Facile construction of a novel metal-imprinted polymer surface without a polymerisation process

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Porous thin films have been prepared by casting water–THF mixed solutions of poly(vinyl chloride-*co*-acrylic acid): when Cu^{2+} ion is imprinted in the casting process, the film obtains a memory for the original Cu^{2+} ion. The imprinting processes can be closely monitored by FTIR spectroscopy.

Introduction

The concept of the molecular imprinting technique attracted considerable attention from many chemists in the 1970's who were interested in molecular recognition in relation to biomimetic chemistry.[1–8] It was first reported by Wulff *et al.*[9,10] The technique basically consists of three steps: (i) synthesis of functional vinyl monomers that can interact with a target template, (ii) radical polymerisation of the vinyl monomers with cross-linking reagents in the presence of the template and (iii) removal of the template from the cross-linked copolymer resin. Actually, this technique has achieved success to some extent. It seems to us, however, that several technical problems which are inherent in this method have remained unresolved or only partially solved. Thus, we have to take the following factors into consideration in order to further elaborate this method: (i) in general, radical polymerisation occurs at high temperatures[11] where the subtle discrimination of enantiomers is energetically unfavourable, (ii) bulk radical polymerisation accompanies shrinkage of the volume: under such a condition the structure of template molecules may be deformed, which would make the retention of the nanometer-sized memory for template molecules difficult, (iii) therefore, the reversible binding capacity is relatively small and (iv) spectroscopic characterisation of the imprinted binding-site is nearly impossible.

It occurred to us that if a polymer bearing functional groups can be quickly '*frozen*' as a thin film in the presence of template molecules, most of the above-mentioned technical problems would be solved. Because of the wide surface area in the thin film system, template molecules can be easily extracted out of the film surface and the structure of the binding-site constructed in the thin film can be easily characterised by various spectroscopic methods. Kobayashi *et al.*[12] recently reported a similar idea for recognition of theophylline but the structure of the imprinted binding-site was not sufficiently characterised by spectroscopic methods. We have succeeded in the preparation of porous thin films by casting a specific water–THF solution of poly(vinyl chloride-*co*-acrylic acid) [Poly(VC-*co*-AA)] and in the spectrophotometric characterisation of the metal imprinting and re-binding processes. The results have clearly disclosed how the memory is imprinted and how the re-binding takes place onto the film surface.

$$-\left(\underset{\mathrm{Cl}}{\mathrm{CH}}-\mathrm{CH_2}\right)_{97.5}\left(\underset{\mathrm{COOH}}{\mathrm{CH}}-\mathrm{CH_2}\right)_{2.5}-$$

Poly(VC-*co*-AA)

Results and discussion

Preparation of porous thin films

In order to prepare porous thin films with which one can acquire a wide surface area, a water–THF mixed solvent was chosen. When the Poly(VC-*co*-AA) solution was cast on a flat polyethylene (PE) plate and uniformly spread with a glass bar, THF (a good solvent) volatilised first to produce a thin film structure and remaining water (a poor solvent) in the film created pores. By this casting method we obtained thin films with 10 µm thickness. Scanning electron microscope (SEM) photographs of the air side and the PE plate side of the resulting films are shown in Fig. 1. It is seen from Fig. 1 that the film surface of the PE side is relatively flat, whereas the surface of the air side has plenty of pores (0.5–5 µm). These cavities are constructed by water droplets generated after volatilisation of THF. When a thin film was prepared from a THF solution of Poly(VC-*co*-AA), even the air side of the film was flat and had no pores. The difference clearly indicates the importance of concomitant water in the casting solvent. We found that the optimum ratio of water *versus* THF is 10:90 wt/wt; below 10 wt% the surface of the air side becomes flatter and above 10 wt% the solution tends to form precipitate.

The surface morphology is scarcely affected by the presence of template metal cations (see Fig. 1). One can expect, however, that the method of casting from a water–THF mixed solution possesses a critical advantage over that from a THF solution in the metal-imprinting efficiency. When the metal-containing THF solution was cast, most metal-complexed sites would be trapped inside the film. In contrast, when the metal-containing mixed solution was cast, the polar metal-complexed sites would be placed onto the interface where water droplets are trapped. This difference should lead to an advantage for the porous thin film in the removal of imprinted metal cations. Furthermore, this method would increase the concentration of the effective metal-binding site on the thin film surface.

