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Polymer 41 (2000) 4793–4802

polymer

Characterization of polyimide gels crosslinked with hexamethylene diisocyanate

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Received 9 June 1999; received in revised form 20 September 1999; accepted 28 September 1999

Abstract

Characterization of the crosslinked structure has been carried out for soft polyimide gels prepared from a soluble high-performance fluorine-containing polyimide consisting of 4,4′-(hexafluoro-isopropylindene)diphthalic anhydride and 3,3′-dihydroxy-4,4′-diaminobiphenyl crosslinked with hexamethylene diisocyanate. Weight-average molecular weight ($M_w = 9.28 \times 10^4$), second and third virial coefficients ($A_2 = 0.82 \times 10^{-3}$ mol ml/g^2, $A_3 = 6.42 \times 10^{-3}$ mol ml^2/g^3) of the linear polyimide in *N*-methylpyrrolidone at 24°C were determined by a static laser light scattering measurement. The average molecular weight between crosslinking points M_c, was calculated based on both swelling and viscoelastic measurements of the polyimide gels. As for the equilibrium swelling data, a concentration-dependent form of the Flory–Huggins parameter (i.e. $\chi = \chi_1 + \chi_2\phi$) has been applied to calculate the M_c. The values of M_c from equilibrium swelling and viscoelastic measurement have been found to be in agreement. By comparing M_c with the results of ^{1}H-NMR, the percentages of effective and ineffective linkages have been evaluated quantitatively for all the polyimide gels. It has been found that the elastically effective crosslinking is less than 20%. Results from classical and improved Flory–Rehner theory have been compared and we believe that the improved theory gives a more reasonable description of M_c at higher crosslink density. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyimide; Gel; Crosslinking

1. Introduction

The volume phase transition of the polymer gels was theoretically predicted by Dušek and Patterson in 1968 [1]. Then in 1977–1978, it was first discovered experimentally by Tanaka et al. for an acrylamide gel in water [2,3]. Since then polymer gels have attracted much more attention than ever before. It is possible to design a wide range of intelligent materials using the volume phase transition (VPT) of gels. By introducing selectively active ingredients into the polymer network, gels can be designed to respond against temperature, pH, electric field, magnetic field, pressure and so on [4–7]. These stimuli-responsive polymer gels are of major interest as novel intelligent materials, e.g., self-oscillating gels [8], optical switching gels [9], and shape memory gels [10].

Vinyl-based polymer networks have been well studied and developed for polymer supports, hygiene products, contact lenses and so on. Many approaches have been applied to study the gelation dynamics and the nature of gels. Dynamic and static light scattering can be used for studying the dynamics of polymer gels [11,12]. Small-angle neutron scattering (SANS) is a good technique to study the microscopic structures of gels [13]. Fluorescence studies have been made on the ionic poly(acrylamide) gels, with dansyl fluorescent probes to investigate the micro-environment changes during volume phase transition, by Hu and Asano et al. [14–16] ^{1}H-NMR studies have been made on the nonionic and ionic poly(*N*-isopropylacrylamide) gels near their phase transition [17]. The morphology of gels can be studied with scanning electron micrograph (SEM) [18]. The gelation dynamics has been studied with real-time pulsed nuclear magnetic resonance measurements [19] and dynamic mechanical behaviors [20].

In order to improve the mechanical properties of the swollen gels, either a physical method (freeze-dry) [6] or a chemical method (using intrinsically high-performance polymers) can be applied. In the case of freeze-dry technique, microcrystallite or microphase separation [18] is introduced as additional physical crosslinking junctions in order to improve the mechanical properties. It is a disadvantage that these junctions dissociate at higher temperatures.

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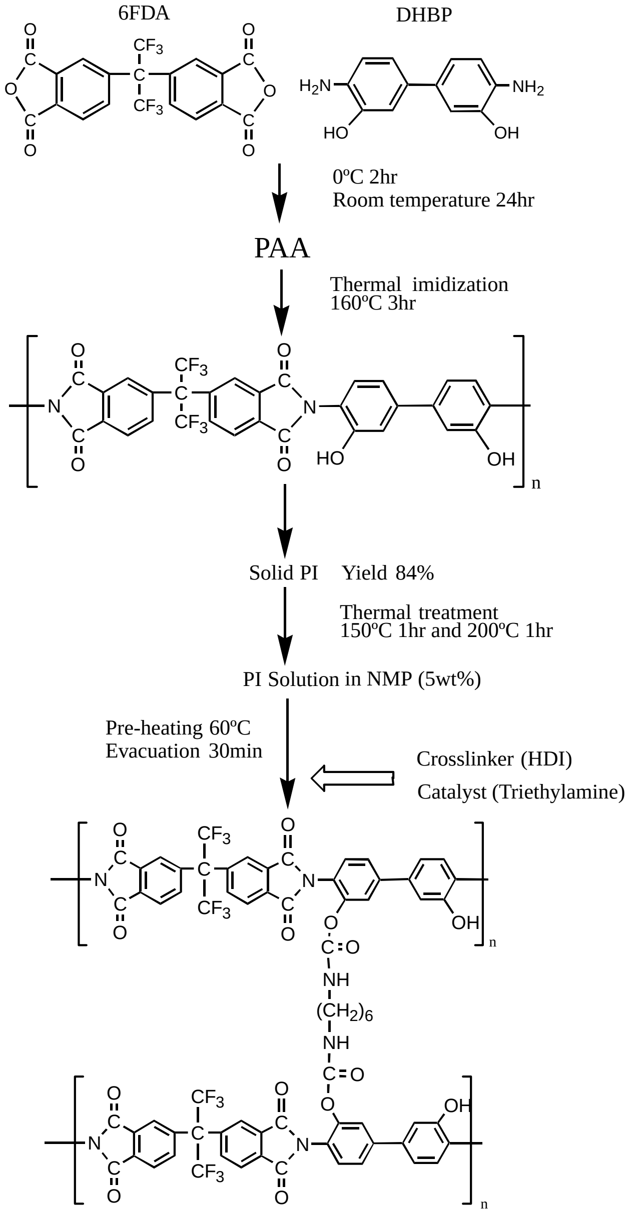
PII: S0032-3861(99)00722-3



Scheme 1.

