

# Postgrafting of Congo Red Dye onto Hyperbranched Mesoporous Silica with Terminal Amino Groups

Turgay Seçkin,<sup>1</sup> Ahmet Gültek<sup>2</sup>

<sup>1</sup>Inonu University, Faculty of Science and Literature Chemistry Department, Malatya 44069, Turkey

<sup>2</sup>Inonu University, Adiyaman Faculty of Science and Literature, Chemistry Department, Malatya 44069, Turkey

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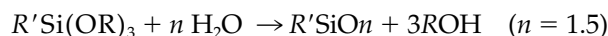
**ABSTRACT:** Congo red dye has been postgrafted onto mesoporous silica that was prepared by the controlled hydrolysis of tetraethyl orthosilicate in the presence of organic agents. Surface grafting of mesoporous silica having amino groups as initiator sites was prepared from  $\gamma$ -aminopropyltrimethoxysilane by sol-gel process. The postgrafting reaction of Congo red onto silica with terminal amino groups was achieved by a repeated step of the addition of methyl acrylate to amine groups followed by the amidation of the resulting ester moieties with ethylene diamine. Postgrafting efficiency of all materials has been outlined. Because postgrafting efficiency values have been found to be smaller than

theoretical values, it is concluded that the resulting product was more likely to be a hyperbranched polymer rather than a true dendrimer at higher generations. The postgrafted structures with amino-terminal groups provide an attractive site for binding Congo red dye that not only persists in its characteristic properties, but also has exceptional hybrid properties possessed by mesoporous silica. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 3905–3911, 2003

**Key words:** pigments; nanocomposites; hyperbranched; silicas

## INTRODUCTION

Aminotrialkoxysilane has great importance in industry not only as coupling agent for much application, but also for novel material synthesis. This compound has been extensively used to modify surfaces as copolymers to synthesize new materials as outlined in the literature.<sup>1</sup> On the same horizon, these materials are seen as the starting materials for a new way of preparing hybrid compounds with application in sensors and electronics. To understand the phenomenon that lies behind this, sol-gel chemistry must be established. Ishida et al.<sup>2</sup> have dealt with aminopropyltriethoxysilanes in aqueous environments, and its polycondensation. The sol-gel reaction of organotrialkoxysilanes is represented by the equation



where  $R$  is the methyl or ethyl group and  $R'$  is an amino-modified organic group. Because of its basicity, and nucleophilicity of the amino group, organosilane compounds are attractive as coupling agents for sol-

gel chemistry. However, the amino group may can act as a basic catalysis for the sol-gel polymerization of alkoxy silanes and may perturb the sol-gel process; therefore, necessary precaution must be taken before proceeding.

The amine groups may undergo a Michael-type addition of the preexisting acrylate group to form aminopropionate ester. Subsequent amidation of the ester moieties with ethylenediamine completes the reaction. As described by Tomolia and coworkers,<sup>3</sup> repetition of these two reactions produces the desired generation of the dendrimers. Polyamidoamine dendrimers, constructed on the surface of silica with rhodium complex, were prepared and tested for hydroformylation reactions.<sup>4</sup> Tsubokawa and coworkers<sup>5</sup> explored the grafting of polyamidoamine dendrimers onto silica core; they concluded that the resulting material is likely to be a highly branched polymer rather than a true dendrimer, especially at higher generations.

The highly branched nature of dendrimers offers many interesting characteristics and applications including multiple sites, not only for metal coordination, but also for the preparation of novel materials.

On the other hand, azobenzenes, well-known photosensitive chromophores, have attracted interest because of their potential uses in photonic applications. The constant interest in azo-group chemistry is well documented in numerous publications.<sup>6</sup> The combination of several well-known classes of azo compounds in organic chemistry with polymer science has led to a great variety of new functional polymers with inter-

Correspondence to: T. Seçkin (tseckin@inonu.edu.tr).

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esting applications in high technology.<sup>7</sup> Recent developments in the low-temperature sol-gel process of oxide glass preparations<sup>8</sup> opened up the possibility of using these materials instead of organic carriers.

These properties of azo dye and hyperbranched mesoporous silica prepared by the sol-gel process prompted us to combine both properties in a material that may possess both properties of the azo dye and the inorganic network.

The present study reports the results of the studies on grafting of Congo red dye on highly branched sol-gel-derived silicate particles, which were first modified with  $\gamma$ -aminopropyltrimethoxysilane. Physicochemical and grafting properties of the modified sol-gel-derived silicates and postgrafted silicates were estimated. A structural elucidation of materials was carried out by conventional instrumental techniques.

