

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Poly(amide-imide)-Silica Gel Hybrids: Synthesis and Characterization

C. V. Avadhani<sup>a</sup>; Y. Chujo<sup>b</sup>

<sup>a</sup> Polymer Science and Engineering Division, National Chemical Laboratory, Pune, Maharashtra, India

<sup>b</sup> Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto, Japan

**To cite this Article** Avadhani, C. V. and Chujo, Y.(2009) 'Poly(amide-imide)-Silica Gel Hybrids: Synthesis and Characterization', Journal of Macromolecular Science, Part A, 46: 7, 663 – 673

**To link to this Article:** DOI: 10.1080/10601320902938871

**URL:** <http://dx.doi.org/10.1080/10601320902938871>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Poly(amide-imide)-Silica Gel Hybrids: Synthesis and Characterization

C.V. AVADHANI<sup>1</sup> and Y. CHUJO<sup>2,\*</sup>

<sup>1</sup>Polymer Science and Engineering Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411008, Maharashtra, India

<sup>2</sup>Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishiyō-ku, Kyoto 615-8510, Japan

Received January 2009, Accepted February 2009

Several poly(amide-imide)-silica gel hybrids containing metal salts were prepared by the sol-gel reaction. Poly(amide-imide)s were prepared by low temperature polycondensation reaction of trimellitic anhydride (TMA) and diisocyanates [isophorone diisocyanate (IPDI), toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), and 4,4'-methylenebis(phenyl isocyanate) (MDI)]. The inherent viscosities of the poly(amide-imide)s obtained ranged from 0.39–0.69 dL/g in DMAc. The hydrolysis and condensation reaction of tetramethoxysilane (TMOS) to form a silica gel network was affected in DMAc containing 5% LiCl, CaCl<sub>2</sub> or ZnCl<sub>2</sub> during the formation of poly(amide-imide)s. Films could be cast from DMAc solution and gradual evaporation of the solvent afforded pale yellow to amber colored hybrids in which the salts were dispersed at the molecular level. About 30–60% polymer was incorporated in the hybrids. Pyrolysis of the polymer silica gel hybrid samples at 600°C resulted in the formation of porous silica. Pore size and surface area studies on representative porous silica gels, SiG-4, SiG-5, and SiG-8, obtained upon the pyrolysis of the corresponding hybrids HPAI-4, HPAI-5 and HPAI-8, indicated that the silica gels were mesoporous in nature and had narrow pore size distribution (pore radius = 1.8 nm) with a surface area of 371 m<sup>2</sup>/g, 335 m<sup>2</sup>/g and 300 m<sup>2</sup>/g, respectively. The bottle shaped pores exhibited a pore volume of 0.227 cm<sup>3</sup>/g, 0.314 cm<sup>3</sup>/g and 0.280 cm<sup>3</sup>/g, respectively. Computer simulation modeling studies indicated that the poly(amide-imide) chains were not coiled and there was no agglomeration of the chains.

**Keywords:** Poly(amide-imide), silica gel hybrids, molecular modeling, porous silica

## 1 Introduction

Organic-inorganic polymer hybrids have gained importance in recent years as candidates or new technologies due to their advantageous performance. Much attention has been paid to the preparation of homogeneous organic-inorganic hybrids *via* the sol-gel technique. Inorganic materials such as glasses have good thermal and optical properties, but are very brittle. Consequently, methods to develop new materials to achieve new combinations of properties have gained importance. Sol-gel reaction process provides an attractive route for the preparation of desirable inorganic networks in which polymers may be incorporated (1, 2). The sol-gel reaction involves the hydrolysis of metal alkoxides such as tetramethoxysilane (TMOS) and 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 (or the metal alkoxide itself) and the polymer (or the polymer itself), the range and composition of the resulting hybrid can be vastly enlarged and tailored at will. It was reckoned that the presence of added metal salts like LiCl, CaCl<sub>2</sub> or ZnCl<sub>2</sub> might result in the formation of new types of hybrids. Hybrids containing poly(2-methyl-2-oxazoline) (3), poly(etherketone) (4), poly(oxyethylene) (5), poly(oxytetramethylene) (6), poly(dimethylsiloxane) (7) and polysiloxane elastomers (8, 9) have been reported. Wang et al. (10) have reported the preparation of polyamide-silica composite materials by the sol-gel reaction, while Morikawa et al. (11) and Nandi et al. (12) have reported the preparation of polyimide-silica gel hybrids with tetraalkoxysilane. Although the dynamics of fluorinated poly(amide-imide)-silica hybrids were studied by solid-state NMR (13), to our knowledge, the preparation of poly(amide-imide)-silica gel hybrids, and porosity and surface area studies of the porous

\*Address correspondence to: Yoshiki Chujo, Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishiyō-ku, Kyoto 615-8510, Japan. E-mail: chujyo@chujyo.synchem.kyoto-u.ac.jp

silica obtained by pyrolysis of poly(amide-imide)-silica gel hybrids has not been reported.

Consequently, in this paper, the preparation of poly(amide-imide)-silica gel hybrids is being reported. PAIs were prepared by the low temperature solution polycondensation of TMA and various diisocyanates, e.g., isophorone diisocyanate (IPDI), toluene diisocyanate (TDI), hexamethylene diisocyanate (HMDI) and 4,4'-methylenebis(diphenyl isocyanate) (MDI). Poly(amide-imide)-silica gel hybrids (HPAIs) were prepared by the hydrolysis-condensation reaction of TMOS in the presence of these polymers in DMAc containing 5% LiCl, CaCl<sub>2</sub> or ZnCl<sub>2</sub>. The presence of salts facilitates the formation of hybrids, as well as contributes to the properties of the resulting hybrids. The porosity and surface area results of the porous silica obtained by the pyrolysis of poly(amide-imide)-silica gel hybrids are also reported. Poly(amide-imides)-silica gel hybrid materials may find use in heat-resistant, electrical insulation and paint applications. An attempt has also been made to visualize the polymer chains employing molecular modeling studies.

## 2 Experimental

### 2.1 Materials

Trimellitic anhydride (TMA) (TCI, Japan) was crystallized from freshly distilled acetic anhydride and sublimed *in vacuo* prior to use. Diisocyanates [isophorone diisocyanate (IPDI), toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI), and 4,4'-methylenebis(phenyl isocyanate) (MDI) (TCI, Japan)] were used as received from freshly opened bottles. Tetramethoxysilane (TMOS) (Shinetsu Chemicals, Japan) was distilled prior to use under an inert atmosphere of nitrogen. N,N-Dimethylacetamide (DMAc) was kept standing over anhydrous P<sub>2</sub>O<sub>5</sub> for 24 h before distillation under reduced pressure. Other reagents were purified using standard laboratory procedures (14).