By using intrinsically high-performance polymers such as polyimides and polyamides, swollen gels are expected to sustain stable mechanical properties in a wide temperature region. Rigid polyamide networks have been intensively studied by Aharoni et al. [21,22] In our previous paper [23], we reported for the first time that a soft gel was successfully prepared from a rigid polyimide chain. By using the polyimide as the framework of the gel, it is expected to demonstrate good thermal stability and high strength. In our previous paper, it was found that there was a side reaction existing during the crosslinking. This is due to the reaction between hexamethylene diisocyanate and trace amounts of water, resulting in a urea linkage in the gel. In the present paper, we have managed to suppress this side reaction.

It is extremely important to control the physical structure and topology of a gel in order to prepare a high-performance gel material. In a well-controlled end-crosslinking reaction, the molecular weight between two crosslinking points M_c, can be precisely estimated from the initial concentrations of the monomer and crosslinker. For a randomly crosslinked system, equilibrium swelling measurement is the method most widely used for studying M_c. However, discrepancies are usually observed between M_c calculated from the reacted amounts of the crosslinker and M_c estimated from equilibrium swelling. There are also some kinds of computer simulations on the structure and elasticity of polymer networks which give us a visual image of the topology of the polymer network [24,25]. In the present paper, we prepared a series of polyimide gels and studied their swelling behaviors and viscoelastic properties. By using the Flory–Rehner theory and the classical rubber elasticity theory [26], we estimated the average molecular weight between two crosslinking points from the data of both equilibrium swelling ratio and compression modulus. The data were also interpreted by using an improved Flory–Rehner equation to give a more realistic view of the gel's structure. It is proved that less than 20% of the linkages form elastically effective crosslinking.

2. Experimental

2.1. Reagents

All reagents were purchased from Tokyo Kasei Organic Chemicals, Wako Chemicals and Aldrich Chemicals, and were used without further purification unless otherwise described. *N*-methylpyrrolidone (NMP) was distilled in the presence of calcium hydride and stored with molecular sieves. *N*,*N*-dimethylacetamide (DMAc) and triethylamine (TEA) were stored with molecular sieves. Spectroscopic grade of tetrahydrofuran (THF) was used.

2.2. Preparations of a polyimide (6FDA/DHBP) and polyimide gels

The preparation of a polyimide, PI(6FDA/DHBP), consisting of 4,4′-(hexafluoro-isopropylindene)diphthalic anhydride (6FDA) and 3,3′-dihydroxy-4,4′-diaminobiphenyl (DHBP) was carried out according to our previous paper [23]. The thermal imidization of the polyimide was confirmed by IR spectra (Jasco IR-700) at the wave number of 1780, 1380 and 725 cm^{-1}. Intrinsic viscosity, $[\eta]$, was equal to 0.89 dl/g in NMP at 30°C. Thermal stability of the polyimide was investigated with a TAI 2050 Thermogravimetry Analyzer showing a 10% weight loss at 490°C (10°C/min, in N_2). PI(6FDA/DHBP) shows good solubility in several common solvents, such as, acetone, NMP, DMAc, and THF. THF was chosen as an extraction solvent for the polyimide gel.

Two series of polyimide gels with initial polyimide weight concentrations of 5 wt% (group "a") and 10 wt%

(group "b") in NMP were synthesized according to the procedure in Scheme 1 (synthesis of polyimide gels). The polyimide solutions were pre-heated at about 60°C and degassed for at least 30 min in order to remove moisture in the solution thoroughly. 2.5 μl/ml of TEA, the catalyst, and various concentrations of hexamethylene diisocyanate (HDI), the crosslinker, were added to polyimide solutions to make polyimide gels with three different crosslinking densities, NCO/OH = 0.1, 0.5 and 1.0, which were coded as G-1, G-2 and G-3 respectively. The side reaction, i.e. the formation of urea linkages, has not been observed in ^{1}H-NMR spectra.

2.3. Static light scattering measurements

Static Laser Light Scattering (LLS) measurements were carried out in Toho University. The linear polyimide was dissolved in NMP to prepare a solution at a concentration of 0.01034 g/ml. The initial solution was then diluted into four solutions and filtered with 5.00 μm-pore filter paper, three times before the measurement. The measurements were carried out at 24°C using a He–Ne laser at 633 nm and the scattering light was collected from an angle of 40 to 140° with an interval of 10° with a Union Giken Automatic Light Scattering Analyzer LS-601. The specific refractive index increment, dn/dC, was measured with a Union Giken Differential Refractometer RM-102.

In static LLS, the angular dependence of the excess absolute time-averaged scattered intensity known as the excess Rayleigh ratio $R_{\mathrm{vv}}(q)$, of a dilute polymer solution at a concentration C (g/ml), and a relatively small scattering angle θ, can be related to the weight-average molecular weight M_{w}, the second and third virial coefficient A_2, A_3 by Eq. (1) [27]

$$\frac{KC}{R_{\mathrm{vv}}(q)} \approx \frac{1}{M_{\mathrm{w}}}\left(1 + \frac{1}{3}\langle R_{\mathrm{g}}^2\rangle q^2\right) + 2A_2C + 3A_3C^2 \tag{1}$$

where $K = 4\pi^2 n^2(\mathrm{d}n/\mathrm{d}C)^2/(N_{\mathrm{A}}\lambda_0^4)$ and $q = (4\pi n/\lambda_0)\sin(\theta/2)$, with N_{A}, n, and λ_0 being Avogadro's number, the refractive index of the solvent, and the wavelength of light in vacuum, respectively. A_2 and A_3 are the second and third virial coefficient. $\langle R_{\mathrm{g}}^2\rangle_z^{1/2}$ (or written as $\langle R_{\mathrm{g}}\rangle$) is the root mean-square z-average radius of gyration. By measuring $R_{\mathrm{vv}}(q)$ at a set of C and q, we are able to determine M_{w}, $\langle R_{\mathrm{g}}\rangle$, A_2 and A_3 from a Zimm plot which incorporates the extrapolations of $q \to 0$ and $C \to 0$ on a single grid.

2.4. Determination of sol-gel fraction

The synthesized polyimide gels were cut into small pieces and dried at 50°C overnight, then vacuum dried at 80°C overnight. The dried gels were dipped into THF to extract the sol fraction out of the gels. THF was changed once every other day and this extraction continued for one week. All the THF extracts were collected and mixed together to determine the polymer content in the THF extracts. A THF solution of the linear polyimide with a known concentration was used as a reference for the ultraviolet measurement. Two absorption peaks are found at 260 and 295 nm. ($\epsilon_{260\ \mathrm{nm}} = 3.10 \times 10^4$ l cm/mol, $\epsilon_{295\ \mathrm{nm}} = 2.34 \times 10^4$ l cm/mol) Ultraviolet spectrum measurement was performed with a Jasco V-570 UV/VIS/NIR spectrophotometer.

