Preparation of end-crosslinked polyimide gels with high moduli

Jionghao He[a],*, Kazuyuki Horie[a], Rikio Yokota[b], Feifeng He[c]

[a]*Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*
[b]*Institute of Space and Astronautical Science, 3-1-1 Yoshinodai, Sagamihara-shi, Kanagawa 229-8510, Japan*
[c]*Shanghai Research Institute of Synthetic Resins, No. 36, Cao Bao Road, Shanghai 200233, People's Republic of China*

Abstract

Crosslinked polyimide gels with pendant hydroxy groups reported previously were found to have only a small fraction of elastically effective junctions. In order to increase the amount of effective junctions and obtain polyimide gels with high modulus, the approach of end-crosslinking with an imide linkage was developed. Methylenedianiline oligomer (pMDA), which has an average amino functionality of 2.6, was used as an amine comonomer as well as a crosslinker to react with $4,4'$-(hexafluoroisopropylindene)-diphthalic anhydride (6FDA), $4,4'$-oxydiphthalic anhydride (ODPA) and $3,3',4,4'$-biphenyltetracarboxylic dianhydride (BPDA) to make different polyimide gels. High compression moduli greater than 1 MPa were found for the ODPA/pMDA polyimide gels at their equilibrium swollen states in N-methylpyrrolidone (NMP). BPDA/pMDA gels did not swell in NMP, while 6FDA/pMDA gels swelled significantly and finally dissolved in NMP. The equilibrium swelling ratio and compression moduli for as-prepared and equilibrium swollen states were correlated to the chemical structure and initial monomer concentrations of the polyimide gels, and found to agree quite well with the prediction of the scaling theory. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Polyimide gel; End-crosslinking; Modulus
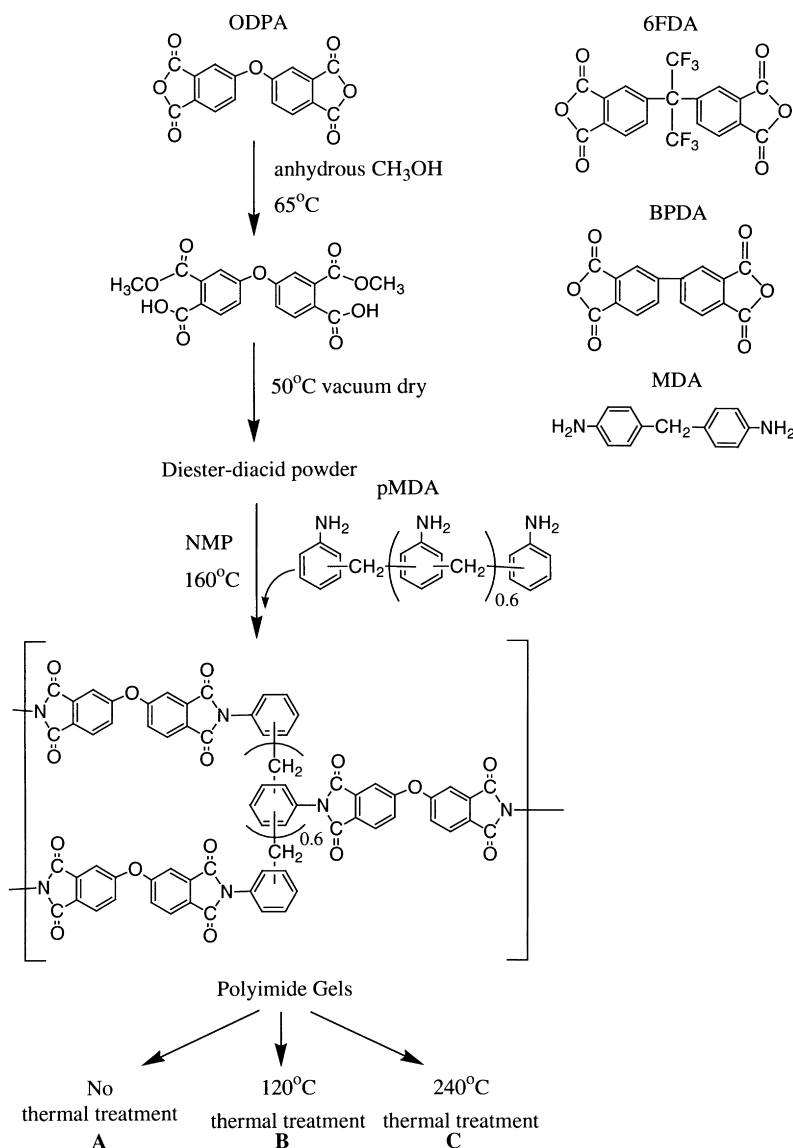
1. Introduction

