

Grafting of Selected Presynthesized Macromonomers onto Various Dispersions of Silica Particles

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Received 24 July 2001; accepted 28 September 2001

ABSTRACT: A new process was developed which enables one to obtain surface-modified silica with a high heavy metal ion complexing ability. The synthetic approach is based on grafting of vinyl-terminated macromonomers onto silica via covalent bonding. A proper selection of the macromonomer structure, molecular weight, and molecular weight distribution allows materials to be obtained with a range of desirable properties. The process has been tested on various dispersions (ranging from 35 and 200 μm) of silica particles and two structurally related macromonomers. Native silica and the resulting mixed organic-inorganic products were fully characterized by IR spectroscopy, SEM, yield of grafting (elemental analysis and calcination), density (helium pycnometry), specific surface area (BET method), and pore size (gas adsorption and mercury porosimetry) measurements. It was found that the corresponding polymers are effectively grafted onto the surface; the density, surface area, and pore size of the silica particles decrease with polymer grafting. Preliminary results on metal-ion uptake indicate that polymer-grafted silica exhibits an excellent complexing ability. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 1287–1296, 2002

Key words: macromonomers; silicas; modification; surfaces; metal-polymer complexes

INTRODUCTION

The importance of silica particles has been recognized for a variety of applications ranging from chemical processes to environment science, mineral recovery, and pharmaceuticals. In this connection, composites of organic polymers and different types of silica, including porous silica and nonporous glass beads, have recently received

considerable interest and have been extensively studied to obtain desired surface properties.

The linking of polymers onto an inorganic surface can be carried out via different strategies. For instance, cationic, anionic, and radical graft polymerization of various vinyl monomers onto inorganic particles can be initiated by introducing suitable groups on the surface,^{1–4} but grafting of reactive polymers has been also reported.^{5,6} In the present article, grafting of vinyl-terminated polyamidoamines onto preaminated silica gel is described to obtain new modified silicas having improved specific properties, in particular, heavy metal ion complexing ability.

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Contract grant sponsor: Brescia University.

Journal of Applied Polymer Science, Vol. 85, 1287–1296 (2002)
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Polyamidoamines (PAAs) are synthetic water-soluble polymers, characterized by the presence of amido and tertiary amino groups regularly arranged along their macromolecular chain. They are obtained, in a linear form, by stepwise polyaddition of primary monoamines or bis-secondary amines, to bisacrylamides.

PAAs carrying additional functions (carboxyl, hydroxyl, and amine) as side substituents can be easily obtained, starting from the appropriate monomers. These polymers have been extensively studied because the versatility of their chemical structures allows a variety of applications ranging from metal-ion complexation^{7,8} to drug delivery.⁹

The weak point of the PAA-based crosslinked resins for industrial applications lies in their rather poor mechanical properties. Organic-inorganic conjugates, in which PAAs are grafted onto silica, have a potential interest because they may combine the properties of multifunctional polymers with the superior mechanical stability and morphology control of inorganic substrates.

The possibility of grafting PAAs by *in situ* polymerization, that is, simultaneous grafting and growing polymer chains onto a silica surface, has already been reported¹⁰ by some of us together with some preliminary data concerning the ion complexing ability of PAAs making them potential absorbers of heavy metal ions such as Cu²⁺ and Co²⁺. We report herein a new synthetic approach which enables the grafting of selected pre-synthesized macromonomers onto various dispersions of silica gel, thereby clearly improving the heavy metal ion complexing ability of the resulting mixed organic-inorganic products up to about one metal ion per grafted polymer repeating unit.

EXPERIMENTAL

Materials

All starting reagents were purchased from Fluka Chemie (Buchs, Switzerland) and used without

further purification, with the exception of 2,2-bis(acrylamido)acetic acid, which was synthesized as described below.

Instruments and Methods

IR spectra were obtained by diffuse reflectance of silica powders (2% in KBr) with a Jasco 5300 FTIR spectrophotometer; SEM analyses were obtained with a Stereo Scan 260 by Cambridge; densities were determined by gas (helium) pycnometry, utilizing an Accupyc 1330 apparatus from Micromeritics.

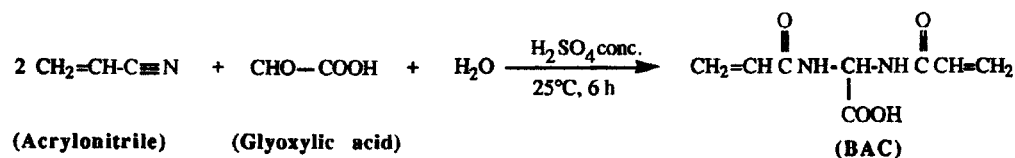
Surface area measurements were performed by gas adsorption in an ASAP (Accelerated Surface Area and Porosimetry) 2000 from Micromeritics, using nitrogen as the adsorptive gas. A micromeritics Poresizer 9320 Mercury porosimeter was utilized for the mercury intrusion/extrusion experiments to access the porosity of the samples.