2.5. ^{1}H-NMR measurements

The dried sol-free polyimide gels were swollen in DMSO-d$_6$ for at least two days. ^{1}H-NMR spectrum measurements were performed with JEOL JNM-GX270 FT-NMR for all the gels.

2.6. Swelling behaviors of polyimide gels

The dried sol-free polyimide gels were dipped into various compositions of NMP/water mixed solvents at a constant temperature (20°C). Cylinder-shaped gels were prepared to study the swelling behaviors of the gels [23]. By measuring the diameter and length of the gels, the swelling ratio was calculated. In contrast, by applying the following equation:

$$Q = \frac{\left(\dfrac{m_1}{\rho_1} + \dfrac{m_2}{\rho_2}\right)}{\dfrac{m_2}{\rho_2}} \tag{2}$$

where m_1 and ρ_1 are the weight and density of the solvent inside the swollen gel, m_2 and ρ_2 are the weight and density of the dried gel before the swelling. We can measure the swelling ratio by weighing the sample even when the shape of the gel is irregular.

2.7. Viscoelastic measurements

Polyimide gels in their as-prepared condition were sandwiched between two circular plates and the complex compression modulus E^* of the gel was measured with a Rheometric RSA II viscoelastic apparatus at frequencies from 0.0159 to 15.9 Hz at 25°C. The compression moduli at 0.159 Hz were used for calculating the M_{c}.

3. Results and discussion

3.1. Molecular weight and Flory–Huggins parameter of the linear polyimide

Static Laser Light Scattering of the linear polyimide, PI(6FDA/DHBP), was measured in a NMP solution at 24°C. The weight-average molecular weight M_{w}, the second and third virial coefficients A_2 and A_3, were obtained from the Zimm plot (Fig. 1). The results are summarized in Table 1. Because the angle dependence of KC/R(θ) is not linear, we used a second-order polynomial approximation to extrapolate the value at zero degree. As for the zero concentration

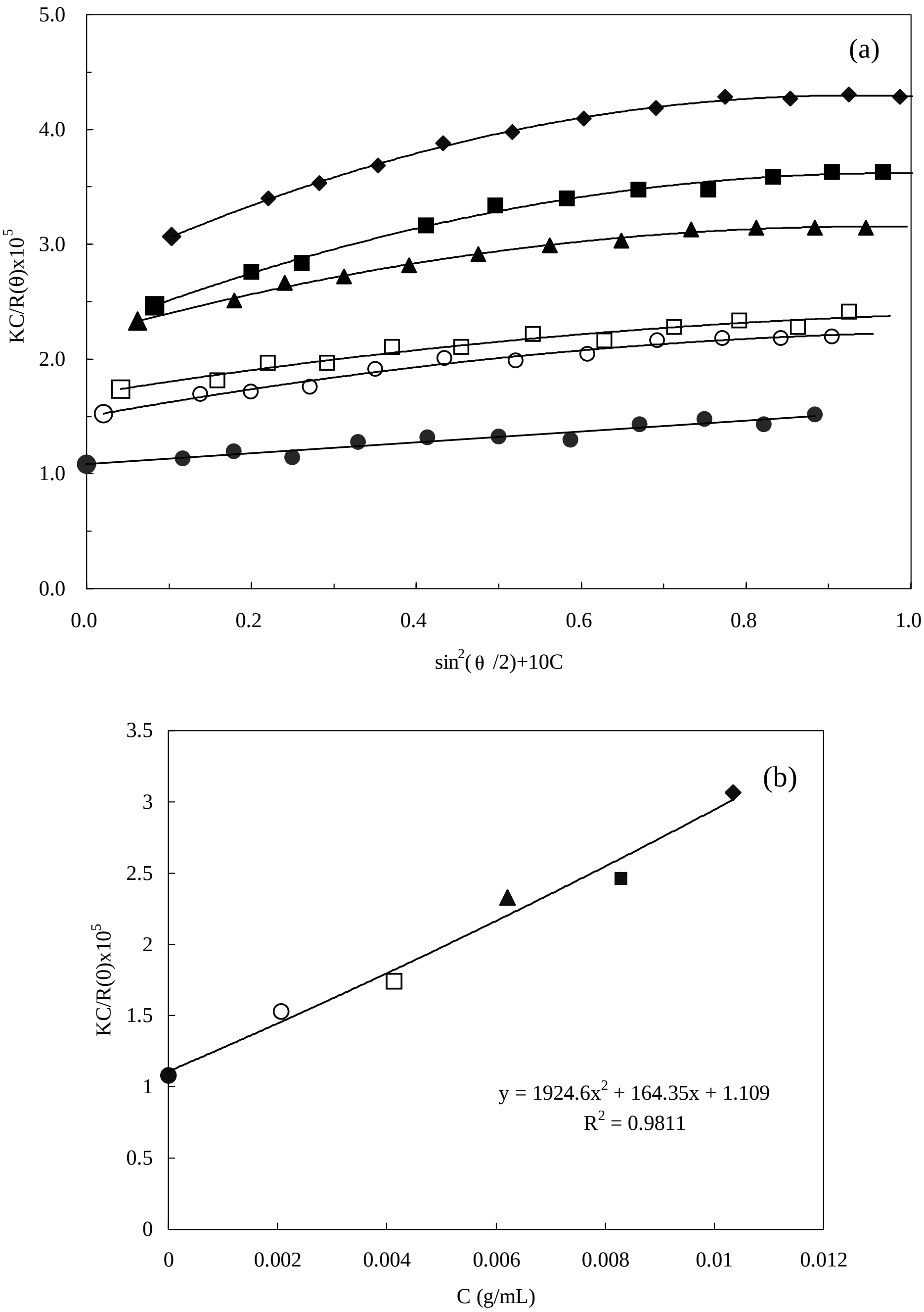


Fig. 1. (a) Zimm plot for a linear PI(6FDA/DHBP) in NMP at 24°C; (b) Fitting from extrapolated values at zero degree with a second-order polynomial $C = 0.01034$ g/ml (◆), $C = 0.008272$ g/ml (■), $C = 0.006204$ g/ml (▲), $C = 0.004136$ g/ml (□), $C = 0.002068$ g/ml (○), $C = 0$ g/ml (●).

extrapolation at various angles, linear approximation is still applicable.