Spectroscopic characterisation of thin films

The metal-imprinted thin films were prepared in the absence or the presence of NaOH according to the following method. Poly(VC-*co*-AA) (0.10 g) was dissolved in THF (1.0 g). In the absence of NaOH, water (0.10 cm^3) was added to this solution. Then water or an aqueous $Cu(NO_3)_2$ solution {10 mm^3, $[Cu(NO_3)_2] = 0.50$ mol dm^{-3}} was further added to this mixture which was then cast on a PE plate. In the presence of NaOH, an aqueous 0.10 mol dm^{-3} NaOH solution (0.10 cm^3) was added to the polymer–THF solution. Then water or an aqueous metal solution {10 mm^3, $[Cu(NO_3)_2] = 0.50$ mol dm^{-3}, $[Fe(NO_3)_3]$ or $[La(NO_3)_3] = 0.33$ mol dm^{-3}} was further added to this mixture which was then cast on a PE plate.

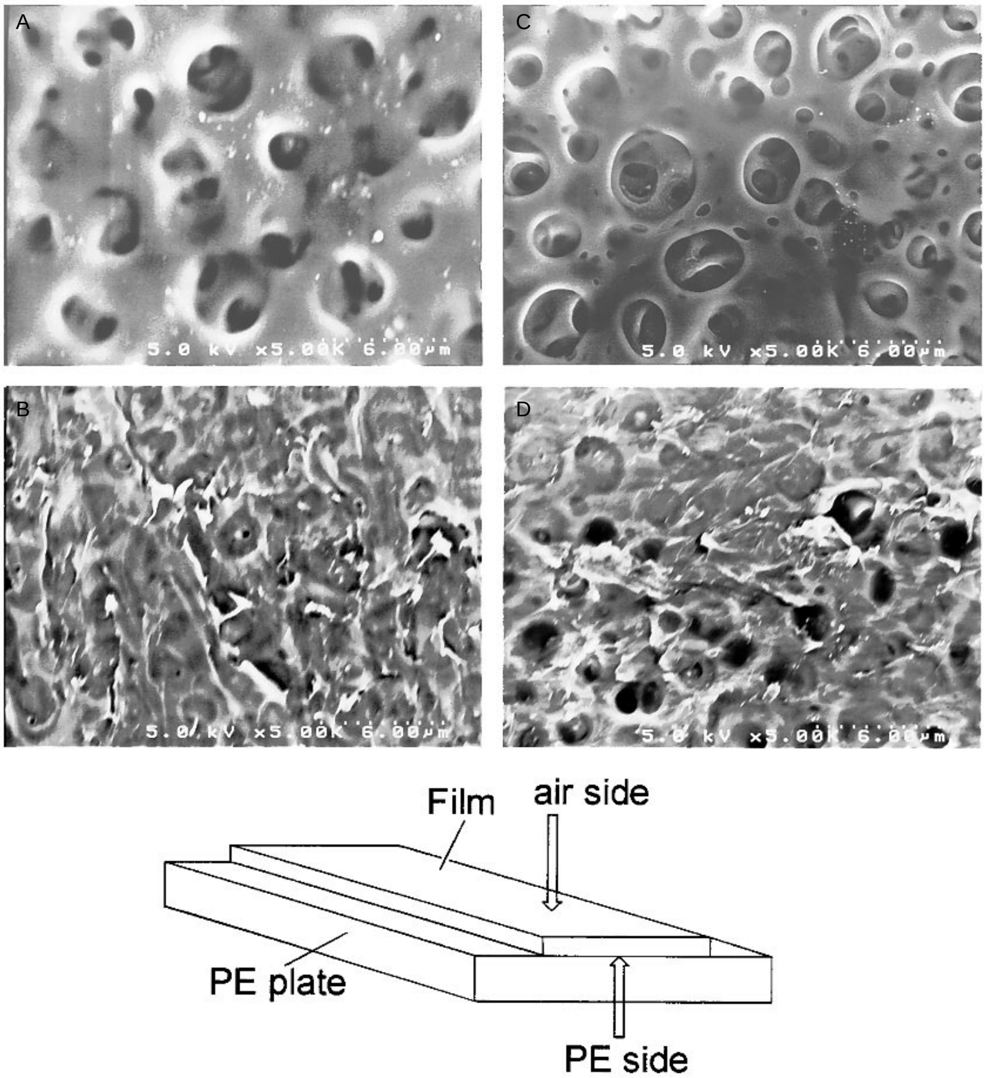

Fig. 1 SEM photographs of the Cu^{2+}-imprinted (A, B) and unimprinted (C, D) films: the upper ones, (A) and (C), are the air side whereas the lower ones, (B) and (D), are the PE plate side

