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# Organic Polymer-Silica Gel Hybrid: A Precursor of Highly Porous Silica Gel

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# ORGANIC POLYMER-SILICA GEL HYBRID: A PRECURSOR OF HIGHLY POROUS SILICA GEL

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## ABSTRACT

In this article I describe two of our discoveries. The first is the preparation of a transparent solid material composed of an organic polymer and silica gel. A novel material called a "hybrid" has successfully been prepared by the sol-gel reaction of ethyl orthosilicate in the presence of an organic polymer consisting of repeating units having an *N*-alkylamide group. The molecular-level dispersion of the organic polymer in the framework of silica gel has been established, which is due to the hydrogen-bond interaction between the organic polymer and silanol group of silica gel. The second discovery is the preparation of porous silica gel, which has been achieved by calcination of the organic polymer-silica gel hybrid at 600°C. Pore sizes ranging from 10 to 20 Å have been attained. A method of controlling pore size has been proposed.

## INTRODUCTION

With the aim of exploring the so-called "high performance" materials, a combination of organic polymers with inorganic materials has been examined. Addition of a filler of ultrafine particle such as silica gel, calcium carbonate, or carbon black to organic polymer has long been utilized to prepare composite materials of high strength. In these classic composite materials, each polymer and inorganic material constitutes an independent phase, in which interaction at the interface between two phases greatly affects the mechanical properties.

The present article reports our recent success in the preparation of two novel materials [1]. The first is a transparent material composed of organic polymer and silica gel, in which the former component is dispersed at molecular level in the framework of the latter. The term "hybrid" has been proposed to express these transparent solid materials. The second material is a novel porous silica gel having pore size of molecular level which has been prepared by calcination of hybrid.

## PREPARATION OF HYBRID

Silica gel may be regarded as a three-dimensional network consisting of $>\!\mathrm{Si{-}O{-}Si}\!<$ linkage, which cannot be dispersed at the molecular level. However, dispersion at the molecular level can be realized at the stage of the precursor, orthosilicate ester (tetraalkoxysilane), in the sol-gel procedure. (See Fig. 1.)

Ethyl orthosilicate and an organic polymer having a specific structure were dissolved together in ethanol. Then, a small amount of aq. HCl was added to the solution to catalyze the sol-gel reaction of orthosilicate, the hydrolysis being followed by condensation at room temperature. With organic polymers that are soluble in ethanol and characterized by a

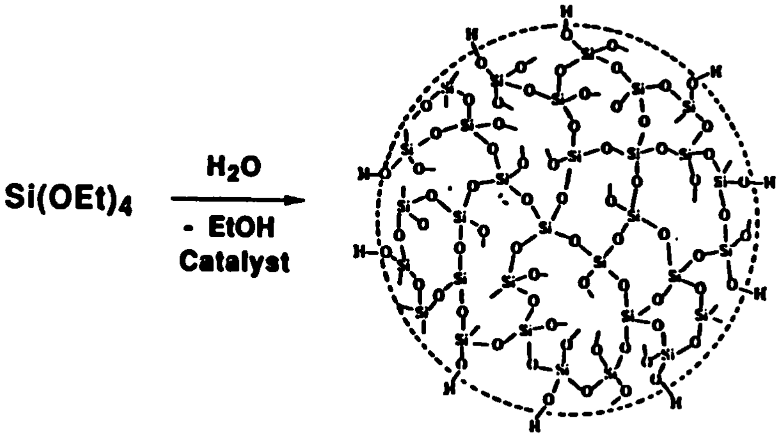
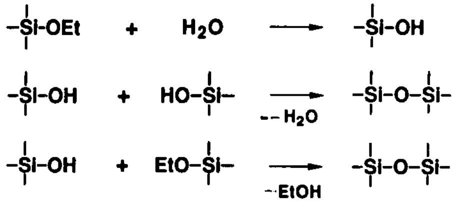


FIG. 1. Sol-gel procedure of $Si(OEt)_4$.

repeating unit structure containing *N*-alkyl carboxylamide, the reaction-mixture remained homogeneous throughout the sol-gel reaction. On evaporation of ethanol, a transparent solid material was produced [1].



