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Silica-graft-polyamidoamine Hybrid Materials: Effect of Constraints on the Polymer Mobility

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Summary: Organic-inorganic hybrid materials with excellent heavy metal ions chelating properties are 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 are prepared and their thermal properties are investigated. Differential Scanning Calorimetry (DSC) is used to study the effects of chain immobilization and ion chelation on the glass-transition temperature (T_g) of the polymers. The T_g of PAA-hybrid materials is elevated with respect to ungrafted PAAs, but when the linear and the corresponding hybrid PAAs are in the complex form with metal ions such as Cu^{2+} and Co^{2+}, the materials arrive to the decomposition temperature and no T_g is detected. To highlight the effect of metal ion on the molecular mobility of these systems, an oligomeric plasticizer is added. The behaviour in the T_g region is analyzed and discussed in term of Tool-Narayanaswamy-Moynihan (TNM) model. In particular the apparent activation energy (Δh^*) is used to discuss overall segmental co-operativity in order to better understand the effect of complex formation on structural mobility.

Keywords: apparent activation energy (Δh^*); differential scanning calorimetry (DSC); hybrid materials; metal polymer complexes; molecular mobility

Introduction

In recent years, organic-inorganic hybrid materials have been attracted significant attention as potential candidates for new generation technologies because of their advantageous performance in comparison with their non-hybrid counterparts.[1] The use of inorganic moieties could greatly expand the range of applications of polymeric materials if some well known disadvantage, such as low mechanical properties and thermal stability, are overcame.[2–4] 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 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 we have developed a new process which enables to obtain surface-modified silica with multifunctional polymers of polyamidoamine (PAA) structure.[5] The synthetic approach is based on grafting of vinyl-terminated PAA onto preaminated silica via covalent bonding. The PAAs are synthetic water-soluble polymers, characterized by the presence of amido and tertiary amino groups regularly arranged along their macromolecular chains. They are obtained in linear form by

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stepwise polyaddition of primary monoamines or bis-secondary amines, to bisacrylamides. PAAs carrying additional functions (carboxyl, hydroxyl and amine groups) as side chain 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 uses, ranging from drug delivery,[6] to metal ion complexation[7] and gas/liquid detector.[8]

In this work two PAAs, synthesized starting from 2,2-bis(acrylamido) acetic acid (BAC) and two bis-secondary amine, respectively N,N′-dimethylethylenediam--dimethylethylenediamine (DMEDA) and ethylenediamine-N,N′-diaceticacid(EDDA), were grafted onto silica particles and the corresponding complexes with Co^{2+} and Cu^{2+} were prepared. To elucidate the effects of the covalent anchoring of chain ends on silica particles and of the complex formation on the molecular mobility of the polymers, the T_gs of hybrid materials in linear and complex forms were studied with respect to the un-grafted ones. The T_g influences many physical properties including elasticity, adhesion, viscosity, gas and solvent adsorption and release, and permeability.[9] In general chemical and diffusion processes are markedly influenced by segmental mobility. Moreover it has been repeatedly proved that the ageing of amorphous polymers is controlled by the type and the rate of their characteristic molecular motion. To highlight the effect of metal ion on the molecular mobility of these systems, a plasticizer was added and the overall segmental co-operativity at T_g were analyzed and discussed in terms of TNM model.

Experimental Part

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]

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 TA Instruments Q100 DSC. A sample weight of about 9 mg and a heating rate of 10 °C/min under nitrogen flow (50 ml/min) were used. Cooling experiments were performed to obtain values of Δh^*. Each sample was heated at 10 °C/min to well above T_g, cooled to below T_g at a controlled rate (q_c) and then reheated at a rate of 10 °C/min through the T_g. q_c is varied from 0.15 to 10 °C/min. The fictive temperature (T_f) was calculated for each cooling rate by extrapolating the liquid and the glassy line to the point of intersection in the enthalpy versus temperature curve.[10] These calculations were done automatically by the DSC Q100 software. $\Delta h^*/R$ was calculated from the slope of $\ln q_c$ versus $1/T_f$.

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 (3 × 30 ml) and water (3 × 50 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 1 mM/g.

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 N, N′- dimethylethylenediamine (DMEDA) or ethylenediamine-N,N′-diacetic acid (EDDA). 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 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%.

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 (3 × 30 ml), methanol (2 × 30 ml), HCl 1 M (2 × 50 ml) and water (3 × 50 ml) and finally dried over desiccator at reduced pressure.

