Preparation and Physical Properties of Polyimide Gels (IV)
Swelling Behavior, Crosslink Density and Dynamic Mechanical Properties

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ABSTRACT

A solvent soluble fluorine-containing polyimide derived from 4,4'-(hexafluoro-isopropylindene) diphthalic anhydride (6FDA) and 3,3'-dihydroxy-4,4'-diaminobiphenyl (DHBP) was prepared and successfully crosslinked with the reaction between hexamethylene diisocyanate (HDI) and hydroxyl group on the phenylene ring, to make a series of soft polyimide gels. The crosslinking reaction was studied with IR, UV and NMR measurements to determine the sol-gel fraction and the actual degree of conversion of hydroxyl groups. The degree and structure of crosslinking are investigated by using swelling experiments in 1-methyl pyrrolidone (NMP) and dynamic mechanical measurements. It has been found that a large amount of crosslinkers form intramolecular loops and the fraction of effective intermolecular linkages is relatively small.

Introduction

Polymer gels recently attract much more attention than ever before. It is possible to design a wide range of intelligent materials using a famous phenomenon of the gel, i.e., volume phase transition. By introducing selectively active ingredients to the polymer network, gels can be made to be responsive against temperature, pH, electric and magnetic field, pressure and etc.[1] In order to prepare a good applicable gel, it is very important to control the physical structure or topology of the gel. There are already some kinds of computer simulations on the structure and elasticity of polymer networks. In this paper, we choose a rigid polymer – polyimide as the framework to synthesize a series of polyimide gels and studied their swelling behaviors and viscoelastic properties. From the data of swelling ratio and modulus, we can speculate the structures, i.e., the fraction of intramolecular linkages and intermolecular linkages, of the crosslinked networks.

Experiments

Preparation of a polyimide, PI(6FDA/DHBP) and polyimide gels

The preparations of a polyimide, PI(6FDA/DHBP), and polyimide gels were carried out according to our previous paper.[2] Two series of polyimide gels crosslinked with hexamethylenediisocyanate (HDI) with initial solid weight concentrations of 5% (group "a") and 10% (group "b") were synthesized.

Static light scattering of the polyimide

The linear polyimide was dissolved in NMP to prepare a solution at a concentration of about 0.01g/ml. The initial solution was then diluted into four solutions. All the solutions were filtered with 5μm filter paper three times before the measurement. The

measurement was carried out at 24°C by using a He-Ne laser at 633nm and the scattering light was collected from an angle of 30°-150° with an interval of 10°.

Determination of hydroxyl group conversion

The dried sol-free polyimide gels were swollen in DMSO-d_6 for at least two days. ^{1}H-NMR spectra measurement was performed on JEOL JNM-GX270 FT-NMR for all the gels.

Studies of the swelling behaviors of polyimide gels

The dried sol-free polyimide gels were dipped into various concentrations of NMP/water mixed solvents at constant temperature (20°C) to study the swelling and volume changes of the gels. Cylinder-shaped gels were prepared. By measuring the diameter and length of the gels, the swelling ratio was calculated. We can also measure the swelling ratio by weighing the sample even if the shape of the gel is irregular.

Dynamic mechanical measurements of polyimide gels

Polyimide gels in their as-prepared condition were sandwiched by two circular plates and the storage and lost compression modulus of the gels were measured with a Rheometric RSA II at a frequency of 1Hz under a room temperature (25°C).

Results and Discussion

Weight-average molecular weight and Flory-Huggins parameter of the polyimide

From the extrapolation of the Zimm plot, we found the weight-average molecular weight M_w is 9.28×10^4 while the second Virial coefficient A_2 is 1.0393×10^{-3} mol•ml/g^2, which means NMP is a very good solvent for the polyimide. Flory-Huggins parameter χ was calculated to be 0.3303. Since the preparation of polyimide is a polycondensation reaction, the theoretical number-average molecular weight is $M_n=M_w/2=4.6\times10^4$.

Determination of the OH conversion ratio

From the NMR spectra of polyimide gels, we calculated the conversion ratio of hydroxyl group on the main polyimide chain. The result is shown in the last column of Table 1. The conversion ratio of hydroxyl group is almost the same as those for the addition ratio of the crosslinker within the error range. This means there is no side reaction occurring during the crosslinking.

Table 1 Sol fraction and conversion ratio of hydroxyl groups of polyimide gels crosslinked with diisocyanate

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

The swelling behaviors of polyimide gels

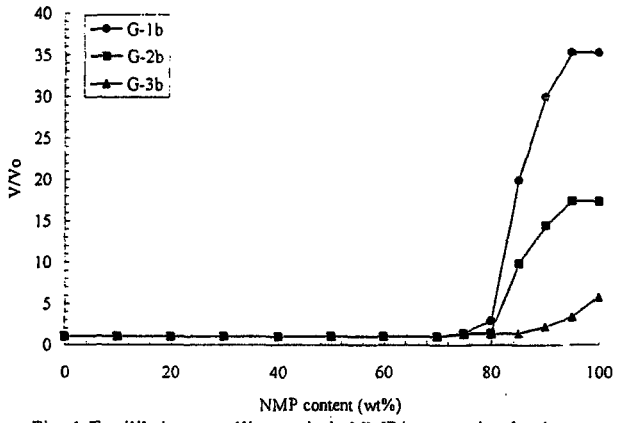

Fig. 1 Equilibrium swelling ratio in NMP/water mixed solvents at 20°C (V_0 corresponds to the volume of the initial dried gels)

Swelling behaviors were studied in NMP/water mixed solvent. In 100% NMP, all the gels reach equilibrium in about two days. For gels with lower crosslinking density, the initial swelling speed is higher. A volume phase transition point is found starting at 80wt% of NMP for all gels. (Figure 1) It is continuous and the maximum swelling ratio is 35, 18, and 9 respectively for G-1b, G-2b and G-3b.