$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OEt} + \mathrm{H_2O} \longrightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} \quad (1)$$

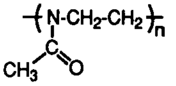
$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{HO}-\overset{|}{\underset{|}{\mathrm{Si}}}- \xrightarrow[-\mathrm{H_2O}]{} -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- \quad (2)$$

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{EtO}-\overset{|}{\underset{|}{\mathrm{Si}}}- \xrightarrow[-\mathrm{EtOH}]{} -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Si}}}- \quad (3)$$

These reactions are catalyzed by acid, e.g., HCl, or by base, e.g., $NH_4OH$. The key intermediate group is $\equiv$Si$-$OH (silanol group), which is mostly converted into $\equiv$Si$-$O$-$Si$\equiv$ linkage by condensations (Eqs. 2 and 3). Some of silanol groups remain after the completion of construction of the network frame, which constitute solid acid sites of the type of Brønsted (protonic) acid.

Usually an organic polymer present in the sol-gel reaction mixture is not incorporated in the framework of silica gel. Silica gel is formed separately. When the polymer molecule has a functional group of strong acceptor of hydrogen-bonding (electron donor), however, it is drawn into the growing framework of silica gel by the hydrogen-bonding interaction with the silanol group.

Polymers that function as a hybrid component in combination with silica gel are exemplified as follows.



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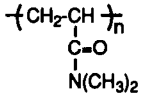

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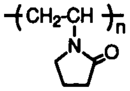

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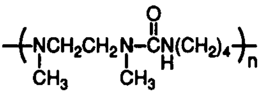

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1: Poly(2-methyl-2-oxazoline)(PMeOXZ) [poly(*N*-acetylethylenimine]
2: Poly(*N*,*N*-dimethylacrylamide)
3: Poly(*N*-vinylpyrrolidone)
4: Polyurea (*N*,*N*′-dimethylethylenediamine + tetramethylene diisocyanate)

All these polymers are combined with orthosilicate to form hybrids of a broad range of compositions up to 80 wt% of polymers. As discussed later, organic polymer is dispersed at molecular level in the framework of silica gel. An important element of homogeneous blending is the formation of hydrogen bonding, which has been supported by the shift of the infrared absorption band of the amide carbonyl group (Fig. 2). Figure 3 shows a schematic expression for the structure of a hybrid between PMeOXZ and silica gel.

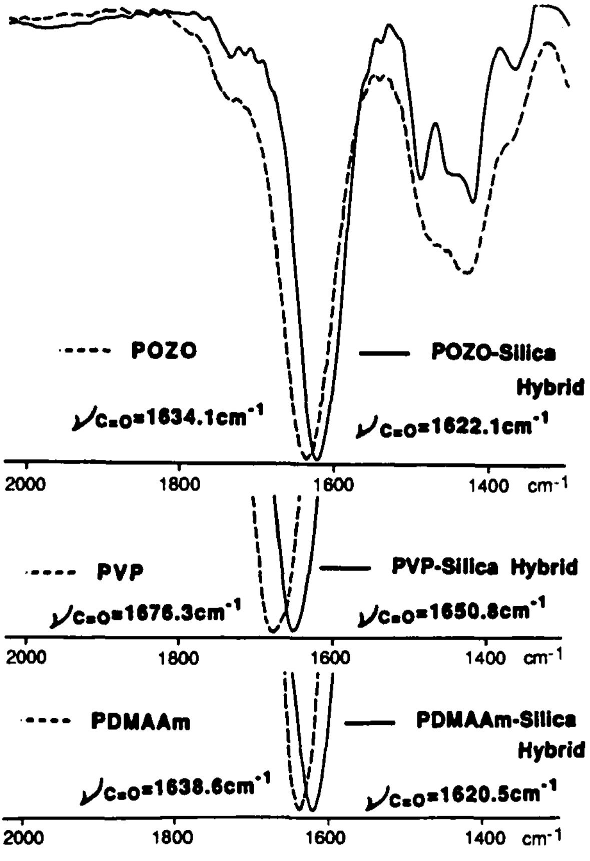


FIG. 2. FT-IR spectra of organic polymers and hybrids.

