Acrylic Copolymers with Pendant 1,2,4-Triazole Moieties as Colorimetric Sensory Materials and Solid Phases for the Removal and Sensing of Cations from Aqueous Media

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ABSTRACT: Linear water-soluble polymers and nets with gel-like behavior were prepared for use as colorimetric sensors and selective extracting agents for naked eye detection and solid–liquid removal of heavy-metal cations from aqueous environments. Triazole is a well-known, heavy-metal cation host. A water-insoluble methacrylamide containing a 1,2,4-triazole receptor derivative was copolymerized with highly hydrophilic and water-soluble methacrylamides to yield a water-soluble polymer or a cross-linked network as a powder or a dense membrane. In powder form, the material selectively removed Hg^{2+}, Pb^{2+}, and Ag^{+} from aqueous media. In the form of swelled dense membranes or films, the material acted as colorimetric sensor for Fe^{3+}. When the membrane was soaked in a yellow aqueous solution of Fe^{3+}, the former colorless, transparent membrane became reddish (but retained its transparency), and the solution became colorless. Aqueous conductivity studies confirmed that both the extraction and the sensing phenomena arose from the interaction of the cations with the triazole moieties. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3817–3825, 2011

KEYWORDS: acrylic polymers; cation elimination; cation sensing; copolymers; membranes; metal-polymer complexes; polymethacrylamides; sensory materials; solid–liquid extraction; supramolecular structures; water-soluble polymers

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INTRODUCTION The selective and reversible interaction of chemical species in aqueous media is a key event in biological systems. The recognition processes, which arise from these selective, highly directional, and weak interactions play a major role in the activity of enzymes, the identification of an antigen by an antibody, the discovery of a drug for a specific biological target, and many other applications.[1–5]

The development of organic and organometallic receptors, in an effort to mimic Nature, gave rise to host–guest or supramolecular chemistry.[6–9] Within this broader area of study, the field of chemosensing is focused on selective interactions that produce a measurable macroscopic signal. Chemosensors have promising possible applications to the fast, cheap detection of chemicals, but their uses are often limited to solution systems in organic media, because most of the sensory molecules have very low aqueous solubility, and they have a lack of mechanical properties that impair the preparation of finished sensory devices.[10]

To overcome these problems with discrete organic or organometallic chemosensors, we propose to use polymers with receptor moieties chemically anchored to the polymer structure.[10–22] Previously, this approach has been undertaken by several other research groups.[10,23–33] We have prepared a water-insoluble methacrylamide containing a triazole receptor and an acid group that we have copolymerized with highly hydrophilic comonomers to yield either a linear, water-soluble, polymer or cross-linked water-swellable gels in two form: as a powder and as a dense membrane or film.

The triazole heterocycle is a well-known cationic receptor.[14,34–48] Our materials interact selectively with heavy-metal cations, allowing them to function as (a) excellent agents for the removal of poisonous Hg^{2+} and Pb^{2+} from effluent water via solid–liquid extraction and (b) colorimetric sensory materials for the naked-eye detection and titration of aqueous Fe^{3+}.

EXPERIMENTAL

All materials and solvents were commercially available and were used as received, unless otherwise indicated. *N*-Methyl-2-pyrrolidone (NMP, Merck) was vacuum distilled over phosphorus pentoxide twice, then stored over 4 Å molecular sieves. 2-Ethoxyethyl methacrylate (EEMA; 99%, Aldrich) was vacuum distilled. Pyridine (Merck) was dried under reflux over sodium hydroxide for 24 h and distilled over 4 Å molecular sieves. Azo-bis-isobutyronitrile (AIBN, Aldrich) was recrystallized twice from methanol.