## EXPERIMENTAL

### Starting materials

The following reagents were purchased from Fluka:  $\gamma$ -aminopropyltrimethoxysilane, methyl acrylate, ethylenediamine, sulfonic acid, tetraethoxy silane (TEOS), ethylene glycol, Congo red dye, and anhydrous methanol. Purity was checked with NMR and monomers were used as received. Ultrapure water filtering system was used to produce deionized water, and ethanol (Merck) was dried over calcium hydride.

### Characterization

The grafting efficiency of Congo red on the silica-gel particles was calculated from the thermal gravimetric analysis (TGA), and thermal behavior was carried out on a Shimadzu System 50 DTA and TGA, respectively. The absorption spectra were measured on a Shimadzu UV 265 spectrometer, and FTIR analysis was performed on a Matsson 1100 FTIR mode spectrometer.

### Procedures and methods

#### Amorphous mesoporous silicate synthesis

TEOS (13,86 g) was dissolved in 8 g ethanol and 8.26 g ethylene glycol with stirring at 80°C in an oil bath. After 1 h of stirring, a mixture of 24 g ethanol, 6 g water, and a catalytic amount of acetic acid was added to the system. After 3 h of reaction under the same conditions, a clear, transparent gel was obtained. The resulting gel was aged at ambient conditions for 2 days, dried in a vacuum oven at 110°C, and calcined at 500°C for 12 h in a flow of O<sub>2</sub>. Surface area of the powder, BET (m<sup>2</sup>/g), was measured to be 317 ± 4 to 550 ± 3 m<sup>2</sup> g<sup>-1</sup> with a pore volume of 0.37 ± 0.02 to 0.55 ± 0.03 mL g<sup>-1</sup>.

#### Preparation of $\gamma$ -aminopropyltriethoxysilane (aps) modified mesoporous silicate

To enhance the number of silanol (SiOH) groups that can be used to attach APS to the surface, etching of the above particles (grain size of 2–20  $\mu$ m) with CH<sub>3</sub>SO<sub>3</sub>H was performed<sup>9</sup> as given in the literature.

Grafting was carried out under nitrogen atmosphere with different amounts of APS, and the silica particles. Each time, the reaction mixture was loaded with 35 g of silica in 100 mL toluene and APS in a 3 : 10 methanol/water ratio; APS was added dropwise to avoid gel formation. The resulting solutions were heated under reflux and stirred for 24 h. The modified particles were then poured off and extracted with methanol in a Soxhlet apparatus for 12 h. Finally, the dried particles were dried under reduced pressure at 120°C for 24 h. The grafting efficiency of APS on silica was optimized as a function of APS concentration, reaction time, and temperature, respectively.

#### Procedure for the preparation of first-generation mesoporous silicate

Aminopropyl silica (0.45 mmol NH<sub>2</sub>, 20.0 g) and methylacrylate (0.18 mol, 15.65 g) were stirred at 50°C under nitrogen for 3 days in methanol (100 mL). The suspension was filtered and washed with methanol (3 × 30 mL). The remaining solvent was removed in high vacuum affording methylpropylaminopropionate silica. To this was added 100 mL ethylene diamine in 100 mL methanol, and it was stirred at room temperature under nitrogen for 1 week. The resulting first-generation material was isolated by filtration and washed with methanol and dichloromethane (3 × 30 mL). The residual solvent was removed in vacuum (88% yield).

The second generation can be prepared by following the above procedure starting with first-generation material (0.61 mmol of NH<sub>2</sub> groups, 20 g) and methyl acrylate, 1.52 mol, and by changing the reaction time to 5 days. After isolation, the ester was added to ethylenediamine (200 mL) in methanol (100 mL) and stirred at room temperature for 1 week (90% yield).

The third (75% overall yield) and the fourth (75% overall yield) generations were prepared in the same manner.

#### Procedure for postgrafting of Congo red on hyperbranched mesoporous silicate

The APS-modified hyperbranched particles (5 g) were dispersed in 50 mL of solvent DMF; then 0.05–0.10 g Congo red was added to the mixture under different pH conditions (adjusted by adding CH<sub>3</sub>SO<sub>3</sub>H). The mixture was heated at 95°C with vigorous stirring for 20 h. The solid particles were collected by filtration and extracted with methanol and dichloromethane in a Soxhlet apparatus for 24 h to remove unreacted dye

molecules that were physically adsorbed. The samples were then dried in a vacuum at 110°C for 2 h.