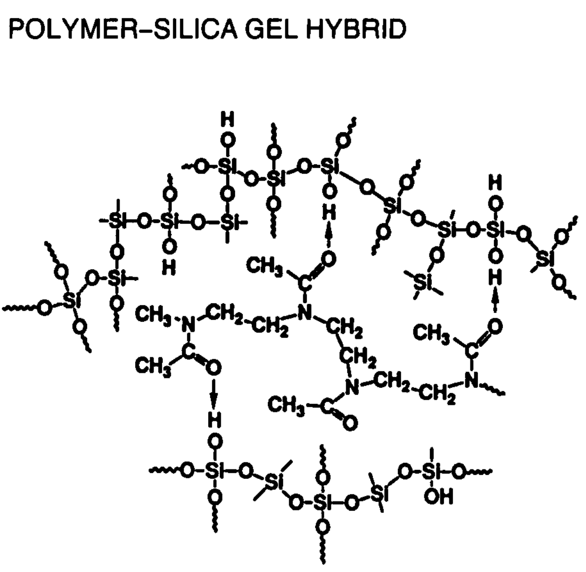
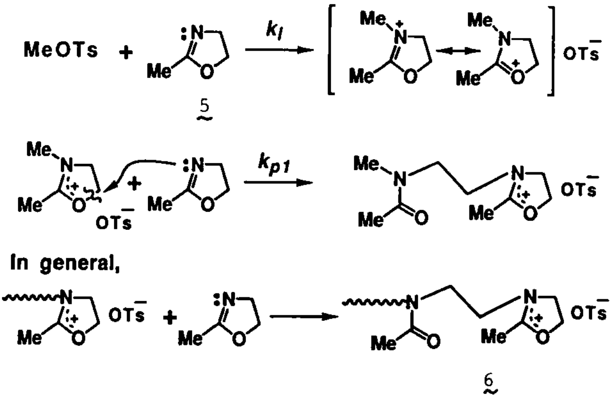


FIG. 3. Schematic expression of PMeOXZ-$SiO_2$ hybrid.

## POLY(2-METHYL-2-OXAZOLINE) (PMeOXZ) HAVING SILYL COUPLING TERMINAL GROUP

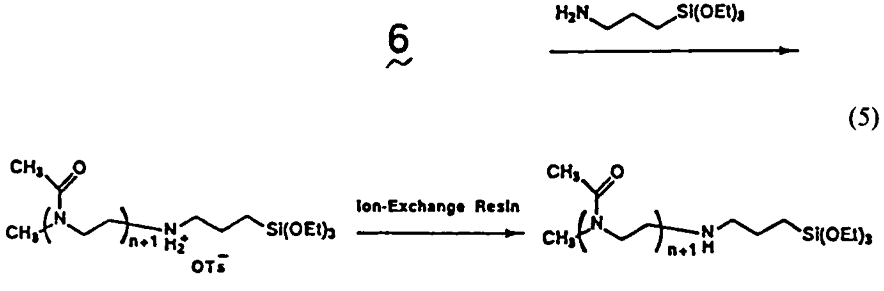
In the preceding section I described hydrids due to the interaction by hydrogen bonding between polymers and silica gel. PMeOXZ having a silane coupling terminal group has been prepared, which can be bonded to silica gel by covalent bond in addition to hydrogen bond [2–4].