Chloride ion determinations were performed by titration with standard silver nitrate and chromate ion as an indicator according to the Mohr method. Calcination data: the products were burned after drying under a vacuum at 80°C. Intrinsic viscosities were measured at 32°C in 0.1M NaCl using Ubbelohde viscometers.

Gel permeation chromatograms were obtained using TSK-GEL G 3000 PW and TSK-GEL G 4000 PW columns connected in series, with 0.1M TRIS buffer, 0.2M NaCl, pH 8, as the mobile phase, and a flow rate of 1 mL/min (Knauer Model HPLC Pump 64), while the samples were checked by a Knauer UV detector operating at 230 nm.

Synthesis of 2,2-Bis(acrylamido)acetic Acid (BAC)

BAC was prepared by the reaction of glyoxylic acid with acrylonitrile in a H₂SO₄ solution, according to the following scheme:



A 3M solution of glyoxylic acid (0.68 mol) in concentrated H₂SO₄ (50% by weight) was prepared and then added dropwise to acrylonitrile (2 mol)

containing a small amount of copper(II) acetate under vigorous stirring and maintaining the temperature between 15 and 30°C. Afterward, the

Table I Extent of Silica Amination and Degree of Grafting

Fraction Size	Extent of Amination— NH ₂ (mM/g)	Degree of Grafting (wt %) ^a					
		S γ [MBA-DMEDA] _x			S γ [BAC—DMEDA] _x		
		b	c	Theoretical	b	c	Theoretical
SI (35–63 μ m)	0.9	2.94	5.78	57.45	4.90	4.79	84.37
SII (63–125 μ m)	1.0	4.20	7.22	60.00	5.58	5.40	85.71
SIII (125–200 μ m)	1.2	8.50	11.38	64.29	8.53	10.03	87.80

^a Weight percentage of polymer in grafted silica as evaluated by calcination.

^b Material prepared by Procedure 1.

^c Material prepared by Procedure 2.

reaction mixture was allowed to stand for 6 h at 25°C, always under stirring. A yellow, slightly viscous solution was obtained, which was diluted with cold distilled water (150 mL). Precipitation of raw BAC took place; the precipitate was collected by filtration, washed with water (2 \times 100 mL), and redissolved by addition of 3M NaOH. BAC was isolated by adding concentrated HCl to pH 2, washing with distilled water (2 \times 100 mL), and drying. Yield: 95%.

Preparation of Linear Vinyl-terminated PAAs, (BAC-DMEDA)_x and [N,N'-methylenebisacrylamide (MBA-DMEDA)_x]

Bisacrylamide, 1.15 mol, and N,N'-dimethylethylenediamine (DMEDA), 1 mol, were thoroughly mixed in the presence of water (about 2 mL/g of the sum of the monomers) or another hydroxylated solvent. If the bisacrylamide was BAC, an equimolecular quantity of 2M NaOH was used. 4-Methoxyphenol (0.02 mol %) was added to avoid radical polymerization of the acrylic monomer. The reaction was run under a nitrogen atmosphere to avoid discoloration. The reaction mixture was allowed to stand for 3 days at 20°C. The product was isolated by ultrafiltration in an Amicon system with a YM 3 membrane and finally lyophilized, with a yield of 70%.

Silica Fractionation (SI, SII, SIII)

Particle-size fractionation of silica gel was obtained by sieving, in dry conditions, a representative sample using a series of standard sieves. Three fractions were obtained: the first between 35 and 63 μ m (SI), the second between 63 and 125 μ m (SII), and the third between 125 and 200 μ m (SIII).

Synthesis of Aminated Silica (SI- γ , SII- γ , SIII- γ)

To a suspension of silica gel, SI, SII, or SIII (10 g), in toluene (50 mL), γ -aminopropyltriethoxysilane (10.8 mL, 23 mM) was added. The reaction mixture was allowed to react at 60°C for 48 h. After this time, silica was collected by filtration and washed with toluene (2 \times 30 mL), methanol (2 \times 30 mL), HCl 3N (3 \times 30 mL), and water (3 \times 50 mL). The product was finally dried to a constant weight and the chloride content (assumed to correspond to the NH₂ content) was titrated according to the Mohr method (see Table I).

