APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 11, 153–161 (1997)

Polyimide–Silica Gel Hybrids Containing Metal Salts: Preparation via the Sol–Gel Reaction

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A facile preparation of polyimide–silica gel hybrids by the simultaneous *in-situ* formation of polyimides during the hydrolysis–condensation of tetramethoxysilane (TMOS) is reported here. The hydrolysis and condensation of TMOS was carried out in a solution of DMAc containing 5% LiCl, $CaCl_2$ or $ZnCl_2$ and the seven-membered cyclic polyimide intermediate. The seven-membered cyclic intermediates, precursors of polyimides, were derived from the low-temperature polycondensation of dianhydrides [benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), and 4,4-bis(hexafluoroisopropylidene)phthalic dianhydride (6FDA)] and di-isocyanates [isophorone di-isocyanate (IPDI), toluene di-isocyanate (TDI), hexamethylene di-isocyanate (HDI) and 4,4′-diphenylmethane di-isocyanate) (MDI)]. These intermediates could readily be converted to the corresponding polyimides. Films were cast from the resulting mixtures and the solvent was gradually evaporated at 130 °C to result in the formation of clear, transparent, pale yellow or amber-colored hybrid films in which the salts were dispersed at the molecular level. Pyrolysis of polyimide–silica gel hybrids at 600 °C gave mesoporous silica. Silica gel obtained from hybrids HPI-8 (containing no salt) and HPI-11 (containing $ZnCl_2$) had a pore radius (BJH method) of 2.9 nm, while that from hybrid HPI-9 (containing LiCl) had a pore radius of 11.4 nm. The surface areas (BET method) obtained were 203 $m^2\,g^{-1}$, 19 $m^2\,g^{-1}$ and 285 $m^2\,g^{-1}$, while the pore volumes were 0.373 $cm^3\,g^{-1}$, 0.158 $cm^3\,g^{-1}$ and 0.387 $cm^3\,g^{-1}$, respectively, for samples obtained from hybrids HPI-8, HPI-9 and HPI-11. © 1997 by John Wiley & Sons, Ltd.

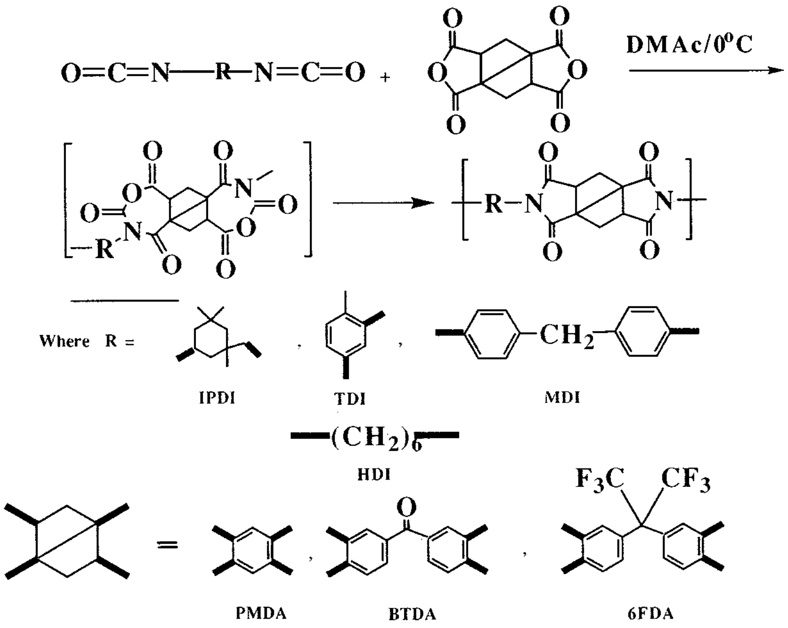
Keywords: polyimides; solution polycondensation; seven-membered cyclic polyimide intermediate; polyimide–silica gel hybrids; sol–gel reaction; pyrolysis; pore size; surface area; adsorption–desorption isotherms