Ring-opening polymerization of 2-methyl-2-oxazoline[MeOXZ] proceeds in a living mechanism under appropriate reaction conditions [5].

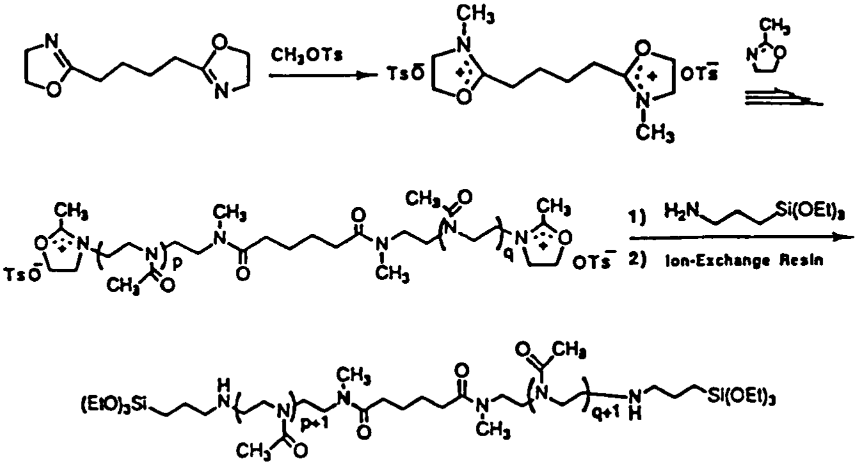


(4)

The oxazolinium growing end is capable of reacting with an amine-containing trialkoxysilyl group. The end-group reaction brings about the stoichiometric introduction of the silane-coupling group (Eq. 5). With an initiator of a bis-oxazolinium salt which is readily prepared *in situ* by the reaction between a bis-oxazoline and a stoichiometric amount of methyl tosylate, a two-directional propagation of MeOXZ can be made to produce PMeOXZ having silane coupling groups at two terminals of the molecule (Eq. 6).

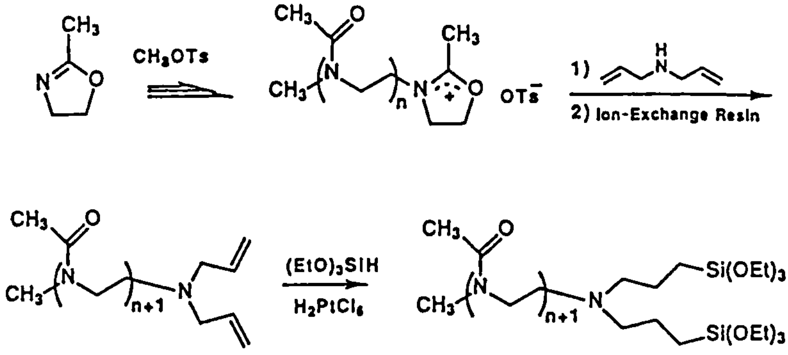


(5)

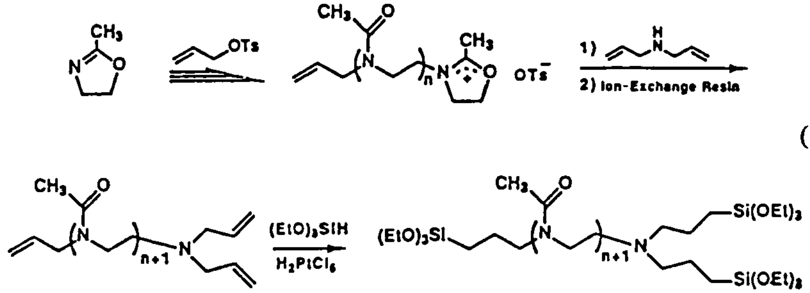


(6)

The silane-coupling group can be introduced also by the hydrosilation of a carbon-to-carbon double bond, which is introduced by means of an olefinic initiator and/or olefinic end-capping agent (terminator). Thus, allyl tosylate is conveniently used as an initiator for this purpose, whereas allylamine or diallylamine is conveniently employed as a terminator. With both olefinic initiator and olefinic terminator, PMeOXZ molecule having reactive groups at both terminals can be prepared. The following illustrates the procedures (Eqs. 7 and 8).