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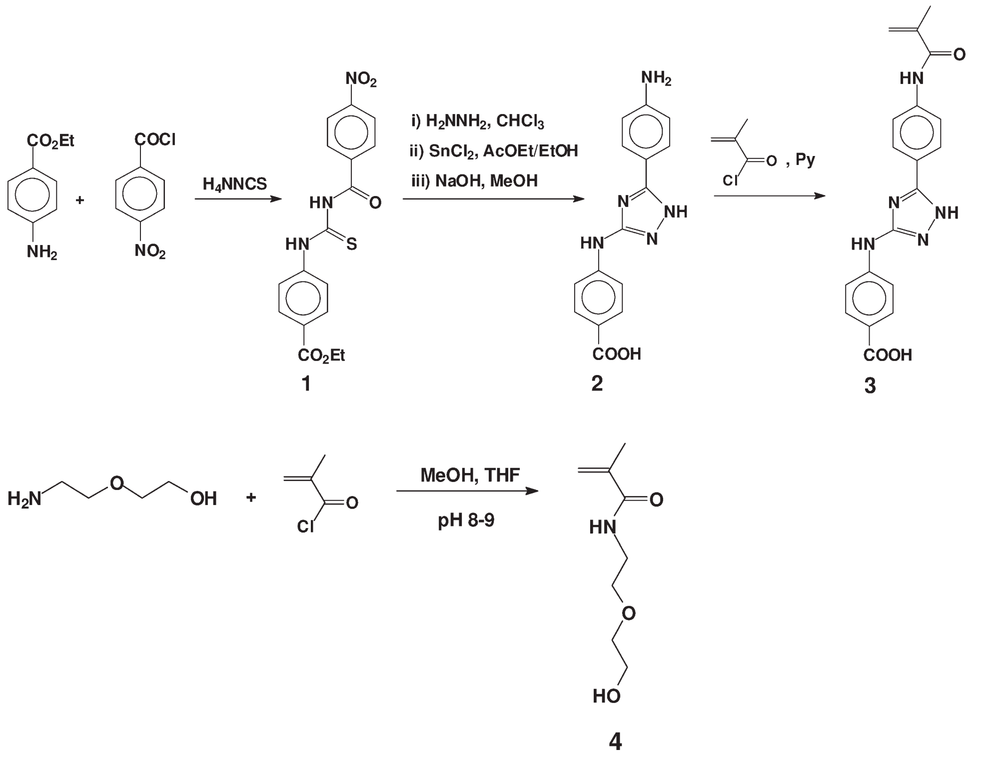


SCHEME 1 Monomer synthesis.

Intermediates and Monomers

The intermediates and monomers were prepared as depicted in Scheme 1. Ethyl 4-(3-(4-nitrobenzoyl)thioureido)benzoate (**1**) and 4-((5-(4-aminophenyl)-1H-1,2,4-triazol-3-yl)amino)-benzoic acid (**2**) were prepared according to the procedures that are described previously.[17]

4-((5-(4-(Methacrylamidophenyl)-1H-1,2,4-triazol-3-yl)-amino)Benzoic Acid (3)

A double-neck, 50-mL-round flask was fitted with a magnetic stir bar, and a condenser was loaded with 5 mmol of 4-((5-(4-aminophenyl)-1*H*-1,2,4-triazol-3-yl)amino)benzoic acid and 15 mL of pyridine. Then, 7.5 mmol of methacryloyl chloride was added dropwise, and the reaction mixture was stirred for 3 h at room temperature (rt). Afterward, the solution was added dropwise to 5% aqueous HCl solution in an ice bath to precipitate the product. The solid was collected by filtration, washed thoroughly with water, and dried in a vacuum oven at 80 °C overnight.

Yield: 97%. M.p.: 285 °C (d). ^{1}H-NMR δ_H (400 MHz, DMSO-d_6, Me_4Si): 13.78 and 12.47 (each signal: 1H, br s, COOH/NH); 10.05 (1H, s, NH); 9.83 (1H, s, NH); 7.96 (2H, d, *J* 8.4, Ph); 7.90–7.88 (4H, m, Ph); 7.69 (2H, d, *J* 8.0 , Ph), 5.88 (1H, s, CH_2), 5.60 (1H, s, CH_2) 2.01 (3H, s, CH_3). ^{13}C-NMR, δ_C (100.6 MHz, DMSO-d_6, Me_4Si): 168.20, 167.94, 160.74, 153.55, 147.01, 141.50, 141.20, 131.61, 127.26, 123.18, 121.75, 121.27, 121.07, 115.83, 19.64. EI-LRMS *m/z*: 363 (M^+, 100), 319 (48), 294 (12), 277 (18), 259 (5), 187 (6), 118 (6), 77 (15), 69 (59). FT-IR [wavenumbers (cm^{-1})]: $\nu_{N—H}$: 3306; $\nu_{acid\ O—H}$: broadband (3096, 2871); $\nu_{C═O}$:1676; $\delta_{N—H}$:1604; $\nu_{Ar\ C═C}$: 1516; $\nu_{C═N}$: 1547.