### 2.2 Characterization Methods

Inherent viscosities were determined in a suspension type Ubbelohde viscometer at a concentration of 0.5 g/dL in DMAc at 30 ± 0.01°C. FT-IR spectra of poly(amide-imide) samples were recorded as KBr pellets on a Perkin-Elmer 1600 series spectrophotometer. Thermogravimetric analysis (TGA) was carried out by heating the samples at 10°C/min in air on a Shimadzu Thermal Analyzer. Glass transition (T<sub>g</sub>) temperatures were measured on a Seiko DSC at a heating rate of 20°C/min in a draft of nitrogen. Pore size and surface area of porous silica were determined on a Belsorp 28 nitrogen adsorption apparatus by the adsorption-desorption isotherm method (15, 16).

### 2.3 Molecular Modeling Studies

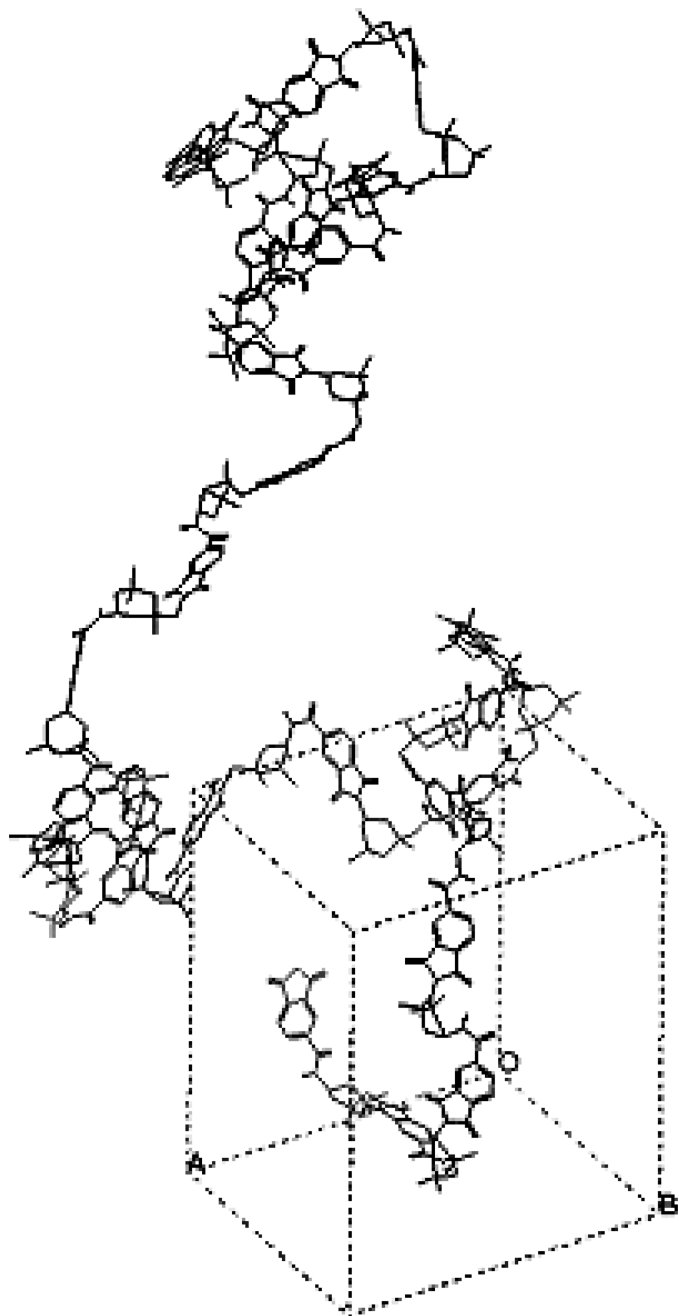
Molecular modeling studies were performed using Cerius 2 molecular modeling software from Molecular Simulations Inc., on Silicon Graphics 2 workstation. Energy Minimization was performed using Dreiding 2.21 force field which employs quadratic polynomial for bond stretching and angle bending and a three term Fourier expansion for torsions.



**Fig. 1.** Energy minimized chain structure of poly(amide-imide) (PAI-1) based on isophorone diisocyanate (IPDI) and trimellitic anhydride (TMA).

### 2.3.1. Preparation of poly(amide-imide)s (PAIs) (PAI-1 to PAI-16)

PAIs were prepared by the reaction of TMA (0.01 mol) with diisocyanates (0.01 mol) at ice-bath temperature in DMAc in a three-neck flask fitted with a nitrogen gas inlet, a reflux condenser, a calcium chloride guard tube and a magnetic stirring bar. Diisocyanate was first dissolved in DMAc and cooled to 0°C. Next, TMA was added in small

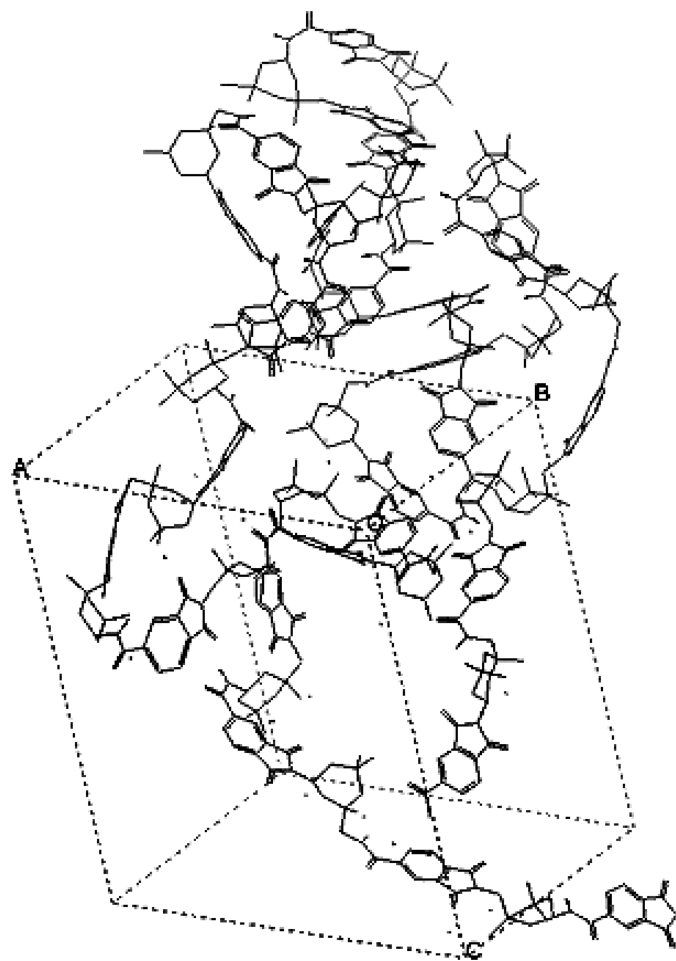


**Fig. 2.** Energy minimized chain structure of poly(amide-imide)s (PAI-1) based on isophorone diisocyanate (IPDI) and trimellitic anhydride (TMA) placed in an arbitrary 3-D periodic cell.

portions over 1 h. After the addition was complete, the reaction mixture was stirred for 2 h at 0°C. The solution was gradually 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 140°C over additional 2 h and left at that temperature for 24 h. Poly(amide-imide)s were isolated by pouring the reaction mixtures into excess methanol, filtering at pump and drying at 100°C in a vacuum oven for 24 h.