#### Procedure for the determination of grafting efficiency

The content of amino groups of the dendritic polyamidoamine-postgrafted silica was determined by consumption of HCl aqueous solutions. In a typical procedure, into a 100-mL flask, 0.10 g polyamidoamine-postgrafted silica and 20 mL of 0.01 mol/L HCl aqueous solution were charged, and the mixture was stirred at room temperature for 2 h and filtrated. Then the filtrate was back titrated with NaOH(aq) by using an indicator. Then the amount of terminal amino groups per 1.0 g ethylenediamine-grafted silica was calculated.

## RESULTS AND DISCUSSION

Silica surfaces are known to exist in a variety of forms that differ both physically and chemically from each other.<sup>10</sup> They can be crystalline, as in crystalline quartz, or amorphous, as in fused silica. They can be hydrophobic, as occurs when the surface chemical groups are mainly siloxane Si—O—Si groups, or hydrophilic, when the surfaces expose silanol Si—OH groups. Hydrophobic silica can be rendered hydrophilic by hydroxylating the siloxane groups into silanol groups. When silica groups are exposed to water for an extended time, their hydroxylation can continue. This produces polymeric chains of Si(OH)<sub>2</sub>—O—Si(OH)<sub>2</sub>—OH groups, which can link up in many different ways to form a three-dimensional network or silica gel.

The chemistry and chemical reactions of silica surfaces in aqueous solutions are generally considered within the above framework. Therefore, mesoporous silica samples were prepared in the presence of alcohols resulting in completely amorphous silica xerogels where polymeric chains formed a three-dimensional network with hydroxyl groups present at the surface.

Porous silica with high surface area was prepared by calcinations of silica/ethylene glycol hybrid network materials. The surface area analysis showed that for all cases, moderate surface areas in the range of 317–550 m<sup>2</sup> g<sup>-1</sup> can be obtained with an optimum ethylene glycol to TEOS weight ratio of 30/50. The pore-size analysis indicated that, for samples with high surface areas, the pores are mesoporous, and for samples with lower surface areas, the pores are microporous.

The introduction of terminal amino groups to silica and the initiator site for postgrafting of Congo red was achieved by the reaction of aminopropyltrimethoxysilane and the molecular architecture of dendron block includes amidoamine (Scheme 1). The synthesis of dendron block onto silica core consists of two steps