2-(2-Aminoethoxyethanol) Methacrylamide (4)[49]

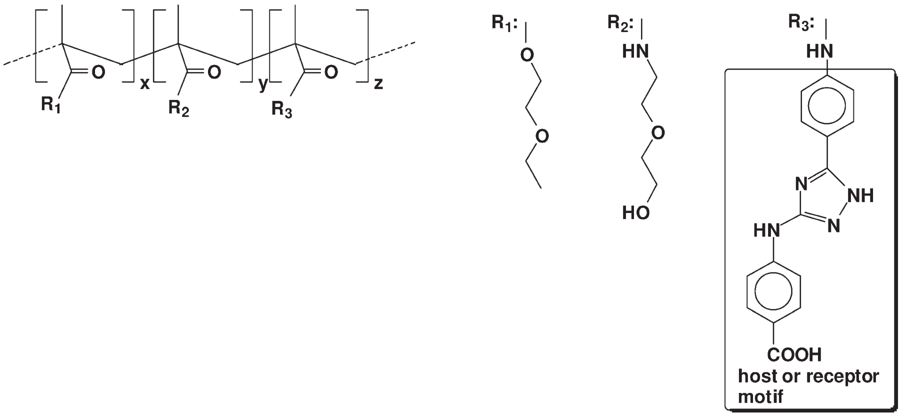
A sample of 25 mmol of methacryloyl chloride was diluted in 20 mL of tetrahydrofuran (THF) under a nitrogen blanket, then slowly added to 20 mL of an ice-cold, methanolic solution of 2-(2-aminoethoxyethanol) (24 mmol). A 1 M aqueous solution of KOH was added to maintain a pH of 8–9 throughout the reaction. The mixture was warmed to room temperature over 4 h. Afterward, it was quenched by addition of HCl to a final pH of 5, and the product was concentrated by distillation. NaCl was added to the crude residue, and the mixture was extracted with dichloromethane. The organic layer was dried with magnesium sulfate, filtered, and concentrated by solvent distillation under vacuum at room temperature, and the final traces of solvent were eliminated by bubbling dry nitrogen to yield the product.

Yield: 97%. ^{1}H-NMR δ_H (400 MHz, DMSO-d_6, Me_4Si): 8.04 (1H, s, NH); 5.66 (1H, s, CH_2); 5.26 (1H, s, CH_2); 4.48 (1H, s, OH); 1.88 (3H, s, CH_3). ^{13}C-NMR, δ_C (100.6 MHz, DMSO-d_6, Me_4Si): 169.34, 139.72, 120.37, 72.42, 69.85, 61.61, 53.65, 39.84. EI-LRMS *m/z*: 174 ($[M+H]^+$, 10), 113 (12), 112 (26), 111 (21), 98 (25), 69 (100), 45 (30), 44 (17), 41 (54), FT-IR [wavenumbers (cm^{-1})]: $\nu_{N—H,\ O—H}$: broadband (3503, 2489) $\nu_{C═O}$:1704; $\delta_{N—H}$:1606.

Polymer Synthesis

Three different copolymers ($\mathbf{I_{COOH}}$, $\mathbf{II_{COOH}}$, and $\mathbf{III_{COOH}}$) were prepared by radical copolymerization of mixtures of the three different comonomers (see Table 1) using ethylene glycol dimethacrylate as a cross-linking agent to obtain the cross-linked materials ($\mathbf{II_{COOH}}$ and $\mathbf{III_{COOH}}$) and AIBN (1.5 mol %) as a radical thermal initiator.

TABLE 1 Chemical Structure of Copolymers



Copolymers	Type	Physical Appearance	$R_1(x)$[a]	$R_2(y)$[a]	$R_3(z)$[a]	CLA[b]	WSP[c]
I$_{\mathbf{COOH}}$[d]	Linear, water soluble	Powder	–	95	5	–	–
II$_{\mathbf{COOH}}$	Cross-linked	Powder	–	95	5	5	–
III$_{\mathbf{COOH}}$	Cross-linked	Membrane or film	30	69	1	1	170

[a] Molar composition ratio of the monomers used for the preparation of the copolymers.

[b] molar percentage of cross-linking agent (1,2-ethanediol-dimethacrylate).

[c] Water-swelling percentage: weight percentage of water uptake by the films upon soaking in pure water until equilibrium.

