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Organic-Inorganic Hybrid Materials with the Ability to Bind Metal Ions: Calorimetric Properties and Thermostability

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Summary: Organic-inorganic hybrid materials with excellent heavy metal ions chelating properties were synthesized by covalent bonding of multifunctional polymers of polyamidoamine (PAA) type onto silica. Two series of polyamidoamine-silica hybrid materials differing in the PAA chemical structure were prepared and their thermal properties were investigated. Differential Scanning Calorimetry was used to study the effects of chain immobilization and ion chelation on the glass-transition temperature (Tg) of the polymers. The Tg of PAA-hybrid materials was elevated with respect to ungrafted PAAs. Complex formation with metal ions such as Cu^{++} or Co^{++} caused total suppression of Tg for both linear polymers as well as the corresponding hybrid materials. Finally, the silica particles slightly influenced the decomposition temperatures of linear polymers increasing their thermal stability.

Keywords: differential scanning calorimetry (DSC); metal polymer complexes; silicas; thermogravimetric analysis (TGA)

1. Introduction

In recent years, organic-inorganic hybrid materials have been attracted significant attention as potential candidates for new technologies in the next generation because of their advantageous performance in comparison with their nonhybrid counterparts [1]. The presence of inorganic moieties in polymers greatly expands the range of their properties and applications and at the same time overcomes some of the disadvantages of conventional polymer chemistry, such as low mechanical properties and thermal stability [2, 3, 4]. The ultimate goal should be the design and the synthesis of macromolecular systems, which match the well known properties of organic polymers with the advantages of inorganic molecules. This field of material research highlights the major role played by chemistry in advanced materials. In this view, the design and the synthesis of

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suitable molecular systems allows the production of new materials with tuneable characteristics in terms of composition, microstructure and functional properties, and new applications in different fields such as sensors, catalysis and chromatography.

In this connection a new process has been developed which enables to obtain surface-modified silica with high heavy metal ions complexing ability [5]. The synthetic approach is based on grafting of vinyl-terminated PAA onto preaminated silica via covalent bonding.

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 bis-acrylamides.

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 [6, 7] to drug delivery [8].

The aim of this work is to elucidate the influence of covalent anchoring of chain ends onto silica particles and of complex formation on the thermal properties of polymers. This investigation would be of real interest for a recent application of PAA based materials as conductive gas sensors [9] and in the preparation of composite materials.

2. Experimental

2.1 Materials

All starting reagents were purchased from Fluka and used without further purification with the exception of 2,2-bis(acrylamido)acetic acid which was synthesised as previously described [5].

2.2 Instruments and methods

IR spectra were obtained by diffuse reflectance of silica powders (2 % in KBr) with a Jasco 5300 FT-IR spectrophotometer;

Chloride ion determinations were performed by titration with standard silver nitrate and cromate ion as indicator according to the Mohr method;

Calcination data: the products were burned after drying under vacuum at 80° C;

Intrinsic viscosities were measured at 32°C in 0.1 M NaCl by means of Ubbelohde viscometers;

Gel Permeation Chromatograms were obtained making use of TSK-GEL G 3000 PW and TSK-GEL G 4000 PW columns connected in series, with 0.1 M TRIS buffer, 0.2 M NaCl pH 8 as 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.

Calorimetric analyses were carried out using a DSC 7 Perkin Elmer instrument.

TGA analysis was run on a Mettler TC11 Thermal analyser equipped with a Mettler TG50 microbalance heating a sample of about 10 mg in an alumina crucible from room temperature to 800 °C under nitrogen flow (20 ml/min).

2.3 Synthesis of aminated silica

To a suspension of silica gel 125 - 200 μm (10 g) in toluene (50 ml), γ-aminopropyl triethoxysilane (10.8 ml 23 mM) was added. The reaction mixture was allowed to react at 60 °C for 48 hours. After this time silica were collected by filtration and purified by solvent extraction with toluene and than washed with HCl 3 N (3x30 ml) and water (3x50 ml). The product was finally dried to constant weight and the chloride content, assumed to correspond to NH_2-content and determined by titration, was 1mM/g .