INTRODUCTION

The sol–gel reaction involves the hydrolysis of metal alkoxides such as tetramethoxysilane (TMOS).[1] This reaction provides a facile route for the preparation of (i) glasses of high purity at processing temperatures much lower than those required conventionally, (ii) molecular dispersions and (iii) organic/inorganic polymer hybrids. The inorganic part of the hybrid is formed by the hydrolysis–condensation of metal alkoxides. By varying the ratio of the metal alkoxide to the polymer, the range and composition of the resulting polymer hybrids can be vastly enlarged and tailored at will. It was reckoned that the presence of added metal salts such as LiCl, $CaCl_2$ or $ZnCl_2$ might result in the formation of the new types of hybrids. Employing the sol–gel reaction, hybrids containing poly(2-methyl-2-oxazoline),[2–4] poly(ether-ketone),[5] poly(oxyethylene),[6] poly(oxytetramethylene),[7, 8] poly(dimethylsiloxane),[9–11] polysiloxane elastomers,[12–17] poly (*N* - vinylpyrrolidone)[18] and polyurea[19] have been reported. In this paper we report the preparation of silica gel hybrids containing polyimides by the acid-catalyzed sol–gel reaction of TMOS to result in the formation of three-dimensional silica-gel networks. The hydrolysis–condensation reaction was carried out in a solution of dimethylacetamide (DMAc) containing 5% LiCl, $CaCl_2$ or $ZnCl_2$ and the seven-membered cyclic intermediate. By the reaction of dianhydrides (BTDA, PMDA and 6FDA) and di-isocyanates (IPDI, TDI, HDI and MDI) in the presence or absence of salts (such as LiCl, $CaCl_2$ or $ZnCl_2$),

CCC 0268–2605/97/020153–09

Received 21 September 1995
Accepted 29 March 1996



Scheme 1. Preparation of polyimides.

48 polyimide–silica gel hybrids were targeted. The potential application of these materials may range from catalysis[20] to non-linear optical (NLO)[21] applications, among others. Porous silica gels were also prepared from these hybrids.

EXPERIMENTAL

Materials

Benzophenonetetracarboxylic dianhydride (BTDA) and pyromellitic dianhydride (PMDA)

Table 1 Preparation of polyimides

Polymer code	Dianhydride (1 equiv.)	Di-isocyanate (1 equiv.)	Yield[a] (%)	η_{inh}[b] (dl g^{-1})
PI-1	PMDA	IPDI	90	0.42
PI-2	PMDA	TDI	91	0.51
PI-3	PMDA	HDI	89	0.32
PI-4	PMDA	MDI	89	0.37
PI-5	BTDA	IPDI	91	0.66
PI-6	BTDA	TDI	90	0.70
PI-7	BTDA	HDI	88	0.51
PI-8	BTDA	MDI	89	0.55
PI-9	6FDA	IPDI	91	0.60
PI-10	6FDA	TDI	90	0.59
PI-11	6FDA	HDI	88	0.53
PI-12	6FDA	MDI	88	0.62

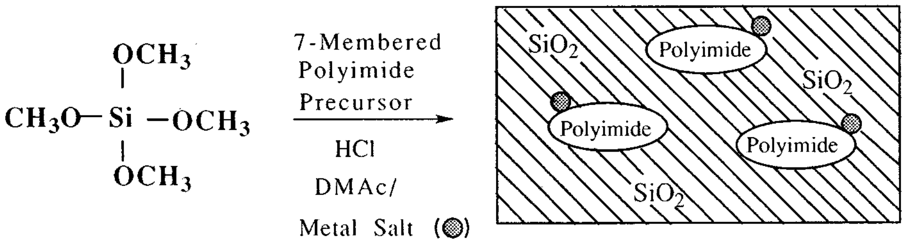
[a] Isolated yield.

[b] Inherent viscosity determined in H_2SO_4 at a concentraton of 0.5 g dl^{-1} at 30±0.01 °C.

Table 2 Solubility[a] of polyimides in various solvents

Polymer	Solvent							
	Acetone	$CHCl_3$	DMF	DMAc	DMSO	NMP	HMPA	H_2SO_4
PI-1	—	—	—	—	—	—	—	++
PI-2	—	—	—	—	—	—	—	++
PI-3	—	—	—	0	—	—	0	++
PI-4	—	—	—	—	—	—	—	++
PI-5	—	—	—	0	—	—	0	++
PI-6	—	—	—	—	—	—	—	++
PI-7	—	—	—	—	—	—	0	++
PI-8	—	—	—	—	—	—	—	++
PI-9	—	—	—	0	—	—	0	++
PI-10	—	—	—	—	—	—	—	++
PI-11	—	—	—	0	—	—	0	++
PI-12	—	—	—	—	—	—	—	++

[a] —, Insoluble; 0, slight swelling at 100 °C; ++, soluble.