(7)

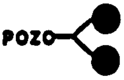
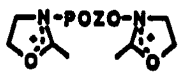
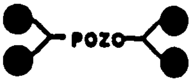


(8)

Table 1 summarizes the methods of introducing silane-coupling groups by the initiation and/or end-capping reactions. PMeOXZ molecules having one to four reactive end-groups can be prepared at will.

PMeOXZ having a silane-coupling group at the end(s) of the molecule was successfully subjected to the preparation of hybrids with silica gel. Transparent solid materials were obtained. A difference between hybrids with PMeOXZ having no reactive end-group and those with end-reactive PMeOXZ has been found in the extent of extraction with polar protic solvent [6]. In addition, covalent bonding at the end of the polymer molecule may have an effect on the mobility of polymer in the framework of silica gel. The effect of the end-group (bonded or unbonded) is an interesting subject for future study.

TABLE 1. Silane Coupling Agents of POZO

| | $HSi(OEt)_3$ | $H_2N(CH_2)_3Si(OEt)_3$ (A) |  and $HSi(OEt)_3$ |
|---|---|---|---|
|  | — |  |  |
|  |  | <br>(A) and $HSi(OEt)_3$<br> |  |
|  | — |  |  |

## POROUS SILICA GEL

An important and interesting characteristic of polymer hybrid with silica gel is the homogeneous dispersion of polymer at the molecular level in the framework of silica gel. At a higher temperature, e.g., 600°C, which is far below the fusion point of silica gel, organic polymer was decomposed to leave silica gel having pores of a size of molecular level. A schematic expression is given in Fig. 4.

Figure 5 illustrates a TGA curve (in air) of a hybrid of PMeOXZ with

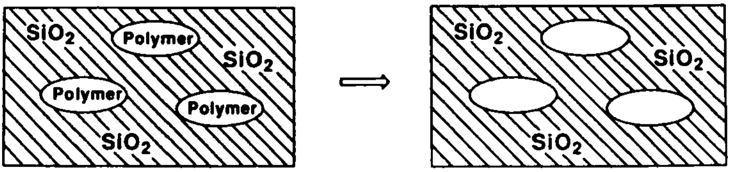


FIG. 4. Schematic expression of calcination of silica gel hybrid.

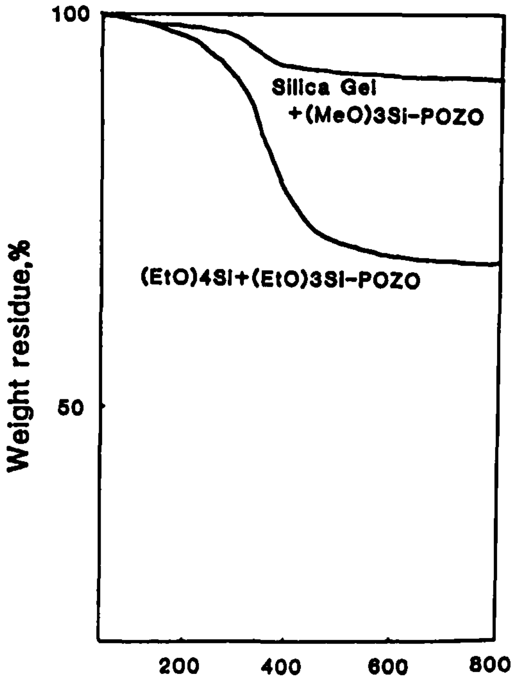


FIG. 5. TGA curve of PMeOXZ-SiO$_2$ hybrid.