Vinyl-based polymer gels are being intensively studied and developed for polymer supports, hygiene products, contact lenses and so on [1,2]. Some disadvantages of these vinyl-based polymer gels are their low mechanical strength and the lack of thermal stability. Because of the high swelling ratio as mostly required for the volume phase transition (VPT) applications [3], the gels are usually very soft and easy to break apart. Therefore, although the VPT of the gels is very attractive to researchers, the softness of the gels prevents them from being used in high pressure and high temperature situations. In order to improve the mechanical properties of the polymer gels, either a physical method or a chemical approach can be applied. Freeze-dry technique is a well-known physical process for improving the strength of the gels [2]. As for the chemical approach, one can either increase the crosslinking density or use intrinsic high-performance polymers. However, when the crosslinking density is increased, the gel becomes difficult

to swell and thus loses its VPT character, which makes it useless. Gels prepared from a high-performance polymer, polyimide, have demonstrated for the first time, in our previous paper [4], very high moduli which are several times greater than those of the vinyl-based networks at the same degree of swelling. The polyimide, a high-performance thermal-resistant engineering polymer widely used in the electronic and space industry [5], was used as the framework of the gel. Due to their stiff aromatic main chain and strong polarity, polyimide gels have extraordinarily high modulus as well as thermal stability. Combined with their superior chemical and thermal stability, polyimide gels with high swelling ability and VPT can be designed as artificial muscles where strength is significant, and high temperature catalyst supports where thermal resistance and chemical stability are required.

In our previous papers [4,6], a soluble polyimide with pendant hydroxy groups was prepared. The crosslinking reaction took place with the pendant hydroxy groups through a diisocyanate crosslinker. This kind of pendant type crosslinking was accompanied by intramolecular loop formation, and the fraction of resulting elastically effective linkages was rather small. Moreover, because of crosslinking with the urethane structure, the polyimide gel tended to decompose when exposed to ultraviolet light or

* Corresponding author. Tel: + 81-3-5841-7289; fax: + 81-3-5841-8658.

E-mail addresses: hejh@horie-lab.chem.t.u-tokyo.ac.jp (J. He), horie@chembio.t.u-tokyo.ac.jp (K. Horie).

ODPA

6FDA

anhydrous CH₃OH
65°C

BPDA

50°C vacuum dry

MDA

Diester-diacid powder

pMDA

NMP
160°C

Polyimide Gels

No
thermal treatment
A

120°C
thermal treatment
B

240°C
thermal treatment
C

Scheme 1.

high temperature. In order to prepare a tough, chemically and thermally stable gel, we used in the present paper an amino compound with more than two amino groups serving as a comonomer as well as a crosslinker to react with dianhydrides. The resulting linkages are all composed of imide structures, which have excellent thermal and chemical stability. A gel material with a compression modulus of more than 1 MPa in its fully swollen state was realized. The equilibrium swelling ratio and compression moduli of the present end-crosslinked polyimide gels were discussed based on the scaling theory.

2. Experimental part

2.1. Reagents

All the reagents were purchased from Tokyo Kasei Organic Chemicals, Wako Chemicals and Aldrich Chemicals, and were used without further purification unless otherwise described. A methylenedianiline oligomer (pMDA) was provided by Nippon Polyurethane Co.

2.2. Preparation of diester–diacids

A dianhydride, 4,4′-(hexafluoroisopropylindene)-diphthalic anhydride (6FDA), 4,4′-oxydiphthalic anhydride (ODPA) or 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA), was added to a baked flask containing anhydrous methanol to make a mixture at a concentration of about 20–30 wt%. The mixture was heated to 65°C to have the methanol refluxed until the mixture became a clear solution. The methanol solution was further refluxed for 1 h after the solution became clear. Then the solution was evaporated and vacuum dried at 50°C overnight to obtain the diester–diacid powder. The esterification was verified by ¹H-NMR.

Table 1
The gelation time of the polyimide gels (initial monomer concentration: 20 wt%; A: without thermal treatment; B: with 120°C thermal treatment; C: with 240°C thermal treatment)

Sample	Amine composition (mol%)		Thermal treatment	Gelation time (h)
	pMDA	MDA		
6FDA–pMDA-50	50	50	B	4.0
			C	
6FDA–pMDA-100	100	0	B	2.5
			C	
ODPA–pMDA-50	50	50	B	3.0
			C	
ODPA–pMDA-100	100	0	A	1.5
			B	
			C	
BPDA–pMDA-50	50	50	B	3.5
			C	
BPDA–pMDA-100	100	0	B	2.0
			C	

2.3. Preparation of end-crosslinked polyimide gels

The diester–diacid derived from 6FDA, ODPA or BPDA was dissolved into *N*-methylpyrrolidone (NMP). A 14.045 wt% NMP solution of pMDA prepared in advance and the solvent NMP were added to the diester–diacid solution to make various initial monomer concentrations ranging from 10 to 45 wt%. 4,4′-Methylenedianiline (MDA) as a diamine comonomer was also introduced when it was necessary to make copolyimide gels. The exact stoichiometry between the ester–acid and amino groups was necessary in preparing the reacting solutions. The monomer solutions were heated at 160°C for several hours to obtain the crosslinked polyimide gels [7]. After the gel preparation, the polyimide gels were subject to further annealing. The gels without further annealing, with 120°C and 240°C thermal treatments under vacuum, were coded as A, B and C series. The whole preparation of the end-crosslinked polyimide gels is illustrated in Scheme 1 and the detailed composition, coding and gelation time for all the gels are summarized in Table 1.

