Preparation and Characterization of Polyimide Gels

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ABSTRACT

Polyimide gel and its precursors–polyamide acid gels were prepared and studied. Several polyamide acids were synthesized and crosslinked by various kinds of diisocyanates. The reaction of the gelation and the volume phase transition point (VTP) of the gels were studied. We found that the gelation times and the swollen rates vary according to the chemical structure of diisocyanates. However all the polyamide acid gels collapse near 0.75 NMP volume fraction of NMP/water mixed solvent at room temperature. We used TGA and DSC for studying the thermal properties of these polyamide acid gels. Polyimide (6FDA/AHHFP) with hydroxide group on the benzene ring was prepared and successfully crosslinked by hexamethylene diisocyanate (HMDI). Its physical properties were studied in the same manner as for polyamide acid gels.

Introduction

Polymeric gels are crosslinked polymer networks swollen with a liquid. Gels have the special properties due to its state between a liquid and a solid. Softness, elasticity, and the capacity to store a fluid make gels unique materials. Recent progress in biology and polymer sciences is unveiling the mystery of marvelous functions of biological molecules and promises new development in gel technologies. The phase transition of gels is one of the most fascinating and important phenomena that allows us to make different applications of the gels. The polymer network changes its volume in response to a change in environment; temperature, solvent composition, mechanical strain, electric field, exposure to light, etc. Gels can be developed to be used as drug delivery system, intelligent sensors, artificial muscles, and so on. In our case, we choose polyimide and polyamide acids to make the polymer framework. This is because polyimide is an engineering plastic and has many excellent thermal, mechanical and electronical properties. Furthermore, most of the polyimides are insoluble and are difficult to process to their end-use forms. The gels can be readily processed and further imidization of the polyamide acid gels is also available. Of course because of crosslinking, the thermal and anti-solvent properties are improved.

Polyamide Acid Gels

Preparation of polyamide acids (BTDA/DEDPM)

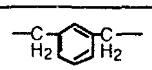
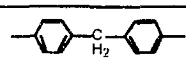
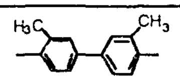
All reagents and solvents in this work were obtained from commercial suppliers and purified before use. PAA(BTDA/DEDPM) was prepared from the DMF solution of 4,4'-methylene-di-o-ethylaniline (DEDPM) added dropwise into 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) in DMF with the total weight concentration of 10% and by subsequent reaction under N_2 atmosphere at 0 °C.

Preparation of polyamide gels

PAA(BTDA/DEDPM) gels were prepared by the dropwise addition of aromatic and aliphatic diisocyanates to the PAA solution and the reaction under N_2 atmosphere at room temperature.

The gelation time of the polyamide acid gels with aromatic diisocyanate crosslinkers is longer than that for gels crosslinked with aliphatic diisocyanate. Also the reaction time increases with the increase in percentage of the crosslinker added. The results are shown in Table 1.

Table 1 Effect of various diisocyanates on the gelation of polyamide acid

Diisocyanates (OCN-R-NCO)		[NCO]/[COOH]	Gelation time (hr.)
Hexamethylene Diisocyanate (HMDI)	$-(CH_2)_6-$	0.5	2.5
		0.75	3
		1	3
m-Xylene Diisocyanate (mXDI)		1	4
4,4'-Diphenylmethane Diisocyanate (DMDI)		1	>7
3,3'-Dimethyldiphenyl 4,4'-diisocyanate (DPDI)		1	>7

Measurements of the properties of gels

Glass tubes were immersed in the solution during the synthesis of gels. After the gelation, gels with the diameter of the glass tube was obtained and cut into slices. The gel cylinders were put into NMP/water mixed solvent for about a week to study the volume phase transition of the gels. IR was measured by Jasco IR-700 and thermal analysis was performed with Shimadzu DSC-50 and TGA-50.

The results of the thermal analysis are shown in Table 2.