[d] $M_n = 3.6 \times 10^4$ g mol^{-1}, $M_w/M_n = 1.71$ [number–average molecular weight (M_n), and weight-average molecular weight (M_w) were determined by gel permeation chromatography using DMF (1% LiBr, 70 °C) as the eluent on the basis of standard poly(methyl methacrylate) calibration].

Linear copolymethacrylamide (**I**$_{\mathbf{COOH}}$) was prepared by radical polymerization of the hydrophilic monomer 2-(2-aminoethoxyethanol) methacrylamide (**4**) and the heterocycle-containing methacrylamide monomer (**3**) in a 95/5 molar ratio as follows: 0.15 mmol of methacrylamide (**3**), 2.85 mmol of methacrylamide (**4**), and 0.075 mmol of AIBN were dissolved in 1.5 mL of dry NMP in an oxygen-free atmosphere and kept at 65 °C for 5 h. The solution was then precipitated in cold acetone. The polymer thus obtained was collected by filtration and purified by dissolved in methanol and reprecipitated in cold acetone, after which it was dried in a vacuum oven at 40 °C overnight.

Cross-linked copolymethacrylamide **II**$_{\mathbf{COOH}}$, used as a solid extraction phase, as described later, was prepared as follows: 0.15 mmol of methacrylamide (**3**) was dissolved in 0.5 mL of dry NMP in a cylindrical mold, then 2.850 mmol of methacrylamide (**4**), 0.150 mmol of ethylene glycol dimethacrylate, and 0.075 mmol of AIBN were added in an oxygen-free atmosphere and kept at 65 °C for 5 h. The solid thus obtained was extracted with methanol for 24 h in a Soxhlet apparatus, dried in a vacuum oven at 60 °C overnight, and crushed to obtain a powdered material.

Films, or dense membranes, having the composition of **II**$_{\mathbf{COOH}}$ prepared by bulk polymerization did not display good mechanical properties after swelling with water. To overcome this problem, copolymer film **III**$_{\mathbf{COOH}}$ was prepared by polymerization of a mixture of the hydrophobic monomer EEMA and the hydrophilic monomer **4** (30:69 mol), using 1% (mol) of the cross-linking agent (ethylene glycol dimethacrylate). This film exhibited excellent mechanical properties, even after swelling with water. To prepare the dense membrane, the reaction was carried out in a 100-μm thick silanized glass mold in an oxygen-free atmosphere at 65 °C for 5 h.

To study the influence of the electronic environment of the triazol moiety on the effectiveness of extraction, the carboxylic acid moiety, which is chemically linked to the heterocycle through a benzene ring, was deprotonated. Cross-linked copolymer **II**$_{\mathbf{COOH}}$ was stirred in 15% aqueous Na_2CO_3 for 30 min, filtered off, and repeatedly washed with distilled water until the pH of the washes was neutral. Then, it was dried in a vacuum oven at 60 °C overnight and crushed to obtain a powder (**II**$_{\mathbf{COO^-}}$). The deprotonation of the film **II**$_{\mathbf{COOH}}$ was accomplished following a similar procedure, without the final crushing, to yield the membrane **III**$_{\mathbf{COO^-}}$. Linear polymethacrylamide **I**$_{\mathbf{COOH}}$ was dissolved in 15% aqueous Na_2CO_3, and the solution was added dropwise to a cold water/acetone mixture (30:70 v/v) to precipitate the deprotonated polymer, **I**$_{\mathbf{COO^-}}$. This material was used to tune and test the deprotonation procedure.

Measurements

^{1}H- and ^{13}C-NMR spectra were recorded with a Varian Inova 400 spectrometer operating at 399.92 and 100.57 MHz, with deuterated dimethylsulfoxide (DMSO-d_6) as solvent.

Infrared spectra (FT-IR) were recorded with a Nicolet Impact spectrometer.