2.4. Amino functionality of pMDA

The C–H–N element analysis was carried out on an EAGER 200 Analyzer to determine the average amino functionality of pMDA which was used as a comonomer and at the same time as a crosslinking agent. pMDA is an intermediate by-product when methylenediphenyl diiso-cyanate (MDI) is produced through the reaction between formaldehyde and aniline. The amino group concentration was found to be 10.45 mol/kg ($N = 14.639\%$) for pMDA and the average amino functionality is around 2.6, which was provided by Nippon Polyurethane Co.

2.5. Determination of imidization ratio

The thermal imidization ratio of the polyimide gels was confirmed by IR spectra (Jasco IR-700) at the wave numbers of 1780, 1380 and 725 cm^{-1}. A model compound derived from phthalic anhydride and pMDA was used as a reference for estimating the imidization ratio of the polyimide gels.

2.6. ^{1}H-NMR measurements

A 5 wt% ODPA–pMDA solution in DMSO-d$_6$ was heated to elevated temperatures, where the formation of methanol, water and acid were traced with the ^{1}H-NMR spectra with the chemical shifts of 3.2, 4.1 and 9.6–10.4 ppm, respectively. The measurements were performed on JEOL JNM-GX270 FT-NMR.

2.7. Determination of sol–gel fractions

The prepared polyimide gels were cut into small pieces and the sol fraction was extracted with NMP in a fat extrac-tor at about 150°C for 6, 24 and 48 h (A, B and C series, respectively). Then the sol-free gels were vacuum dried at 240°C for 3 h. Another method of extraction was also applied for the A series samples. The dried gels (A series) were dipped into NMP at 45°C for two weeks to extract the sol fraction, and the solvent was replaced every other day. Gels were weighted before and after the extraction as well as in the dry state to calculate the sol–gel fraction inside the polyimide gels.

2.8. Swelling behaviors of polyimide gels

Since we did not observe any remarkable temperature dependence of the equilibrium swelling ratio, the sol-free polyimide gels after the extraction were considered to be in their equilibrium swelling state. By applying the following Eq. (1), the equilibrium degree of swelling in weight can be

Table 2
Integration of proton peaks for ODPA–pMDA-100 gel upon heating (initial monomer concentration: 5 wt%; solvent: DMSO-d_6)

Procedure	CH$_3$OH 3.2 ppm	–COOH 9.6–10.4 ppm	–NH$_2$ 4.4–6.4 ppm	H$_2$O 4.1 ppm	Aromatic 6.3–8.0 ppm	DMSO 2.5 ppm
50°C, 5 min	0.065	0.029	0.397	0	1.000	0.048
80°C, 5 min	0.055	0.019	0.508	0	1.000	0.045
100°C, 5 min	0.044	0.015	0.520	0	1.000	0.045
120°C, 5 min	0.063	0.016	0.533	0	1.000	0.040
150°C, 5 min	0.105	0.023	0.564	0.002	1.000	0.040
150°C, 15 min	0.158	0.035	0.527	0.004	1.000	0.041
150°C, 45 min	0.168	0.048	0.236	0.014	1.000	0.032
150°C, 90 min	0.238	0.020	0.000	0.081	1.000	0.044
160°C, 120 min	0.178	0	0	0.095	1.000	0.048

calculated:

$$Q_{\mathrm{w}} = \frac{W_{\mathrm{PI}} + W_{\mathrm{NMP}}}{W_{\mathrm{PI}}}, \tag{1}$$

where W_{PI} and W_{NMP} are the weights of the polyimide and the solvent inside the swollen gel, respectively. The sol-free polyimide gels were also dried and dipped into NMP at 75°C in order to measure their swelling speed and stability.

2.9. Modulus measurements

Dynamic mechanical measurements were performed on a Rheometric RSA II viscoelastic apparatus. Polyimide gels in their as-prepared and equilibrium swelling states were cut into cubes and sandwiched between two circular plates imposed with a compressive pre-tension ranging from 20 to 200 g. The dynamic strain sweep test ($\varepsilon = 0.5$–10%, 1 Hz) was carried out to study the modulus–strain correlation of the gels. The dynamic frequency sweep test (0.1–15 Hz) was carried out for frequency dependent studies. The stress relaxation test was carried out for gels that were too hard to be measured by the first two tests. The complex compression modulus E^* of the gels was measured at 25–30°C. The storage part of the complex compression moduli (E') at 1 Hz was used as a characteristic value in the present study.