The distribution of carboxylic acid groups was characterised by FTIR spectroscopy. The thin film prepared in the absence of NaOH gave two carbonyl peaks at 1747 and 1710 cm^{-1}, which are assigned to monomeric and dimeric carboxylic acids, respectively (solid line in Fig. 2A). When this film was washed with a methanolic 0.10 mol dm^{-3} HNO_3 solution, two carboxylic acid peaks were scarcely affected (solid line in Fig. 2B). When $Cu(NO_3)_2$ was added to the neutral cast solution, a new peak appeared at 1620 cm^{-1} which is assignable to $COO^-{\cdot}Cu^{2+}$ (dotted line in Fig. 2A).[13] This peak nearly disappeared with HNO_3 treatment, indicating that Cu^{2+} can be extracted out of the thin film (dotted line in Fig. 2B).

In the presence of NaOH, the thin film gave a broad carbonyl peak around 1570 cm^{-1} for $COO^-{\cdot}Na^+$ (solid line in Fig. 3A).[14] When this film was washed with a methanolic 0.10 mol dm^{-3} HNO_3 solution, the weak peak disappeared while a peak at 1747 cm^{-1} which is attributable to monomeric carboxylic acid became stronger (solid line in Fig. 3B). The peak for dimeric carboxylic acid (1710 cm^{-1}) was just observable as a shoulder in the 1747 cm^{-1} peak. The comparison with Fig. 2B indicates the following: (i) the COOH group tends to dimerise owing to the hydrogen-bonding interaction and (ii) the $COO^-{\cdot}Na^+$ group is discretely dispersed in the film and trapped as an isolated COOH group after the HNO_3 treatment. When $Cu(NO_3)_2$ was added to the alkaline cast solution, a strong $COO^-{\cdot}Cu^{2+}$ peak appeared at 1620 cm^{-1} (dotted line in Fig. 3A). When this film was washed with a methanolic 0.10 mol dm^{-3} HNO_3 solution, the 1620 cm^{-1} peak became very weak while a dimeric carboxylic acid peak at 1710 cm^{-1} was selectively intensified (dotted line in Fig. 3B). The results indicate that Cu^{2+} can gather two carboxylic acids to construct preorganised binding-sites for Cu^{2+} which remain as dimeric carboxylic acids even after removal of Cu^{2+}.

Similar experiments were performed with trivalent metal ions. We chose Fe^{3+} and La^{3+} which tend to adopt a coordination structure different from the square-planar Cu^{2+} complex. When the films were prepared from alkaline solution, the carbonyl peaks ascribable to $COO^-{\cdot}Fe^{3+}$ and $COO^-{\cdot}La^{3+}$ appeared at 1595 and 1545 cm^{-1}, respectively. When the Fe^{3+}-imprinted film was washed with a methanolic 0.10 mol dm^{-3} HNO_3 solution, the $COO^-{\cdot}Fe^{3+}$ peak intensity did not decrease. We used neutral EDTA solution instead of a methanolic HNO_3 solution but could not extract Fe^{3+} out of the film. On the other hand, when the La^{3+}-imprinted film was subjected to similar HNO_3 treatment, the $COO^-{\cdot}La^{3+}$ peak totally disappeared and a new peak ascribable to dimeric carboxylic acid appeared at 1710 cm^{-1}. The difficulty in the extraction of imprinted Fe^{3+} ions may be rationalised by two different explanations. (i) The metal complex is trapped deeply inside the film or (ii) the stability constants are too large to remove the metal ion by solid (film)–liquid extraction. In the present system, the second rationale is more likely because the order of the stability constants[15] for the bis-acetato complexes is $Fe^{3+} \gg Cu^{2+} > La^{3+}$. This implies that the stability constant for Fe^{3+} is too large for it to be removed by solid–liquid extraction.