### 2.3.2. Preparation of poly(amide-imide)-silica gel hybrids (HPAIs) (HPAI-1 to HPAI-16)

The diisocyanate (0.01 mol) was dissolved in 25 ml DMAc (containing 5% salt based on the weight of the diisocyanate and TMA) and was taken in a three-neck flask fitted with a nitrogen gas inlet, a reflux condenser attached with a calcium chloride guard tube and a stirring bar, and cooled



**Fig. 3.** Energy minimized chain structure of poly(amide-imide)s (PAI-1) based on isophorone diisocyanate (IPDI) and trimellitic anhydride (TMA) placed in arbitrary 3-D periodic cell in presence of Li (from LiCl) (shown as black dots) (placed randomly on the energy minimized chain structure before constructing the 3-D periodic cell and subsequent energy minimization).

to ice-bath temperature. To this solution, was added TMA in small portions over 1 h. After the addition was complete, the reaction mixture was stirred for 2 h at ice-bath temperature. To this reaction mixture was added TMOS (one equivalent based on the weight of one repeat unit of the PAI). The reaction mixture was stirred for 2 h at ice-bath temperature. Two drops of 0.1 N HCl were added and stirred for 2 h and then allowed to attain ambient temper-

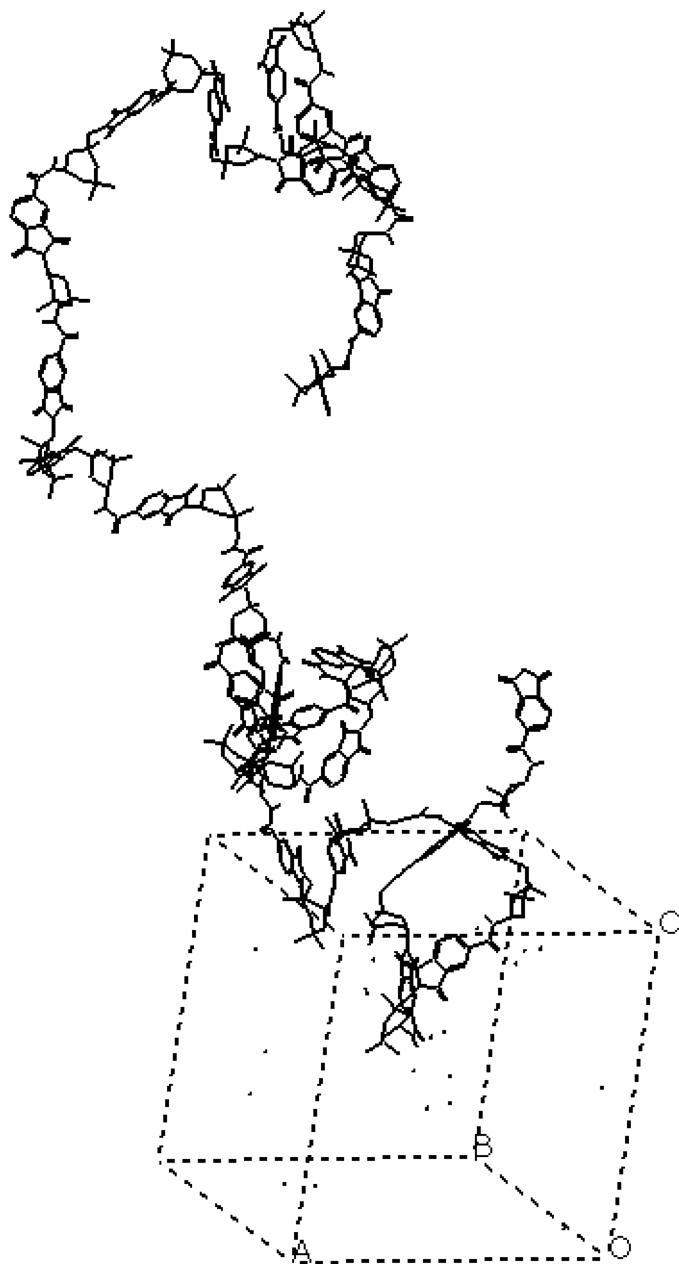
ature. The temperature was then raised to 40°C over 1 h, 80°C over the next 2 h and finally to 120°C over 2 h. The reaction mixture was kept at this temperature for several days to allow the solvent to evaporate gradually and afford a poly(amide-imide)-silica gel hybrid.

### 2.3.3. Preparation of porous silica gels

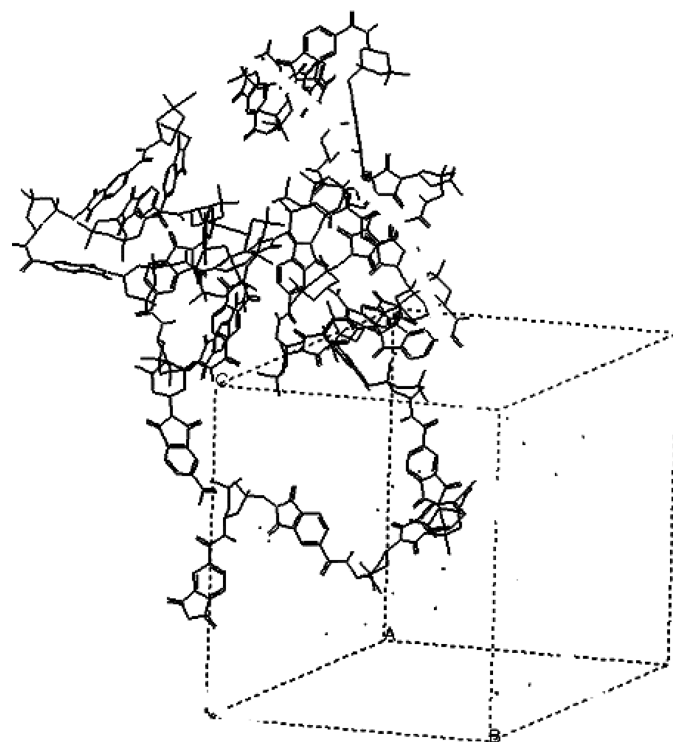
Pyrolysis of poly(amide-imide)s hybrids at 600°C for 24 h resulted in porous silica gels.

## 3 Results and Discussion

Poly(amide-imide)s (PAIs) combine the excellent thermal properties of polyimides and the ease of processing of polyamides and may be intermediate in properties between polyimides and polyamides (17–19). PAIs can be prepared by the reaction of (i) excess diamine with tetracarboxylic dianhydride to form a low molecular weight amine-terminated polyamic-acid; this is then treated with a diacid chloride to form poly[amide(amic-acid)] which is then converted to the PAI; (ii) excess diamine with diacid chloride to form a low molecular weight amine-terminated polyamide, which is then treated with a dianhydride to form



**Fig. 4.** Energy minimized chain structure of poly(amide-imide)s (PAI-1) based on isophorone diisocyanate (IPDI) and trimellitic anhydride (TMA) placed in arbitrary 3-D periodic cell in presence of Ca (from  $\text{CaCl}_2$ ) (shown as black dots) (placed randomly on the energy minimized chain structure before constructing the 3-D periodic cell and subsequent energy minimization).