Heavy Metal Ions Complexation

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

General Procedure to Prepare Plasticized PAA and Plasticized PAAs Complexing Heavy Metal Ions

To a solution of PAA (80 mg) in water (10 ml), tetraethylene glycol dodecyl ether (Brij 30, 30 mg) was added. Each sample was prepared by spraying the polymer plasticizer solution onto a clean microscope slide and allowing the film to dry in air for at least 24 h. After deposition, the films were removed from glass and placed into aluminium pans.

The same procedure was followed to prepare plasticized PAAs complexing heavy metal ions. Those systems were obtained adding to PAA water solution, at pH 7.5, $CuCl_2 \cdot 2H_2O$ or $CoCl_2 \cdot 6H_2O$ (30 mg), and isolated as above described.

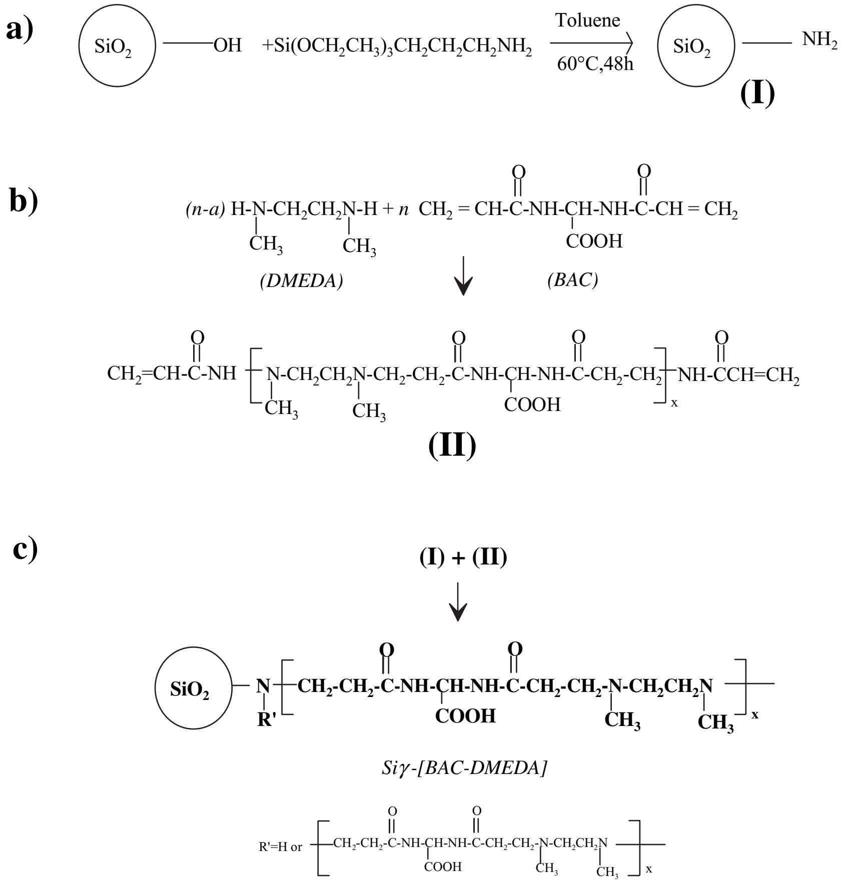
Results and Discussion

Preparation of Hybrid Materials

The chemical process involves three steps: a) surface functionalisation of inorganic particles, b) preparation of vinyl-terminated macromonomers, and c) macromonomers grafting onto functionalised silica particles, as indicated in Scheme 1.

The adopted chemical approach as well as the optimisation of reaction conditions have been discussed in a previous paper.[5] Two structurally related PAAs namely BAC-DMEDA and BAC-EDDA, which in linear form have shown excellent complexing ability, were selected for this study.

Polymerisation of the PAAs takes place through a stepwise mechanism and vinyl terminated macromonomers can be obtained by employing an excess of bis-acrylamide (15 mol %). After ultrafiltration to eliminate low molecular weight fractions, the products were characterized in terms of molecular weights distributions by



Scheme 1.

analytical GPC (see Table 1), making use of PAAs purposely prepared and analysed *via* NMR.[5]

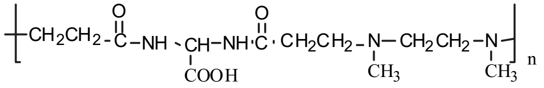
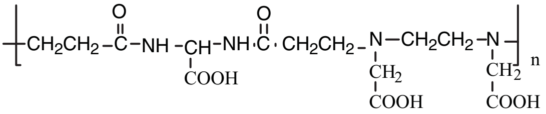
The grafting reaction was carried out in water at 25 °C, where the polymerization of linear PAA yields higher molecular weight products. Native silica and the resulting mixed organic-inorganic products have been fully characterized by IR spectroscopy, SEM, yield of grafting, and density. It has been 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% respectively for BAC-DMEDA and BAC-EDDA grafting. These results were confirmed by calcinations.