TABLE 2. POZO Modified Silica Gel After Pyrolysis

| POZO (D.P.) | Feed ratio (POZO/TEOS) | Pore volume (cc/g) | Surface area (m$^2$/g) |
|---|---|---|---|
| 9 | 1/10 | 0.090 | 136 |
| 16 | 1/10 | 0.108 | 179 |
| 14 | 1/5 | 0.195 | 348 |
| 50 | 1/5 | 0.238 | 409 |
| 3 | 1/2 | 0.280 | 509 |
| 14 | 1/2 | 0.273 | 443 |
| 16 | 1/2 | 0.283 | 473 |
| 50 | 1/2 | 0.504 | 810 |
| 100 | 1/2 | 0.308 | 540 |
| – | 0 | 0.073 | 114 |

silica gel, which shows that a temperature of 600°C is high enough to decompose almost completely the component of organic polymer.

Table 2 shows the total pore volumes and total surface areas of the porous silica gel samples that were prepared by calcining various hybrid samples with various feed ratios (compositions) using one-end reactive PMeOXZ having various molecular weights. It is important to note that total surface area data as high as 810 $m^2/g$ have been recorded.

Figure 6 shows a linear plot of the total surface area vs. total pore volume. On the basis of an assumption of spherical shape of pores, the average value of the radii of pores has been calculated at 18.4 Å. It is of interest that the pore size is independent of the molecular weight of PMeOXZ, which is the polymer component of hybrid before calcination. In other words, the pore size cannot be controlled by the molecular weight of PMeOXZ in the mother hybrid. Probably the pore size corresponds to the size of coil consisting of a part of PMeOXZ molecule. The size of coil is controlled by the conformation of PMeOXZ molecule at the time of inclusion in the framework of silica gel. Elucidation of this problem is an interesting topic for future study.

An indication of the possibility of controlling the pore size has been obtained by a silica gel hybrid with a starburst dentrimer as the polymer

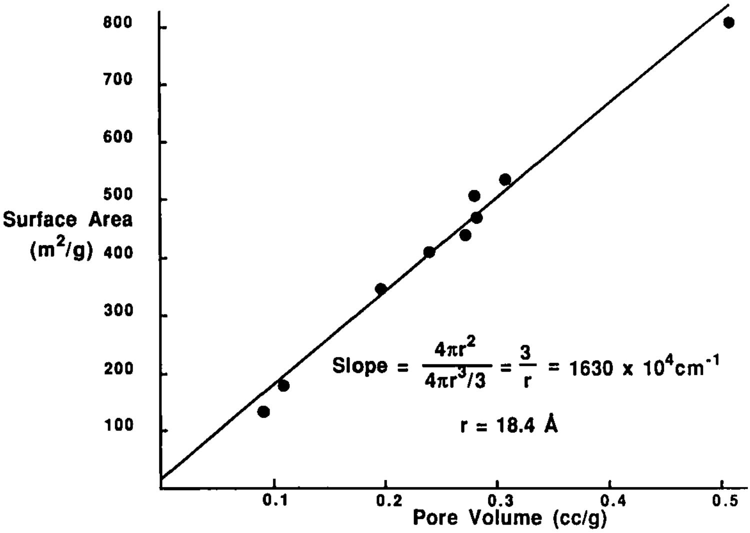


FIG. 6. Total surface area vs. total pore volume of porous $SiO_2$.

component. A special molecular shape has been established by Tomalia, the pioneer of starburst dentrimer [7]. In a series of our experiments, the dentrimers prepared with ammonia (core), methyl acrylate, and ethylenediamine have been found to give transparent hybrid with silica gel. It should be pointed out that these dentrimers contain *N*-alkyl amide group in the repeating units.

The size of the dentrimer is determined by the number of "generations." The radius of the dentrimer of 3.5 generations (Fig. 7) has been calculated by Tomalia at 12.9 Å, which was employed to prepare a hybrid. The peak of the pore-size distribution curve of porous silica gel after calcination is located at about 13 Å (Fig. 8). Change of the pore size has been found to follow that of the generation of the dentrimer in the mother hybrid.