Scheme 2. Preparation of polyimide–silica gel hybrids.

Table 3 Combinations of di-isocyanates, dianhydrides and added metal salts that resulted in clear and transparent polyimide–silica gel hybrids

Dianhydride	Di-isocyanate	Added metal salt
6FDA	MDI, HDI	None, LiCl, $CaCl_2$ and $ZnCl_2$
BTDA	TDI	None, LiCl, $CaCl_2$ and $ZnCl_2$
6FDA	IPDI, TDI	None, LiCl and $ZnCl_2$
BTDA	IPDI	None, LiCl and $ZnCl_2$
PMDA	IPDI	None, LiCl and $ZnCl_2$
BTDA	HDI	None

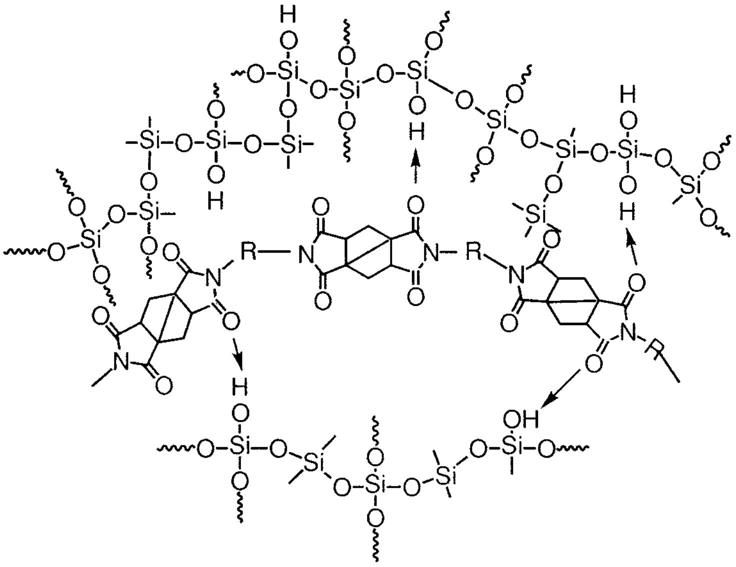


Figure 1 Schematic representation of polyimide–silica gel hybrid.

were recrystallized from freshly distilled acetic anhydride and sublimed *in vacuo* before use. 4,4-bis(Hexafluoroisopropylidene)phthalic dianhydride (6FDA) and di-isocyanates [isophorone di-isocyanate (IPDI), toluene di-isocyanate (TDI), hexamethylene di-isocyanate (HDI), and 4,4′-diphenylmethane di-isocyanate) (MDI)] were used as such, without further purification, from freshly opened bottles. Tetramethoxysilane (TMOS) was distilled under an inert atmosphere of nitrogen prior to use. Dimethylacetamide (DMAc) was kept standing over anhydrous P_2O_5 for 24 h before distillation under reduced pressure. Other reagents were purified using standard laboratory procedures.[22]

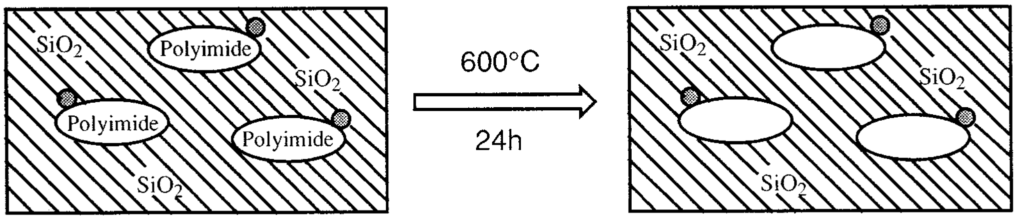
Characterization methods

Inherent viscosities were determined in a suspension-type Ubbelohde viscometer at a concentration of $5\ \mathrm{g\ dm^{-3}}$ in sulfuric acid at 30±0.01 °C. A Perkin-Elmer 1600 Series FTIR spectrophotometer was used to record the spectra of KBr pellets. Thermogravimetric analysis (TGA) was carried out by heating the samples at $10\ °\mathrm{C\ min^{-1}}$ in air on a Shimadzu Thermal Analyzer. Glass transition temperatures (T_g) were measured on a Seiko DSC at a hearing rate of $20\ °\mathrm{C\ min^{-1}}$ in a current nitrogen. The pore size, pore volume and surface area of porous silica were determined by the nitrogen adsorption–desorption isotherm method[23–25] on a Belsorp 28 nitrogen adsorption apparatus.