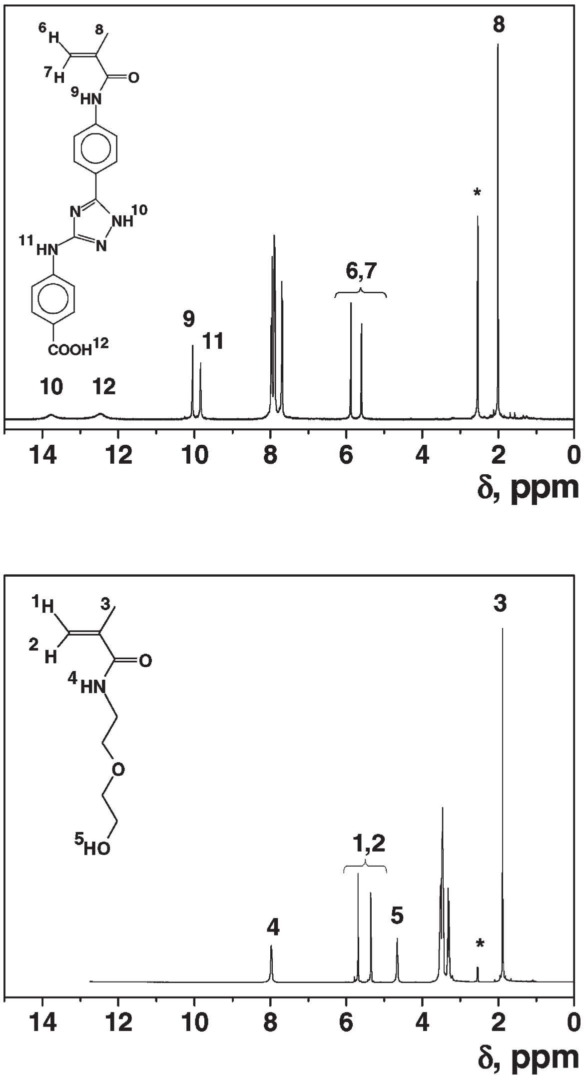


FIGURE 1 ^{1}H-NMR spectra of monomers **3** (top) and **4** (bottom) in DMSO-d_6 (* = solvent signals).

Thermogravimetric analysis (TGA) of a 5 mg sample was performed under a nitrogen or oxygen atmosphere on a TA Instrument Q50 TGA analyzer at a scan rate of 10 °C min^{-1}.

The solid–liquid extraction of Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} as the nitrate or chloride salt was carried out as follows: ~10 mg of the copolymethacrylamide $\mathbf{II}_{\mathbf{COOH}}$ or deprotonated polymethacrylamide $\mathbf{II}_{\mathbf{COO^-}}$ was shaken with 1 mL of an aqueous solution of the metal salt for a week at 25 °C. The molar ratio of each cation to the triazol heterocycle subunits was 1:1. After filtration, the concentration of each cation in the liquid phase was determined by inductively coupled plasma mass spectrometry (Agilent 7500 i), and direct information regarding the percentage of extraction of the metal ions by the polyamides was obtained. Consecutive dilutions of sample aliquots with ultra pure water/nitric acid (5% v/v) were performed to reach concentrations in the range of the calibration curve (0–40 ppb).

RESULTS AND DISCUSSION

Monomer and Polymer Synthesis and Characterization

A straightforward synthesis following common organic procedures yielded the methacrylamide comonomers **3** and **4** in high purity. The NMR spectra of the monomers, shown in Figure 1, display a clean pattern with signals corresponding to the expected chemical structure of the monomers.

The polymeric materials were prepared in two different architectures: as linear, water-soluble polymers and as cross-linked polymer networks. The cross-linked materials, in turn, had two forms: a powder and a film or dense membrane, both of which displayed gel-like behavior.

The linear copolymer $\mathbf{I}_{\mathbf{COOH}}$ was obtained by conventional radical polymerization in solution, followed by precipitation in a nonsolvent. It was purified by solvation/reprecipitation to yield a water-soluble powder. Figure 2 shows the ^{1}H-NMR spectrum of the copolymer; the signals of the monomer containing the triazole core are amplified and assigned. Integration of the spectrum confirmed that the molar ratio of monomer **3** to monomer **4** within the copolymers corresponded to the feed ratio used in the synthesis (5:95). The feed molar ratio was chosen to produce a water-soluble polymer with a high content of the water-insoluble triazole-containing monomer **3**, but an increase in the content of **3** beyond this value gave rise to water-insoluble material. Treatment of $\mathbf{I}_{\mathbf{COOH}}$ with a base to deprotonate the acid functionality produced the polymer $\mathbf{I}_{\mathbf{COO^-}}$. Deprotonation caused the polymer to become insoluble in organic solvents, such as DMSO, but obviously did not affect the solubility in water.