3. Results and discussion

3.1. Gelation mechanism

The reaction of the present polyimide gel formation upon heating has two possible routes. For the first one, the ester–acid group converts to anhydride at first due to the removal of methanol when heated. Then the dianhydride and diamine follow the normal way to form polyamic acid and polyimide. The second is that the amine reacts with diester–diacid first to form polyamide ester, then it is imidized when methanol is removed. However, the diester–diacid preparation method for polyimide synthesis was confirmed to follow the first reaction route [8]. In the present paper, we have also traced the formation of water, methanol, amino group and acid in ^{1}H-NMR spectra during the crosslinking

reaction. The results are summarized in Table 2 and Fig. 1. The integration of the aromatic peaks (6–8 ppm) was taken as the reference. There was a peak for the proton of carboxylic acid around 10 ppm at first. It began to decrease when the temperature rose from 50°C and started to increase again from 120°C. This suggests that the formation of anhydride took place first, which led to the decrease in acid. Then the anhydride reacted with amine to form amide acid again. Meanwhile, the peak of methanol at 3.2 ppm increased steadily. In Fig. 1, it is clear that the peak of water (4.1 ppm) began to increase at 150°C which indicated the imidization process. Finally, when it was heated at 160°C for 2 h, the peaks for carboxylic acid and amine (4.4–6.4 ppm) all disappeared, which means the reaction was complete. As for the amino group (4.4–6.4 ppm), it shifted gradually upon heating from the lower to the higher magnetic field, which indicates the dissociation of ion interaction between the carboxylic acid and the amine. When further heated, the amino group began to decrease and finally disappeared as a consequence of amide and imide formation. Therefore, the gelation mechanism in our case for the ODPA–pMDA system is the same as that described in the literature [8]. The gelation takes a longer time in the order from ODPA, BPDA to 6FDA as the dianhydride comonomer (Table 1).

3.2. Imidization ratio of polyimide gels

The absorbance ratio of the band at 1380 cm^{-1} (C–N stretching) to the band at 1500 cm^{-1} (benzene ring vibration) was taken to estimate the imidization ratio of the polyimide gels [9]. A model compound derived from phthalic anhydride and pMDA which is assumed to have a 100% imidization ratio was taken as the reference. For the present preparation condition, i.e. heating at 160°C for 8 h, the gels had an imidization ratio of around 80% (A series). When the gels were thermal treated at 240°C for 3 h (C series), they showed an imidization ratio of above 90%. Those thermally treated at 120°C (B series) did not have a significant change in the IR spectra compared to the A series. Thus, in order to achieve high thermal and chemical stability for the polyimide gels, thermal treatment at 240°C
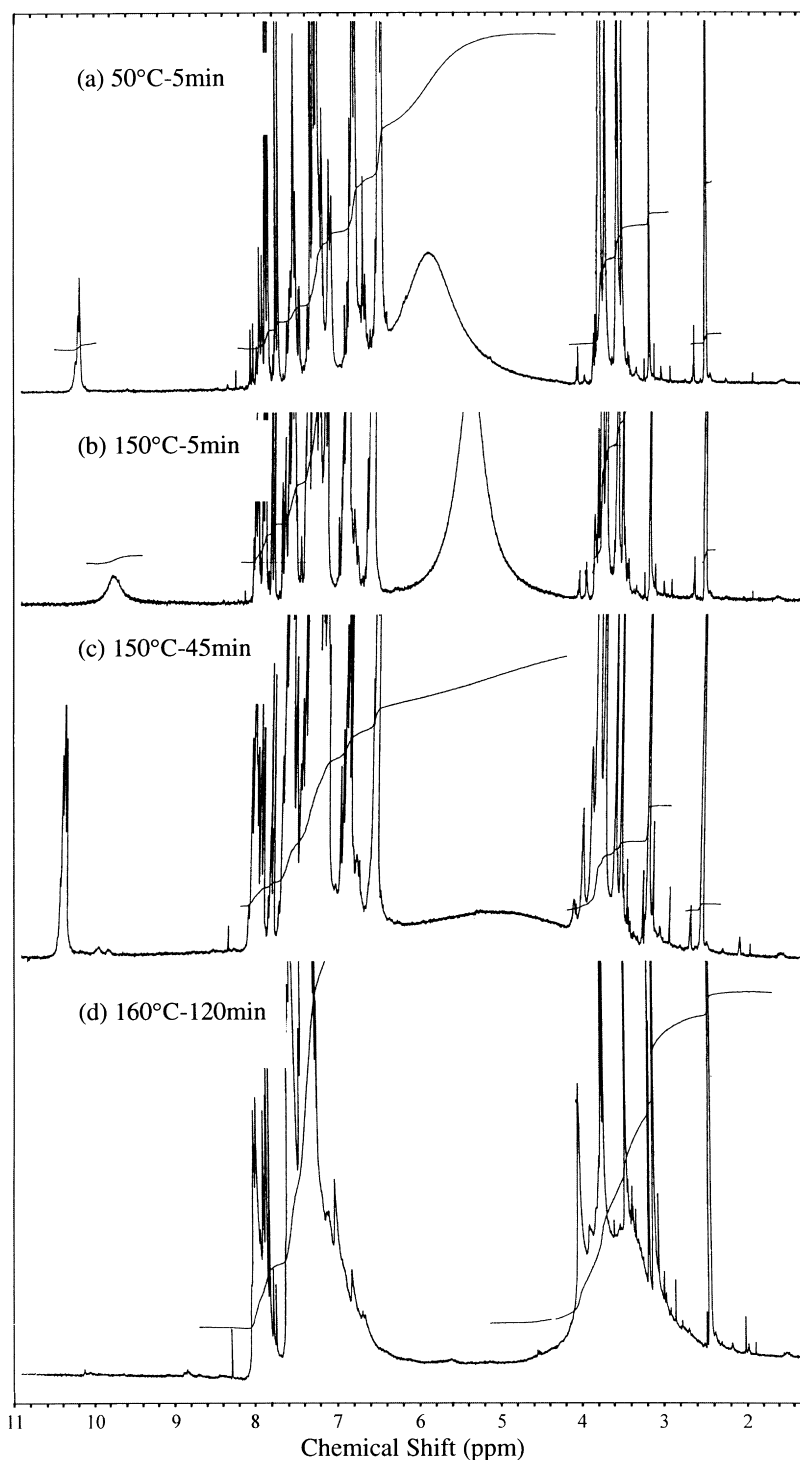
Fig. 1. ^{1}H-NMR spectra of ODPA–pMDA-100 in DMSO-d$_6$ at various temperatures and reaction times.