PAA-grafted Silica

Procedure 1

To a solution of vinyl-terminated PAA, (BAC-DMEDA)_x or (MBA-DMEDA)_x (45 g) in water (145 mL), a small amount of 4-methoxyphenol as a radical inhibitor was added. The solution was added to aminated silica (30 g). The reaction mixture, carefully degassed and purged with nitrogen, was allowed to react under stirring in the dark at room temperature for 5 days. The product was collected by filtration, washed with water (3 \times 30 mL), methanol (2 \times 30 mL), HCl 1M (2 \times 50 mL), and water (3 \times 50 mL), and finally dried over a desiccant at reduced pressure.

Procedure 2

The procedure was the same as that employed in case 1 with the only difference that the PAA solution was added to aminated silica under a vacuum. The final product was isolated and purified as described above.

Heavy Metal Ion Complexation

Typical complexation experiments with Cu²⁺ and Co²⁺ were performed in batch in 0.5M acetate

Table II Complexing Capacity Toward Cu^{2+} and Co^{2+}

Products	Degree of Grafting	Cu^{2+} (wt%)	Cu^{2+} per Polymer Repeating Units	Co^{2+} (wt %)	Co^{2+} per Polymer Repeating Units
$\text{S}\gamma$ [MBA-DMEDA]	11.38	3.05	1.02	1.19	0.43
$\text{S}\gamma$ -[BAC-DMEDA]	10.03	2.34	1.05	1.43	0.70
$\text{S}\gamma$ -[BAC-DMEDA] <i>in situ</i>	20.70	n.d.	n.d.	0.36	0.085
$\text{S}\gamma$	9.89 ^b	0.040	0.006	0.022	0.003

^a Polymer as described in ref. 10.

^b γ -Aminopropyltriethoxysilane weight percent.

buffer under a controlled pH (4–6.5). The products were equilibrated with an excess 0.1M solution of the proper salt ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), washed exhaustively with acetate buffer (5×20 mL), and finally with water (20 mL). The amount of chelated ions was determined by atomic absorption (Table II).

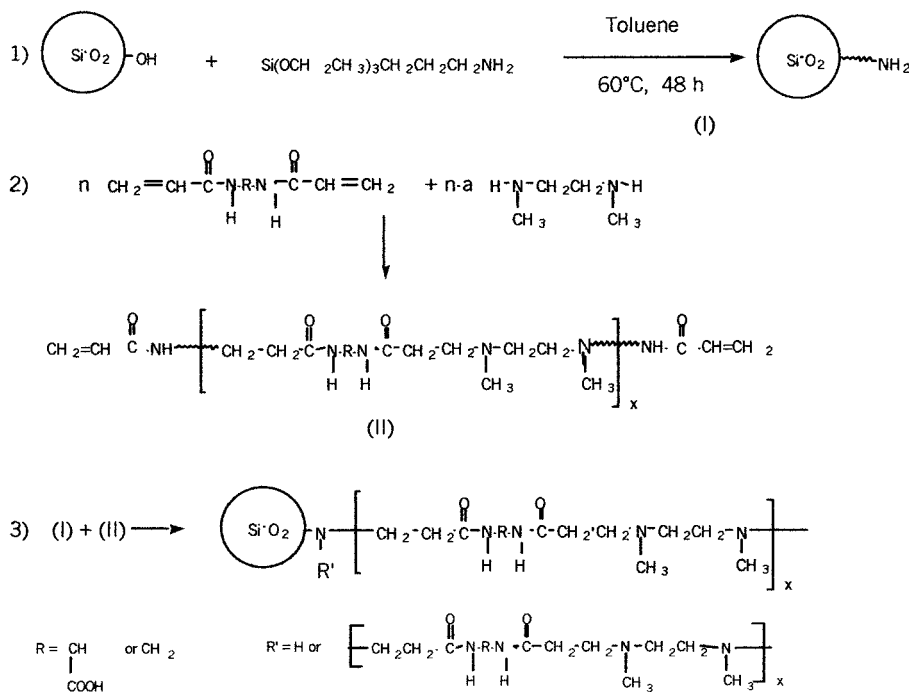
RESULTS AND DISCUSSION

Grafting of Macromonomers

With respect to a previous approach in which organic-inorganic products were obtained by *in situ* polymerization of monomers, where grafting

and polymerization occur simultaneously,¹⁰ in this work, presynthesized selected macromonomers were grafted by a covalent bond onto inorganic matrices. To evaluate the effect of the silica morphology on the grafting efficiency, the new procedure was employed on various dispersions of silica particles. The chemical process (Scheme 1), involves three steps: preparation of vinyl-terminated macromonomers, surface functionalization of inorganic particles, and, finally, grafting of the macromonomers onto functionalized silica particles.

