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Polyamide-silica gel hybrids containing metal salts: Preparation via the sol-gel reaction

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Summary

The hydrolysis and condensation of tetramethoxysilane in a DMF solution of polyamides containing LiCl, $CaCl_2$ or $ZnCl_2$, both in presence and absence of polyoxazoline, resulted in the facile formation of polyamide-silica gel hybrids. Films were cast from the resulting mixtures and evaporation of the solvent resulted in the formation of clear, transparent hybrids with the salts dispersed at the molecular level. Pyrolysis of hybrids at 600°C gave porous silica. Pore size and surface characteristics of these silica gel samples indicated a porous nature with a pore radius of 1.1 nm for silica gels obtained from hybrids HPA-6 (containing no salt) and HPA-9 (containing $ZnCl_2$) and a surface area of 213 m^2g^{-1} and 310 m^2g^{-1}, respectively. Silica gel from hybrid HPA-7 (containing LiCl) had a pore radius of 1.9 nm and a surface area of 15 m^2g^{-1}. The silica gel samples obtained from hybrids HPA-6, HPA-7 and HPA-9 exhibited narrow slit-like pores with a pore volume of 0.68 cm^3g^{-1}.

Introduction

The sol-gel reaction involves the controlled hydrolysis and condensation of metal and non-metal alkoxides and is an attractive route for the facile formation of high purity glasses at relatively low processing temperatures, molecular dispersions, composites, as well as organic-inorganic polymer hybrids (1). The inorganic component of the hybrid is formed by the hydrolysis-condensation of metal alkoxides such as TMOS. Transparent organic-inorganic glassy gels are easily prepared by effecting the hydrolysis-condensation of the alkoxide in a solution of a preformed polymer. The range and composition of the polymer-silica gel hybrids can be tailored by changing the ratio of the metal alkoxide and the polymer. Structure of organic and inorganic component, phase morphology, degree of penetration and covalent

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bonds contribute to a wide variety of properties in the hybrids (2). The presence of metal salts like LiCl, $CaCl_2$ or $ZnCl_2$ might result in the formation of new types of hybrids.

Silica gel hybrids containing poly(2-methyl-2-oxazoline) (3), poly(ether-ketone) (4), poly(oxyethylene) (5), poly(oxytetramethylene) (6), poly(dimethylsiloxane) (7), polysiloxane elastomers (8), poly(*N*-vinylpyrrolidone) (9), polyurea (10), and polyimide (11) have been reported. Wang, et al. (12) have reported the preparation of polyamide-silica gel composites via the sol-gel reaction.

The present paper reports the preparation of silica gel hybrids by the acid-catalyzed hydrolysis-condensation reaction of TMOS in a solution of polyamide to result in the formation of multi-dimensional silica gel network. By the reaction of diamines and diacid chlorides several polyamides were targeted. The hydrolysis-condensation of TMOS was carried out in a solution of dimethylformamide (DMF) containing 5% LiCl, $CaCl_2$ or $ZnCl_2$ and the polyamide both in the presence and absence of polyoxazoline (POZO). The potential application of these materials may be in catalysis (13), in non-linear optics (14), in coatings, films and in semi-permeable membrane applications. Porous silica gels were also prepared by the pyrolysis of these hybrids at 600°C in a furnace.

Experimental

Materials

Tetramethoxysilane (TMOS) was distilled prior to use under an inert atmosphere of nitrogen. Isophorone diamine was used as such from freshly opened bottle. Hexamethylene diamine was sublimed in vacuum. Adipoyl chloride, isophthaloyl chloride and terephthaloyl chloride were distilled under reduced pressure. Dimethylformamide (DMF) was distilled over calcium hydride under reduced pressure.