From the linear approximation of the extrapolated values to zero concentration (solid circle in Fig. 1a), we found that the weight-average molecular weight M_w, is 9.28×10^4. This extrapolation data was also used for approximating the curve at zero degree. With five extrapolation data at zero degree plus one from the extrapolation at zero concentration and zero degree, the second-order polynomial fitting gives the values of radius of gyration, the second and third virial coefficients, $\langle R_g \rangle$, A_2 and A_3 as 39 nm, 0.82×10^{-3} mol ml/g^2, 6.42×10^{-3} mol ml^2/g^3, respectively (Fig. 1b). The value of A_2 is comparable with that of another polyimide, PI(BCPOBDA/DMMDA), which was derived from 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride (BCPOBD) and 2,2′-dimethyl-4,4′-methylenedianiline (DMMDA) at the same order of magnitudes of the molecular weight ($M_w = 1.24 \times 10^5$, $A_2 = 1.6 \times 10^{-3}$ mol ml/g^2, $\langle R_g \rangle = 25$ nm) [27]. The $\langle R_g \rangle$ of PI(6FDA/DHBP) is larger than that of PI(BCPOBDA/DMMDA), because

Table 1
M_w, A_2 and A_3 from the Zimm plot for the linear PI(6FDA/DHBP). ($C_0 = 0.01034$g/ml, Solvent: NMP Temperature: 24°C; Refractive Index of NMP: $n_d^{20} = 1.470$ (589 nm); Laser: He–Ne (633 nm), (dn/dC) = 0.169)

Function	Second-order extrapolation	
	$\theta \to 0$	$C \to 0$
M_w	9.26×10^4	9.28×10^4
A_2 (mol ml/g^2)	0.82×10^{-3}	
A_3 (mol ml^2/g^3)	6.42×10^{-3}	
$\langle R_g \rangle$ (nm)		39.2
Correlation coefficient	0.9811	0.9118

PI(6FDA/DHBP) is stiffer thus leading to a more expanded conformation. The A_2 and A_3 are measures of the deviation of a polymer solution from the ideal condition. It is related to the Flory–Huggins parameter χ, in a concentration dependent form by Eqs. (3)–(5), [28]

$$A_2 = \frac{\frac{1}{2} - \chi_1}{V_1 \rho^2} \tag{3}$$

$$A_3 = \frac{\frac{1}{3} - \chi_2}{V_1 \rho^3} \tag{4}$$

$$\chi = \chi_1 + \chi_2 \phi \tag{5}$$

where V_1 (= 96.6 cm^3/mol) is the partial molar volume of the solvent, ρ (= 1.30 g/ml) is the density of the dry polyimide, and ϕ is the volume fraction of the polymer in the solution. $\chi_1 = 0.36$ and $\chi_2 = -1.03$ have been obtained for the present polyimide in NMP at 24°C. Many experimental data have shown that χ indeed has a concentration dependence in polymer-solvent systems with quite strong interactions such as polar, ionic, or hydrogen bonding between a polymer and a solvent [28–30]. Since the polyimide is prepared with a polycondensation reaction, the theoretical number-average molecular weight is assumed to be $M_n = M_w/2 = 4.6 \times 10^4$.

3.2. Sol-gel fraction of polyimide gels

Two groups of polyimide gels, a and b, have been synthesized. It has been confirmed from ^{1}H-NMR spectra that there exists no side reaction between the crosslinker and water during the crosslinking. In each group, three samples with different initial ratios of isocyanate group to hydroxyl group varying from 0.12 to 0.97 are listed in Table 2. Group "a" has an initial polyimide concentration of 5 wt% while group "b" has 10 wt%. This is to investigate the initial concentration effect on the final properties of the gels. We will discuss it later in this paper. All the gels have dark brown colors, but are clear. After being washed with THF, sol fraction was extracted. There is only a small amount of sol fraction (less than 10 wt%) found in all gels. Sol fraction decreases with increasing crosslinking density. For G-3a and G-3b, almost no sol fraction was found. It implies that the crosslinker reacts with hydroxyl group thoroughly at a high degree of conversion and leads to form a three-dimension network with relatively less soluble fraction.

Table 2
Sol fraction and conversion ratio of hydroxyl groups of the polyimide gels crosslinked with hexamethylene diisocyanate

Sample	Initial polyimide concentration (wt%)	NCO/OH	Sol fraction by weight	OH conversion ratio
G-1a	5	0.13	7.2%	0.15
G-1b	10	0.12	6.7%	0.19
G-2a	5	0.48	0.7%	0.58
G-2b	10	0.47	1.5%	0.52
G-3a	5	0.97	0.0%	1.00
G-3b	10	0.92	0.6%	1.00

3.3. Determination of the OH conversion ratio

From the ^{1}H-NMR spectra (Fig. 2) of the polyimide gels, we calculated the degree of conversion of hydroxyl group on the primary polyimide chain. It is noticed that in ^{1}H-NMR spectra a peak at 10.2 ppm represents the proton of hydroxyl group, while peaks at 7–9 ppm belong to the protons of the aromatic rings. The urethane formation by the reaction between isocyanate group and hydroxyl group has been ascertained by using a model reaction [23], but the proton of urethane linkage (7.3 ppm) is overlapped by the hydroxyl-substituted phenylene protons in Fig. 2. By integrating the peaks at 10.2 ppm and 7–9 ppm, we are able to estimate the reacted hydroxyl groups on the primary polyimide chain. The results are shown in the last column of Table 2.

The degree of conversion of the hydroxyl group is almost the same as that calculated from the initial ratio of the crosslinker within the error range. This means there is no side reaction occurring during the crosslinking. In our previous paper [23] trace amounts of water were found to react with diisocyanate and form urea linkages between two crosslinkers which appeared at 5.7 ppm. Dehydration has been carried out carefully in the present work so that there is no urea linkage seen in the polyimide gels, which is ascertained by the observation of no peak in ^{1}H-NMR spectra of any gels at 5.7 ppm which belongs to the proton of urea.

3.4. The swelling behavior of polyimide gels

Swelling behavior was studied in NMP/water mixed solvents. In a 100% NMP solution, all the gels reach equilibrium in about two days (Fig. 3). For gels with lower crosslinking density, the initial swelling speed is faster. As to the solvent composition dependence of swelling, all the gels start swelling at 80 wt% of NMP in NMP/water mixed solvents. (Fig. 4) It is a continuous volume phase transition and the maximum degree of swelling for G-1b, G-2b and G-3b is 35, 18, and 9, respectively.