Molecular Mobility: Effect of Grafting and Metal Ions Chelation

The effect of polymer immobilisation by covalent anchoring of the chain ends onto inorganic particles can be examined by T_gs comparison of Si-bound and unbound PAAs. Two different hybrid materials differing in the PAA chemical structure, as well as the corresponding linear polymers, were studied with differential scanning calorimeter. For all samples it was found that the silica core did not undergo any transition in the experimental temperature window (60–160 °C); therefore thermal transitions were observed in PAA only.

All samples were stabilized by heating from room temperature to 160 °C; after this preliminary thermal treatment the second

Table 1.
Polymer structures, viscosities, molecular weights and T_gs.

Structure	$\eta_{sp}/C^{a)}$ (dl/g)	M_w (g/mol)	M_n (g/mol)	T_g (°C)	$T_g^{b)}$ (°C)
 $[-CH_2CH_2-C(=O)-NH-CH(COOH)-NH-C(=O)-CH_2CH_2-N(CH_3)-CH_2CH_2-N(CH_3)-]_n$ BAC - DMEDA	0.12	6,050	4,820	99	116
 $[-CH_2CH_2-C(=O)-NH-CH(COOH)-NH-C(=O)-CH_2CH_2-N(CH_2COOH)-CH_2CH_2-N(CH_2COOH)-]_n$ BAC-EDDA	0.10	6,900	5,900	122	133

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

and subsequent scans gave identical DSC curves. The transition temperatures reported in Table 1 were evaluated on the second scan.

Concerning unbound PAAs, the glass transitions of BAC-DMEDA and BAC-EDDA occurred at 99 °C and 122 °C, respectively (see Table 1); the higher T_g value of the latter oligomer was ascribed to the presence of three carboxyl groups as side-chain substituent *per* repeating unit instead of one of the former. On the other hand, the T_g of silica-grafted PAAs were 116 °C and 133 °C, that means an increase respectively of 17 °C and 11 °C in comparison with unbound BAC-DMEDA and BAC-EDDA. This behaviour may be interpreted taking into account that T_g is strongly dependent on the mobility of the polymer chains. It is known that the addition of a solid filler to a polymer increases T_g if strong attractive forces between the polymer and the filler are present. The covalent attachment of the chain-ends on Si particles decreases the mobility of the oligomers.

Linear PAAs as well as polymer-grafted silica have been 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 are in the complex form with heavy metal ions, such as Cu^{2+} and Co^{2+} as model ions, no heat capacity step typical of the glass transition was observed in the DSC curve, as shown in Figure 1. This indicates the total suppression of the glass transition co-operative segmental motions in the temperature range under study (from 20 °C up to 200 °C, the onset degradation temperature). The same behaviour was observed for unbound PAAs. These results clearly show the effect of the metal complex formation on the thermal properties of PAAs, both in unbound and in silica grafted PAA. When metal ions are chelated, the cyclic structure occurring around the ions[11] highly constrains the oligomers causing changes in molecular packing and suppressing T_g.

The high organization and rigidity of such systems play a very important role for a recent application of PAA-based materials. We have indeed set new vapour