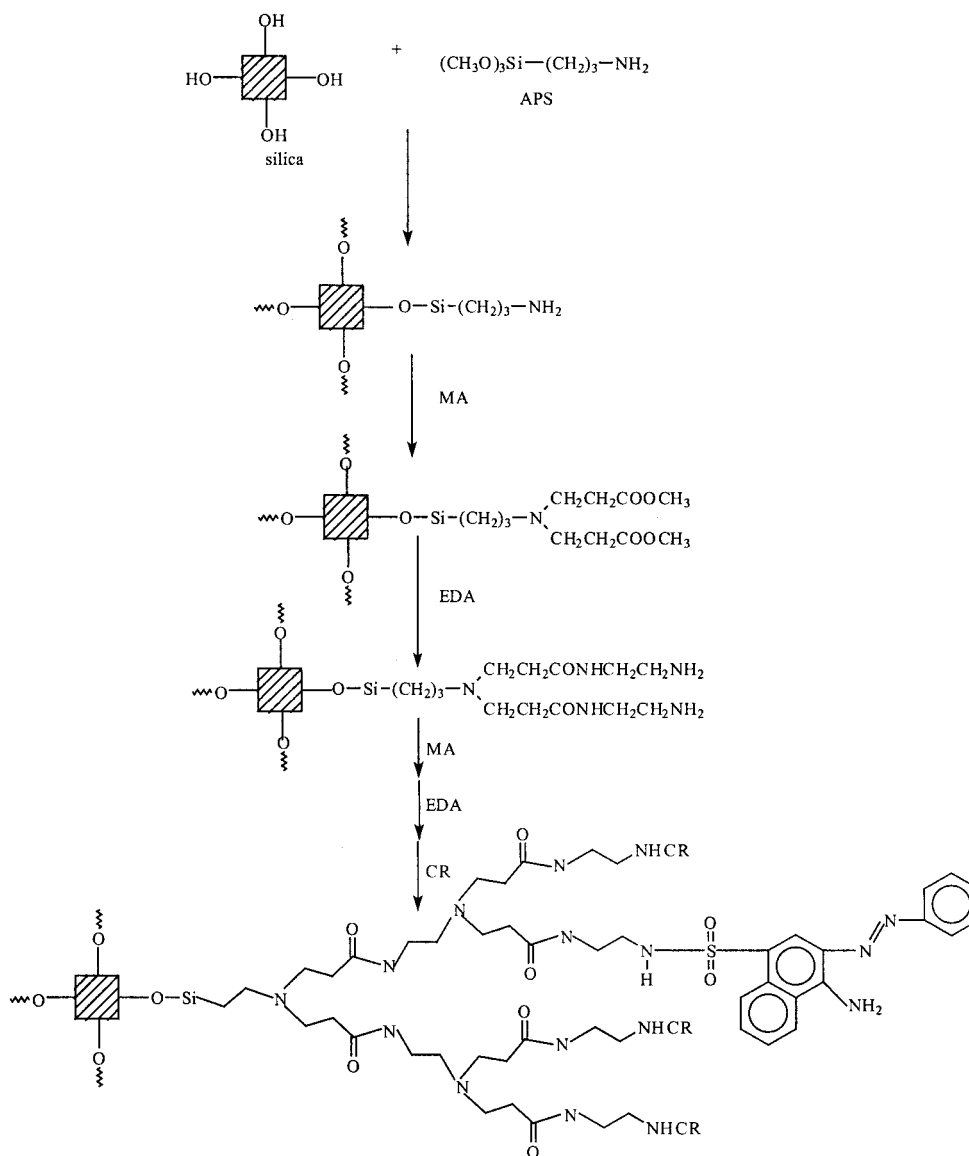
alternately repeated to achieve higher generations and follows the divergent synthesis technique. In the first step, exhaustive Michael addition of methylacrylate to the primary amine terminal groups of the silica core results in tertiary amine branch point with methyl ester terminal groups. The methyl ester terminal group is reacted in the second step with ethylenediamine to regenerate the primary amine terminal groups. By using this scheme, four series of amidoamine as end group on silica were synthesized and postgrafted with Congo red.

The grafting of  $\gamma$ -aminopropyltrimethoxysilane on silica network was investigated by FTIR, TGA, and elemental analysis. In Figure 1, FTIR spectra of starting materials were given for comparison purposes, and in Figure 2, the FTIR spectra of APS-modified silica, 0.5 generation with methylacrylate, generation 1–2, and the Congo red postgrafted onto the second generation silicas were given. APS-grafted silica apart from the characteristic vibration bands for silica, the CH<sub>2</sub> absorption bands at 2955 cm<sup>-1</sup> (asymmetric stretching), and 2880 cm<sup>-1</sup> (symmetric stretching), and 1640 cm<sup>-1</sup> (amino group), can be clearly observed, which are also present as the strongest peaks in FTIR spectrum of APS. This suggests that APS was successfully grafted onto the silica surface. It has found that the silanol groups, SiOH, on the silica surface, which are the reactive site for silylation reaction, play an important role in the surface modification process. The tentative assignments for the spectra of silica were as follows: 1174 cm<sup>-1</sup>  $\nu_{as}$ (Si—O—Si), 1060 cm<sup>-1</sup>  $\nu$ (Si—O—), 938, 785 cm<sup>-1</sup>  $\nu'_s$  (Si—O—Si), 620, 550 cm<sup>-1</sup>  $\nu_s$ (Si—O—Si). Polysiloxanes made up T units, [RSiO<sub>1.5</sub>]<sub>x</sub>, and show a broad, structureless absorption covering the entire region of 1160–1000 cm<sup>-1</sup>.

TGA analysis showed 3.4% weight loss for silica etched with CH<sub>3</sub>SO<sub>3</sub>H and 16.1% for APS-modified silica. This was considered to be APS grafted on silica surface as shown in Scheme 1. Three types of interactions between aminosilane molecule and silica surface might take place as shown in Scheme 2. Due to these types of interactions that might take place in every experimental condition, grafting efficiency was found to be smaller than the theoretical values.