**Fig. 5.** Energy minimized chain structure of poly(amide-imide)s (PAI-1) based on isophorone diisocyanate (IPDI) and trimellitic anhydride (TMA) placed in arbitrary 3-D periodic cell in presence of Zn (from  $\text{ZnCl}_2$ ) (shown as black dots) (placed randomly on the energy minimized chain structure before constructing the 3-D periodic cell and subsequent energy minimization).

the poly[amide(amic acid)], which is then converted to the PAI; (iii) anhydride acid [e.g., trimellitic anhydride, (TMA) or TMA derivatives, like acid chlorides, with diamines to form the poly[amide(amic acid)] which is then converted to the PAI (20, 21); (iv) TMA with diisocyanate to form the PAI; the reaction is believed to proceed *via* the formation of a seven-membered cyclic intermediate (22, 23); (v) diacylhydrazide with a dianhydride where the reaction proceeds *via* the formation of polyamide(hydrazide-acid), the cyclodehydration of which yields PAI (24–29); (vi) pre-formed imide group containing diacid chloride with a diamine (30–36) and (vii) a dicarboxylic acid and a diamine in the presence of triphenyl phosphate (37).

### 3.1 Preparation of Poly(amide-imide)s (PAI-1 to PAI-16)

Poly(amide-imide)s (PAIs) were prepared by the low temperature solution polycondensation of equimolar quantities of the diisocyanate and TMA in DMAc (Scheme 1). The polymers were isolated in the range of 88–92% by pouring the reaction mixtures into a large excess amount of methanol and drying at pump. The inherent viscosities of the polymers (PAI-1 to PAI-16) were determined in DMAc and were in the range of 0.39 to 0.69 dL/g. Temperature at 10% weight loss and the glass transition temperatures are incorporated in Table 1. The solubility of PAI is given in Table 2.

**Table 1.** Preparation of poly(amide-imide)s

Polymer code	Diisocyanate (0.01 mol)	Salt <sup>a</sup>	Yield <sup>b</sup> (%)	$\eta_{inh}^c$ (g/dL)	$T_{10}^d$ (°C)	$T_g^e$ (°C)
PAI-1	IPDI	No	90	0.43	230	ND
PAI-2	IPDI	LiCl	89	0.40	230	110
PAI-3	IPDI	CaCl <sub>2</sub>	88	0.39	210	105
PAI-4	IPDI	ZnCl <sub>2</sub>	92	0.51	225	105
PAI-5	TDI	No	89	0.69	225	120
PAI-6	TDI	LiCl	89	0.50	215	105
PAI-7	TDI	CaCl <sub>2</sub>	89	0.49	210	116
PAI-8	TDI	ZnCl <sub>2</sub>	92	0.67	210	108
PAI-9	MDI	No	90	0.66	220	147
PAI-10	MDI	LiCl	91	0.52	225	95
PAI-11	MDI	CaCl <sub>2</sub>	90	0.50	260	162
PAI-12	MDI	ZnCl <sub>2</sub>	92	0.59	265	160
PAI-13	HMDI	No	88	0.44	275	148
PAI-14	HMDI	LiCl	88	0.41	250	137
PAI-15	HMDI	CaCl <sub>2</sub>	89	0.40	260	183
PAI-16	HMDI	ZnCl <sub>2</sub>	90	0.44	230	140

Anhydride-Acid (0.01 M) = TMA;

<sup>a</sup>5% based on weight of TMA and diisocyanate;

<sup>b</sup>Isolated yield;

<sup>c</sup>Determined in DMAc at a concentration of 0.5 g/dL at 30 ± 0.01°C;

<sup>d</sup> $T_{10}$ , temperature corresponding to 10% weight loss in TGA measured at 10°C/min in air;

<sup>e</sup>From DSC, measured at 20°C/min in a draft of nitrogen.

ND = Not detected.

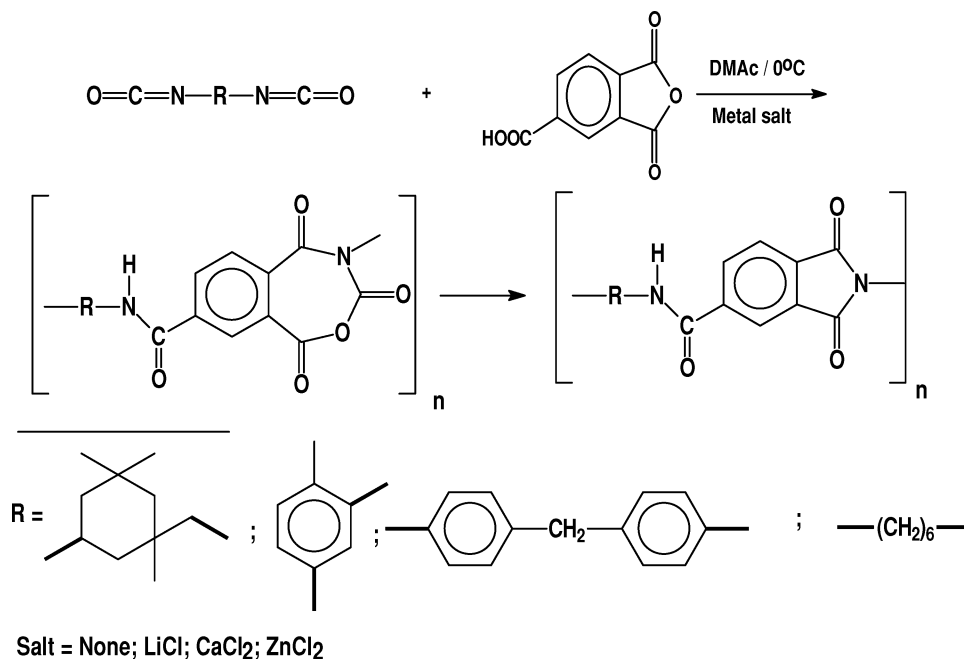
**Table 2.** Solubility of poly(amide-imide)s in different solvents

Polymer code	Solvents					
	DMF	DMAc	DMSO	NMP	HMPA	H <sub>2</sub> SO <sub>4</sub>
PAI-1	+	+	+	+	+	++
PAI-2	+	+	+	+	+	++
PAI-3	+	+	+	+	+	++
PAI-4	+	+	+	+	+	++
PAI-5	+	+	+	+	+	++
PAI-6	+	+	+	+	+	++
PAI-7	+	+	+	+	+	++
PAI-8	+	+	+	+	+	++
PAI-9	+	+	+	+	+	++
PAI-10	+	+	+	+	+	++
PAI-11	+	+	+	+	+	++
PAI-12	+	+	+	+	+	++
PAI-13	+	+	+	+	+	++
PAI-14	+	+	+	+	+	++
PAI-15	+	+	+	+	+	++
PAI-16	+	+	+	+	+	++

+ = Soluble on standing; ++ = Soluble with degradation.