Two structurally related PAAs which, in linear form, have been shown to possess an excellent complexing ability^{7,8} were selected for this study.

**Scheme 1**

Polymerization of PAAs takes place through a stepwise mechanism¹¹; therefore, vinyl-terminated macromonomers could be obtained by employing an excess of bisacrylamide (15 mol %). After ultrafiltration to eliminate low molecular weight fractions, the products were characterized in terms of molecular weights and molecular weight distributions by analytical GPC (Table III), making use of PAAs purposely prepared and analyzed by NMR techniques.¹² The FTIR and ¹H-NMR spectra of the two PAAs were consistent with their expected structure.⁷

Silica functionalization was achieved through the introduction of primary amino groups, which were capable of reacting with vinyl-terminated macromonomers in the subsequent grafting step. To this purpose, silica was reacted with γ -aminopropyltriethoxysilane in toluene for 48 h at 60°C.

The extent of amination was 0.9–1.2 mM amino groups per gram of inorganic material, and it was observed to increase with the particle size (Table I). This result can be explained by the increase in surface area observed passing from fraction SI to SIII (Fig. 5). Such an unexpected behavior may be explained by supposing that the porosity of native silica is so high that the total area is more dependent on the porosity than on the particle size.

The grafting reaction was carried out in water at 25°C, where the polymerization of linear PAAs is known to yield the highest molecular weight products. To optimize the reaction conditions and to achieve optimal results, the influence of the reaction time and of the mixture composition on the degree of grafting was investigated. Figure 1 shows that, generally, after 120 h, the conversion limit is reached. From Figure 2, it can be noticed that the degree of grafting increases up to a polymer/silica weight ratio of 1.5–2, while it is constant for higher ratios. The same trend is noticed with different polymer structures and silica fractions.

Figure 3 shows IR spectra of unmodified silica, aminated silica, and polymer-grafted materials obtained from the above procedure. Infrared spectra of grafted silica show the appearance of new absorptions in the 2870–2990, 1620–1655, and 1440 cm⁻¹ regions. The first one is characteristic of methylene groups and becomes evident after functionalization with γ -aminopropyltriethoxysilane. The other two absorptions are typical bands of the corresponding linear products which appear after PAA grafting and are ascribed to CO amidic stretching and CH₂ bending, respectively.

Table III Polymer Structure, Viscosity, and Molecular Weights

No.	Code	Structure	η_{sp}/C^a (dL/g)	\overline{M}_w	\overline{M}_n	d
1	MBA-DMEDA	$\left[\begin{array}{c} \text{O} \\ \parallel \\ -\text{CH}_2-\text{CH}_2-\text{C}-\text{NH}-\text{CH}_2-\text{NH}-\text{C}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}- \\ \parallel \qquad \qquad \qquad \parallel \qquad \qquad \qquad \parallel \qquad \qquad \qquad \parallel \\ \text{O} \qquad \qquad \qquad \text{O} \qquad \qquad \qquad \text{O} \qquad \qquad \qquad \text{O} \\ \text{---} \qquad \qquad \qquad \text{---} \qquad \qquad \qquad \text{---} \qquad \qquad \qquad \text{---} \end{array} \right]_x$	0.14	2160	1500	1.44
2	BAC-DMEDA	$\left[\begin{array}{c} \text{O} \\ \parallel \\ -\text{CH}_2-\text{CH}_2-\text{C}-\text{NH}-\text{CH}-\text{NH}-\text{C}-\text{CH}_2-\text{CH}_2-\text{N}-\text{CH}_2-\text{CH}_2-\text{N}- \\ \parallel \qquad \qquad \qquad \parallel \qquad \qquad \qquad \parallel \qquad \qquad \qquad \parallel \\ \text{O} \qquad \qquad \qquad \text{O} \qquad \qquad \qquad \text{O} \qquad \qquad \qquad \text{O} \\ \text{---} \qquad \qquad \qquad \text{---} \qquad \qquad \qquad \text{---} \qquad \qquad \qquad \text{---} \\ \text{COOH} \qquad \qquad \qquad \text{CH}_3 \qquad \qquad \qquad \text{CH}_3 \end{array} \right]_x$	0.265	8400	6000	1.40

^a C = 0.2% in 0.1 M NaCl.