The foregoing results indicate that the metal ion useful for

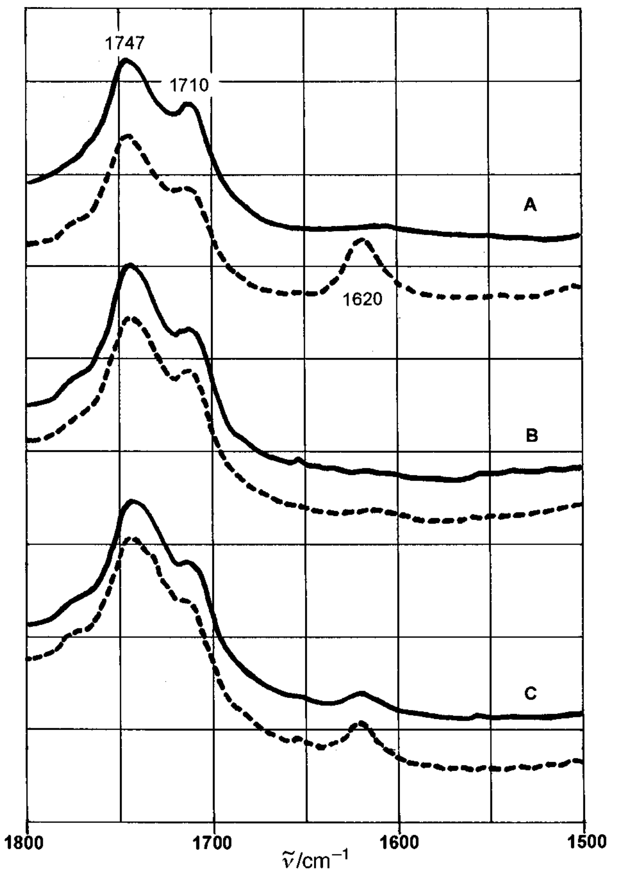

Fig. 2 Partial FTIR spectra of the thin films prepared from neutral solution. The solid lines denote the thin film in the absence of template $Cu(NO_3)_2$ whereas the dotted lines denote the thin film in the presence of template $Cu(NO_3)_2$: (A) cast from NaOH-containing water–THF solution and washed with a water–MeOH (1 : 9 w/w) mixed solvent for 10 h, (B) after washing with a methanolic 0.10 mol dm^{-3} HNO_3 for 10 h and (C) after immersion in methanolic 1.0 mmol dm^{-3} $Cu(NO_3)_2$ for 10 h.

metal-imprinting must have a 'moderate' stability constant: it should be large enough to allow efficient deposition in the metal-imprinting process but it should be small enough to allow efficient extraction in the de-metallation.

Stoichiometry of the imprinted metal complexes

In order to obtain a stoichiometrical insight into the metal-imprinting process, we measured the $COO^-{\cdot}M^{n+}$ ($M^{n+} = Cu^{2+}$, Fe^{3+} and La^{3+}) peak intensity in the FTIR spectra as a function of the metal concentration in the cast solution. As shown in Fig. 4A, the peak intensity was saturated at $[Cu(NO_3)_2]/[NaOH] = 0.5$. This ratio indicates that the imprinted Cu^{2+} undergoes the coordination of two COO^- groups and the complex has the stoichiometry $(RCOO^-)_2{\cdot}Cu^{2+}$. Surprisingly, a similar saturation curve with a break-point at $[Fe(NO_3)_3]/[NaOH] = 0.5$ was also obtained from the $Fe(NO_3)_3$ system (Fig. 4B). The result suggests that the imprinted Fe^{3+} complex consists of $(RCOO^-)_2{\cdot}Fe^{3+}{\cdot}X^-$ ($X^- = NO_3^-$ or OH^-). It is not yet clear why $(RCOO^-)_3{\cdot}Fe^{3+}$ is not formed as an imprinting species. Presumably, the $(RCOO^-)_2{\cdot}Fe^{3+}{\cdot}X^-$ species is already stable enough to be buried in the film phase (judging from the difficulty of its removal) or the local concentration of the carboxylic acid group is too low to gather three ligands. We applied the same technique to $La(NO_3)_3$ but could not observe a clear break-point due to the broad peak for $RCOO^-{\cdot}La^{3+}$.

Evaluation of the metal re-binding ability

The metal re-binding ability was tested for the Cu^{2+}- or La^{3+}-imprinted and unimprinted films. The FTIR spectrum of the La^{3+}-imprinted film changed only slightly even after immersion