after gel formation at 160°C is necessary for the present end-crosslinked system.

3.3. Sol–gel fraction and stability of polyimide gels

The soluble fraction was extracted for all the polyimide gels and is shown in Table 3. It is clear that after the thermal treatment (B and C series), the polyimide gels contained only smaller amounts of sol fraction and became more stable in NMP. It was also found that the polyimide gels without any thermal treatment (A series) had poor stability in NMP at high temperatures. For example, ODPA–pMDA gels (A series) became dissolved in NMP at 75°C after one month. Even with a certain thermal treatment (B and C

Table 3
Soluble fraction in the polyimide gels (initial monomer concentration: 20 wt%; A series: without thermal treatment; B series: with 120°C thermal treatment; C series: with 240°C thermal treatment)

Sample	A series	B series	C series
6FDA–pMDA-50		dissolved	0.12
6FDA–pMDA-100		0.54	0.28
ODPA–pMDA-50		0.77	0.06
ODPA–pMDA-100	0.37	0.24	0.07
BPDA–pMDA-50		0.19	0.02
BPDA–pMDA-100		0.19	0.03

series), 6FDA–pMDA gels became decomposed in NMP at 75°C, also in one month. However, they are all quite stable in NMP at room temperature. The chemical and thermal stability of the polyimide gels is probably influenced by the imidization ratio of the gels. It is believed that there is some residual amide structure remaining in the polyimide gels. These amides with pendant carboxylic groups at *ortho* positions tend to be intramolecular-acidolyzed to form an anhydride. In the presence of water and in a polar aprotic solvent like NMP at high temperatures, this decomposition reaction is further enhanced [5]. The breakdown of the amide linkages leads to the decomposition of the polyimide gels. ODPA–pMDA and BPDA–pMDA gels which have been thermally treated at 240°C are very stable and show no significant change in the weight of the gels after three months in NMP at 75°C.

3.4. Gelation conditions

In order to find a suitable gelation condition for synthesizing the polyimide gels, the reaction time and initial monomer concentration dependencies of the ODPA–pMDA system were investigated in detail. The sol fraction and equilibrium degree of swelling are the key parameters to

set the criterion. The reaction temperature was chosen as 160°C according to the reference [7]. The reaction time was investigated from 1 to 8 h. The results of the sol fraction and equilibrium degree of swelling in weight are shown in Fig. 2. The formation of the gel was observed after 3 h of heating at 160°C. The sol fraction drops from 70 to 25% when heated for 8 h. The same trend was also observed for the equilibrium degree of swelling in weight. It can be speculated that the sol fraction and the equilibrium degree of swelling in weight will not change much beyond 8 h. Therefore, the reaction time was set to be 8 h. Next, we changed the initial monomer concentration from 15 to 35 wt% and studied their properties. As shown in Fig. 3, the sol fraction decreases almost linearly down to 10 wt% with the increase in the initial monomer concentration. There is a discrepancy for the 15 wt% gel here compared with the data in Fig. 2. In the initial monomer concentration study, the gels were dipped into NMP at 75°C for ten days in order to extract the sol fraction, which was different from using the fat extractor in the reaction time study. Since the gels are not very stable in NMP at the high temperature, it could have resulted in a higher sol fraction and equilibrium swelling ratio. However, this will not affect the results of the comparison here. For those above 35 wt%, because of the removal of methanol at high solid concentrations, the gels had big pores inside and became inhomogeneous, which made the measurement inaccurate. In order to make a high modulus gel with a swelling ratio of around 10, a concentration of 20 wt% is preferred in the present end-crosslinked system. Thus, all the polyimide gels were synthesized at 20 wt% under 160°C for 8 h unless otherwise specified.