Preparation of polyimides PI-1 to PI-12, e.g. PI-6

Polyimides were prepared by reacting equimolar amounts of the appropriate dianhydride and di-isocyanate at ice-bath temperature in dimethylacetamide (DMAc).

For example to prepare TDI (0.380 g) was dissolved in DMAc ($10\ \mathrm{cm^3}$) and cooled to ice-bath temperature in a three-necked flask



Scheme 3. Pyrolysis of polyimide–silica gel hybrid to give porous silica.

Table 4 Preparation of polyimide–silica gel hybrids[a] and their properties

Hybrid code	Dianhydride (1 equiv.)	Di-isocyanate (1 equiv.)	Metal salt[b]	Polymer[c] (%)	T_{10} (°C)[c]	T_g[d] (°C)
HPI-1	PMDA	IPDI	None	68	210	151
HPI-2	PMDA	IPDI	LiCl	66	320	—
HPI-3	PMDA	IPDI	$ZnCl_2$	70	240	162
HPI-4	BTDA	HDI	None	70	265	156
HPI-5	BTDA	IPDI	None	68	250	168
HPI-6	BTDA	IPDI	LiCl	68	240	196
HPI-7	BTDA	IPDI	$ZnCl_2$	67	240	174
HPI-8	BTDA	TDI	None	70	330	—
HPI-9	BTDA	TDI	LiCl	69	300	—
HPI-10	BTDA	TDI	$CaCl_2$	70	345	188
HPI-11	BTDA	TDI	$ZnCl_2$	69	350	178
HPI-12	6FDA	HDI	None	70	265	154
HPI-13	6FDA	FDI	LiCl	69	285	194
HPI-14	6FDA	HDI	$CaCl_2$	70	250	149
HPI-15	6FDA	HDI	$ZnCl_2$	70	240	151
HPI-16	6FDA	IPDI	None	69	230	156
HPI-17	6FDA	IPDI	LiCl	64	250	183
HPI-18	6FDA	IPDI	$ZnCl_2$	68	310	182
HPI-19	6FDA	MDI	None	70	250	152
HPI-20	6FDA	MDI	LiCl	60	325	176
HPI-21	6FDA	MDI	$CaCl_2$	70	260	174
HPI-22	6FDA	MDI	$ZnCl_2$	70	320	177
HPI-23	6FDA	TDI	None	70	350	188
HPI-24	6FDA	TDI	LiCl	69	400	200
HPI-25	6FDA	TDI	$ZnCl_2$	65	420	173

[a] Feed ratio of polyimide: TMOS, 1:1.
[b] 5% based on combined weight of dianhydride and di-isocyanate.
[c] From TGA at a heating rate of 10 °C min^{-1} in air.
[d] From DSC measured at a heating rate of 20 °C min^{-1} in nitrogen.

equipped with a nitrogen gas inlet, a reflux condenser fitted with a $CaCl_2$ guard tube and a stirring bar. BTDA (0.7038 g) was then added in small portions of 10–20 mg, ensuring that the earlier amount dissolved completely before a fresh portion was added. After the addition was complete, the reaction mixture was stirred for 2 h at ice-bath temperture. There was a perceptible increase in the viscosity of the solution. Next the solution was allowed to attain ambient temperature gradually. The temperature was then raised to 40 °C over 1 h (several polymers separated out of the solution at the end of this stage), to 80 °C over the next 2 h and finally to 140 °C over a further 2 h, and left at that temperature for 24 h. Polyimide PI-6 was iso-

Table 5 Some surface characteristics of porous silica gels obtained upon the pyrolysis of polyimide–silica gel hybrids

Hybrid code	Compositon	Surface area[a] ($m^2 g^{-1}$)	Pore volume[b] ($cm^3 g^{-1}$)	Pore size[b] (nm)
HPI-8	BTDA–TDI/No salt	203	0.373	2.9
HPI-9	BTDA–TDI/LiCl	19	0.158	11.4
HPI-11	BTDA–TDI/$ZnCl_2$	285	0.387	2.9

[a] BET Method.
[b] BJH Plot.