The cross-linked polymers were prepared by bulk radical polymerization using 1,2-ethanedioldimethacrylate as the cross-linking agent. To obtain the powder form of the material, $\mathbf{II}_{\mathbf{COOH}}$, the cross-linking agent was added to a final molar content of 5%, along with a small amount of NMP to promote solubility, keeping the same 5:95 ratio of comonomers **3–4** as in the linear copolymer **I** (Table 1). Figure 3 shows the IR-FT spectrum of $\mathbf{II}_{\mathbf{COOH}}$ with assignments of relevant

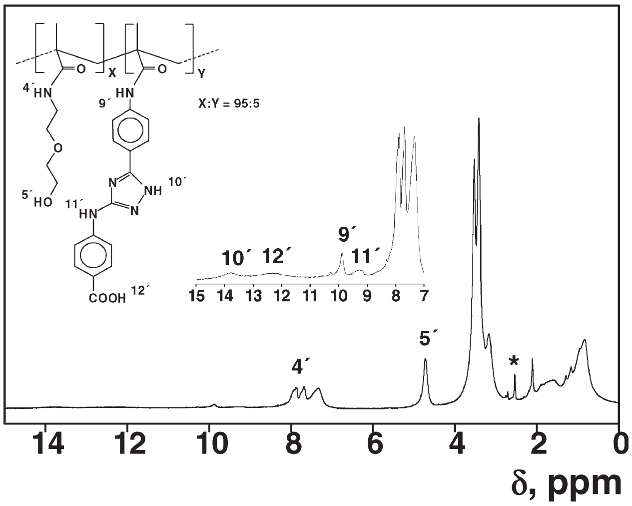


FIGURE 2 ^{1}H-NMR spectrum of polymer $\mathbf{I}_{\mathbf{COOH}}$ in DMSO-d_6 (* = solvent signal).

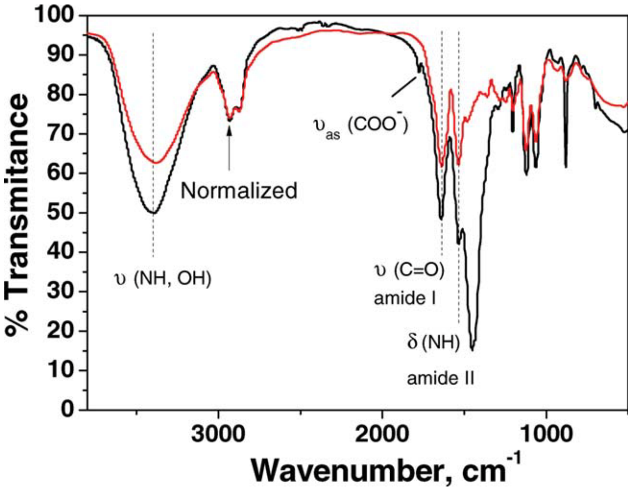


FIGURE 3 Normalized FT-IR spectra of polymers **II**:**II$_{COOH}$** (red line) and **II$_{COO^-}$** (black line). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

stretching and bending bands corresponding to the functional groups of the copolymer structure. Treatment of **II$_{COOH}$** with a base deprotonated the acid functionality to give **II$_{COO^-}$**, and a clear change in the IR-FT spectrum was observed. A new shoulder corresponding to the asymmetric stretching of the carboxylate groups was detected.

The film, or dense membrane, forms of the material, **III$_{COOH}$**, were prepared with a lower content of triazole-containing monomer **3** to obtain films that could be analyzed by UV/vis spectroscopy. The hydrophobic monomer EEMA was used as comonomer to give tractable films following swelling with water. A lower content of the cross-linking agent was used so as to not excessively reduce the hydrophilic character, or gel behavior, of the membrane. The water uptake of the membrane, following soaking in pure water at rt until uptake equilibrium was reached, was 170% by weight (Table 1).[14] This result shows that water-solvated species, such as anions and cations, can access and interact with the isolated hydrophobic sensing motifs within the polymer structure via diffusion into the predominantly hydrophilic swelled membrane.

Properties of the Polymers

Thermal Properties

Thermal resistance is a key parameter of the suitability of organic materials for technological applications. The thermal resistance of polymers **I$_{COOH}$**, **II$_{COOH}$**, and **III$_{COOH}$** was evaluated by thermogravimetry, and the decomposition temperatures that resulted in 5% and 10% weight loss, T_5 and T_{10}, are shown in Table 2. The results indicate that the materials have from moderate to good thermal stability, in both inert and oxidizing atmospheres. The cross-linked materials exhibited higher degradation temperatures, because the thermal breakage of a bond is less probable to produce a volatile residue in a network than in a linear structure. The different thermal behaviors of the linear and cross-linked copolymers **I$_{COOH}$** and **II$_{COOH}$** are shown in Figure 4. The first degradation step corresponds broadly with the loss of part of the pendant aliphatic residue.