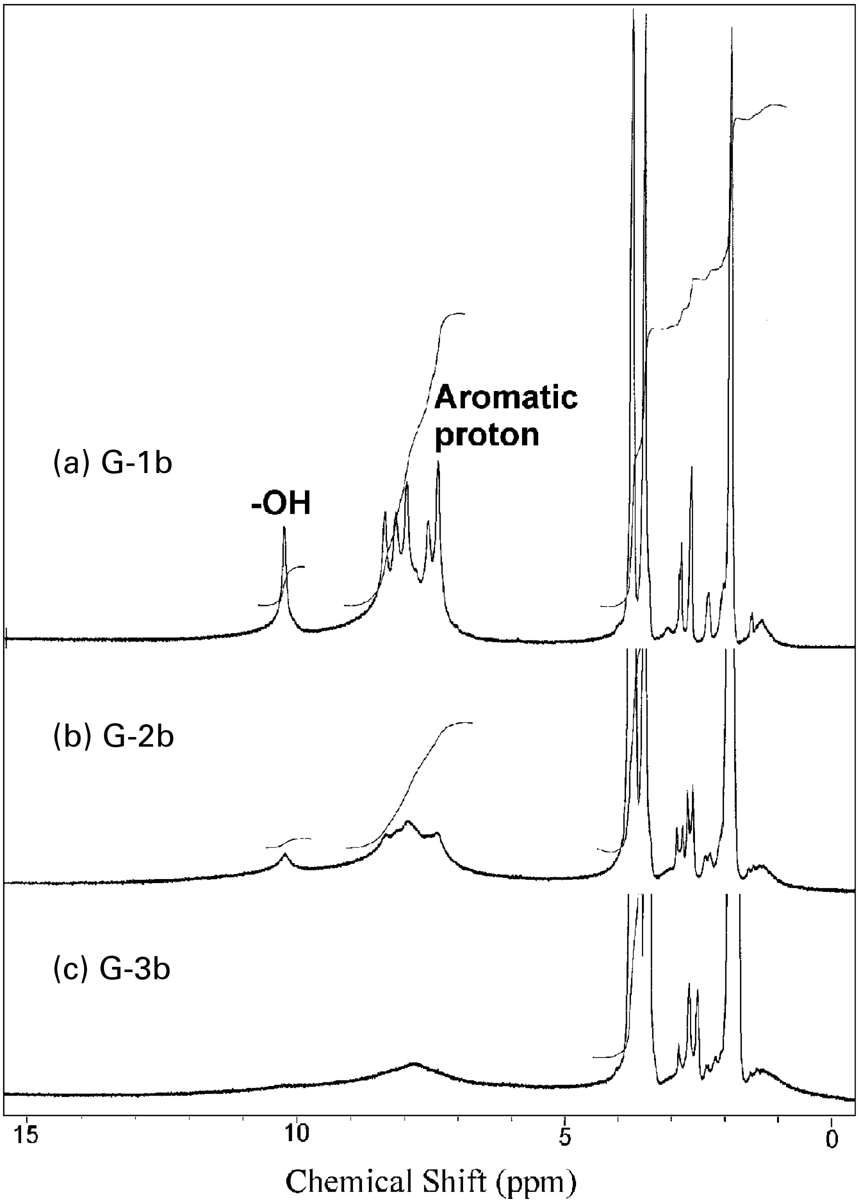


Fig. 2. ^{1}H-NMR spectra of (a) G-1b, (b) G-2b and (c) G-3b polyimide gels in DMSO-d$_6$.

The equilibrium swelling ratio measurement is a typical approach to characterize polymer networks [31]. By combining Flory–Huggins theory of polymer solution and the elasticity theory of rubbers, Flory–Rehner's equation, Eq. (6), is derived [26]. We are able to estimate the average molecular weight between two crosslinking points, M_c, by using this equation.

$$\ln(1-\phi)+\phi+\chi_1\phi^2+\chi_2\phi^3 + \frac{\rho V_1\left(1-\dfrac{2M_c}{M_n}\right)}{M_c}\left(\phi^{\frac{1}{3}}-\frac{\phi}{2}\right)=0 \qquad (6)$$

Here ϕ is the volume fraction of the polyimide inside the gel, which is related to the equilibrium swelling ratio of the gel, Q, by $Q=1/\phi$. V_1 is the molar volume of the solvent ($V_1=96.6$ cm^3/mol for NMP), $\rho=1.30$ g/cm^3 the density of the dried gel, M_n the number-average molecular weight of the primary polymer. The term ($1-2M_c/M_n$) is a correcting factor that takes the influence of dangle primary chain ends into account. An effective crosslinking point is a crosslinker with both ends connected to polymers, both of which can reach other crosslinking points. By applying this equation, we calculated M_c for our gels as is given in Table 3.

It is obvious that from the values of M_n/M_c being larger than unity, the primary polymer chains are divided into several effective crosslinking units. In other words, there are several effective crosslinking points on one primary polymer chain. Assuming that an effective crosslinking point consists of two effective urethane linkages connecting

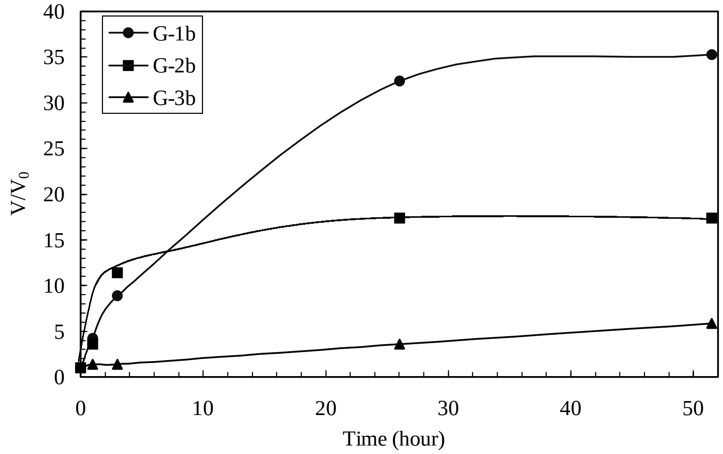


Fig. 3. The swelling rates of G-1b, G-2b and G-3b in pure NMP at 20°C (V_0 corresponds to the volume of the initial dried gels).

different polymers, we can estimate the percentage of effective linkages for these polyimide gels by the following calculations. From the ^{1}H-NMR spectra, the total number of linkages can be determined by integrating the peak of hydroxyl group. The number of effective linkages per primary polymer chain is estimated to be M_n/M_c. Thus based on chemical (^{1}H-NMR) and physical (equilibrium swelling) measurements, we get a quantitative concept of the crosslinking structure inside these kind of gels. The results are summarized in Table 3.