### 3.2 Preparation of Poly(amide-imide)-Silica Gel Hybrids (HPAI-1 to HPAI-16)

HPAIs were prepared by the simultaneous formation of the PAIs during the hydrolysis condensation of TMOS. PAIs were prepared by the low temperature condensation of TMA and diisocyanates in DMAc containing 5% LiCl,



Sch. 1. Preparation of poly(amide-imide)s.

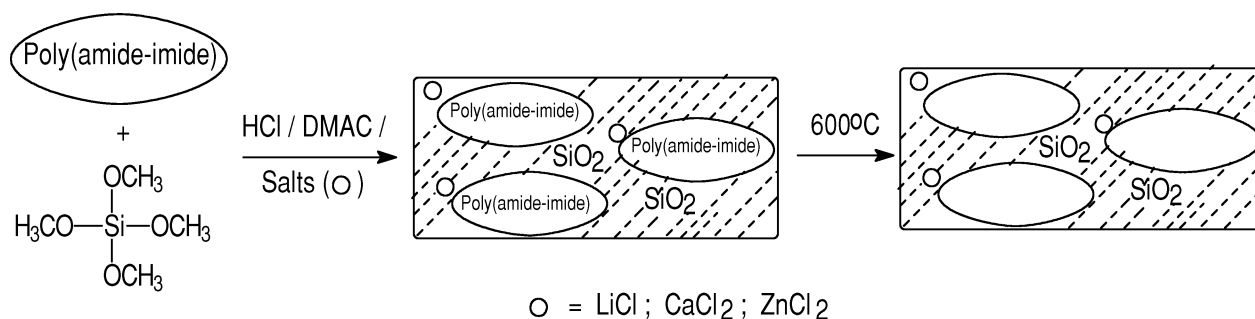
CaCl<sub>2</sub> or ZnCl<sub>2</sub> (based on the combined weight of TMA and diisocyanate). To the resulting solution at 0°C was added TMOS (1 weight equivalent based on the weight of the repeating unit of the PAI such that the weight feed ratio of polymer to silica gel was 1:1). The hydrolysis and condensation were effected by the addition of 2 drops of 0.1 N HCl. The solution was cast on a Teflon mold and the solvent was removed gradually at 120–130°C over several days to give pale yellow amber colored films in which the salts were dispersed at the molecular level (Scheme 2). Clear, transparent and homogeneous hybrids were formed (Table 3).

HPIA formation was confirmed by FT-IR spectra which showed absence of a peak due to diisocyanate group at 2270 cm<sup>-1</sup> and the appearance of peaks at 3300 cm<sup>-1</sup>, 1640 cm<sup>-1</sup> (amide stretching) and 1785 cm<sup>-1</sup> and 1736 cm<sup>-1</sup> characteristic of the cyclic imide structure. A shift to lower wavenumber of the amide carbonyl stretching band at 1640 cm<sup>-1</sup> in the hybrids was observed in the

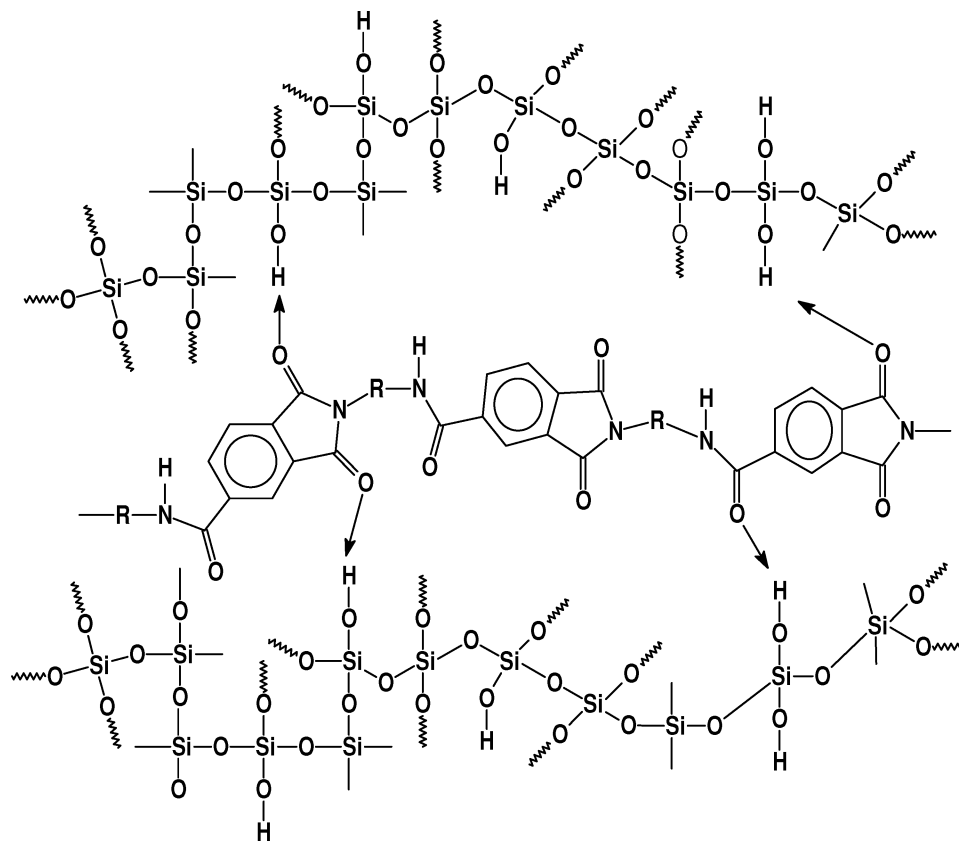
IR spectra of the hybrids. This is evidence of the hydrogen bonding between the amide and imide carbonyl groups of the polymer and the residual silanol groups of the silica gel.

PAI hybrid formation may be deemed to be through the operation of the hydrogen bond between the residual silanol groups (the Brønsted Acid) formed during the hydrolysis of TMOS and the carbonyl of amide and imide groups of poly(amide-imide)s and also the entrapment of the polymer chains during the condensation of silanol groups to form the three-dimensional Si-O-Si network. The schematic representation of such a hybrid is illustrated in Scheme 3.

Thermogravimetric analysis and DSC measurements were carried out on the hybrid samples. About 30–60% polymer was observed in the hybrid samples. The temperature at 10% (T<sub>10</sub>) weight loss was higher in the hybrid samples compared to those of the poly(amide-imide)s. The T<sub>g</sub> values, too, were higher in the hybrids than the values observed for poly(amide-imide)s. Polymer chains appeared



Sch. 2. Preparation of poly(amide-imide)-silica gel hybrids and porous silica.



Sch. 3. Schematic representation of poly(amide-imide)-silica gel hybrid.