Table 2 Thermal properties of PAA gels

Diisocyanate	Evaporation of Solvents (°C)	Imidization and local relaxation of side chain (°C)	Tg (°C)
HMDI	110.1	138.3	196.4
mXDI	99.3	128.0	318.0
DMDI	98.3	142.7	322.3
DPDI	100.0	143.8	335.1

The volume phase transition point (VTP) was found at about 75% -80% volume fraction of NMP in NMP/water mixed solvent at room temperature for all the polyamide acid gels. The results are shown in Figure 1.

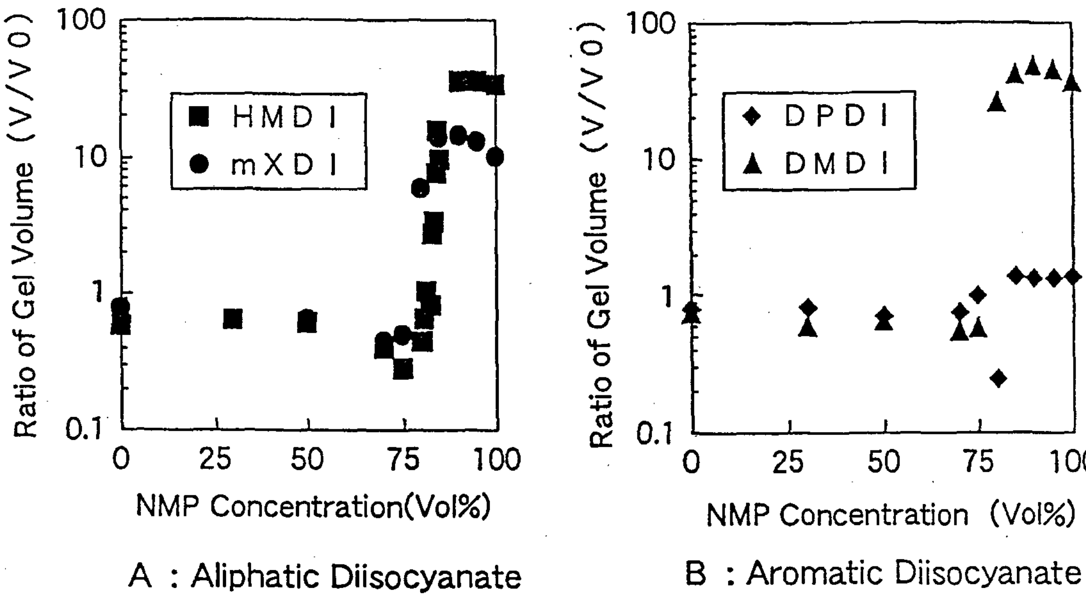


Fig. 1 Volume change of PAA gels of NMP/water in mixed solvent
Effect of various diisocyanates

Polyimide Gels

Preparation of polyimide (6FDA/AHHFP)

4,4'-(hexafluoroisopropylindene) diphthalic anhydride (6FDA) was added stepwise into the NMP solution of 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (AHHFP) to make a polyamide acid solution. Then the polyamide acid was thermally imidized at 160°C with the addition of xylene for 2 hours. Polyimide was obtained by precipitating the polyimide solution in water and drying in vacuum oven at 70°C overnight.

The thermal imidization was confirmed by IR spectrum at the wave number of 1780cm^{-1} and 725cm^{-1}. PI(6FDA/AHHFP) is soluble in most common solvents, such as, acetone, DMF, ethyl acetate and THF.

Preparation of polyimide gel (6FDA/AHHFP)

PI(6FDA/AHHFP) was dissolved in NMP with a weight concentration of 10% and hexamethylene diisocyanate (HMDI) was added dropwise into the solution to make the polyimide gel.

PI(6FDA/AHHFP) gel was successfully synthesized. The IR spectrum of the dried crosslinked PI showed no characteristic viberation of the isocyanate group. So we can conclude that diisocyanate reacts with hydroxyl group and connects PI chains together. The volume phase transition and its thermal properties will also be discussed.

References

1. O. Yamazaki, T. Yamashita, K. Horie, Polym. Prepr. Jpn., 45, 263, (1996)