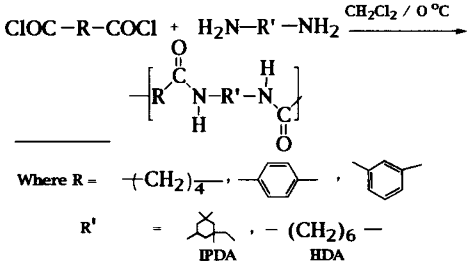
Poly(2-methyl-2-oxazoline) (DP=100) was synthesized by the ring-opening polymerization of 2-methyl-2-oxazoline by the procedure reported earlier (3). Other reagents were purified using standard laboratory procedures (15).

Characterization methods

Inherent viscosities were determined in a suspension type Ubbelohde viscometer at a concentration of 0.5g/dL in dimethylformamide or in sulfuric acid at 30±0.01°C. Thermogravimetric analysis was carried out by heating the samples at 10°C/min in air. Glass transition temperatures (Tg) were measured at a heating rate of 20°C/min in a draft of nitrogen. The pore size, pore volume, and surface area of porous silica samples were determined by nitrogen adsorption-desorption isotherm method (16,17) on a Belsorp 28 nitrogen adsorption apparatus.

Polyamide Preparation (PA-1 to PA-6)

Polyamides were prepared by reacting diamines (0.01 mol) and diacid chlorides (0.01 mol) in presence of an equivalent amount of pyridine at ice-bath temperature in dichloromethane in a three-necked flask fitted with a nitrogen gas inlet, a reflux condenser fitted with a calcium chloride guard tube and a stirring bar. The reaction mixture was washed with water to remove the pyridinium salt. The dichloromethane solution was dried over anhydrous Na_2SO_4 before concentration. Polymer samples were isolated by pouring the reaction mixtures into excess of methanol or n-hexane, filtering at pump and drying at 100°C in vacuum for several hours (Scheme 1 and Table 1).



Scheme 1: Preparation of Polyamides.

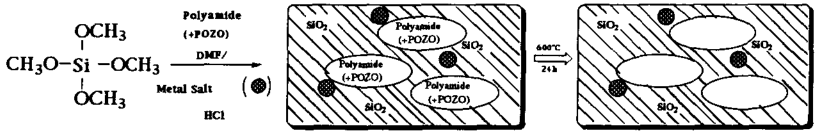
Table 1 : Preparation of Polyamides.

Polymer code	Diamine (0.01 mol)	Diacid chloride (0.01 mol)	Yield[a] (%)	η_{inh}[b] (dL/g)
PA-1	Hexamethylene diamine	Adipoyl chloride	90	0.42
PA-2	Isophorone diamine	Adipoyl chloride	91	0.51
PA-3	Hexamethylene diamine	Terephthaloyl chloride	88	0.32
PA-4	Isophorone diamine	Terephthaloyl chloride	89	0.37[c]
PA-5	Hexamethylene diamine	Isophthalolyl chloride	91	0.66[c]
PA-6	Isophorone diamine	Isophthalolyl chloride	90	0.70

a = Isolated yield; b = Determined in DMF at a concentration of 0.5 g/dL at 30±0.01 °C; c = Determined in H_2SO_4 at a concentration of 0.5 g/dL at 30±0.01 °C.

Polyamide-Silica Gel Hybrid Preparation (HPA-1 to HPA-32)

To a solution of a polyamide in DMF, TMOS was added (weight-feed ratio employed was polyamide : TMOS :: 1 : 1 or polyamide : TMOS :: 1 : 5). The reaction mixture was stirred for 2 hours at ambient temperature. Two drops of 0.1 N HCl were added and stirred for 2 additional hours. The temperature was then raised gradually to 110°C



Scheme 2 : Preparation of Polymer-Silica Gel Hybrids and Porous Silica.

Table 2: Preparation of Polyamide-Silica Gel Hybrids and Some Properties.