Table 3. Preparation and characterization of poly(amide-imide)-silica gel hybrids

Polymer Code	Diisocyanate (0.01 mol)	Salt <sup>a</sup>	Polymer incorporated <sup>b</sup> (%)	$T_{10}^c$ (°C)	$T_g^d$ (°C)
HPAI-1	IPDI	None	35	235	156
HPAI-2	IPDI	LiCl	58	265	159
HPAI-3	IPDI	CaCl <sub>2</sub>	47	265	180
HPAI-4	IPDI	ZnCl <sub>2</sub>	39	240	171
HPAI-5	TDI	None	60	235	151
HPAI-6	TDI	LiCl	60	250	163
HPAI-7	TDI	CaCl <sub>2</sub>	60	240	166
HPAI-8	TDI	ZnCl <sub>2</sub>	57	230	186
HPAI-9	MDI	None	60	235	157
HPAI-10	MDI	LiCl	60	240	167
HPAI-11	MDI	CaCl <sub>2</sub>	60	260	166
HPAI-12	MDI	ZnCl <sub>2</sub>	46	280	168
HPAI-13	IPDI	None	30	315	153
HPAI-14	IPDI	LiCl	55	260	164
HPAI-15	IPDI	CaCl <sub>2</sub>	49	310	ND
HPAI-16	IPDI	ZnCl <sub>2</sub>	51	230	184

Anhydride-Acid = TMA;

<sup>a</sup>5% based on the weight of TMA and diisocyanate;

<sup>b</sup>Based on thermogravimetric analysis carried out at 10°C/min;

<sup>c</sup>Based on DSC, carried out at 20°C/min in nitrogen.

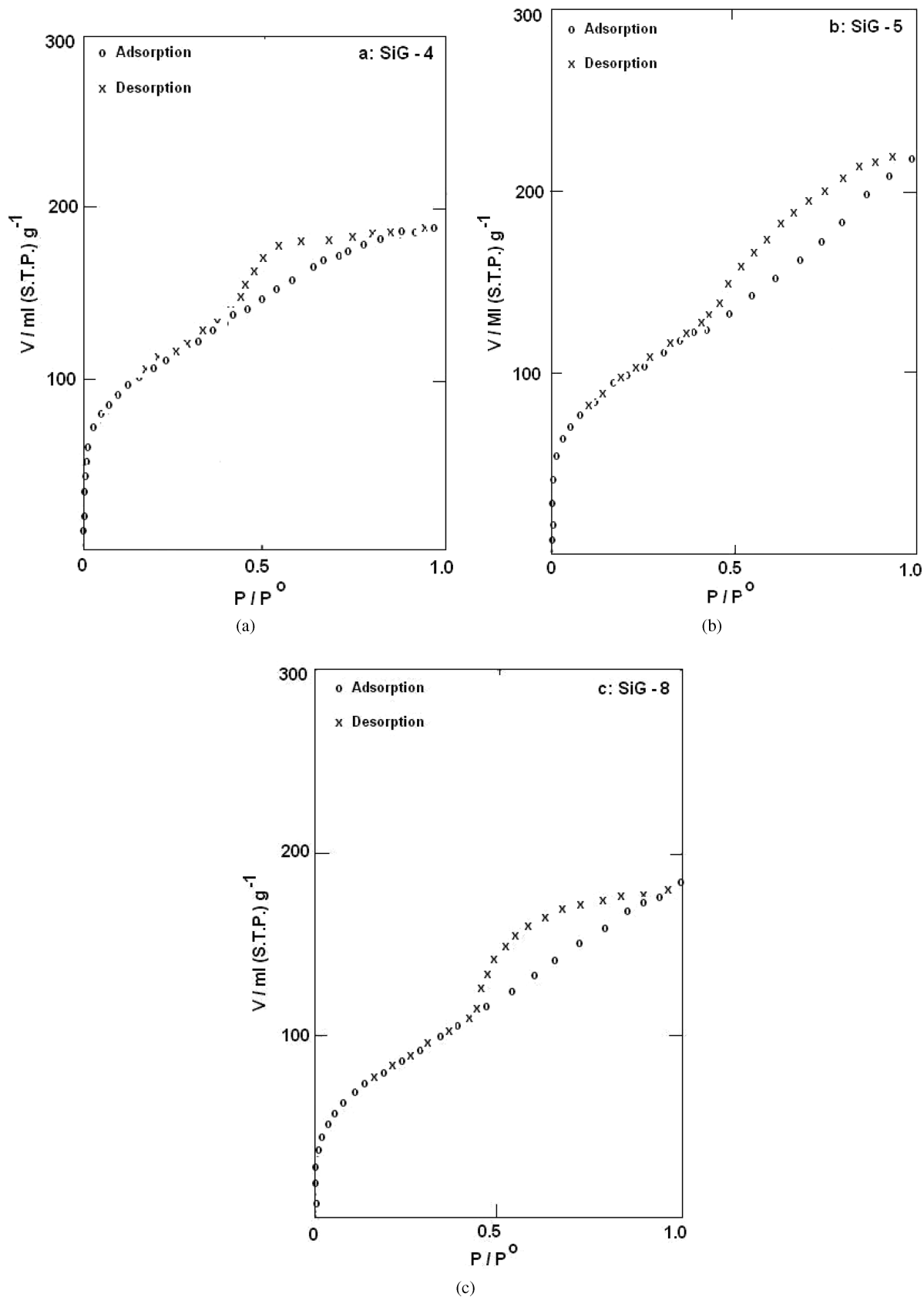
ND = Not detected.

to be still mobile despite the rigid silica gel network formed due to the condensation of the silanol groups. These values are incorporated in Table 3.

### 3.3 Molecular Modeling Studies

Molecular parameters of chain structure based on trimellitic anhydride (TMA) and isophorone diisocyanate (IPDI) were estimated by molecular modeling studies. A poly(amide-imide) chain with 24 repeat units was constructed and energy was minimized using standard molecular modeling software. The total energy of the energy minimized chain structure (relaxed system) was 1897 kcal/mol while the chain end-to-end distance was found to be 182.7 Å (Figure 1). An arbitrary 3-D periodic cell was constructed and the energy of the polymer chain was minimized. The chain end-to-end distance for the 3-D periodic cell for cells without any salt, with Li ions, Ca ions and Zn ions was found to be 54.0 Å, 17.5 Å, 31.6 Å, and 11.15 Å, respectively. The total energy of the energy minimized chain structure (relaxed system) for the 3-D periodic cell without any salt, with Li ions, with Ca ions and with Zn ions was found to be 1560 kcal/mol, 3461 kcal/mol, 3697 kcal/mol and 9205 kcal/mol, respectively. Figures 2, 3, 4, and 5, respectively, represent 3-D periodic cell without any salt, with Li





**Fig. 6.** Adsorption-desorption isotherms of silica gels (SiG-4, SiG-5, and SiG-8) obtained upon the pyrolysis of corresponding poly(amide-imide)-silica gel hybrids [HPAI-4 (TMA-IPDI/ $\text{ZnCl}_2$ ), (HPAI-5 (TMA-TDI/No Salt), and (HPAI-8 (TMA-TDI/ $\text{ZnCl}_2$ )).