There are about 74 monomer units per primary polyimide chain and each monomer unit has two hydroxyl groups. Therefore there are totally 148 reactive hydroxyl groups per polyimide chain. According to the initial ratio of the crosslinker and the calculated hydroxyl conversion ratio from ^{1}H-NMR data for G-1a, it is believed that 13% of the hydroxyl groups have reacted with the crosslinker. So there are $n_{\text{link}} = 148 \times 13\% = 19$ linkages per polymer chain. However not all the linkages are elastically effective, as is shown by the M_c data, and it is postulated that the crosslinkers are likely to form loops by reacting with the adjacent hydroxyl groups of the same polymer chain [32] (Scheme 2, Illustration of the crosslinking structure for G-1a (crosslinkers are in bold lines)). These small loops formed by the crosslinkers do not make any contributions to the elasticity of the network. In our case, pendent crosslinkers do not exist because the initial ratio of the crosslinker to the hydroxyl group agrees with the result measured with ^{1}H-NMR. For an original polyimide chain in G-1a, there are 19 hydroxyl groups having reacted but only 2.18 are elastically effective, i.e. 11% of the total OH group which reacted. We can see from Table 3 that with increasing crosslinker content, the effective linkage fraction f_{eff}, decreases to only 3.6%. The distance between two isocyanate groups is estimated to be 1.26 nm in average for HDI [25], and the minimum distance between two adjacent OH groups on the same monomer unit of the polyimide would be 0.75 nm. If the average distance between two polymer chains is larger than the length of HDI and the distance between two adjacent OH groups, the effective crosslinking reaction between two different polymer chains would be suppressed to take place, compared to the adjacent loop-forming reaction. In

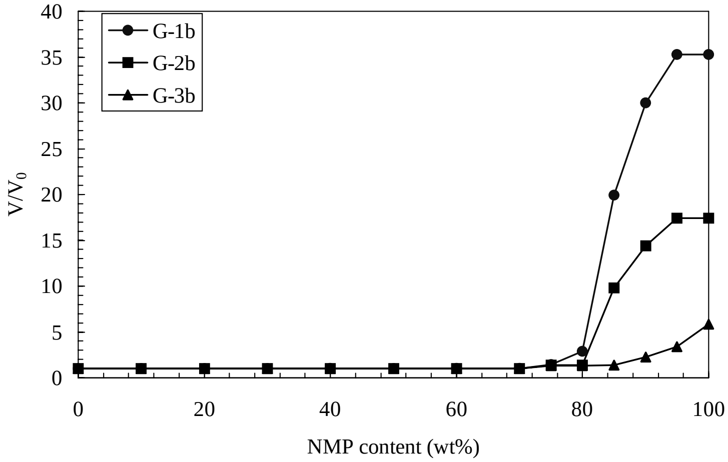


Fig. 4. Equilibrium volume change of gels in NMP/water mixed solvents at 20°C (V_0 corresponds to the volume of the initial dried gels).

our case, by considering polymers as parallelly arranged cylinders with a diameter of 0.75 nm uniformly dispersed in the solvent, there would be a space of approximately 2.6 and 1.6 nm between polymer chains in average for the polyimide concentration of 5 and 10 wt%, respectively. In other words, the average distance between two hydroxyl groups attached to different polymer molecules is larger than the length of the crosslinker. Therefore HDI has much more priority to react with an OH group nearby on the same polymer chain than with OH groups on other polymer chains in a distance. That is why the percentage of effective linkages is so small and we have seen no significant difference in degree of swelling for the two groups of polyimide gels after raising initial polyimide concentration from 5 wt% (group a) to 10 wt% (group b).

3.5. Viscoelastic measurements

Dynamic mechanical measurements were performed for the gels in their as-prepared conditions. The shear modulus, *G*, derived from the classical rubber theory is given by [33]

$$E = 3G = \frac{3dRT}{M_c}\left(1 - \frac{2M_c}{M_n}\right) \tag{7}$$

where *d* is the density of the swollen network at the time of the measurement, M_c is the molecular weight between elastically-active junction points and M_n is the number-average molecular weight of the primary polymer. A typical frequency dependence of the dynamic modulus measurement for the polyimide gel G1-b, is shown in Fig. 5. Storage modulus E', almost keeps constant from 0.0159 Hz to 15.9 Hz. The values of M_c are calculated from Eq. (7) and are summarized in Table 4. We found that the values of M_c calculated from viscoelastic measurements agree quite well with those calculated from the equilibrium swelling ratio. The M_c is almost the same for group “a” and “b” of the same crosslinking density. Practically speaking, changing the initial polymer concentration from 5 to 10 wt% has no effect on the final properties of the present gels. It should be noticed that the polyimide gels have higher moduli than those of vinyl polymer networks. For example, a 8 wt% poly(vinyl alcohol) (PVA) gel containing 4 wt% residual acetyl group swollen in water showed a tensile modulus of 1.0×10^4 Pa [34]. Here, at almost the same liquid content, all the polyimide gels have compression moduli several times larger than 1.0×10^4 Pa, and for G-3a, it even reaches 7.8×10^5 Pa. This improvement of the strength is mainly due to the nature of the rigid polyimide framework.

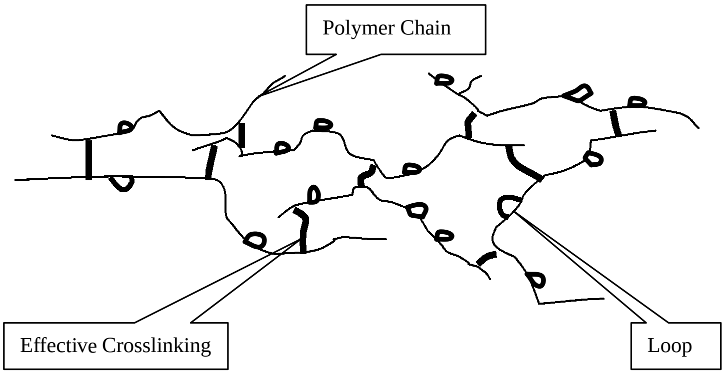
3.6. Improved Flory–Rehner equation

The classical theory applied above describes the crosslinking structure of the polyimide gels. However, a quantitative agreement between the theory and experiments has not yet been attained in general for the practical application to swollen polymer gels. The discrepancy appears to be due to oversimplification employed in the theory, such as Gaussian statistics of the polymer chains which ignores the segment-segment correlation and phantom assumption which ignores the topological constraints. In the case of a real polymer network, the polymer segment distribution is given by the self-avoiding walk (SAW) statistics. In equilibrium swelling Eq. (8) has been proposed [35],