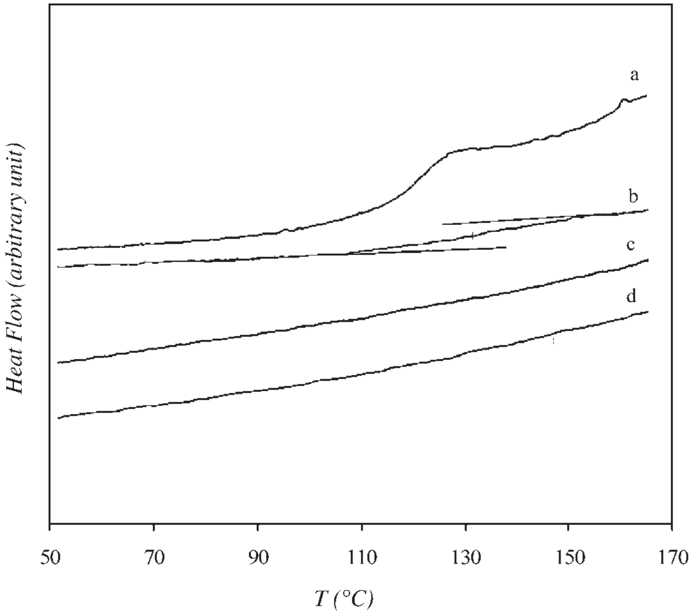


Figure 1.
DSC traces of BAC-EDDA (a), Si-BAC-EDDA (b), BAC-EDDA Co^{2+} (c) and Si-BAC-EDDA Co^{2+} (d). The thermograms were obtained under nitrogen flow (50 ml/min) and with a heating rate of 10 °C/min.

detectors formed from nanocomposites of conductive carbon-black and PAA-based insulating polymers.

The PAA composite detector clearly exhibited a significantly enhanced sensitivity as compared to other polymer composite detector films. Generally the new material can detect a mean value of analyte concentration approximately 1000 fold smaller than that of a traditional composite vapour detector. We have demonstrated that the higher sensitivity of these systems can not be attributed to the difference in polymer/gas partition coefficient but to changes in polymer conformation during the adsorption process.[12]

Molecular Mobility: Effect of a Plasticizer

As previously discussed, when the linear and the corresponding hybrid PAAs are in the complex form with metal ions such as Cu^{2+} and Co^{2+}, the materials arrive to the decomposition temperature and no T_gs are detected.

To highlight the effect of metal ion on the molecular mobility of these systems, a plasticizer made of tetraethylene glycol dodecyl ether (Brij 30) was added to a BAC-DMEDA series and the behaviour in the T_g-region was analyzed.

In Table 2 are reported the detected transition temperatures of un-plasticized BAC-DMEDA and of BAC-DMEDA and BAC-DMEDA · Co^{2+} both with 27.3% by weight of Brij 30 (P-BAC-DMEDA and P-BAC-DMEDA · Co^{2+} respectively). As expected, the plasticizer drastically

Table 2.
Transition temperatures (T_g) and apparent activation energies (Δh^*) evaluated for unmodified BAC-DMEDA and for plasticized BAC-DMEDA and BAC-DMEDA · Co^{2+}.

Samples	T_g (°C)	Δh^* (kJ/mol)	R^2
BAC-DMEDA[a)]	120	1776	0.998
P-BAC-DMEDA[b)]	30	550	0.997
P-BAC-DMEDA · Co^{2+}[b)]	109	n.d.	—

[a)] $M_w = 8{,}100$ g/mol, $M_n = 6{,}270$ g/mol.
[b)] Plastified with tetraethylene glycol dodecyl ether (Brij 30) (27.3 wt%).

decreases the T_g which goes from 120 °C to 30 °C for BAC-DMEDA and P-BAC-DMEDA, respectively. Also in the case of P-BAC-DMEDA·Co^{2+}, a transition temperature was detected at 109 °C.

The effect of the plasticizer and the complex formation with metal ions on the molecular mobility of these systems were studied adopting a procedure for the analysis of DSC data which follows a well-recognized approach. It is assumed that the relaxation time(s) $(\cdot\tau)$ for enthalpy relaxation depends on both the temperature (T) and the structure of the glass, identified by its fictive temperature (T_f), according to the so called **Tool-Narayanaswamy-Moynihan** (TNM) model.[13–15]

The intention, here, is to evaluate the apparent activation energy Δh^*, introduced in this model, in order to estimate the effect of the plasticizer and the complex formation with metal ions as Co^{2+} on the relaxation processes. In this respect, a set of experiments in which the sample is cooled at different constant rates before immediately scanning in DSC is required. As example, Figure 2.a shows the behaviour of plasticized BAC-DMEDA. The dependence of the T_f from the cooling rate q_c may be written as follows:[16]

$$-\frac{\Delta h*}{R} = \frac{d[\ln(|q_c|)]}{d[1/T_f]} \tag{3}$$

The T_f was calculated for each cooling rate and Δh^* is then evaluated from the slope of the plot of $\ln[|q_c|]$ vs $[1/T_f]$, as illustrated in Figure 2.b. The results for all the samples tested are summarized in Table 2.