The DTA analysis was performed on APS-modified silica, Congo red, 0.5–2.0 g hybrids, and the Congo red postgrafted silica. The respective DTA curves are shown in Figure 3. In the case of the modified silica [Fig. 3(a)], exothermic effects have been disclosed with maximum at around 300 and 375°C. The diffuse peak corresponds to silane decomposition at the surface. No such effects have been noted for unmodified silica. Moreover, a slight exotherm at 550°C has been observed because of decomposition of the adsorbed silane.

DTA analysis of the hybrid materials from generation 0.5–2 g and the postgrafted Congo red showed



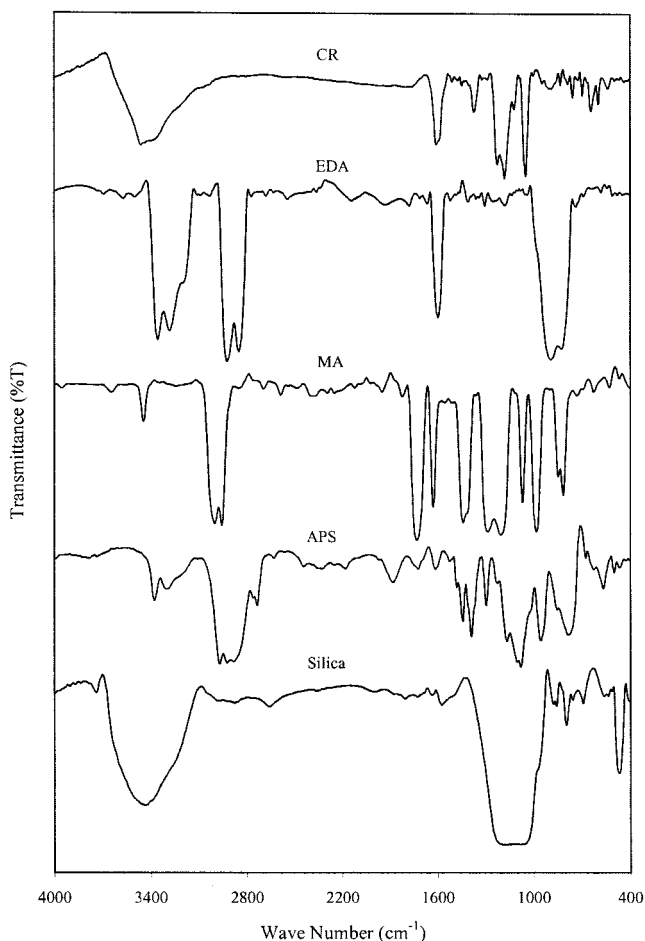
**Scheme 1** Sketching illustration of dendritic Congo red postgrafted silica.

that an exotherm that appeared at around 300°C was broadened, and a slight exotherm appeared at around 575°C. These results are in accord with the theory as expected. Silane decomposition at the surface rationalized in terms of the increase in organic moieties in higher generations was increased.

All evidence from FTIR, TGA, DTA, and elemental analysis supported the successful grafting of APS on the surface of silica. The grafting efficiency of APS on silica was studied as a function of reaction temperature, which was changed from room temperature to the boiling point of the solvent. The results showed that the grafting efficiency was improved by raising the temperature. The grafting efficiency of APS as a function of reaction time was also studied from 4 to 24 h. It was found that the reaction time between 18 and 24 h was necessary for optimal

grafting. The effect of APS concentration on grafting efficiency was revealed depending upon the amount of silanol (SiOH) groups present on the silica surface that is less than 0.034 mol/g; the theoretical amount of APS for 1 g of silica is  $0.034/3 = 0.011$  mol. This evidence was supported by TGA analysis, from 0.01 to 1 mol ratio: the grafting efficiency was increased from 9.2 to 12.7% and then remained constant with further increase in APS concentration, so the optimum APS concentration was found to be 0.025 mol/g silane.

A monomolecular layer of silane on every particle is necessary in theory for optimum adhesion promotion. If the surface area of the filler and the specific wetting area of the silane is known, the quantity of the silane required for a monomolecular coating can be calculated from the formula



**Figure 1** FTIR spectra of silica,  $\gamma$ -aminopropyltrimethoxy silane (APS), methylacrylate (MA), ethylenediamine (EDA), and Congo red (CR).

$$gS = \left( \frac{gFxsF}{sW} \right)$$

where  $gS$  is silane;  $gF$  is filler;  $sF$  is the specific surface area of the filler in  $m^2/g$ ; and  $sW$  is the specific wetting area of the silane in  $m^2/g$ . The required quantity of the silane was found to be 4.49 g ( $gF = 5$  g;  $sF = 317$   $m^2/g$ ;  $sW = 353$   $m^2/g$ ).