3.5. Moduli of polyimide gels

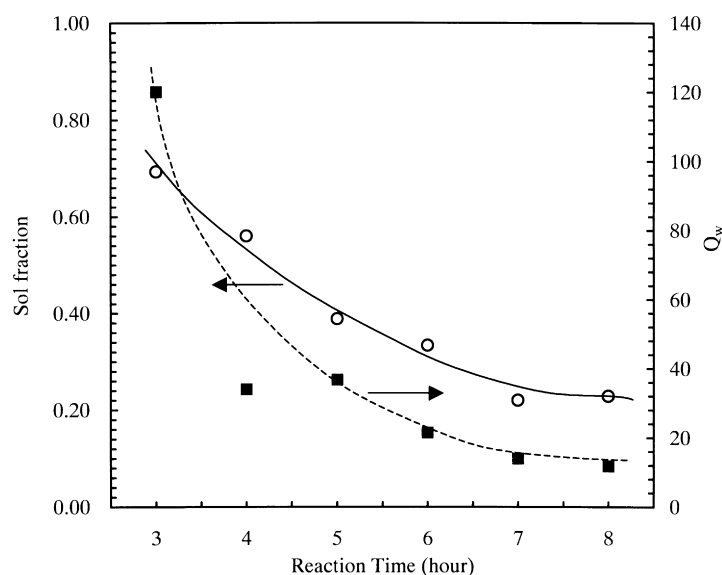It has long been known that the properties of a crosslinked

Fig. 2. (○), sol fraction and (■), equilibrium swelling ratio in weight Q_w for ODPA–pDMA-100 — 15 wt% gels prepared at 160°C in various reaction times.
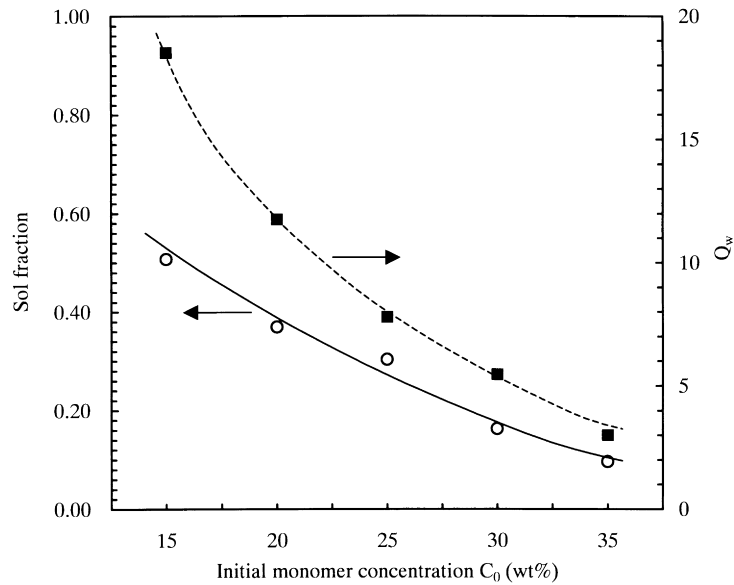
Fig. 3. (○), sol fraction and (■), equilibrium swelling ratio in weight Q_w for ODPA–pDMA-100 gels prepared at 160°C for 8 h with various initial monomer concentrations C_0.

network depend on the preparation conditions (solvent class and concentration at preparation). Many theoretical studies have been carried out to deal with the elasticity of a real network containing trapped entanglements and chain defects [10–12]. Scaling theory appears to be quite good at predicting the modulus as a function of preparation conditions and final testing conditions, including the dry and equilibrium swollen states [13,14]. There are two kinds of network. One is the strongly crosslinked network which has no permanent (trapped) entanglements. However, in practice, most networks have modulus and swelling dominated by trapped entanglements, which can be called lightly crosslinked network. The relationship between the modulus and the swelling ratio of the lightly crosslinked

network is given by the following equations [13]:

$$\frac{Gb^3}{kT} \cong \left(\frac{b}{a_1}\right)^2 \begin{cases} \phi_0^{5/3}\phi^{7/12} & (T \gg \theta) \\ \phi_0^2\phi^{1/3} & (T = \theta) \end{cases} \tag{2}$$

$$Q \cong \begin{cases} (a_1/b)^{6/5}\phi_0^{-1} & (T \gg \theta) \\ (a_1/b)^{3/4}\phi_0^{-3/4} & (T = \theta) \end{cases} \tag{3}$$

where G is the shear modulus, T the absolute temperature, k the Boltzmann constant, a_1 the tube diameter in the melt, b the monomer size (Kuhn length), ϕ the volume fraction of the polymer at the test condition, ϕ_0 the volume fraction of the monomer during preparation and θ the temperature of the polymer. The equilibrium swelling ratio Q is defined as
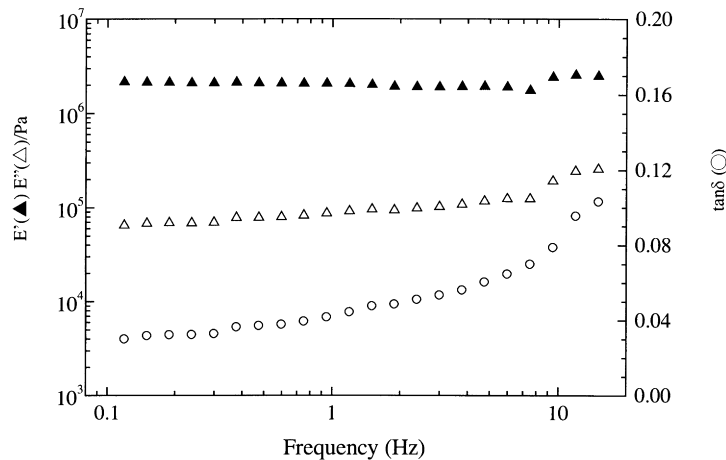