Hybrid	Weight Feed Ratio[a]				Salt	% Polymer	T_{10}[c]	Tg[d]
Code	Polyamide		POZO[b]	TMOS	(5%)	in Hybrid[c]	(°C)	(°C)
HPA-1	PA-1	1	-	5	None	37	260	136
HPA-2		1	-	5	ZnC_2	36	235	167
HPA-3		1	1	1	None	35	305	140
HPA-4		1	1	1	LiCl	60	235	140
HPA-5		1	1	1	$ZnCl_2$	66	260	150
HPA-6	PA-2	1	-	1	None	55	271	158
HPA-7		1	-	1	LiCl	53	225	184
HPA-8		1	-	1	$CaCl_2$	60	263	185
HPA-9		1	-	1	$ZnCl_2$	57	255	148
HPA-10		1	-	5	None	35	300	174
HPA-11		1	-	5	LiCl	35	300	-
HPA-12		1	-	5	$CaCl_2$	35	295	-
HPA-13		1	-	5	$ZnCl_2$	35	310	170
HPA-14		1	1	1	None	55	260	146
HPA-15		1	1	1	LiCl	63	265	164
HPA-16		1	1	1	$CaCl_2$	60	300	166
HPA-17		1	1	1	$ZnCl_2$	67	300	163
HPA-18	PA-3	1	-	1	None	35	331	-
HPA-19		1	-	1	LiCl	67	285	-
HPA-20		1	-	1	$ZnCl_2$	70	259	-
HPA-21		1	-	5	None	46	300	-
HPA-22		1	-	5	$ZnCl_2$	35	300	-
HPA-23		1	1	1	None	70	291	-
HPA-24		1	1	1	LiCl	70	283	-
HPA-25		1	1	1	$ZnCl_2$	64	295	-
HPA-26	PA-6	1	-	1	None	70	275	-
HPA-27		1	-	1	LiCl	63	300	-
HPA-28		1	-	1	$ZnCl_2$	60	300	-
HPA-29		1	-	5	None	41	295	-
HPA-30		1	1	1	None	56	310	-
HPA-31		1	1	1	LiCl	70	260	-
HPA-32		1	1	1	$ZnCl_2$	64	265	-

a = Combinations which gave clear and transparent hybrids; b = POZO of DP=100;
c = As observed from the thermogravimetric analysis at a heating rate of 10°C/min in air;
d = As observed in the DSC measured at a heating rate of 20°C/min in nitrogen.

to 120°C and kept at that temperature for several days to allow the solvent to evaporate gradually and afford a hybrid. Silica gel hybrids containing polyamides and POZO were also prepared in a similar manner. The weight-feed ratio employed was polyamide : polyoxazoline: TMOS :: 1:1:1 (Scheme 2). Table 2 incorporates the combinations that resulted in clear, homogeneous and transparent hybrids.

Preparation of Porous Silica Gels

Polyamide-silica gel hybrids were pyrolysed in a muffle furnace at 600°C for 24 hours to obtain porous silica gels (Scheme 2).

Results and Discussion

The sol-gel reaction affords the preparation of composites and hybrids of organic-inorganic polymers in which the components are intermingled with each other at a molecular level. There are no covalent linkages and the hybrid might be composed of a single, transparent and homogeneous phase (18).

On account of their superior thermal stability, lower density and specific strength, aromatic polyamides, particularly Kevlar and Nomex, find pervasive applications in aerospace and automobile industries, among others (12).

Polyamides Preparation (PA-1 to PA-6)

Polyamides were prepared by the polycondensation of equimolar amounts of diamines and diacid chlorides in dichloromethane, in presence of an equivalent amount of pyridine as an acid trap (Scheme 1). The polymers were isolated in yields in the range 88-91%. The inherent viscosities of the polyamides were in the range 0.32 to 0.70 dL/g (Table 1). These polyamides were insoluble in many protic solvents tried. PA-1, PA-2, PA-3, and PA-6 were soluble in DMF, DMAc, and DMSO on heating to 100°C. However, all polyamides dissolved readily in sulfuric acid.