2.4 Preparation of linear vinyl-terminated PAAs: $(BAC\text{-}DMEDA)_n$ and $(BAC\text{-}EDDA)_n$

2,2-bis(acrylamido)acetic acid (BAC) (1.15 mole) dissolved in an equimolecular quantity of 2 M NaOH was added of 1 mole of a bis-secondary amine. The reaction mixture was thoroughly mixed in the presence of water (about 2 ml/g of the sum of the monomers) or another hydroxylated solvent. If the bis-secondary amine was N,N'-ethylethylenediamino diacetic acid (EDDA), triethylamine (TEA) (3 mol) was added. 4-Methoxyphenol (0.02 mol %) was added to avoid radical polymerization of the acrylic monomer. The reaction was run under nitrogen atmosphere to avoid discolorations. The reaction mixture was allowed to stand for 8 hrs at 20°C. The product was isolated and fractionated by ultrafiltration in an Amicon system with a YM 3 membrane and finally lyophilized with a yield of 70%.

2.5 General procedure to prepare PAA-grafted silica

To a solution of vinyl-terminated PAA (45 g) in water (145 ml), a small amount of 4-methoxyphenol as radical inhibitor was added. The solution was added to aminated silica (30 g) under vacuum. The reaction mixture, carefully degassed and purged with nitrogen, was allowed to react under stirring in the dark at room temperature for three days. The product was collected by filtration, washed with water (3x30 ml), methanol (2x30 ml), HCl 1 M (2x50 ml) and water (3x50 ml) and finally dried over desiccator at reduced pressure.

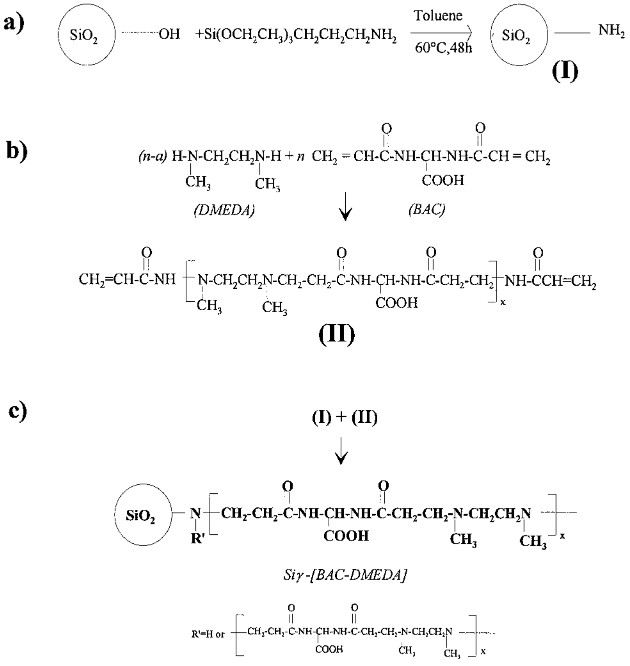
2.6 Heavy metal ions complexation

Typical complexation experiments with Cu^{2+} and Co^{2+} were performed in batch in 0.5M acetate buffer under controlled pH (6.5). The products were equilibrated with excess 0.1M solution of the proper salt ($CuSO_4 \bullet 5H_2O$ and $CoCl_2 \bullet 6H_2O$), washed exhaustively with acetate buffer (5x20 mL) and finally with water (20 mL).

3. Results and discussion

3.1 Preparation of hybrid materials

The chemical process involves three steps: preparation of vinyl-terminated macromonomers, surface functionalisation of inorganic particles, and, finally, grafting of the macromonomers onto functionalised silica particles (Scheme 1).



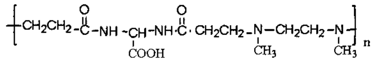
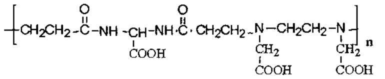
Scheme 1

The adopted chemical approach as well as the optimisation of reaction conditions were discussed in a previous paper [5]. In this section we report the results obtained with different PAA-Si hybrid materials differing in the PAA chemical structure.

Two structurally related PAAs namely BAC-DMEDA and BAC-EDDA, which, in linear form, have been shown to possess excellent complexing ability were selected for this study. Polymerisation of the PAAs takes place through a stepwise mechanism; 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 1), making use of PAAs purposely prepared and analysed by NMR techniques [5, 10].

The grafting reaction was carried out in water at 25 °C where the polymerization of linear PAAs is known to yield higher molecular weight products. Native silica and the resulting mixed organic-inorganic products have been fully characterized by IR spectroscopy, SEM, yield of grafting, and density. It has been found that the corresponding polymers are effectively grafted onto the surface through the formation of real chemical bonds. The PAA content, evaluated by elemental analyses was 10% and 15.6% when BAC-DMEDA or BAC-EDDA are grafted, respectively. The results were confirmed by calcinations.