Fig. 4. Dynamic frequency sweep test for ODPA–pMDA-100 gel after 240°C thermal treatment in its equilibrium swollen state in NMP at 75°C.
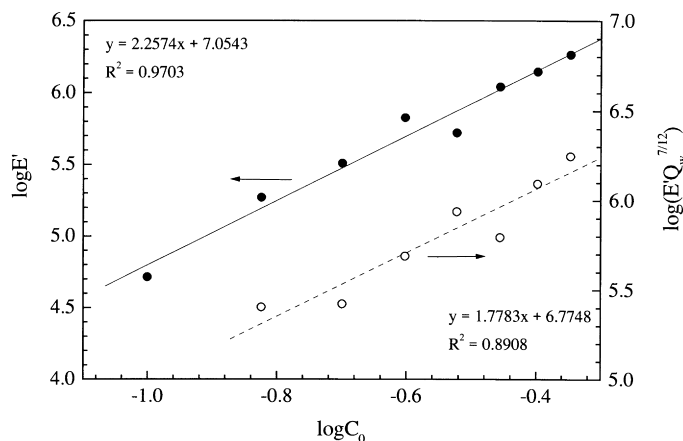
Fig. 5. Correlation of initial monomer concentration C_0 and compression modulus E' in the (●), as-prepared and (○) equilibrium swelling states for the ODPA–pMDA-100 polyimide gels prepared at 160°C for 8 h with various initial monomer concentrations.

the ratio of the volumes of the gel in the fully swollen and dry states, which is simply the reciprocal of the volume fraction in the fully swollen state ($Q = 1/\phi$).

From Eq. (2), the initial monomer concentration dependency of the shear modulus in as-prepared state for the lightly crosslinked network can be derived by applying $\phi = \phi_0$ which leads to $G \sim \phi_0^{9/4}$ for different preparation concentrations in a good solvent. On the other hand, as for the measurements in the fully swollen state in good solvent where $\phi = 1/Q$, the correlation between the shear modulus and the equilibrium swelling ratio can be expressed as $G|_{\phi=1/Q} \sim Q^{-9/4}$. This relation is valid for both strongly and lightly crosslinked networks.

In our case, the complex compression moduli of the polyimide gels were measured by both the dynamic strain sweep test and the dynamic frequency sweep test. It was found that the storage compression moduli (E') keep almost constant at various strains and that the polyimide gels can stand a strain of at least 7%. The typical dynamic frequency sweep test of the ODPA–pMDA-100 gel in its equilibrium swollen state is given in Fig. 4. It is clear that the storage compression modulus (E') does not have a frequency dependence. Based on the fact that the compression modulus is proportional to the shear modulus ($E' \sim G$) under small strain while the weight concentration and swelling ratio in weight are approximately in proportion to the volume fraction and swelling ratio in volume ($C_0 \sim \phi_0$, $Q_w \sim Q$), we have plotted in Fig. 5 (left Y axis) the compression modulus E' in the as-prepared state against the initial monomer concentration C_0, double-logarithmically for the ODPA–pMDA-100 gels prepared at various concentrations. We found that it could be scaled as $E' \sim C_0^{2.26}$ which was almost the same as the value of 9/4 deduced from Eq. (2) for lightly crosslinked networks. In Fig. 5 (right Y axis), for the equilibrium swollen ODPA–pMDA-100 gels prepared under various concentrations, the correlation can be scaled as $E'Q_w^{7/12} \sim C_0^{1.78}$, which is in quite a good agreement with $G \sim \phi_0^{5/3}\phi^{7/12}$ suggested in Eq. (2). It implies that there

were a lot of trapped entanglements inside the polyimide gels in their preparation states, even though after the reaction at 160°C for 8 h, there are some uncrosslinked parts remaining due to the incompleteness of the reaction. As we can see from Table 3, the polyimide gel immediately after the preparation (A series) has a sol fraction as much as 30%. These chain defects form entanglements and lead to a stronger dependence of E' and Q on the initial concentration. In Fig. 6, the compression modulus in their equilibrium swollen states was plotted against the equilibrium degree of swelling in weight, double-logarithmically for different kinds of polyimide gels. Although their chemical structures and conditions of preparation and thermal treatment are different, almost all of them appear on a line which can be correlated as $E' \sim Q_w^{-2.19}$. This exponent is pretty close to $-9/4$. It is noteworthy that this exponent in the relationship between E' and Q_w holds for both strongly crosslinked and lightly crosslinked networks. The present end-crosslinked polyimide gels show dynamic and swelling characteristics which agree well with those predicted by the scaling theory.
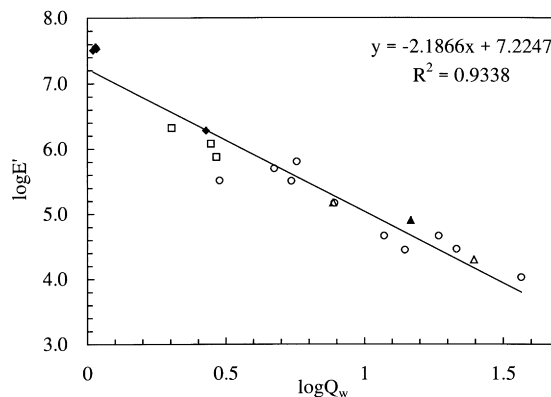

