	C.E	M_c (kg/mol)
8	0.7	BIS, 2.50	IA, 2.50	0.0154	0.2235	1858	8.17	0.33	134.6
9	0.7	BIS, 2.50	IA, 5.00	0.0028	0.0868	415	6.05	0.24	181.8
10	2.0	BIS, 1.25	IA, 2.50	0.0279	0.3089	2196	6.39	0.51	172.1
11	2.0	BIS, 2.50	IA, 2.50	0.0581	0.2170	9084	26.19	1.05	42.0

Table 3

Polymer volume fractions (v_{2r} , v_{2s}), compression moduli (S) and polymer-water interaction parameters (χ) at swelling equilibria at 25°C for PNIPAAm hydrogels prepared in the presence of two different molecular weight of hydrophilic crosslinker, VTPDMS

Sample no.	Crosslinker ($\times 10^{-2}$ mol/L)	Comonomer (mol%)	v_{2s}	v_{2r}	S (Pa)	v_e (mol/m ⁻³)	C.E	M_c (kg/mol)
6 ^a	VTPDMS, 1.25	—	0.1935	0.2158	40115	77.77	6.22	14.1
12 ^a	VTPDMS, 1.25	IA, 1.00	0.1557	0.1904	25332	57.39	4.59	19.2
12 ^a	VTPDMS, 1.25	IA, 1.00	0.1385	0.2257	20946	44.05	3.52	24.9
13 ^a	VTPDMS, 1.25	IA, 2.50	0.1198	0.2686	10896	21.41	1.71	51.4
14 ^a	VTPDMS, 1.25	IA, 7.50	0.0904	0.3761	7482	12.90	1.03	85.3
15 ^a	VTPDMS, 2.50	IA, 7.50	0.2516	0.2068	65274	119.29	4.77	9.2
15 ^a	VTPDMS, 2.50	IA, 7.50	0.2095	0.2477	55144	94.96	3.79	11.6
7 ^b	VTPDMS, 1.25	—	0.1149	0.1976	12879	31.50	2.52	34.9
16 ^b	VTPDMS, 1.25	IA, 1.00	0.0659	0.2794	3969	9.27	0.74	118.7
17 ^b	VTPDMS, 1.25	IA, 2.50	0.0456	0.3895	1523	3.22	0.26	341.6
18 ^b	VTPDMS, 1.25	IA, 7.50	0.0108	0.3729	206	0.73	0.06	1517.2

[NIPAAm] = 2.0 mol/L.

^aTegomer VSi 2250; M.W = 2000 g/mol.

^bTegomer VSi 2150; M.W = 1000 g/mol.

Table 4
Swollen diameters of the samples given in Tables land 3

Sample no.	Crosslinker ($\times 10^{-2}$ mol/L)	Comonomer (mol%)	d (mm) (at swelling equilibrium)	d (mm) (3 months later)
3	BIS, 2.50	—	8.40	8.21
4	BIS, 1.25	—	9.29	9.37
5	BIS, 1.25	—	22.35	21.62
6 ^a	VTPDMS, 1.25	—	11.20	11.17
7 ^b	VTPDMS, 1.25	—	14.36	14.38
12 ^a	VTPDMS, 1.25	IA, 1.00	12.71	15.71
15 ^a	VTPDMS, 2.50	IA, 7.50	11.42	15.59
14 ^a	VTPDMS, 1.25	IA, 7.50	17.45	33.45
13 ^a	VTPDMS, 1.25	IA, 2.50	14.20	18.60
16 ^b	VTPDMS, 1.25	IA, 1.00	17.56	25.35

[NIPAAm] = 2.0 mol/L.

^aTegomer VSi 2250; M.W = 2000 g/mol.

^bTegomer VSi 2150; M.W = 1000 g/mol.

efficiencies dependent on the compression moduli of the hydrogels were decreased sharply, with increasing IA content (Table 3). This effect can be explained by the fact that electrostatic repulsive force between $-\text{COO}^-$ groups of weakly ionized IA units attached covalently on the main chain structures of NIPAAm networks destroy the intramolecular hydrophobic interactions arising from the methylsiloxane units of VTPDMS chains. To support these findings and propose the optimum conditions for the materials having high mechanical strength and water absorption capacity, i.e., optimum combination of hydrophilic and hydrophobic constituents, Tegomer content of the products was increased while IA content was taken as constant for its higher value used in this work (Samples 14, 15). The results showed that the increase in the number of hydrophobic siloxane units suppressed the effect of physical crosslink-destroyers, i.e., COO^- groups. From the comparison of the compression moduli of the Samples in Table 3 with the diameters of the corresponding ones in Table 4 (because they are used for the determination of the effective crosslinking densities), it was observed that the preparation highly swollen, but mechanically stable NIPAAm hydrogels was mainly related to the ration of hydrophilic/hydrophobic constituents. For example, the diameter of the natural and so weakly swollen NIPAAm hydrogels were nearly stable during the observation period chosen as 3 months whereas in the case of the ionic hydrogels crosslinked with hydrophobic crisslinker, surprisingly, the diameters of the samples increased in the course of time, except Samples 12 and 15. The results indicates that for these two samples hydrophobic interactions are balanced with the hydrophilic ones.

Conclusions

We studied the effects of VTPDMS, being a hydrophobic macrocrosslinker on the physical parameters such as polymer volume fraction (v_{2s}), effective density (v_e) polymer-solvent interaction parameter, χ and average molecular weight between crosslinking points (M_c)

of neutral and ionic NIPAAm hydrogels, in comparison with those of the ones cross-linked with BIS. It was revealed that the compressive elastic moduli of VTPDMS-crosslinked neutral NIPAAm hydrogels were 50 times higher than those of the ones crosslinked with conventional tetra functional monomer, i.e., BIS in 1,4-dioxane. The lower mechanical responses of the neutral NIPAAm hydrogels crosslinked with Tegomer VSi 2150, having half of the dimethylsiloxane units in the molecular structure of Tegomer VSi 2250 supported the importance of the nature of secondary forces, being highly effected on the degree of physical crosslinkings. For both Tegomer VSi 2250 and Tegomer VSi 2150, the compression moduli of the ionic NIPAAm hydrogels were decreased sharply, with increasing IA content. As for these results, the electrostatic repulsive force between the ionized carboxyl groups of IA units destroyed the strong intramolecular hydrophobic interactions arising from the dimethylsiloxane units of VTPDMS chains. From the starting point of these findings, it can be said that the most productive combinations of the hydrophilic component which absorbed large amount of water and the hydrophobic component which improved the mechanical performance are necessary to designate the materials having the right balance of repulsive and attractive forces, being responsible for swelling and mechanical behaviors of the networks. For this study, the indicated combinations of hydrophobic and hydrophilic constituents correspond to the ratios of VTPDMS 2250 (1.25×10^{-2} mol/L)/IA (1.0, mol%) for Sample 12 and VTPDMS 2250 (2.50×10^{-2} mol/L)/IA (7.50 mol%) for Sample 15. The absorption capacities of these hydrogels and their applications in drug delivery are subject to further studies.

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