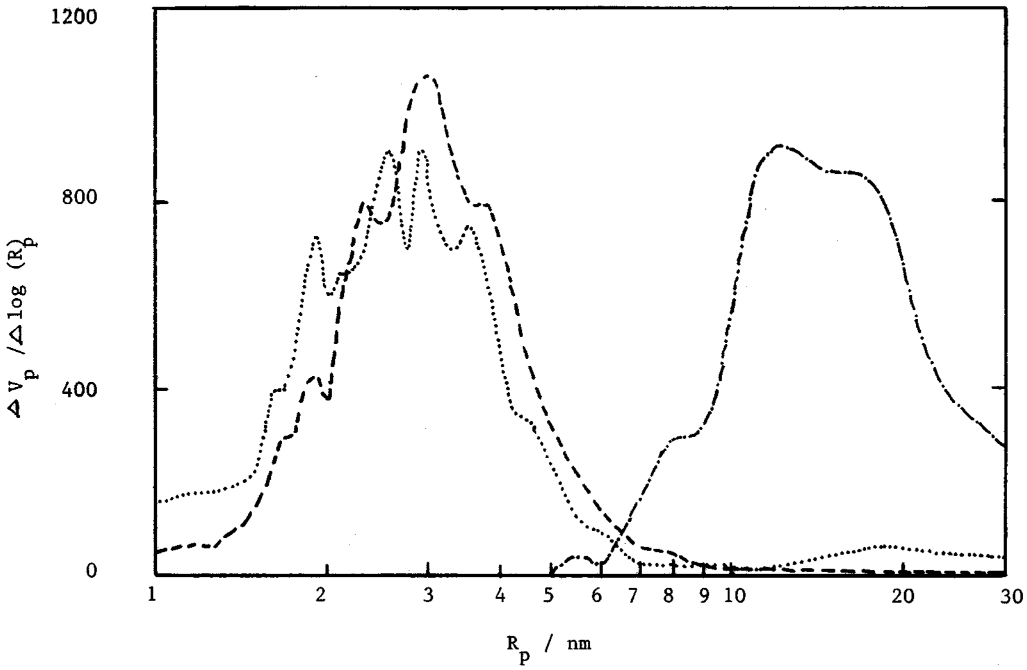


Figure 2 Pore size distribution plots of porous silica obtained after the pyrolysis of hybrids HPI-8 (— — —), HPI-9 (— · — · —)and HPI-11 (· · · ·).

lated by pouring the reaction mixture into methanol (200 cm^3), filtering at the pump and drying at 100 °C in vacuum for 8 h.

Preparation of polyimide–silica gel hybrids HPI-1 to HPI-25, e.g. HPI-9

TDI (0.3783 g) was dissolved in DMAc (25 cm^3) containing LiCl (0.054 g) (5% salt based on the weight of the di-isocyanate and the dianhydride), placed in a three-necked flask fitted with a nitrogen gas inlet, a reflux condenser fitted with a $CaCl_2$ guard tube and a stirring bar and cooled to ice-bath temperature. To this solution was added BTDA (0.700 g) in small portions of 10–20 mg over 1 h. After the addition was complete, the reaction mixture was stirred for 2 h at ice-bath temperature. To this reaction mixture TMOS (0.887 g) was added (one equivalent based on the weight of one repeat unit). The reaction mixture was stirred for 2 h at ice-bath temperature. Two drops of 0.1 M HCl were added and stirred for 2 h and then allowed to attain ambient temperature. The temperature was then raised to 40 °C over 1 h, 80 °C over the next 2 h and finally to 120 °C over 2 h; the mixture was kept at that temperature for several days to allow the solvent to evaporate gradually and afford hybrid HPI-9.

Preparation of porous silica gels

Porous silica gels were prepared by the pyrolysis of the polyimide–silica gel hybrids in a furnace at 600 °C for 24 h.