It was found in practice, however, that the use of the calculated amount of silane did not necessarily achieve optimum improvement of adhesion. The distribution of the silane over the whole surface of the filler (Scheme 2) was dependent on the activity of the surface and the pretreatment method used.

Finally, the maximum grafting efficiency was obtained at 80°C, with 0.052 mol APS to silica ratio, and 24 h of reaction time.

It is expected that hyperbranched amidoamine up to fourth generation would be constructed on the surface of the silica surface with aminopropyl groups 2.20 mmol/g protruding from the surface. We conclude

that the resulting product after the fourth generation was likely to be hyperbranched polymer rather than a true dendrimer, as shown in Scheme 2.

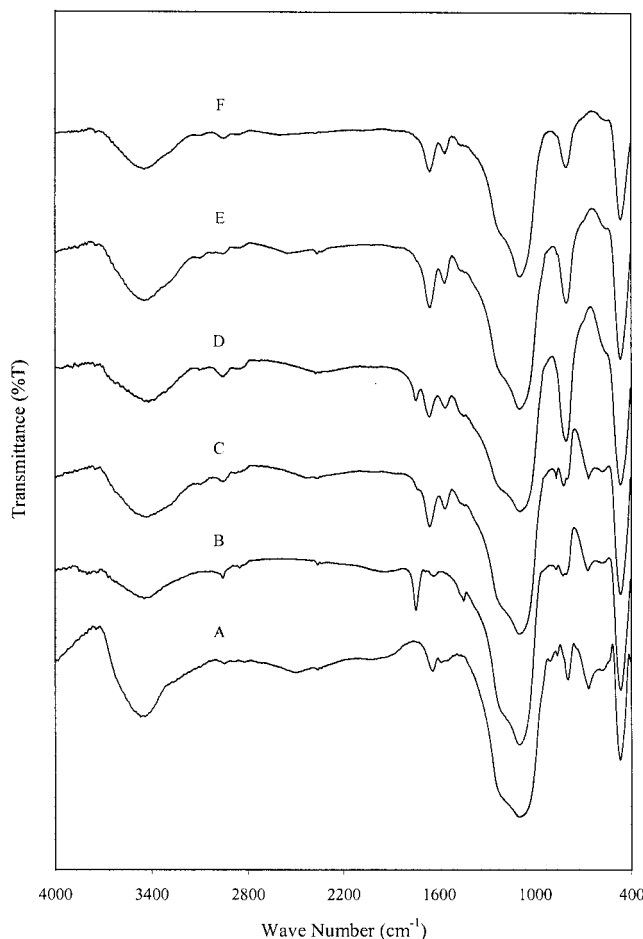
The grafting efficiency was calculated as

$$\text{Amino groups (mmol/g)} = \frac{[\text{HCl}(\text{mmol})/0.10]}{\{1 + (\text{PG}(\%)/100)\}}$$

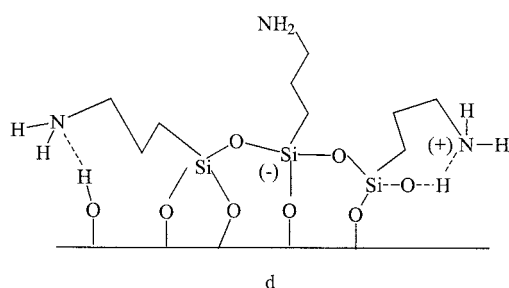
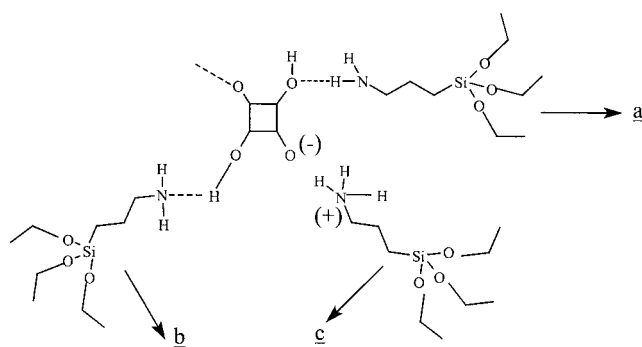
where HCl (mmol) is the number of moles of HCl consumed for the reaction with ethylenediamine-post-grafted silica, and PG(%) is the percentage of post-grafting value of aminopropyltrimethoxy silane groups observed;

$$\text{Grafting (\%)} = \frac{[\text{H}_2\text{N-terminated silica}(\text{g})]}{\text{Silica charged}(\text{g})} \times 100$$

The content of amino groups of the dendritic amine postgrafted silica was determined by weight loss when postgrafted silica was heated at 500°C by use of thermal analyzer;



**Figure 2** FTIR spectra of APS-modified silica (A), 0.5 generation with MA (B), first generation (C), 1.5G (D), second generation (E), and Congo red postgrafted silica (F).