By using Flory-Rehner's equation, [3] we are able to estimate the average molecular weight M_c between two crosslinking points.

$$\frac{M_c}{V_1\rho}\left(\frac{1}{2}-\chi\right)=Q^{\frac{5}{3}} \qquad (1)$$

Table 2 The equilibrium swelling ratio Q and calculated M_c of the polyimide gels

Sample	Q	M_c	M_c/M_n*
G-1a	35.3	2.8×10^5	6.1
G-1b	32.8	2.5×10^5	5.4
G-2a	17.8	9.0×10^4	2.0
G-2b	14.6	6.4×10^4	1.4
G-3a	8.9	2.8×10^4	0.6
G-3b	9.1	2.9×10^4	0.6

M_c(g/mol): Average molecular weight between two crosslinking points
V_1(=96.62 cm^3/mol, NMP): Molar volume of the solvent
ρ(=1.30 g/cm^3): Density of the dried gel
χ(=0.3303): Flory-Huggins parameter
Q: Equilibrium swelling ratio of the gel
*Least number of polymers between two crosslinking points ($M_n=M_w/2=4.6\times10^4$)

It is obvious for G-1 and G-2 that M_c is larger than the molecular weight of the linear polymer. This implies that several linear polymers linked together and act as one crosslinking unit contributing to the properties of the whole network. For example, there could be at least six polyimide chains connected together as one long crosslinking chain.

Table 3 Estimated effective linkage fraction of polyimide gels

Sample	OCN/OH	n_{link} [a]	n_{eff} [b]	$f_{eff}=n_{eff}/n_{link}$ [c]
G-1a	0.13	19	2.3	12.1%
G-1b	0.12	18	2.6	14.4%
G-2a	0.48	71	3.0	4.2%
G-2b	0.47	69	4.3	6.2%
G-3a	0.97	144	4.9	3.5%
G-3b	0.92	136	4.8	3.5%

a) Reacted OH per polymer = $N_{OH}\times$OCN/OH (DP=M_n/624=74, N_{OH}=2DP=148)
b) Effective branch point per polymer c) Effective linkage fraction

Not all the linkages are "effective" crosslinking, as shown by the M_c data, the polymers are postulated to have quite a great amount of intramolecular linkages, i.e., loops. Loops do not make any contributions to constrain the network. The crosslinker which connects two polymers is considered as an "effective" linkage. The effective junction fraction is estimated in Table 3. By increasing initial solid concentration from 5wt% to 10wt%, we see no significant difference.

Dynamic mechanical measurements

The compression modulus (E) was measured for the gels in their as-prepared states. The shear modulus G derived from the classic rubber theory [3] is given by:

$$G = \frac{1}{3}E = \frac{dRT}{M_c}$$

where (2) the density of the dry network is d, M_c is the effective molar mass between elastically active junction points.

Table 4 Compression modulus of polyimide gels in their as-prepared condition

Sample	Dimension (mm)	E' (Pa)	E'' (Pa)	d(g/ml)	M_c
G-1a	11.5×9.5×4.5	6.9×10^4	2.0×10^3	1.05	1.1×10^5
G-1b	5.0×5.5×5.5	4.7×10^4	7.9×10^2	1.05	1.7×10^5
G-2a	6.5×8.5×4.0	8.6×10^4	1.2×10^3	1.05	9.1×10^4
G-2b	3.5×5.0×5.5	7.5×10^4	2.1×10^3	1.05	1.0×10^5
G-3a	7.5×8.0×3.0	7.8×10^5	8.2×10^4	1.05	1.0×10^4
G-3b	4.5×5.0×4.5	4.6×10^5	6.2×10^3	1.06	1.7×10^4

From equation (2), M_c is calculated. It can be understood that because of entanglement of polymer chains, the values of M_c obtained from dynamic mechanical measurement may contain some kinds of physical junctions contributing to the modulus of the network. On the other hand, the equilibrium swelling ratio, as a static method, only consider the static equilibrium condition which all the polymer chains are well extended and physical junctions are relatively small. The M_c in Table 4 is almost the same for the same crosslinking density of group "a" and "b".

Conclusion

A gel with rigid polyimide chains has been synthesized. Gel formation is greater than 90% and almost all the crosslinkers successfully reacted with hydroxyl group. The M_c has been calculated from both the measurements of equilibrium swelling ratio and compression modulus. It is estimated that a large number of crosslinkers in fact only form intramolecular loops. The viscoelastic measurement has been approved to be an important approach to study the gels.

Acknowledgment

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