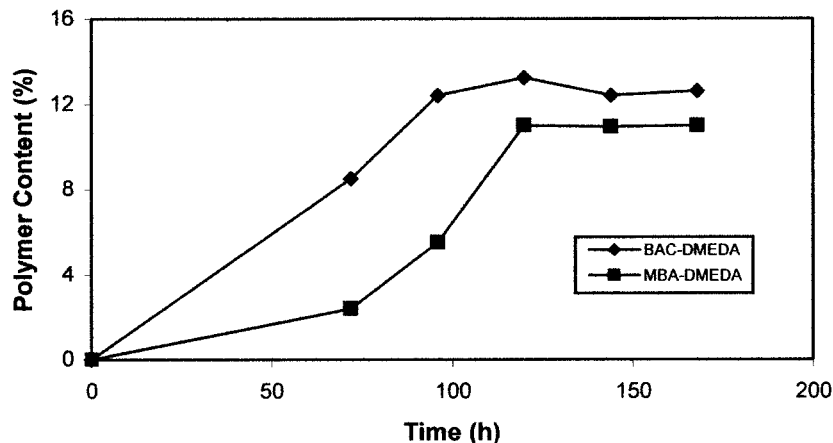


Figure 1 Effect of reaction time on degree of grafting. Aminated silica 1 g/4.5 mL H₂O; polymer/silica (wt/wt) = 1.5.

If unfunctionalized silica were used in the grafting step, no absorption at 1655 cm^{-1} was observed in the final product; the same was noticed if amino-terminated instead of vinyl-terminated PAAs were used. This indicates that, in both cases, no polymer was present on the surface and suggests that the proposed process, involving vinyl-terminated PAAs and aminated silica, leads to the grafting of PAA chains onto silica particles through the formation of real chemical bonds, physical adsorption being neglectable.

As far as the degree of grafting is concerned, the PAA content, determined by calcination, ranged from 2.9 to 11.4% (Table I) and increased with the extent of amination. These results were confirmed by elemental analyses. The amount of grafted polymer was always considerably smaller than was the maximum expected value. This may be because grafting hardly proceeds because of

the heterogeneous reaction system and of the steric hindrance exerted by grafted chains. Accordingly, grafting by *in situ* polymerization, where low molecular weight monomers are involved, leads to products with about 20 wt % of organic material, which is at least twice higher than the amount obtained in the present work.¹⁰

A second procedure (Procedure 2), where the polymer solution was added to silica under a vacuum, was adopted to increase the extent of grafting. As in Procedure 1, the amount of the grafted polymer was observed to increase with the extent of amination. In contrast, MBA-DMEDA turned out to be grafted more efficiently than did BAC-DMEDA. In fact, the degree of grafting of the former was improved compared to the results obtained when the reaction was carried out at ambient pressure, while no significant differences were noticed in the case of BAC-DMEDA. It is likely that the vacuum enhances penetration of the polymer solution into the pores and, thus, an increased fraction of these become accessible to polymer chains, increasing the degree of grafting for MBA-DMEDA, while such an increment is neglectable in the case of BAC-DMEDA, owing to its higher molecular weight.

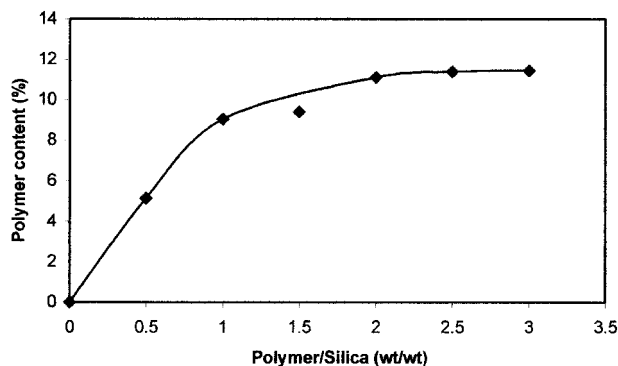


Figure 2 Effect of polymer concentration on degree of grafting. Aminated silica fraction II 1 g/4.5 mL H₂O; 120 h; polymer = [BAC-DMEDA]_x.

Surface Characterization

To evaluate the effect of functionalization and polymer grafting on the morphology of the material, the three fractions of the starting silica as well as the same ones after amination and grafting were analyzed by scanning electron microscopy (SEM) and characterized in terms of the density, specific surface area (BET), total pore