$$\frac{\left(\frac{1}{2} - \chi_1\right)}{\left(1 - \frac{2M_c}{M_n}\right)} = \frac{\Phi_F}{\frac{M_c}{M_0}} \times \frac{5}{6}\left[\frac{6}{5}\left(f + \frac{1}{2}\right)\right]^{\frac{5}{2}}\left[Q^{\frac{25}{12}} - Q^{\frac{5}{4}}\right] - A_3\left[\frac{6}{5}\left(f + \frac{1}{2}\right)\right]^{-\frac{9}{10}} Q^{-\frac{3}{4}} \tag{8}$$

where *Q* is the equilibrium swelling ratio, *f* is the degree of ionization which we can disregard, A_3 is the third virial coefficient, Φ_F is the volume fraction of the polymer at the time of gel preparation which is 0.040 at 5 wt% and 0.081 at 10 wt%, M_0 is the molecular weight of the repeating unit, M_n is the number-average molecular weight of the primary polymer. The results are summarized in Table 5.

The values of M_c calculated from this improved equation (Eq. (8)) are smaller than those calculated from the classical equation (Eq. (6)), and the discrepancy becomes more marked with increasing crosslinking density. The classical Flory–Rehner equation ignores the segment-segment correlation that leads to the underestimation of the number of the



Scheme 2.

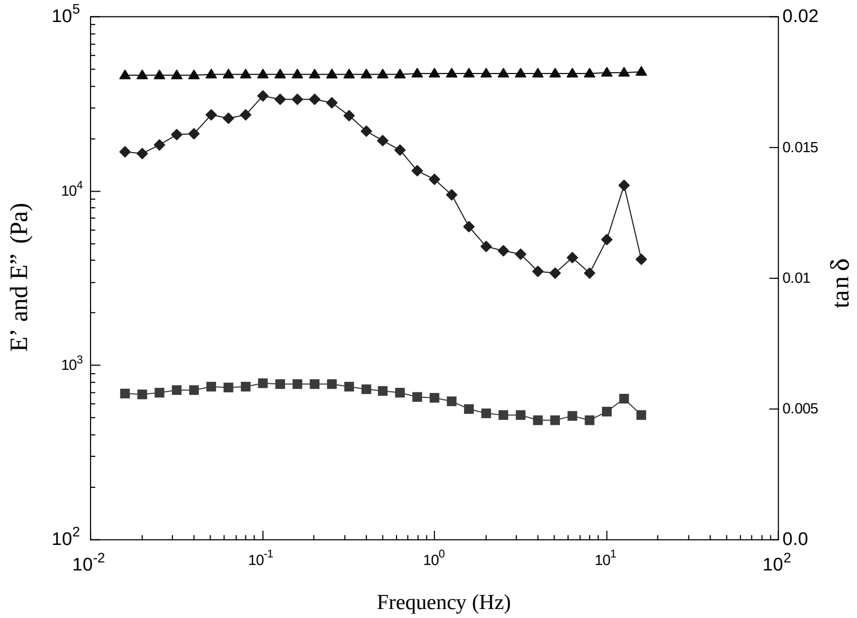


Fig. 5. E′ (▲), E″ (■), and tan δ (◆) vs. frequency for the polyimide gel G-1b.

Table 3
The equilibrium degree of swelling Q, calculated M_c and estimated fraction of effective linkage of the polyimide gels

Sample	NCO/OH	Q	M_c	n_{link}[a]	n_{eff}[b]	$f_{eff} = n_{eff}/n_{link}$[c]
G-1a	0.13	35.3	2.11×10^4	19	2.18	0.11
G-1b	0.12	32.8	2.08×10^4	18	2.21	0.12
G-2a	0.48	17.8	1.70×10^4	71	2.70	0.038
G-2b	0.47	14.6	1.50×10^4	69	3.07	0.044
G-3a	0.97	8.9	0.88×10^4	144	5.23	0.036
G-3b	0.92	9.1	0.91×10^4	136	5.05	0.037

[a] Number of reacted OH group per polymer $= N_{OH} \times$ NCO/OH (DP $= M_n/624 = 74$, $N_{OH} = 2DP = 148$).
[b] Effective linkage per polymer $n_{eff} = M_n/M_c$.
[c] Effective linkage fraction.

effective linkages. On the other hand, the improved equation uses the (SAW) statistics that makes the polymer chains have a more expanded conformation than the Gaussian distribution of the polymer chains. Therefore, at the same degree of swelling, the improved equation is supposed to give a smaller M_c. When the gel is highly crosslinked, the entanglement of polymer chains and segment-segment correlation in the as-prepared state exist more markedly than in the weakly crosslinked gel. Therefore we believe the improved Flory–Rehner theory gives a more accurate calculation of M_c at higher crosslinking densities. As for the values of f_{eff}, although varying from 0.06 to 0.14 they can be considered as the same around 0.10 within the experimental error range. The elastically effective crosslinking and loop forming reactions are a pair of competitive reactions. The crosslinking reaction involves two steps: at first one isocyanate group of the crosslinker reacts with one OH group on a polyimide chain, and second the remaining isocyanate group of the crosslinker reacts with an adjacent OH group which is either on the same or another polyimide chain relative to the first reacted OH group. This second step determines the final fractions of effective and loop linkages. For the pendent isocyanate group of the crosslinker bound to a polyimide chain, the ratio of concentration of OH groups on the same polyimide chain to that on other polyimide chains is always kept constant during the crosslinking reaction independent of initial crosslinker concentrations. Therefore the final fraction of effective linkage f_{eff}, can also be considered constant regardless of the initial crosslinker concentration. The average value of 0.10 means the probability ratio of the effective crosslinking with another polymer to the loop-forming reaction with the same polymer is 1 to 9, or in other words, the local concentration of OH group from the same polymer is 9 times larger than that of the OH group from another polymer within the reactive domain of the isocyanate group.