Since the relaxation is a highly co-operative process, the measured apparent activation energy is not in itself representative of the activation energy of the fundamental molecular process. In fact, it can be shown[17] that the primary activation energy E_a of the fundamental molecular process is related to the apparent activation energy through the non-exponentiality parameter (β):

$$E_a = \Delta h^* \beta \tag{4}$$

The implication is that for any given primary process, the broader the distribution of the relaxation times is, the greater will be the co-operativity necessary between molecular segments participating in the relaxation, and the greater will be the apparent activation energy.

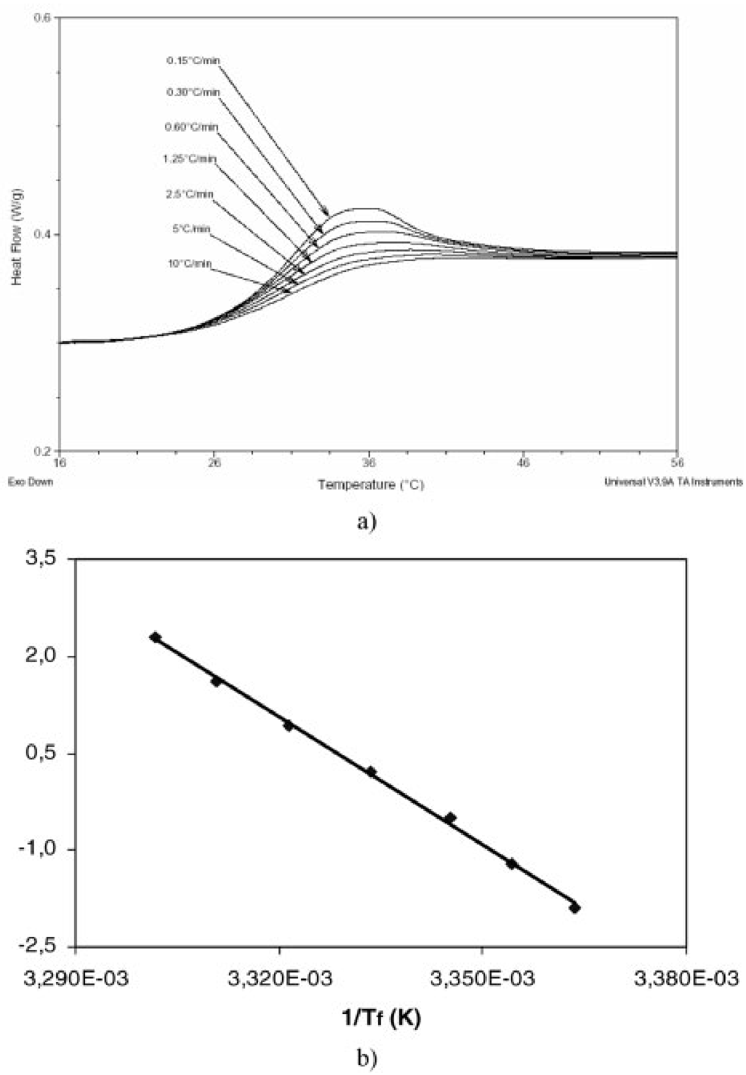
Moreover, Δh^* is considered an energy barrier that must be exceeded during structural relaxation, and the decreasing Δh^* activates less energy demanding relaxation.

As reported in Table 2, the addition of the plasticizer to BAC-DMEDA produces a substantial decrease in Δh^*, from 1776 kJ/mol to 550 kJ/mol. This parameter has not been evaluated for the grafted polymer due to experimental limits (low Δc_p, Figure 1 trace b).

The results reported above, could be also interpreted in terms of fragility concept, developed by Angel in 1985[18] for classifying the simple glass forming liquids behaviours. In this view, strong liquids are characterised by stable structure and properties that do not dramatically change from the liquid state to the glassy state. On the other hand, for fragile liquids such structures are unstable and properties changes are more evident. This is valid for the thermodynamic response (e.g. specific heat capacity) and the transport properties (e.g. viscosity).

Generally, the fragility can be defined from the relaxation time associated with the glass transition, plotted as a function of $T_g\backslash T$: in this representation, it describes the departure from the linear Arrhenius behaviour (strong liquid). The fragility parameter (m) corresponds to the limiting slope of the curve described above. While it is known that m increases with T_g[19] and the transition temperatures of BAC-DMEDA and P-BAC-DMEDA are respectively 120 °C, and 30 °C, we can deduce that the plasticizer in the polymers gives a reduction of fragility.