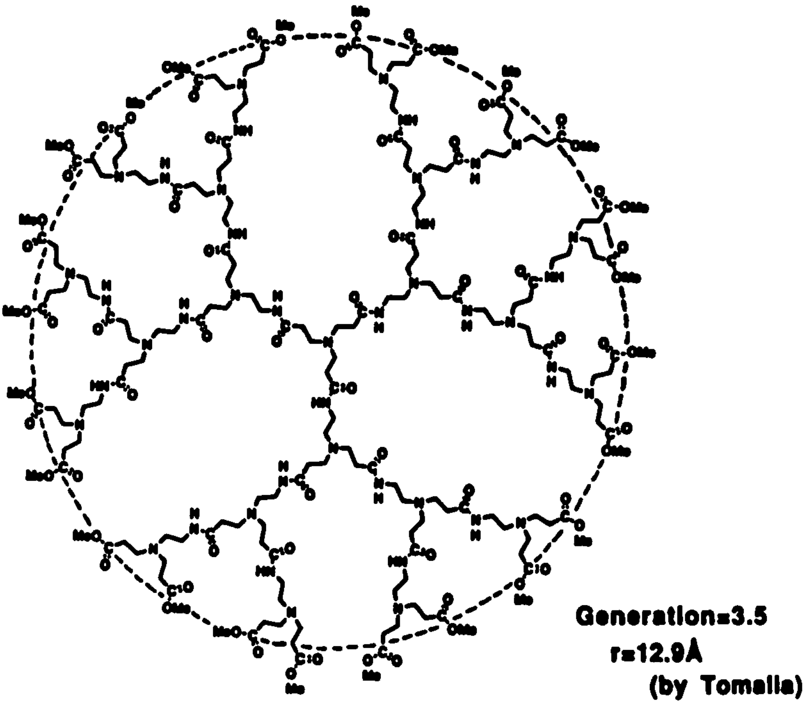


FIG. 7. Schematic expression of a starburst dentrimer of 3.5 generations.

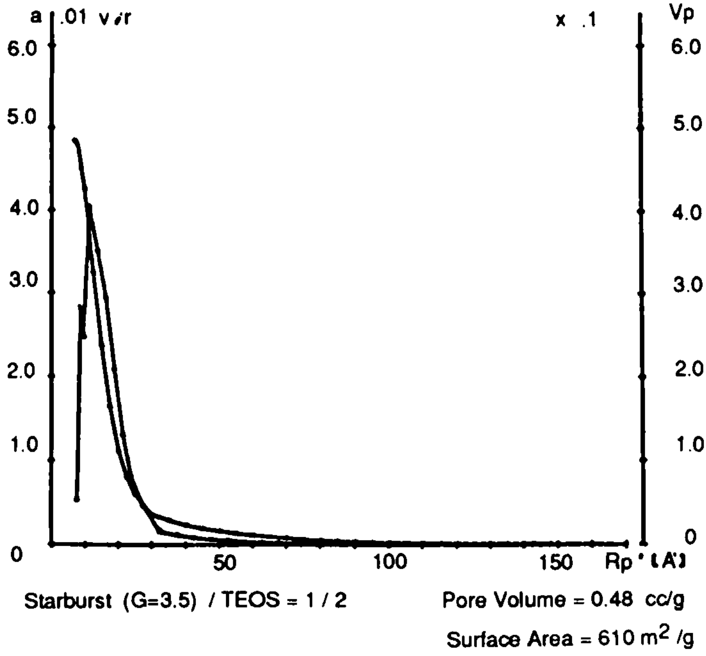


FIG. 8. Starburst (G = 3.5)/Si(OEt)$_4$ = 1/2. Total pore volume: 0.48 cc/g. Total surface area: 610 m$^2$/g.

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