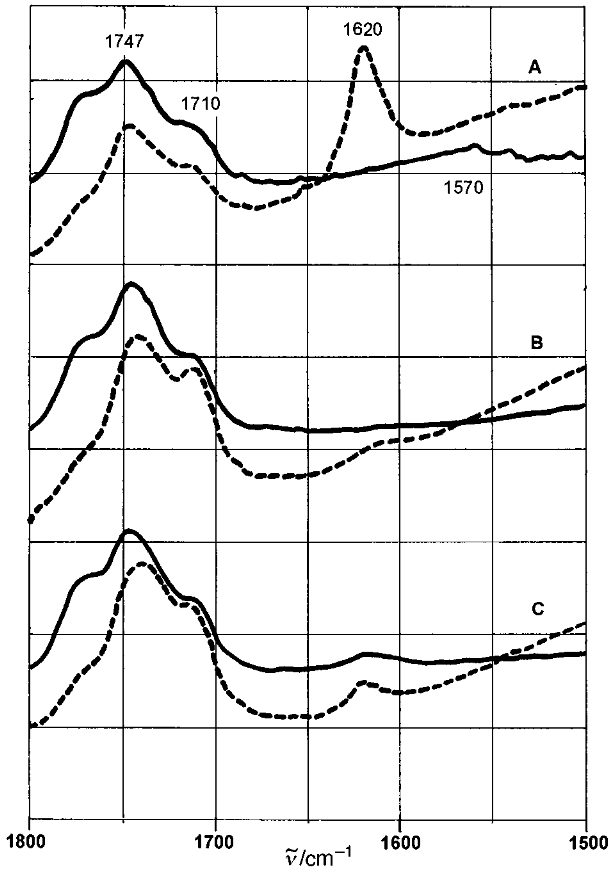

Fig. 3 Partial FTIR spectra of the thin films prepared from alkaline solution. The explanations are recorded in the caption to Fig. 2.

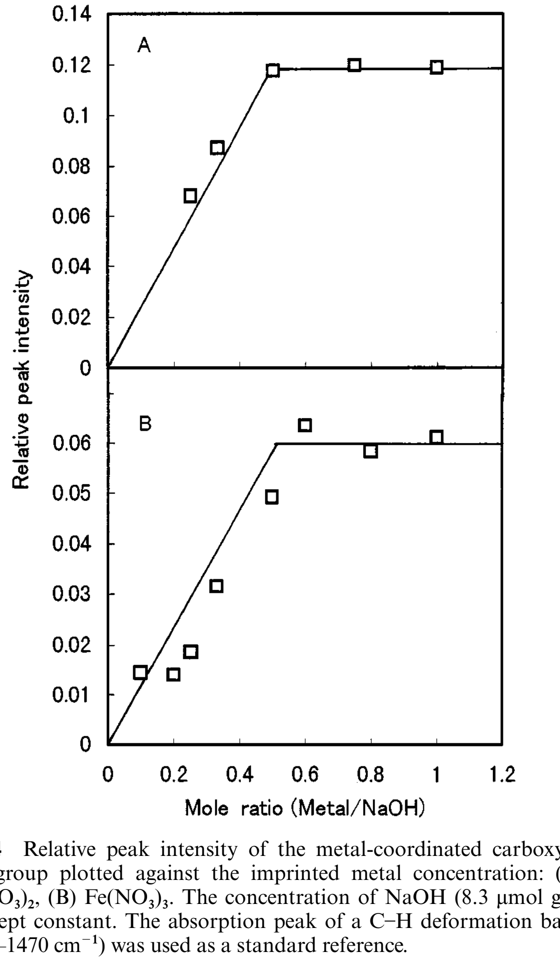

Fig. 4 Relative peak intensity of the metal-coordinated carboxylic acid group plotted against the imprinted metal concentration: (A) $Cu(NO_3)_2$, (B) $Fe(NO_3)_3$. The concentration of NaOH (8.3 µmol g^{-1}) was kept constant. The absorption peak of a C–H deformation band (1400–1470 cm^{-1}) was used as a standard reference.