In this respect, the experimental data reported in Figure 3 show a decrease both of ΔC_p and enthalpy relaxation peak, going from BAC-DMEDA to P-BAC-DMEDA. The decrease of fragility can be attributed



a)

b)

Figure 2.

a) Heating scans at 10 °C/min for plasticized BAC-DMEDA sample (8.5 mg) cooled at the rates indicated against each curve and immediately reheated in the DSC. All the cooling and reheating scans, concerning an experiment, were run on the same sample. Only a part of the complete scans from 16 to 56 °C are shown here for clarity. b) Plot of ln(cooling rate) vs reciprocal fictive temperature for cooling traces shown in a). The full line represents the least-squares fit to the data.

to the modified ability for intermolecular coupling or cooperativity: in fact, as Plazek and Ngai pointed out,[20] there is a clear correlation between fragility and cooperativiy parameter determined in the coupling model. In this view, the addition of tetraethylene glycol dodecyl ether reduces the thermal energy necessary for promoting the cooperative chain motions associated with the glass transition.

On the other hand, when the material is in the complex form, the addition of the plasticizer allows measuring a transition temperature at 109 °C but, under the

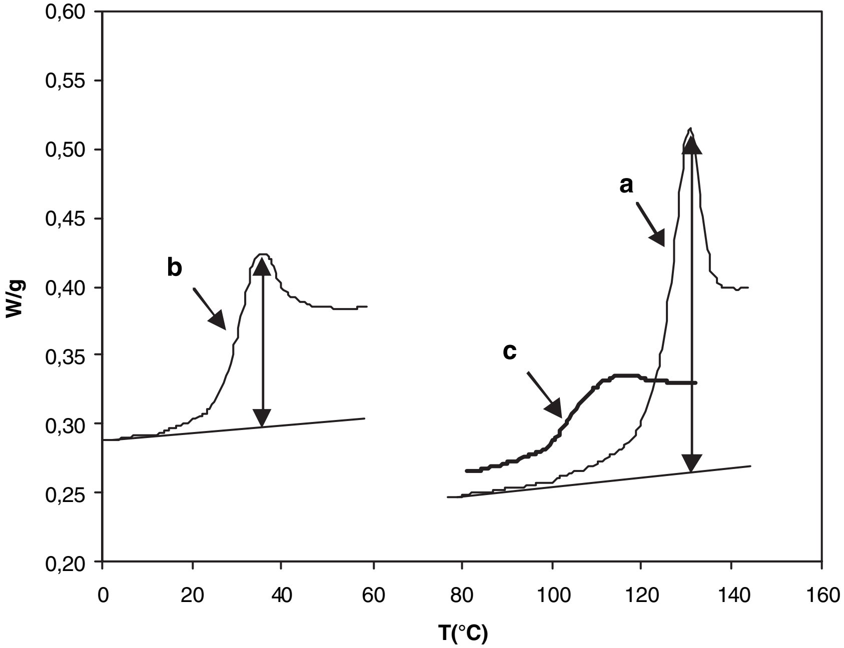


Figure 3.
Heating scans at 10 °C/min for BAC-DMEDA (a), P-BAC-DMEDA (b) and P-BAC-DMEDA · Co^{2+} (c) cooled at 0.15 °C/min.

experimental conditions, P-BAC-DMEDA · Co^{2+} does not have relaxation peak, also at the lowest cooling rate ($q_c = 0.15\,°C/min$), as shown in Figure 3. This result means that the motions involved in the relaxation processes are prevented probably because the macromolecules are constrained in a cyclic structure around the metal ions.[11]

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 the effects of chain immobilization and ion chelation on the molecular mobility of the polymers were investigated. From the behaviour of Si-bound and unbound PAAs and PAA metal complexes, the following considerations may be drawn:

1. the covalent anchoring of chain ends onto silica particles decreases the mobility of polymers enhancing the T_g of PAA;
2. the complex formation, occurring through a cyclic structure around the metal ions, highly constrains polymer as shown from the absence of T_g until the degradation temperature.

The addition of a plasticizer to a selected PAA produces a substantial decrease in Δh^*, reducing the thermal energy necessary for promoting the cooperative chain motions associated with the glass transition, as shown comparing the Δh^* P-BAC-DMEDA and BAC-DMEDA, moreover in the case of P-BAC-DMEDA · Co^{2+} allows to measure a glass transition temperature. Nevertheless, the plasticized PAA metal complexes does not show a well- rendered relaxation peak indicating that probably a change in the relaxation mode is occurred.

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