RESULTS AND DISCUSSION

The use of polyimides as high-performance/high-temperature thermoplastic materials in various applications stems from the attractive combination of chemical, mechanical and physical properties.[26–28] Polyimides may be prepared by the reaction of a diamine and a dianhydride.[29, 30] Here the reaction proceeds via the formation of the polyamic acid intermediate, which may be cyclodehydrated to the polyimide either thermally or chemically. Polyimides may also be conveniently prepared by the reaction of a di-isocyanate and a dianhydride.[31] Here the reaction proceeds via the formation of a seven-membered cyclic intermediate which on loss of carbon dioxide forms the polyimide. Morikawa *et al.*[32] and Nandi *et al.*[33] have reported the preparation of polyimide by the diamine–dianhydride route and the subsequent preparation of polymer hybrid with tetra-alkoxysilane. In this paper we report the preparation of three-dimensional silica-gel networks containing polyimides by the acid-catalyzed sol–gel reaction of TMOS. The polyimides were prepared by the reaction of a di-isocyanate with a dianhydride owing to the ease of formation of the seven-membered cyclic intermediate, and subsequent formation of the polyimide at fairly low temperatures.

Preparation of polyimides PI-1 to PI-12

Polyimides were prepared by the low-temperature solution polycondensation of equimolar quantities of di-isocyanates and dianhydrides in DMAc. The seven-membered cyclic intermediates formed were soluble in DMAc at 0 °C and on heating eliminate carbon dioxide to form the polyimides (Scheme 1). Polymers were isolated in yields in the range 88–91% by pouring the reaction mixtures into a large excess of methanol, filtering and drying at 100 °C in vacuum. The inherent viscosities of the polyimides were in the range 0.32–0.70 dl/g^{-1} in sulfuric acid (Table 1). The polyimides PI-3. PI-5, PI-9 and PI-11 swelled slightly in DMAc and HMPA on heating to 100 °C, whilst polyimide PI-7 swelled only in HMPA. However, all polyimides dissolved in sulfuric acid (Table 2).

Preparation of polyimide–silica gel hybrids HPI-1 to HPI-25

Polyimide–silica gel hybrids were prepared by the simultaneous *in-situ* formation of the polyimides during the hydrolysis and condensation of TMOS. The seven-membered cyclic polyimide intermediate was prepared by the low-temperature polycondensation of a di-isocyanate and a dianhydride in DMAc containing LiCl, $CaCl_2$ or $ZnCl_2$ (5% based on the weight of the di-isocyanate and the dianhydride). To the resulting solution at 0 °C, TMOS was added so that the PI/TMOS feed ratio was 1:1. The hydrolysis and condensation was effected by the addition of two drops of 0.1 M HCl. The solution was cast on a Teflon mold and the solvent was evaporated gradually at 120–130 °C over several days to give pale yellow or amber-colored films in which the salts were dispersed at the molecular level (Scheme 2). By the reaction of dianhydrides [benzophenonetetracarboxylic dianhydride (BTDA), pyromellitic dianhydride (PMDA), and 4,4-bis(hexafluoroisopropylidene)phthalic dianhydride (6FDA) and di-isocyanates [isophorone di-isocyanate (IPDI), toluene di-isocyanate (TDI), hexamethylene di-isocyanate (HDI), and 4,4′-diphenylmethane di-isocyanate) (MDI)] and salts such as LiCl, $CaCl_2$ or $ZnCl_2$ and TMOS, 48 polyimide–silica gel hybrids were targeted. Clear, transparent and homogeneous hybrids were formed in several combinations of di-isocyanates, dianhydrides and added metal salts, as shown in Table 3. All other combinations resulted in either phase separation or formation of opaque lumps.

Polyimide formation was characterized by the absence of the isocyanate stretching band at 2270 cm^{-1} and the appearance of the imide bands at around 1770 cm^{-1} and 1713 cm^{-1} in the FTIR spectra of the polymers and the polymer–silica gel hybrids.

Polyimide–silica gel hybrid formation may be thought to be through the operation of hydrogen bonding between the residual silanol groups (the Brønsted acid), formed during the hydrolysis of TMOS, and the carbonyl groups of the polyimide; and the entrapment of the polyimide chains during the condensation of the already hydrolyzed TMOS to form the three-dimensional Si—O—Si network. The schematic representation of such a hybrid is illustrated in Fig. 1. It is expected that polyimide–silica gel hybrids with salts dispersed at the molecular level would find semi-conductor, semi-permeable membrane and NLO applications among others.