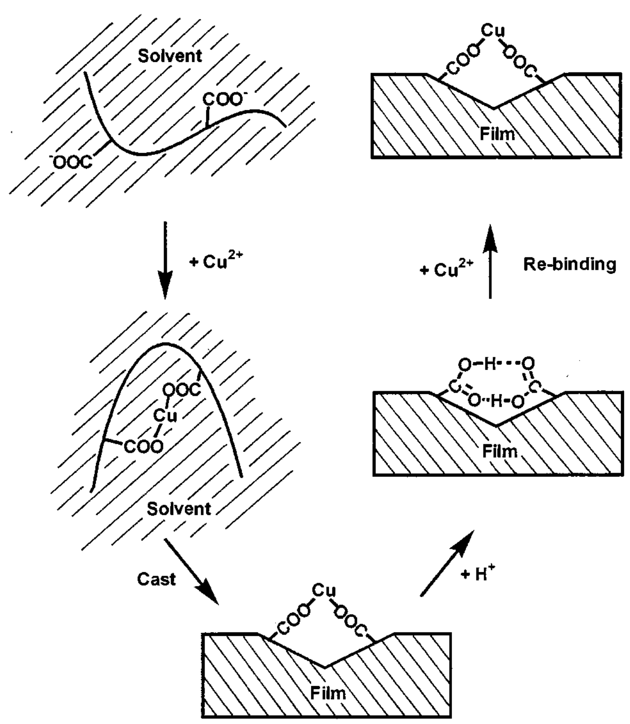

Fig. 5 Schematic representation of the Cu^{2+} imprinting and re-binding processes for a thin film prepared from alkaline solution

in a MeOH solution containing $La(NO_3)_3$ (1.0 mmol dm^{-3}). The poor re-binding ability is associated with the low stability constant and the less preorganised carboxylic acid groups. We thus decided to evaluate the '*memory effect*' by comparing the Cu^{2+}-imprinted film with the unimprinted film in the Cu^{2+} re-binding process.

To quantitatively estimate the Cu^{2+} concentration present in the film phase by FTIR spectroscopy we prepared a calibration curve from cast films containing known amounts of $Cu(NO_3)_2$. We found that the peak area (1620 cm^{-1} for $COO^-{\cdot}Cu^{2+}$) is linearly proportional to the $Cu(NO_3)_2$ concentration in the range 0–30 μmol g^{-1}. In the Cu^{2+}-imprinted film prepared from alkaline solution, the Cu^{2+} concentration after the HNO_3 treatment was 2.9 μmol g^{-1} (dotted line in Fig. 3B). It increased up to 8.6 μmol g^{-1} after immersion in the $Cu(NO_3)_2$ solution (1.0 mmol dm^{-3}; dotted line in Fig. 3C). Thus, the re-binding capacity maintaining the memory for original template Cu^{2+} was estimated to be 5.7 μmol g^{-1}. On the other hand, the re-binding capacity for the unimprinted film was estimated to be 4.6 μmol g^{-1} (solid line in Fig. 3C). The difference (1.1 μmol g^{-1}) is ascribable to the metal-template effect. In the film prepared from the neutral solution, the re-binding capacity maintaining the memory for original template Cu^{2+} was estimated to be 12.2 μmol g^{-1} (dotted line in Fig. 2C). In contrast, the re-binding capacity for the unimprinted film was estimated to be 6.5 μmol g^{-1} (solid line in Fig. 2C). Provided that all carboxylic acid groups form the $(RCOO^-)_2{\cdot}Cu^{2+}$ complex, 6.0 and 3.2% of all carboxylic acid groups are used for the reversible Cu^{2+} ion binding in the Cu^{2+}-imprinted and the unimprinted films, respectively. One can thus conclude that the difference (5.7 μmol g^{-1}: 2.8% of all carboxylic acid groups) is created by the metal-imprinting effect.[16] These Cu^{2+} imprinting and re-binding processes are illustrated in Fig. 5.

It is quite understandable that the Cu^{2+} template effect was observed for the thin film prepared from alkaline solution, because the $COO^-{\cdot}Na^+$ groups tend to disperse discretely while they gather together in the presence of Cu^{2+}. In fact, however, the larger Cu^{2+} imprinting effect was observed for the thin film prepared from the neutral solution. Conceivably, the dimeric carboxylic acid groups associated by the hydrogen-bonding interaction are not very efficient as a Cu^{2+}-binding site whereas the two carboxylic acid groups preorganised by Cu^{2+} (*e.g.*, into a square-planar coordination structure) can act as an efficient Cu^{2+}-binding site.

Conclusion

The present study showed that the thin film system is very advantageous to facile metal-imprinting: *i.e.* the wide surface area useful for the metal-imprinting is secured, the imprinted metal ion is easily removed from the film and the metal imprinting and re-binding processes are conveniently monitored by the spectroscopic method. One must note, however, that only a metal ion with a '*moderate*' stability constant can be loaded by this method. The results imply that polymerisation is not obligatory to construct the memory for the original template ions and molecules. Further studies are currently continuing in this laboratory.

Experimental

Poly(VC-*co*-AA) was purchased from Aldrich. The SEM pictures were taken with a Hitachi S-4500 scanning electron microscope and the infrared spectra were measured with a Shimadzu FT-IR 8100M spectrophotometer.

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