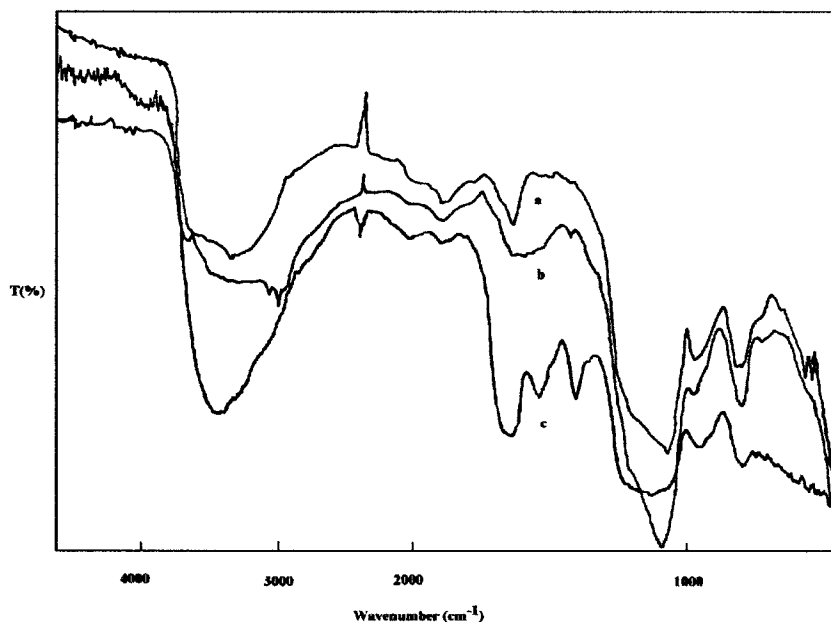


Figure 3 FTIR spectrum of (a) starting silica, (b) aminated silica, and (c) BAC-DMEDA grafted material.

volume (TPV), and total pore area (TPA). SEM analyses of the starting silica [Fig. 4(A–C)] shows that the particles have the same shape in the different fractions and that their size is homogeneous and in agreement with the diameters expected from sieving classification. Comparison with polymer-grafted silica [Fig. 4(D–F)] indicates that the treatments and experimental conditions adopted do not alter either the shape or the aspect of the particles compared to native silica and that no fragmentation occurs. The silica density [Fig. 5(A)] decreases with an increasing particle size from 2.12 to 2.10. A pronounced reduction to 1.88–1.83 and 1.85–1.80 is observed when BAC-DMEDA or MBA-DMEDA are grafted, respectively.

Silica functionalization and polymer grafting induce a decrease of both the surface area and the pore volume on all silica fractions, as can be noticed from inspection of Figure 5. For instance, the specific surface area of fraction II decreases from 454.7 m²/g for unmodified silica to 354.3 m²/g for aminated silica to 241.3 or 260.7 m²/g after BAC-DMEDA or MBA-DMEDA grafting, respectively. Similar trends are observed for the total pore volume and the total pore area.

As regards the effect of particle size, in passing from native silica to the corresponding aminated fraction, the drop in the pore volume and surface area generally increases with the size. This may

be a consequence of the different extents of amination. On the other hand, such a difference makes the degree of grafting to increase with the particle size. Accordingly, the density, BET, TPV, and TPA values in polymer-grafted silica are found to decrease from fraction I to fraction III.

Preliminary Results on Heavy Metal Ion Uptake

Although a detailed study will be published in a forthcoming article, we report here some results on Cu²⁺ and Co²⁺ ion uptake to show the effectiveness of such materials as heavy metal ion complexing systems. To this purpose, the fractions with a higher polymer content were employed as complexing materials and, for comparison purposes, both native and aminated silica were also tested. According to previous results, the Cu²⁺ uptake was studied at pH 4 and that of Co²⁺ at pH 6.5.^{10,13}

In both cases, the products were equilibrated with an excess 0.1M buffered solution of the proper salt, then washed exhaustively with pure buffer until no heavy metal ions were present in the solution and the total amount of fixed ions was finally determined by atomic adsorption. From Table II, it should be noticed that, while native and aminated particles exhibit only a negligible complexing ability, polymer-grafted silica shows excellent uptake properties, demonstrating