About 60–70% polyimide was incorporated in the polymer hybrid, as observed by thermogravimetric analysis. The temperature at 10% weight loss (T_{10}) and glass transition temperature (T_g) values are incorporated in Table 4.

Preparation of porous silica

Porous silica gels were prepared by the pyrolysis of the polymer hybrids at 600 °C for 24 h in a furnace (Scheme 3). Adsorption and desorption studies were carried out according to the literature method[23–25] to determine the pore size, pore volume and surface area of the porous silica thus obtained. Preliminary studies on representative samples of porous silica obtained after the pyrolysis of hybrids HPI-8 (containing no salt) and HPI-11 (containing $ZnCl_2$) indicated a Type

IV isotherm and a Type H2 hysteresis loop. Type IV isotherm is associated with capillary condensation occurring in the mesopores and is also indicative of monolayer–multilayer adsorption. This type of isotherm is exhibited by mesoporous industrial samples. Type H2 hysteresis loops are exhibited by porous adsorbents. This type of hysteresis loop is indicative of capillary condensation occurring in pores with narrow necks and wide bodies (commonly referred to as bottle-shaped pores). Silica obtained from hybrid HPI-9 (containing LiCl), on the other hand, had a Type 4 isotherm and a hysteresis loop resembling Type H1 hysteresis. Type H1 hysteresis loops are associated with porous materials which are known to consist of agglomerates or compacts of approximately uniform spheres.[23–25] Silica samples from hybrids HPI-8 and HPI-11 had a pore radius (Barrett, Joyner and Halenda (BJH) method) of 2.9 nm, while that from HPI-9 had a pore radius of 11.4 nm. The surface areas [Brunauer, Emmett and Teller (BET) method] obtained were 203 $cm^2 g^{-1}$, 19 $cm^2 g^{-1}$ and 285 $cm^2 g^{-1}$, while the pores had a volume of 0.373 $cm^3 g^{-1}$, 0.158 $cm^3 g^{-1}$, and 0.387 $cm^3 g^{-1}$, respectively, for the three silica-gel samples obtained from hybrids HPI-8, HPI-9 and HPI-11 (Table 5). The pore size distribution plot of porous silica gel samples is illustrated in Fig. 2.

CONCLUSIONS

Polyimide–silica gel hybrids were successfully prepared by the simultaneous *in situ* formation of the polyimides during the hydrolysis and condensation of TMOS. Pale yellow or amber-colored films could be cast in which the metal salts were dispersed at the molecular level from a solution of the polyimide precursor and TMOS. Mesoporous silica gels could be obtained by the pyrolysis of the hybrids at 600 °C. Preliminary adsorption–desorption studies on representative porous silica samples indicated that hybrids HPI-8 (containing no salt) and HPI-11 (containing $ZnCl_2$) upon pyrolysis gave silica gels with smaller pores (pore radius 2.9 nm) while HPI-9 (containing LiCl) gave larger pores (pore radius 11.4 nm). Silica gels obtained from hybrids HPI-8 and HPI-11 had a larger surface area (203 $m^2 g^{-1}$ and 285 $m^2 g^{-1}$, respectively), while that from hybrid HPI-9 gave a surface area of only 19 $m^2 g^{-1}$. Hybrid HPI-9 (containing LiCl) gave silica gel with a smaller pore volume (0.158 $cm^3 g^{-1}$), while hybrids HPI-8 (containing no salt) and HPI-11 (containing $ZnCl_2$) gave silica gels that had a larger pore volume (0.373 $cm^3 g^{-1}$ and 0.387 $cm^3 g^{-1}$, respectively). By judicious choice of the salt it might be possible to control such characteristics as pore size, pore volume and the surface area of the silica gels obtained by the pyrolysis of the hybrids. Presence of metal salts favors the formation of the hybrids, as well as helping to tailor properties suitable for potential applications. Controlled pyrolysis of hybrids may result in porous silica gel with domains of polymer still embedded in the silica-gel network. Such materials could have very interesting properties, useful for potential applications. Further studies are in progress.

Acknowledgement The authors thank Dr T. Yazawa and Mr K. Kuraoka of Osaka National Research Institute, Ikeda, Osaka, Japan, for their help in the pore size determination studies using Belsorp 28.