Fig. 6. Correlation of equilibrium swelling ratio in weight Q_w and compression modulus E' for the polyimide gels. [(○), ODPA — A series; (△), ODPA — B series; (□), ODPA — C series; (◆), BPDA — B and C series; and (▲), 6FDA — B series].

Table 4
The compression moduli of polyimide gels in their as-prepared state and equilibrium swollen states of C series

PI Gels C series	As-prepared state (A series)		Equilibrium swelling state at 75°C (C series)	
	PI concentration (wt%)	E' (Mpa)	PI concentration (wt%)	E' (MPa)
6FDA–pMDA-50 — C	20	0.04	34	dissolved
6FDA–pMDA-100 — C	20	0.06	40	dissolved
ODPA–pMDA-50 — C	20	0.06	36	1.2
ODPA–pMDA-75 — C	20	0.10	34	0.8
ODPA–pMDA-100 — C	20	0.14	50	2.1
BPDA–pMDA-50 — C	20	0.06	92	34.0
BPDA–pMDA-75 — C	20	0.28	95	32.0
BPDA–pMDA-100 — C	20	0.24	93	36.0

It should be noticed that the modulus for the equilibrium swollen gel of ODPA–pMDA-100 has reached a value greater than 2 MPa with a weight swelling ratio of 2.0. The moduli of other polyimide gels are summarized in Table 4. For the as-prepared states, all the gels have almost the same moduli, around 0.1–0.2 MPa, although different monomers were used. For example, a typical soft contact lens has a tensile strength less than 0.2 MPa in its swelling state with a weight swelling ratio of 2 [2]. In our case, a high modulus above 1 MPa was reached by using the intrinsic high-performance polymer to make the gels. Furthermore, these kinds of gels swell and are quite stable in the organic solvents at high temperatures.

The correlations of the modulus of the gel with its preparation and swelling conditions have been discussed above. However, in order to design a gel material with specified modulus and swelling ratio, the discussion with the scaling law alone is not sufficient. We have to predict the absolute value of the modulus or swelling ratio of a given gel material. Because of the chain defects or intramolecular loops inside the gels, the modulus of a real network can never reach the modulus of a perfect network. It has been noticed that there are quite a lot of intramolecular loops formed in almost all the crosslinking systems [15,16]. For a real network, the modulus can be estimated by Eq. (4),

$$E = 3G = \frac{3ART\rho\phi_2^{1/3}(V_u/V_F)^{2/3}}{M_c}\left(1 - \frac{2M_c}{M_n}\right) \qquad (4)$$

where ϕ_2 is the network volume fraction at equilibrium swelling, ρ the density of the dried network, V_u the volume of the dried, unstrained network, V_F the volume of the network at formation, (V_u/V_F) the dried network volume fraction at formation, M_c the molecular weight between elastically active junction points, M_n the number-average molecular weight of the linear polymer and T the temperature in the measurement; A has the value of $(1 - 2/f)$ for phantom networks and the value of 1 for affine networks [17]. $(1 - 2M_c/M_n)$ is the correcting term for the influence of dangle primary chain ends. For our end-crosslinked polyimide gel systems, M_c is estimated to be

1000 g/mol, the density of the dried gel is about 1.3 g/cm^3, the monomer volume fraction at preparation is 0.2 and the temperature of the measurement is 300 K. Therefore, for the affine network when the dangle chain end is ignored, the compression modulus of the gel must be 2.6 MPa and 1.5 MPa when the gel has a swelling ratio of 2.0 and 10.0, respectively. The modulus of the ODPA–pMDA-100 gel in C series (2.1 MPa) almost reaches the theoretical prediction value for an equilibrium swelling ratio of 2.0. The moduli of the BPDA–pMDA gels (C series) are about one order larger because the gels hardly swell and look like solids.

4. Conclusions

The end-crosslinked polyimide gels consisting of imide linkage alone are proved to have high modulus as well as chemical and thermal stability. ODPA–pMDA gels showed an equilibrium swelling ratio of 2.0 together with a compression modulus above 1 MPa. We are convinced that the high modulus has been achieved by using the stiff aromatic polyimide chains. The correlation between the moduli in preparation state and equilibrium swollen state, and the equilibrium degree of swelling in weight was elucidated. We found that it agrees quite well with the scaling theory. It would be possible to design a polyimide gel material with specified modulus and equilibrium swelling ratio in the extended direction of the present research.

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