**Scheme 2** Three types of interactions (a) between aminosilane molecule and silica surface; (b) hydrogen bonds; (c) proton transfer; (d) groups of silica surface following modification with  $\gamma$ -aminopropyltrimethoxysilane.

**TABLE I**  
The Grafting Efficiency and the Amount of Amino Groups of Silica, and Dendritic Blocks Prepared by Divergent Synthesis

Amino groups (mmol/g) <sup>a</sup>	Generation	Postgrafting <sup>b</sup> (%)	Overall grafting (%)
0.45	0	—	12.7
0.61	1	1.5	14.0
0.89	2	4.2	20.1
1.53	3	9.5	22.7
2.20	4	11.7	24.1

<sup>a</sup> Observed.

<sup>b</sup> Determined by TGA at 500°C.

Postgrafting (%)

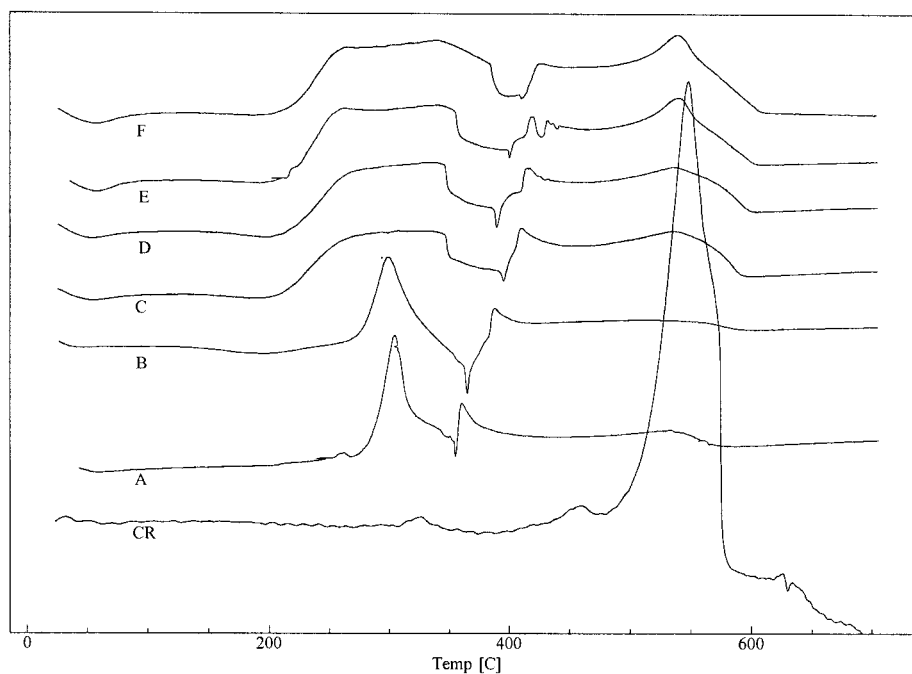
$$= \frac{[\text{Ethylenediamine postgrafted (g)}]}{(\text{H}_2\text{N-terminated silica (g)})} \times 100$$

Overall grafting (%)

$$= \frac{[\text{Total polymer grafted (g)/Silica (g)}]}{\times 100}$$

The amount of amidoamine postgrafted and total polymer grafted onto the silica was determined by TGA as mentioned above. Table I shows the amino group content of silica after APS grafting and after the postgrafting reaction of hyperbranched amidoamine silicas.

By using DMF and  $\text{Et}_3\text{N}$  as catalysts, we investigated the Congo red grafting efficiency on all generations



**Figure 3** DTA (10°C/min in  $\text{O}_2$  atm.) of Congo red (CR), APS-modified silica (A), 0.5 generation with MA (B), first generation (C), 1.5G (D), second generation (E), and Congo red postgrafted silica (F).