Table 1. Polymer structure, viscosity, molecular weights and Tg's

Structure	$\eta_{sp}/C^{a)}$ (dl/g)	$\boxed{\overline{M}_w}$	$\boxed{\overline{M}_n}$	Tg (°C)	$Tg^{b)}$ (°C)
 $-\!\!\left[CH_2CH_2-\overset{O}{\overset{\Vert}{C}}-NH-\underset{COOH}{CH}-NH-\overset{O}{\overset{\Vert}{C}}-CH_2CH_2-\underset{CH_3}{N}-CH_2CH_2-\underset{CH_3}{N}-\right]_n$ BAC-DMEDA	0.12	6050	4820	99	116
 $-\!\!\left[CH_2CH_2-\overset{O}{\overset{\Vert}{C}}-NH-\underset{COOH}{CH}-NH-\overset{O}{\overset{\Vert}{C}}-CH_2CH_2-\underset{\underset{COOH}{CH_2}}{N}-CH_2CH_2-\underset{\underset{COOH}{CH_2}}{N}-\right]_n$ BAC-EDDA	0.10	6900	5900	122	133

a) C= 0.2% in 0.1 M NaCl; b) Silica-grafted polymers.

3.2 Thermal Properties

The effect of polymer immobilisation by covalent anchoring the chain ends onto inorganic particles can be examinated by a comparison of Tg's of bound and unbound PAAs. Two different hybrid materials, differing in the PAA chemical structure, as well as the corresponding linear polymers were studied with DSC. For all samples it was found that the silica core did not undergo any transition in the experimental temperature window; therefore only thermal transitions in PAA were observed. Sample stabilisation was attained by preliminary heating of the samples to 160°C. In such cases the second and subsequent scans showed identical DSC curves.

DSC traces of unbound PAAs revealed Tg's of 99 and 122 °C for BAC-DMEDA and BAC-EDDA respectively. The higher value for the latter oligomer was ascribed to the presence of three carboxyl group as side substituent per repeating unit instead of the one of the former (Table 1).

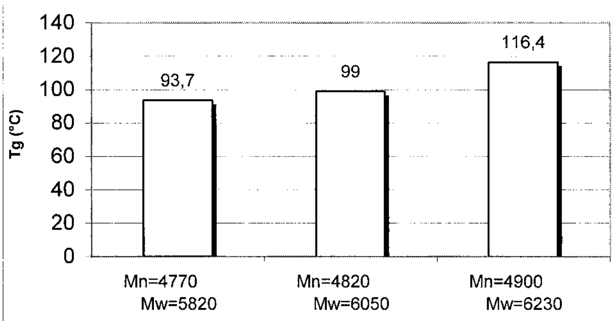


Figure 1. Tg of BAC-DMEDA possessing various molar masses.

Furthermore, as expected the Tg of linear polymers was observed to increase with molecular weight as reported in Figure 1 for BAC-DMEDA.

The DSC traces revealed that the Tg of surface immobilized PAAs was increased relative to ungrafted free polymers (Table 1). In particular the Tg of silica-grafted PAAs was elevated by 17 and 11 °C in comparison with free BAC-DMEDA and BAC-EDDA respectively. This effect, which has been reported for other hybrid materials [3, 4], may be interpreted taking into account that Tg is strongly dependent on the mobility of the polymer chains. The covalent attachment of chains to a surface decreases the mobility of the polymer at the grafted surface.

Linear PAAs as well as polymer-grafted silica are extensively studied for their heavy metal ions chelating properties. In particular, PAA chains retain their complexation ability even in the grafted form and the complexing capacity is of the same order (one metal ion per repeating unit) as in their free counterparts [5]. When PAA-Si hybrid materials chelated heavy metal ions such as Cu^{++} and Co^{++} no heat capacity step typical of the glass transition was observed in the DSC curve (Figure 2). This indicates total suppression of cooperative segmental motion over the temperature range under study (up about 200 °C, the polymer degradation onset). The same results were obtained when unbonded PAAs chelated Cu^{++} and Co^{++}.