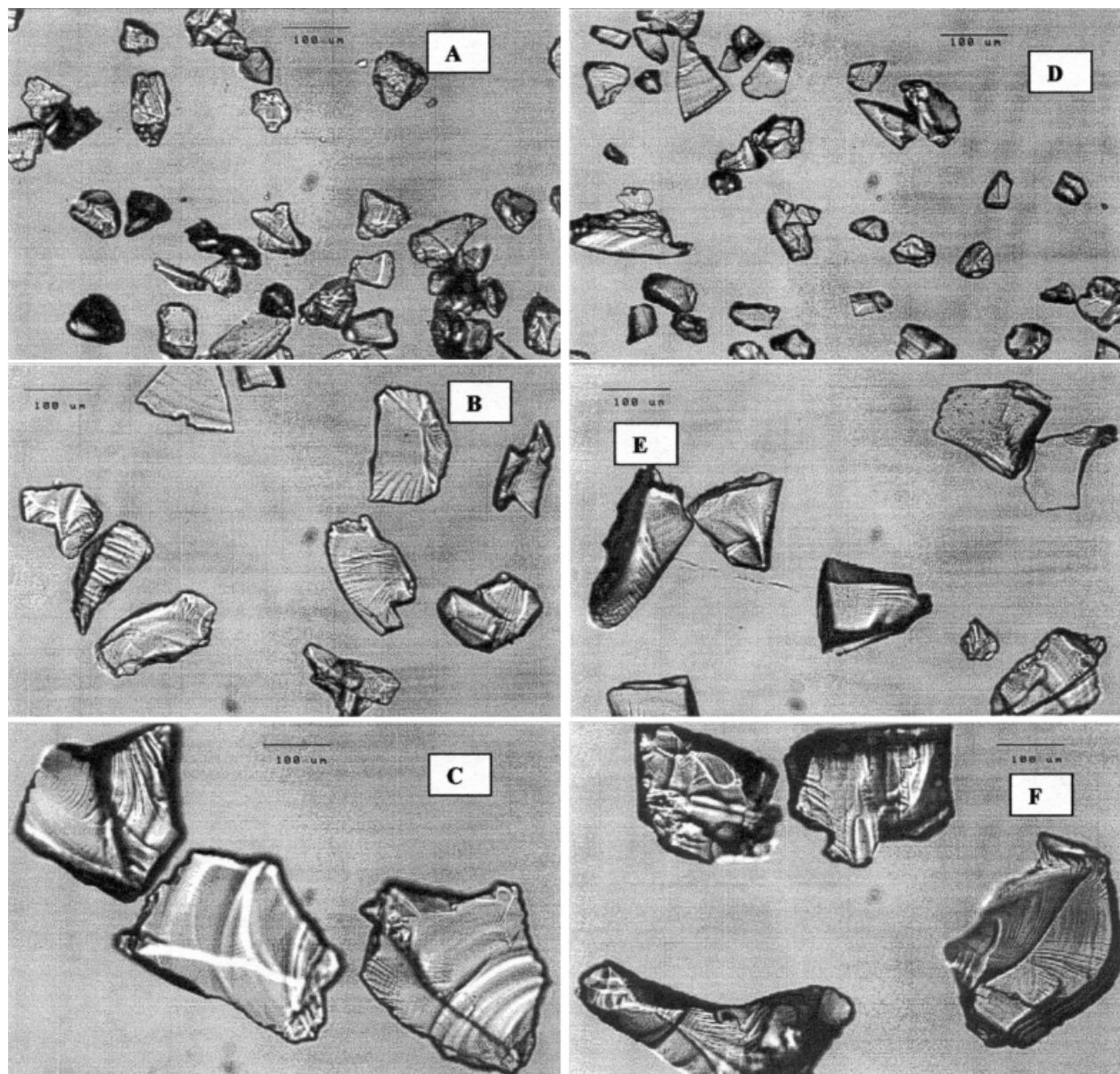


Figure 4 Scanning electron micrographs of (A) pure silica gel fraction I, (B) pure silica gel fraction II, (C) pure silica gel fraction III, (D) MBA-DMEDA-grafted fraction I, (E) MBA-DMEDA-grafted fraction II, and (F) MBA-DMEDA-grafted fraction III.

that PAA chains retain their complexation ability even in the grafted form. Although the complexing capacity of $S\gamma$ [MBA-DMEDA] and $S\gamma$ [BAC-DMEDA] toward Cu^{2+} is of the same order (one metal ion per polymer repeating unit)¹³ as in their free counterparts in aqueous media, for Co^{2+} and other tested ions, a better uptake was exhibited by $S\gamma$ [BAC-DMEDA]. This is in agreement with the behavior observed in linear polymers and is ascribed to the presence in $S\gamma$ [BAC-

DMEDA] of carboxy groups which can participate in ion chelation increasing the stability of the complexes thus formed.

The complexing capacity is lower toward Co^{2+} than Cu^{2+} ions; however, it is worth considering that the capacity of $S\gamma$ [BAC-DMEDA], for instance, is at least three times higher than that shown by the same material prepared by *in situ* polymerization in spite of the lower degree of grafting achieved by the novel procedure. It is