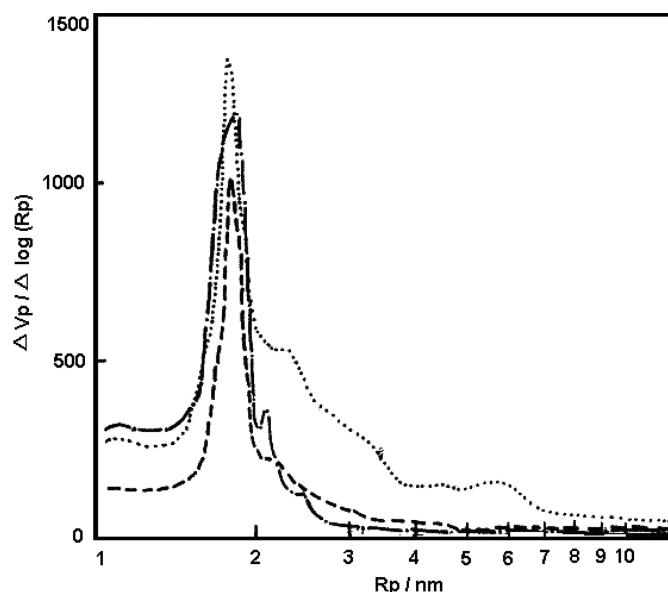
**Table 4.** Some characteristics of chain structure of poly(amide-imide)s PAI-1) based on isophorone diisocyanate (IPDI) and trimellitic anhydride (TMA)

Chain end-to-end distance (from NCO to Anhydride end group) ( $\text{Å}^\circ$ )				183
Total energy of the energy minimized chain structure (relaxed system) (Kcals/mol)				1897
Chain end-to-end distance (from NCO to Anhydride end group) in 3-D Periodic cell ( $\text{Å}^\circ$ )				54.0
Total energy of the energy minimized chain structure (relaxed system) in 3-D Periodic cell (Kcals/mol)				1560
Chain end-to-end distance (from NCO to Anhydride end group) in 3-D Periodic cell in presence of Zn from LiCl ( $\text{Å}^\circ$ )				17.5
Total energy of the energy minimized chain structure (relaxed system) in 3-D Periodic cell in presence of Li from LiCl (Kcals/mol)				3461
Chain end-to-end distance (from NCO to Anhydride end group) in 3-D Periodic cell in presence of Zn from $\text{CaCl}_2$ ( $\text{Å}^\circ$ )				31.6
Total energy of the energy minimized chain structure (relaxed system) in 3-D Periodic cell in presence of Ca from $\text{CaCl}_2$ (Kcals/mol)				3697
Chain end-to-end distance (from NCO to Anhydride end group) in 3-D Periodic cell in presence of Zn from $\text{ZnCl}_2$ ( $\text{Å}^\circ$ )				11.5
Total energy of the energy minimized chain structure (relaxed system) in 3-D Periodic cell in presence of Zn from $\text{ZnCl}_2$ (Kcals/mol)				9205
Dimensions of 3-D Periodic Cell ( $\text{Å}^\circ$ )	a	25.4	$\alpha$	85.8
	b	21.6	$\beta$	91.1
	c	26.5	$\gamma$	84.4
Dimensions of 3-D Periodic Cell in presence of Li from LiCl ( $\text{Å}^\circ$ )	a	21.6	$\alpha$	98.4
	b	23.5	$\beta$	108.9
	c	25.4	$\gamma$	93.2
Dimensions of 3-D Periodic Cell in presence of Ca from $\text{CaCl}_2$ ( $\text{Å}^\circ$ )	a	26.7	$\alpha$	98.0
	b	21.0	$\beta$	89.3
	c	26.3	$\gamma$	83.1
Dimensions of 3-D Periodic Cell in presence of Zn from $\text{ZnCl}_2$ ( $\text{Å}^\circ$ )	a	20.7	$\alpha$	78.5
	b	26.4	$\beta$	92.5
	c	28.1	$\gamma$	82.0

ions, Ca ions and Zn ions. The 3-D periodic cell dimensions without any salt, with Li ions, Ca ions and Zn ions are shown in Table 4. From these results, it can be seen that the chains are fairly distended and not in any particular coiled state. There is a tendency for the polymer chain to be “distended” and not agglomerated or coiled. Table 4 incorporates some characteristics of chain structure of the poly(amide-imide) based on TMA and IDI.

### 3.4 Preparation of Porous Silica

Porous silica gel was prepared by the pyrolysis of the polymer hybrids at  $600^\circ\text{C}$  for 24 h in a furnace (Scheme 2). Adsorption and desorption studies were carried out on representative porous silica gel samples, SiG-4, SiG-5, and SiG-8, obtained upon the pyrolysis of HPAI-4, HPAI-5 and HPAI-8 to determine the pore size, surface area and pore volume. These silica gels exhibited a Type IV adsorption-desorption isotherm and Type H2 hysteresis loops. Type IV isotherm is indicative of capillary condensation occurring in bottle-shaped pores, i.e., pores with narrow necks with wide bodies (15, 16). Figure 6 (a, b, and c) incorporates the adsorption-desorption plots of porous silica gels. All the samples exhibited mesoporous nature and had a narrow



**Fig. 7.** Pore size distribution plots of porous silica gels obtained upon the pyrolysis of hybrids HPAI-4 (---), HPAI-5 (···) and HPAI-8 (- · - ·).

**Table 5.** Surface Characteristics of Porous Silica Gels Obtained upon the Pyrolysis of Poly(amide-imide)-Silica Gel Hybrids

Silica gel code	Composition of parent silica gel hybrid	Surface area <sup>a</sup> (m <sup>2</sup> /g)	Pore volume <sup>b</sup> (cm <sup>3</sup> /g)	Pore radius <sup>b</sup> (nm)	Remarks
SiG - 4	TMA-IPDI/ZnCl <sub>2</sub>	371	0.227	1.8	Mesoporous, Bottle-shaped pores <sup>c</sup>
SiG - 5	TMA-TDI/No Salt	335	0.314	1.8	Mesoporous, Bottle-shaped pores <sup>c</sup>
SiG - 8	TMA-TDI/ZnCl <sub>2</sub>	300	0.280	1.8	Mesoporous, Bottle-shaped pores <sup>c</sup>

<sup>a</sup>BET Method.<sup>b</sup>BJH Method.<sup>c</sup>From adsorption isotherms.

pore size distribution with pore radius of 1.8 nm (Barrett-Joyner-Halenda (BJH Method)) (38) and a surface area of 371 m<sup>2</sup>/g, 335 m<sup>2</sup>/g, and 300 m<sup>2</sup>/g (Brunauer-Emmett-Teller (BET Method)) (39), respectively. The bottle-shaped pores exhibited a pore volume of 0.227 cm<sup>3</sup>/g, 0.314 cm<sup>3</sup>/g, and 0.280 cm<sup>3</sup>/g, respectively (Table 5). The pore size distributions of porous silica gel samples obtained from the pyrolysis of hybrids HPAI-4, HPAI-5 and HPAI-8 are illustrated in Figure 7.