REFERENCES

1. Y. Chujo and T. Saegusa, *Adv. Polym. Sci.* **100**, 11 (1992).
2. Y. Chujo, E. Ihara, H. Ihara and T. Saegusa, *Macromolecules* **22**, 1030 (1989).
3. Y. Chujo, E. Ihara, S. Kure, K. Suzuki and T. Saegusa, *Makromol. Chem.—Macromol. Symp.* **42**/**43**, 303 (1991).
4. Y. Chujo, E. Ihara, S. Kure and T. Saegusa, *Macromolecules* **26**, 568 (1993).
5. J. L. W. Noell, G. L. Wilkes, D. K. Mohanty and J. E. McGrath, *J. Appl. Polym. Sci.* **40**, 1177 (1990).
6. M. Fujita and K. Honda, *Polym. Commun.* **30**, 200 (1989).
7. H. Huang and G. L. Wilkes, *Polym. Bull.* **18**, 455 (1987).
8. H. Huang, G. L. Wilkes and J. C. Carlson, *Polymer* **30**, 2001 (1989).
9. (a) H. Huang, B. Orler and G. L. Wilkes, *Macromolecules* **20**, 1322 (1987).
10. R. H. Glaser and G. L. Wilkes, *Polym. Bull.*, **19**, 51 (1988).
11. H. Huang, B. Orler, and G. L. Wilkes, *Polym. Bull.* **14**, 557 (1985).
12. Y.-P. Ning, M.-Y. Tang, C.-Y. Jiang, J. E. Mark and W. C. Roth, *J. Appl. Polym. Sci.* **29**, 3209 (1984).
13. Y.-P. Ning and J. E. Mark, *J. Appl. Polym. Sci.* **30**, 3519 (1985).

14. J. E. Mark, C.-Y. Jiang and M.-Y. Tang, *Macromolecules* **17**, 2613 (1984).
15. G. S. Sur and J. E. Mark, *Makromol. Chem.* **187**, 2861 (1986).
16. C.-Y. Jiang and J. E. Mark, *Makromol. Chem.* **185**, 2609 (1984).
17. J. E. Mark, Y.-P. Ning, C.-Y. Jiang, M.-Y. Tang and W. C. Roth, *Polymer* **26**, 2069 (1985).
18. T. Saegusa and T. Chujo, *Makromol. Chem.—Macromol. Symp.* **64**, 1, (1992).
19. Y. Chujo, S. Kure, H. Matsuki, H. Hokazono and T. Saegusa, *Polym. Prepr. Jpn* **41**, 733 (1992).
20. R. J. St Pierre and M. A. El-Sayed, *J. Phys. Chem.* **91**, 763 (1987).
21. T. Kobayashi (ed.), *Non-linear Optics of Organics and Semiconductors*, Part II, Springer, Berlin, 1989.
22. D. D. Perrin and W. L. F. Armarego (eds), *Purification of Laboratory Chemicals*, 3rd edn, Pergamon, New York, 1988.
23. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.* **57**(4), 603 (1985).
24. S. J. Gregg and K. S. W. Sing, (eds), *Adsorption, Surface Area and Porosity*, 2nd edn, Academic Press, New York, 1982.
25. E. P. Barrett, L. G. Joyner and P. P. Halenda, *J. Am. Chem. Soc.* **73**, 373 (1951).
26. P. M. Hergenrother, *Angew. Makromol. Chem.* **145**/**146**, 323 (1986).
27. C. E. Sroog, *J. Polym. Sci. Macromol. Rev.* **11**, 161 (1976).
28. K. L. Mittal, *Polyimides: Synthesis, Characterization and Applicatons*, Plenum, New York, 1984.
29. G. M. Bower and L. W. Frost, *J. Polym. Sci. Part A* **1**, 3135 (1963).
30. S. R. Sandler and W. Karo, *Polymer Synthesis*, Academic Press, New York, 1974.
31. R. A. Meyers, *J. Polym. Sci. A-1* **7**, 2757 (1969).
32. A. Morikawa, H. Yamaguchi, M. Kamimoto and Y. Imai, *Chem. Mater.* **6**(7), 913 (1994).
33. M. Nandi, J. A. Conklin, L. Salvati Jr and A. Sen, *Chem. Mater.* **2**, 772 (1990).