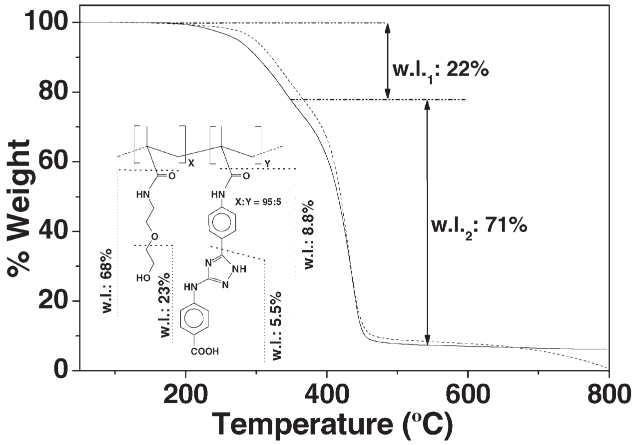


FIGURE 4 TGA of linear polymethacrylamide **I$_{COOH}$** (straight line) and cross-linked polymethacrylamide **II$_{COOH}$** (dashed line) in a nitrogen atmosphere (w.l.: weight loss percentage).

TABLE 2 Thermal TGA Data of the Polymers in an Inert (N_2) Atmosphere

Polymer	T_5[b] (°C)	T_{10}[c] (°C)	Char Yield (%)
I$_{COOH}$[a]	273 (262)	301 (293)	6.2 (0)
II$_{COOH}$	298	321	0.5
III$_{COOH}$	305	331	0.0

[a] Data shown in parentheses correspond to results in an oxidizing (O_2) atmosphere.

[b] 5% weight loss.

[c] 10% weight loss.

Hydrophilicity of the Polymers

Polymer structures need to have a highly hydrophilic character to be useful for solid–liquid extraction from aqueous

TABLE 3 Solid–Liquid Extraction of Metal Cations from Aqueous Solution by Solid-Phase Polymethacrylamide **II$_{COOH}$** and Its Deprotonated Derivative **II$_{COO^-}$** Extraction Percentage (% *E*), Distribution Coefficient (K_d), and Selectivity (α) Under Noncompetitive Conditions

	II$_{COOH}$			**II$_{COO^-}$**		
Salt	% *E*	K_d (L mol^{-1})	α ($K_{d_i}/K_{d_{Pb}}$)	% *E*	K_d (L mol^{-1})	α ($K_{d_i}/K_{d_{Pb}}$)
$Cr(NO_3)_3$	22	69	0.02	37	14×10	0.02
$Fe(NO_3)_3$	30	10×10	0.03	33	12×10	0.02
$Co(NO_3)_2$	34	13×10	0.04	44	19×10	0.02
$Ni(NO_3)_2$	10	28	0.01	43	18×10	0.02
$Cu(NO_3)_2$	25	22	0.01	74	69×10	0.09
$ZnCl_2$	12	33	0.01	37	14×10	0.02
$AgNO_3$	88	17×10^2	0.56	97	78×10^2	1.00
$Cd(NO_3)_2$	14	38	0.01	47	21×10	0.03
$Hg(NO_3)_2$	90	23×10^2	0.75	85	14×10^2	0.18
$Pb(NO_3)_2$	93	31×10^2	1.00	97	78×10^2	1.00