Polyamide-Silica Gel Hybrid Preparation (HPA-1 to HPA-32)

To a solution of polyamide in DMF, TMOS was added. The hydrolysis and condensation was effected by the addition of 2 drops of 0.1N HCl. Silica gel hybrids containing polyamides and POZO were also prepared in a similar manner. The solution was cast on Teflon mold and the solvent was removed gradually at 110-120°C over several days to give a pale yellow to amber-colored films (Scheme 2). Polyamide-silica gel hybrid formation was favoured in the presence of POZO. Table 2 incorporates the combinations that resulted in clear, homogeneous and transparent hybrids.

Polyamide formation was characterized by the amide bands at 3300 cm^{-1} and 1640 cm^{-1} in the infrared spectra of the polymers. However, the 1640 cm^{-1} band shifted to lower wavenumber in the polymer-silica gel hybrids. Polyamide-silica gel hybrid formation may be reckoned to be through the operation of the hydrogen bond between the residual silanol groups (the Brφnsted acid) formed during the hydrolysis of TMOS and the carbonyl groups of polyamide and POZO (when present) and the entrapment of the polymer chains during the condensation of the already hydrolyzed TMOS to form the three-dimensional Si-O-Si network. The schematic representation of such a

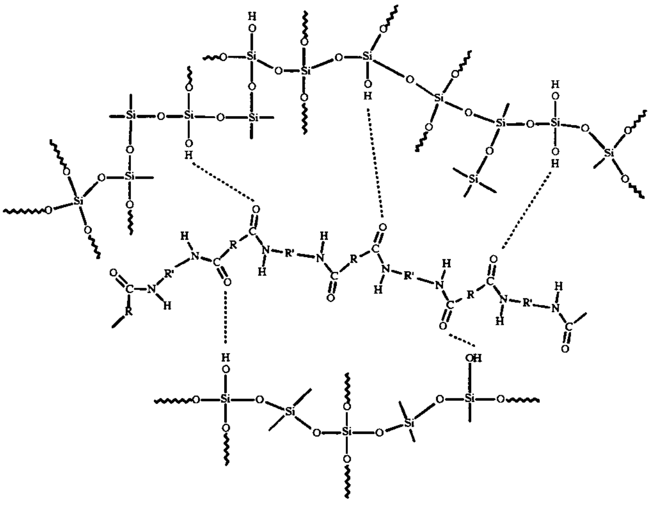


Figure 1: Schematic Represenatation of Polyamide-Silica Gel Hybrid.

hybrid is illustrated in Figure 1. It is expected that polymer-silica gel hybrids with salts dispersed at a molecular level would find usage in semi-conductor, semi-permeable membrane, and NLO applications, among others.

Nearly 35-70% polymers were incorporated in the organic-inorganic polymer hybrids as observed in the thermogravimetric analysis. Table 2 incorporates the temperature at 10% (T_{10}) weight loss and the glass transition temperatures.

Preparation of Porous Silica Gels

Porous silica gels were prepared by the pyrolysis of the polymer hybrids at 600°C for 24 hours in a furnace. Adsorption-desorption studies were carried out according to literature method (16,17) to determine the pore size, pore volume and surface area of the porous silica thus obtained. Preliminary studies were carried out on representative silica gel samples obtained from hybrids HPA-6 (containing no salt), HPA-7 (containing LiCl) and HPA-9 (containing $ZnCl_2$). Silica gel samples from hybrids HPA-6 and HPA-9 gave a Type IV isotherm and Type H4 hysteresis loop. Type IV isotherm is associated with capillary condensation taking place in the mesopores. It is also indicative of monolayer-multilayer adsorption. Type H4 hysteresis loop is indicative of narrow slit-like pores, but the Type I isotherm character is indicative of microporosity. Silica from hybrid HPA-7 also exhibited a Type IV isotherm and a Type H3 hysteresis loop. Type H3 hysteresis loop is normally observed with aggregates of plate-like particles giving rise to slit-shaped pores (16,17). Silica from

Table 3. Some Surface Characteristics of Porous Silica Gels Obtained upon the Pyrolysis of Polyamide-Silica Gel Hybrids.