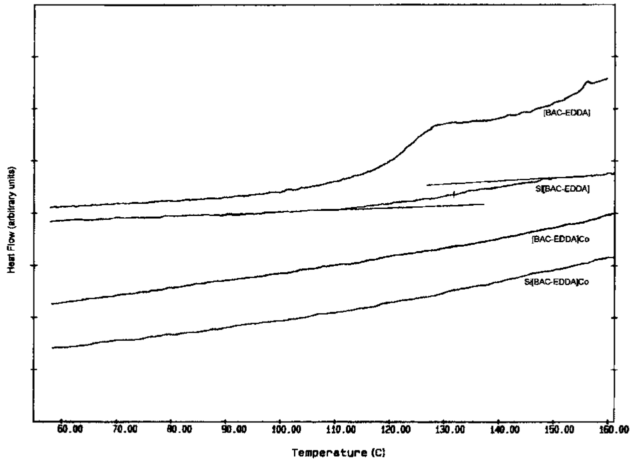


Figure 2. DSC traces of free and silica-grafted BAC-EDDA, and of the corresponding Co chelated materials.

The effect described, characterizing the anomalous glass-transition behaviour of bound and unbound PAA and PAA metal complexes, may be interpreted as follows: the covalent anchoring of chain ends to silica particles, which implies strong interactions between polymer and rigid core, decreases the mobility of the polymer and increases the Tg of PAA. When metal ions are chelated the cyclic structure occurring around the ions [11] highly constrains polymers causing changes in molecular packing and suppression of Tg.

To investigate the thermal stability of the PAA hybrid materials, we carried out TGA measurements under nitrogen as shown in Figure 3. For comparison purposes thermogravimetric measurements were performed for aminated silica and starting PAAs. The silica particles slightly influenced the decomposition temperatures of linear PAAs; the general tendency was increasing thermal stability with hybridisation. Two degradation processes, that can be ascribed to the presence of PAAs and aminopropyl silica gel respectively, could be noticed.

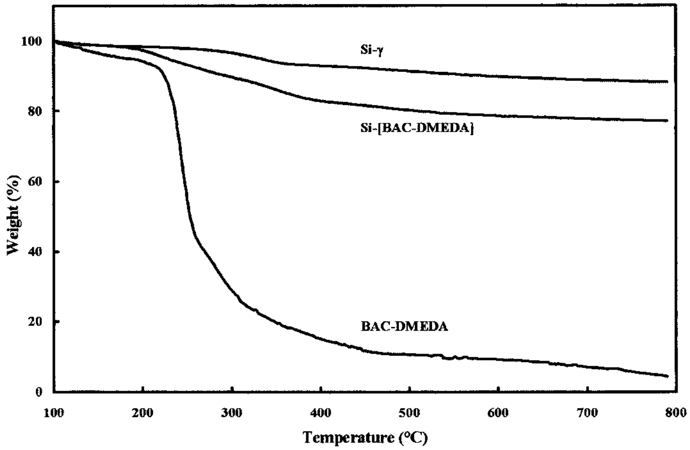


Figure 3. TGA curves of aminated silica , BAC-DMEDA grafted silica and BAC-DMEDA free polymer, obtained at a heating rate of 20 °C/min under nitrogen.

The polymer weight loss determined by TGA is somewhat lower than expected on the basis of the degree of grafting evaluated by elemental analyses and calcinations. On the other hand, the thermal decomposition in a solid medium is a complex process associated with different chemical reactions and processes. In solid polymers, chemical and diffusion processes are markedly influenced by segmental mobility and the situation becomes even more complicated in composites in which the presence of an inorganic phase may influence the kinetics of products transfer. Therefore the data obtained by TGA can be used only for a comparative estimation of thermal stability and not for a quantitative evaluation of the degree of grafting.

4. Conclusions

Organic-inorganic hybrid materials with excellent heavy metal ions chelating properties were synthesized by covalent bonding of vinyl-terminated PAAs onto silica. Two series of polyamidoamine-silica hybrid materials differing in the PAA structure were prepared and their thermal properties were investigated. All materials are stable below 200 °C under the analytical conditions employed. Furthermore, from the behaviour of bound and unbound PAA and PAA metal complexes, the following considerations may be drawn:

1. the covalent anchoring of chain ends to silica particles decreases the mobility of polymers enhancing the Tg of PAA;
2. the complex formation occurring through a cyclic structure around the metal atoms highly constrains polymer chains causing changes in molecular packing and suppression of segmental motion.

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