Table 4
Compression moduli of polyimide gels in their as-prepared states measured at 0.159 Hz, 25°C and the resulting M_c calculated from Eq. (7)

Sample	Dimension (mm)	E′ (Pa)	E″ (Pa)	d[a] (g/ml)	M_c
G-1a	$11.5 \times 9.5 \times 4.5$	6.9×10^4	2.0×10^3	1.05	1.9×10^4
G-1b	$5.0 \times 5.5 \times 5.5$	4.7×10^4	7.9×10^2	1.05	2.0×10^4
G-2a	$6.5 \times 8.5 \times 4.0$	8.6×10^4	1.2×10^3	1.05	1.8×10^4
G-2b	$3.5 \times 5.0 \times 5.5$	7.5×10^4	2.1×10^3	1.05	1.9×10^4
G-3a	$7.5 \times 8.0 \times 3.0$	7.8×10^5	8.2×10^4	1.05	0.70×10^4
G-3b	$4.5 \times 5.0 \times 4.5$	4.6×10^5	6.2×10^3	1.06	0.98×10^4

[a] The densities of the swollen gels in their as-prepared state which are calculated from the densities and weights of the dried gels and the solvent.

Table 5
Calculated M_c and estimated fraction of effective linkage, f_{eff}, of the polyimide gels using the improved Flory–Rehner's equation

Sample	NCO/OH	Q	M_c	n_{link}	n_{eff}	$f_{eff} = n_{eff}/n_{link}$
G-1a	0.13	35.3	1.70×10^4	19	2.7	0.14
G-1b	0.12	32.8	1.91×10^4	18	2.4	0.13
G-2a	0.48	17.8	0.91×10^4	71	5.0	0.070
G-2b	0.47	14.6	1.07×10^4	69	4.3	0.062
G-3a	0.97	8.9	0.29×10^4	144	15.9	0.11
G-3b	0.92	9.1	0.54×10^4	136	8.5	0.062

4. Conclusion

Swollen gels with rigid polyimide chains have been synthesized. The crosslinking reaction proceeded between hydroxyl groups on the polyimide chains and isocyanate groups in a crosslinker. No side reaction is observed under well-controlled conditions. All polyimide gels show a volume phase transition in a mixed NMP/water solvent with NMP content larger than 80 wt%. The average molecular weight between two crosslinking points M_c, has been calculated from the measurements of both equilibrium swelling ratio and complex compression modulus. By combining the data from ^{1}H-NMR and M_c, it is estimated that a lot of crosslinkers form small loops with the adjacent OH, while only several percents of them form elastically effective crosslinkages. Viscoelastic measurements showed compression modulus of 7.8×10^5Pa for as-prepared polyimide gels containing 95 wt% solvent. We are convinced that by using polyimides, it is possible to improve thermal and mechanical properties of the gels.

Acknowledgements

The authors would like to appreciate Dr. Masatoshi Hasegawa, Prof. Yoichi Shindo, and their students in Toho University for their help in measuring the static light scattering of the linear polyimide solution.

References

[1] Dušek K, Patterson D. J Polym Sci Part A-2 1968;6:1209.
[2] Tanaka T, Ishiwata S, Ishimoto C. Phys Rev Lett 1977;39:474.
[3] Tanaka T. Phys Rev Lett 1978;40:820.
[4] Dušek K, editor. Responsive gels: Volume Transition I Advances in Polymer Science, 109. Berlin: Springer, 1993.
[5] DeRossi D, Kajiwara K, Osada Y, Yamauchi A, editors. Polymer gels, fundamentals and biomedical aApplications New York: Plenum Press, 1991.
[6] Ikada Y. Kikan kagaku sosetsu, polymer gels, 8. Tokyo: Japan Chemical Society, 1990 p. 59.
[7] Osada Y, Okuzaki H, Hori H. Nature 1992;355:242.
[8] Yoshida R, Takahashi T, Yamaguchi T, Ichijo H. Adv Mater 1997;9:175.
[9] Suzuki A, Ishii T, Maruyama Y. J Appl Phys 1996;80:131.
[10] Li Y, Hu ZB, Chen YY. J Appl Polym Sci 1997;63:1173.
[11] Tanaka T, Hocker LO, Benedek GB. J Chem Phys 1973;59:5151.
[12] Jacques GJ, Jennifer LM, Peter NP. Macromolecules 1991;24:6690.
[13] Kanaya T, Ohkura M, Misawa M. Macromolecules 1994;27:5609.
[14] Hu Y, Horie K, Ushiki H, Tsunomori F, Yamashita T. Macromolecules 1992;25:7324.
[15] Hu Y, Horie K, Torii T, Ushiki H, Tang X. Polym J 1993;25:123.
[16] Asano M, Winnik FM, Yamashita T, Horie K. Macromolecules 1995;28:5861.
[17] Tokuhiro T, Amiya T, Mamada A, Tanaka T. Macromolecules 1991;24:2936.
[18] Callister S, Keller A, Hikmet RM. Makromol Chem, Macromol Symp 1990;30:19.
[19] Tanaka H, Fukumori K, Nishi TJ. Chem Phys 1988;89:3363.
[20] Liavsky M, Bubenikova Z, Bouchal K. Polymer 1996;37:3851.
[21] Aharoni SM, Edwards SF. Macromolecules 1989;22:3361.
[22] Aharoni SM. Macromolecules 1991;24:4286.
[23] He J, Yamashita T, Horie K. Macromol Chem Phys 1998;199:949.
[24] Akgiray O. Makromol Chem, Macromol Symp 1993;76:211.
[25] Lee KJ, Eichinger BE. Polymer 1990;31:406–14.
[26] Flory PJ. Principles of polymer chemistry, 11. Cornell University Press, 1953 chap. 11 and 13.
[27] Siddiq M, Hu H, Ding M, Li B, Wu C. Macromolecules 1996;29:7426.
[28] Erman B, Flory PJ. Macromolecules 1986;19:2342.
[29] Moerkerke R, Koningsveld R, Berghmans H, Dušek K, Šolc K. Macromolecules 1995;28:1103.
[30] Moerkerke R, Meeussen F, Koningsveld R, Berghmans H, Mondelaers W, Schacht E, Dušek K, Šolc K. Macromolecules 1998;31:2223.
[31] Mita I, Horie K, Masuda M. Polym Bull 1981;4:369.
[32] Stepto RFT, editor. Polymer Networks, principles of their formation, structure and properties UK: Blackie, 1998.
[33] Tobolsky AV, Carlson DW, Indictor NJ. Polym Sci 1961;54:175.
[34] Poser CI, Ofstead RF. Proc ACS Polym Mater Sci Engng 1987;57:366.
[35] Dušek K, editor. Responsive gels: Volume Transition I Advances in Polymer Science, 109. Berlin: Springer, 1993. p. 7.