Hybrid Code	Composition	Surface Area [a] (m^2g^{-1})	Pore Volume [b] (cm^3g^{-1})	Pore Radius[b] (nm)	Remarks [c]
HPA-6	(IPDI+C4):TMOS::1:5/No Salt	213	0.68	1.1	Microporous, Narrow slit-like pores
HPA-7	(IPDI+C4):TMOS::1:5/LiCl	15	0.68	1.9	Mesoporous, Narrow slit-shaped pores
HPA-9	(IPDI+C4):TMOS::1:5/$ZnCl_2$	310	0.68	1.1	Microporous, Narrow slit-like pores

a - BET Method; b - BJH Method; c - From adsoption - desorption isotherm

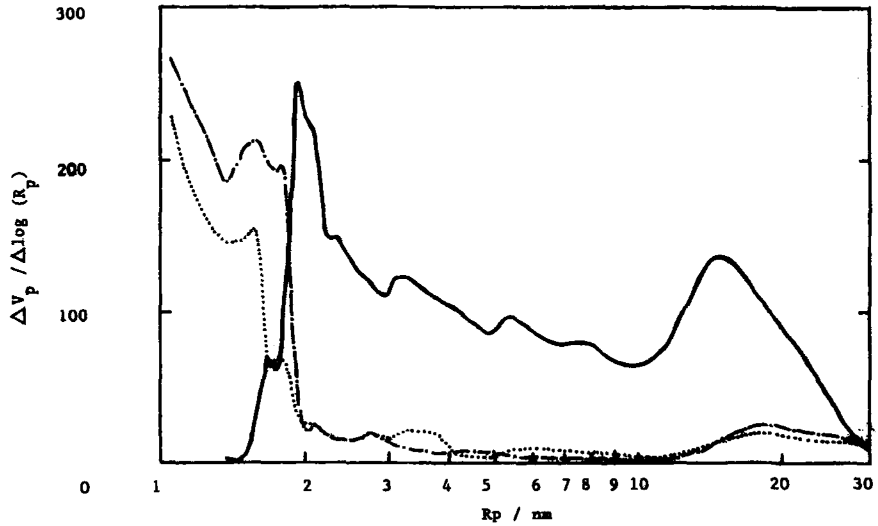


Figure 2: Pore size distribution plots of porous silica obtained after the pyrolysis of hybrids HPA-6 (---), HPA-7 (——) and HPA-9 (—-).

hybrids HPA-6 and HPA-9 had a pore radius of 1.1 nm (BJH Method) and a surface area of 213 m^2g^{-1} and 310 m^2g^{-1}, respectively, while silica from hybrid HPA-7 (containing LiCl) had a pore radius of 1.9 nm (BJH method) and surface area of 15 m^2g^{-1} (BET method). The pore volume observed was 0.68 cm^3g^{-1} for the silica gels obtained from hybrids HPA-6, HPA-7, and HPA-9 (Table 3). The pore size distribution plots of these porous silica gel samples are illustrated in Figure 2.

Conclusions

Polyamide-silica gel hybrids were prepared by the hydrolysis and condensation of TMOS. Films could be cast in which the metal salts are highly dispersed from the solution of the polymer and TMOS. Porous silica gels could be obtained by the pyrolysis of the hybrids at 600°C. Adsorption-desorption studies on representative porous silica samples indicated a porous nature. Hybrids HPA-6 (containing no salt) and HPA-9 (containing $ZnCl_2$) gave silica with smaller pore sizes and larger surface areas, while hybrid HPA-7 (containing LiCl) gave silica with a larger pore size and a smaller surface area. Presence of LiCl in the hybrid seems to favor the formation of larger pores and smaller surface areas. It appears that pore size, surface area and pore volume could be controlled by a judicious choice of metal salts. Controlled pyrolysis of hybrids may result in porous silica gels with domains of polymers still embedded in the silica gel network. Such materials could have interesting properties for potential applications.

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