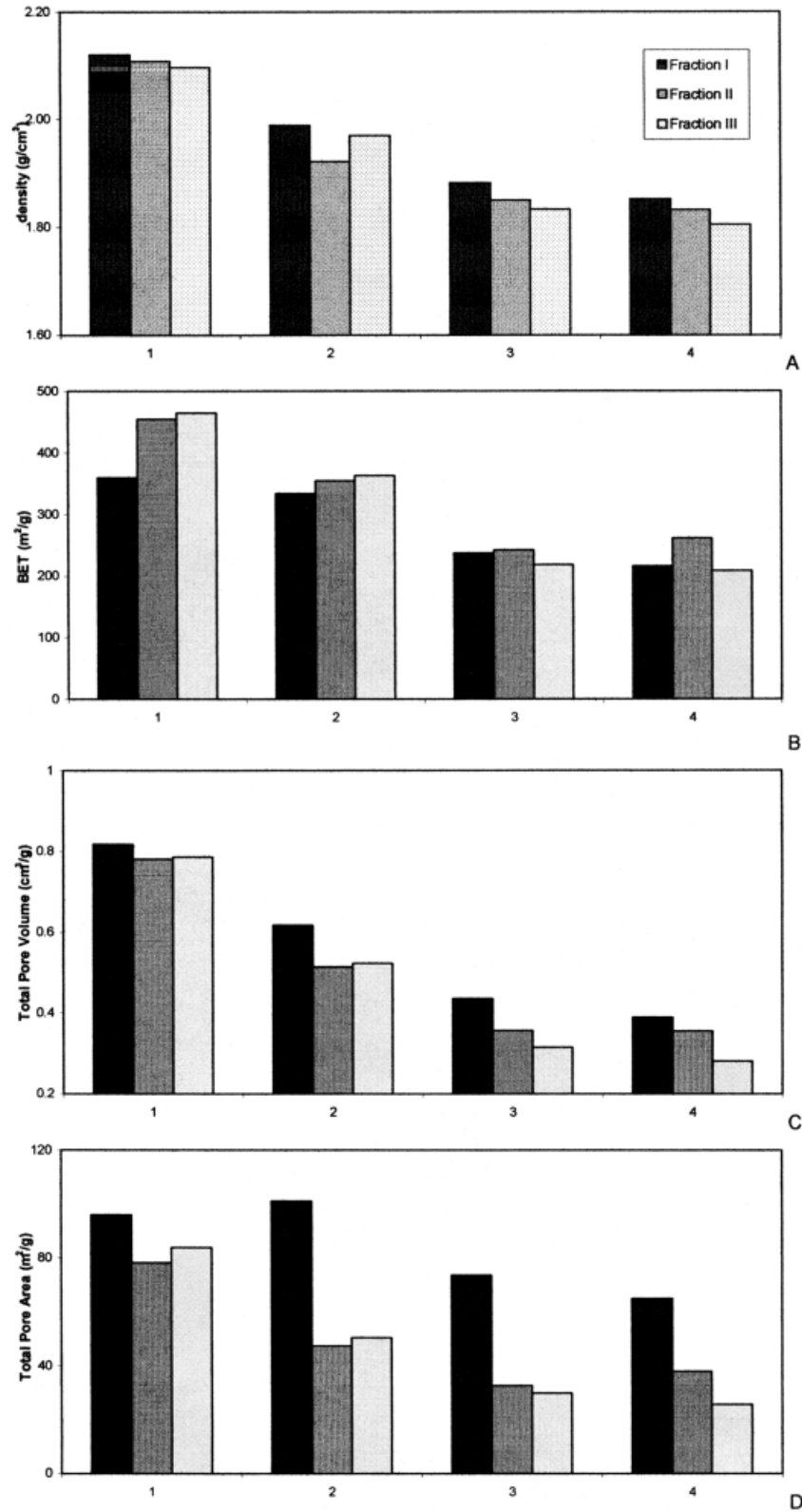


Figure 5 Effect of silica amination and PAA grafting on the three fractions of silica particles: (A) density; (B) specific surface area; (C) total pore volume; (D) total pore area. (1) Starting silica; (2) aminated silica; (3) [BAC-DMEDA]-grafted material; (4) [MBA-DMEDA]-grafted material.

likely that, while the synthetic approach here developed enables to one to graft polymer chains of controlled molecular weight, the *in situ* procedure leads to the grafting of a mixture of very low molecular weight chains or monomers which are endowed with a lower complexing capacity.

CONCLUSIONS

A novel procedure to prepare polymer-grafted silica with an excellent heavy metal ion complexing ability was developed. Grafting, which involves an addition reaction of end-functionalized macromonomers onto aminated silica, takes place through covalent bonding. Although lower polymer contents are obtained compared to a previous procedure where grafting was achieved by polymerization of the monomers in the presence of aminated silica, the heavy metal ion uptake exhibited by the novel procedure is higher. This can be interpreted by supposing that, in the latter case, grafted chains are longer and therefore possess superior ion-chelating properties.

This work was partially financed by a grant (MURST 60%) from Brescia University.

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