#### 4 Conclusions

Poly(amide-imide)-silica gel hybrids were prepared by the hydrolysis and condensation of TMOS during the formation of PAIs. Pale yellow to amber colored films could be obtained by solution casting in which the metal salts were highly dispersed at the molecular level. Higher T<sub>10</sub> and T<sub>g</sub> values were observed in the hybrid samples as compared to the virgin polymers. The polymer chains are significantly mobile despite the rigid silica gel network formed due to the condensation of the silanol groups. Porous silica gel could be obtained by the pyrolysis of the hybrids at 600°C for 24 h. Preliminary adsorption-desorption studies on representative porous silica gel samples, SiG-4, SiG-5, and SiG-8, obtained as a result of the pyrolysis of hybrid HPAI-4, HPAI-5 and HPAI-8 indicated a mesoporous nature and large surface area, while the bottle-shaped pores had a fairly large pore volume. Molecular modeling studies indicated that the poly(amide-imide) chains are fairly distended and there was no evidence of being coiled or being agglomerated. This is also evident from the narrow pore sizes obtained for these silica gels. Domains of PAIs still embedded in the silica gel matrix may be obtained by the controlled pyrolysis of hybrids. Such partially pyrolyzed hybrids might have interesting properties and applications.

#### References

- Kim, K.-M. and Chujo, Y. (2003) *J. Polym. Sci. Part A: Polym. Chem.*, 41, 1306.
- Zhang, Y.-H., Li, Y., Fu, S.-Y., Xin, J.H. and Daoud, W.A., and Li, L.-F. (2005) *Polymer*, 46, 8373.
- Chujo, Y., Ihara, E., Kure, S. and Saegusa, T. (1993) *Macromolecules*, 26, 5681.
- Noell, J.L.W., Wilkes, G.L., Mohanty, D.K. and McGrath, J.E. (1990) *J. Appl. Polym. Sci.*, 40, 1177.
- Fujita, M. and Honda, K. (1989) *Polym. Commun.*, 30, 200.
- Huang, H., Wilkes, G.L. and Carlson, J.C. (1989) *Polymer*, 30, 2001.
- Huang, H., Orler, B. and Wilkes, G.L. (1987) *Macromolecules*, 20, 1322.
- Ning, Y.-P. and Mark, J.E. (1985) *J. Appl. Polym. Sci.*, 30, 3519.
- Mark, J.E., Jiang, C.Y. and Tang, M.-Y. (1984) *Macromolecules*, 17, 2613.
- Wang, S., Ahmad, Z. and Mark, J.E. (1993) *Polym. Bull.*, 31, 323.
- Morikawa, A., Yamaguchi, H., Kakimoto, M. and Imai, Y. (1994) *Chem. Mater.*, 6, 913.
- Nandi, A., Conklin, J.A., Salvati, L. and Sen A. (1990) *Chem. Mater.*, 2, 772.
- Wang, G.P., Chang, T.C., Hong, Y.S. and Chiu, Y.S. (2002) *Polymer*, 43, 2101.
- Perrin, D.D. and Armarego, W.L.F. Purification of Laboratory Chemicals, 3rd Ed. Pergamon Press: New York, 1988.
- Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., Pierotti, R.A., Rouquerol, J. and Siemieniewska, T. (1985) *Pure and Appl. Chem.*, 57, 603.
- Gregg, S.J. and Sing, K.S.W. Adsorption, Surface Area and Porosity, 2nd Ed. Academic Press: New York, 1982.
- Cassidy, P.E. Thermally Stable Polymers—Synthesis and Properties, Marcel Dekker, Inc.: New York, 1980.
- Hsiao, S.H. and Yang, C.P. (1990) *J. Polym. Sci. Polym. Chem. Ed.*, 28, 1149.
- Loncrini, D.F. (1966) *J. Polym. Sci. Polym. Chem.*, A-1, 4, 1531.
- Stephens, C.W. (1962) U.S. Pat. 3,049,518.
- Lavin, E., Markhart, A.H. and Santer, J.O. (1966) U.S. Pat. 3,260,691.
- Ulrich, H. in *Encycl. Polym. Sci. Engg.*, 2nd Ed. Mark, H.F., Bikales, N.M., Overberger, C.G. and Menges, G. Eds. Wiley: New York, Vol. 8, p. 448, 1987.
- Avadhani, C.V., Wadgaonkar, P.P. and S.P. Vernekar in *Polymer Science—Contemporary Themes (Polymers'91)*, Sivaram, S., Ed. Tata McGraw-Hill: New Delhi, India, Vol. 1, 21–26, 1991.
- Terney, S., Keating, J., Zielinski, J., Hakala, J. and Sheffer, H. (1970) *J. Polym. Sci. A-1*, 8, 683.
- Avadhani, C.V., Wadgaonkar, P.P. and Vernekar, S.P. (1990) *J. Appl. Polym. Sci.*, 40, 1325.
- Comanita, V.E., Sass, O.E. and Vollmert, B. (1972) *Angew. Makromol. Chem.*, 21, 105.
- Unishi, T. (1965) *J. Polym. Sci. Polym. Part B., Polym. Lett.*, 3, 679.
- Loncrini, D.F., Walton, W.L. and Huges, R.B. (1966) *J. Polym. Sci. A-1: Polym. Chem.*, 4, 440.
- Sivaraj, K. and Nanjan, M.J. (1983) *Makromol. Chem. Rapid Commun.*, 4, 669.
- Wrasidlo, W. and Augl, J.M. (1969) *J. Polym. Sci. A-1*, 7, 321.

31. de la Campa, J.G., de Abajo, J. and Nieto, J.L. (1982) *Makromol. Chem.*, 183, 571.
32. de Abajo, J., Gabarda, J.P. and Fontan, J. (1978) *Angew. Makromol. Chem.*, 71, 143.
33. Nieto, J.L., de la Campa, J.G. and de Abajo, J. (1982) *J. Makromol. Chem.*, 183, 557.
34. Maiti, S. and Ray, A. (1983) *J. Polym. Sci. Polym. Chem. Ed.*, 21, 999.
35. Maiti, S. and Ray, A. (1982) *J. Appl. Polym. Sci.*, 27, 4345.
36. Ghosh, M. and Maiti, S., (1985) *J. Macromol. Sci., Chem.*, A22, 1463.
37. Yang, C.P. and Hsiao, S.H. (1989) *Makromol. Chem.*, 190, 2119.
38. Barrett, E.P., Joyner, L.G. and Halenda, P.J. (1951) *J. Am. Chem. Soc.*, 73, 373.
39. Brunauer, S., Emmett, P.H. and Teller, E. (1938) *J. Am. Chem. Soc.*, 60, 309.