(Table II). TGA showed that the grafting efficiency of Congo red decreases significantly beyond second generation, arising from the steric crowding. Therefore, optimum conditions for attaching Congo red to hyperbranched silicas as a function of dye concentration, and pH were studied by using the second-generation hyperbranched silica.

The APS-modified silica and hyperbranched silica with amino end groups were white in color, but Congo red modified hyperbranched silica was red in color, which was not possible by removal by Soxhlet extraction. This suggests that Congo red was bonded. TGA data indicated that Congo red modified hyperbranched silica lost more weight than APS-modified silica. The grafting efficiency of Congo red was increased by increasing its concentrations. This was corroborated by the UV-visible absorption spectra (Fig. 4). The intensity of the absorption band of Congo red in the matrix at  $\lambda_{\text{max}} = 510$  nm increases about threefold in the investigated temperature range. The increase in absorption intensity is accompanied by a bathochromic shift of the  $\lambda_{\text{max}} = 537$  nm to  $\lambda_{\text{max}} = 550$  nm.

### CONCLUSION

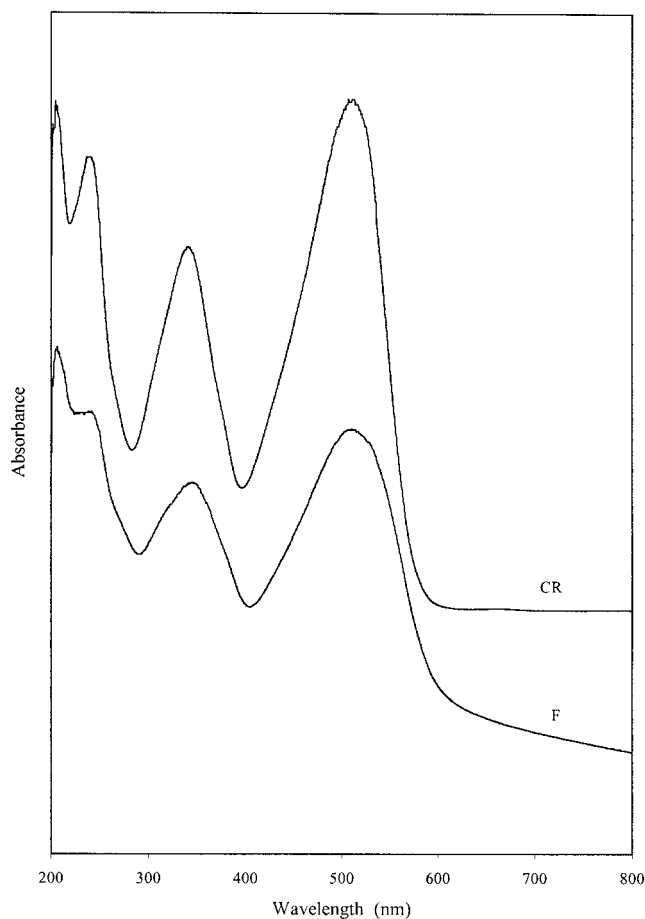
The postgrafting reaction of Congo red onto amidoamine-functionalized dendritic blocks was achieved from the terminal amino groups. Divergent synthesis was applied for the dendritic block preparations. The grafting efficiency and overall grafting efficiency were observed by TGA. These results indicate that the resulting hybrid materials are hyperbranched dendritic block rather than a true dendrimer because the observed grafting efficiency was much smaller than the calculated values. The postgrafting efficiency of Congo red dye was smaller in higher generations because of steric crowding; however, novel hybrid pigments obtained with second-generation dendritic blocks showed exceptional thermal stability and UV stability, as shown in the figures. The detailed investigation of the UV effect onto hybrid pigments and overcoming steric hindrance via long-chain diamine were still a concern in our laboratory.

**TABLE II**  
The Postgrafting and Overall Grafting Efficiency of Congo Red Dye

Amino groups (mmol/g) <sup>a</sup>	Generation	Postgrafting <sup>b</sup> (%)	Overall grafting (%)
0.45	0	0.4	11.5
0.61	1	1.6	14.0
0.89	2	2.92	26.1
1.53	3	0.8	21.7
2.20	4	0.5	19.1

<sup>a</sup> Observed.

<sup>b</sup> Determined by TGA at 500°C.



**Figure 4** UV absorption spectra of Congo red and Congo red postgrafted silica (F) in ethylene glycol at 25°C.

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