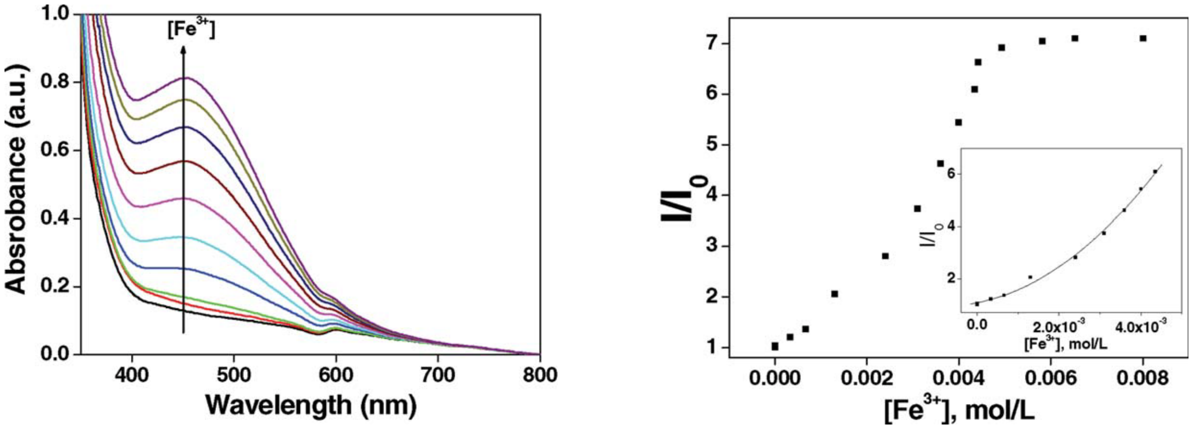


FIGURE 5 Left: UV/vis titration curve of film $\mathbf{III_{COOH}}$ with aqueous Fe^{3+}. Right: I/I_0 versus Fe^{3+} concentration at 455 nm; inset: expansion of the I/I_0 versus Fe^{3+} concentration curve. The reference was an aqueous solution of Fe^{3+} with the same concentration as that of the sample cuvette. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

media and to behave as sensory materials for the detection of water-solvated species. Because the highly hydrophilic monomer **4** was known to produce water-soluble linear polymers, we chose it as the high molar fraction comonomer for our materials, both linear and cross-linked. Upon increasing the molar content of water-insoluble monomer **3** relative to that of monomer **4** in the solution polymerization, starting at 1%, the linear polymer product remained water soluble until the content of **3** reached 5%.

The comonomer composition for membrane $\mathbf{III_{COOH}}$ was chosen to produce a material with good tractability after soaking in water, while maintaining a gel behavior. A hydrophobic comonomer, EEMA, was therefore added to the mixture of hydrophilic monomer **4** and triazole-containing monomer **3** along with the cross-linker to give the terpolymer. The molar content of the hydrophobic monomer was chosen to give films with good mechanical properties after swelling with water while maintaining the overall hydrophilic character of the membrane. The water-swelling percentage of $\mathbf{III_{COOH}}$ was 170% by weight, confirming the desired gel behavior of the material.

Applications of the Polymer

Solid–Liquid Extraction

A solid–liquid extraction takes place whenever a solution containing different target or guest molecules is in contact with a solid phase that can interact selectively with these guest molecules, thus acting as a solid host. In our materials, the heterocyclic triazole moieties of the solid polymethacrylamide act as host molecules for water-solvated cations. The selectivity and effectiveness of the extraction can be described in terms of the extraction percentage (% *E*) and the distribution coefficient (K_d). The distribution coefficient is a measure of the capacity of the material to extract cations under competitive conditions and is here defined as the ratio of the concentrations of the cation in both phases, eq 1, where *n* is the molar amount of polymer structural units and, *V* is the solution volume in liters.[17–22]

$$K_d = \left(\frac{\%E}{100 - \%E}\right)\left(\frac{V}{n}\right) \tag{1}$$

The solid–liquid extraction selectivity, $\alpha_{S,L}$, is the ratio of two distribution coefficients as shown in eq 2. The cation (Pb^{2+}) with the highest distribution coefficient ($K_{d_{M2}}$) is taken as the reference.

$$\alpha_{S,L} = \frac{K_{d_{M1}}}{K_{d_{M2}}} \tag{2}$$

The ability of the cross-linked powder material **II** to perform solid–liquid of heavy-metal cations from aqueous media was tested with both protonated and deprotonated pendant acid groups ($\mathbf{II_{COOH}}$ and $\mathbf{II_{COO^-}}$). The extraction of the environmentally deleterious cations Hg^{2+} and Pb^{2+} by $\mathbf{II_{COOH}}$ was significantly high, 90% or higher, and was selective with respect to other cations, although the extraction of Ag^+ was also noteworthy. The high extraction percentage of Hg^{2+} was consistent with the literature data regarding the favorable host–guest interaction between the triazole heterocycle and the mercury cation. Upon deprotonation of the polymer to give $\mathbf{II_{COO^-}}$, the extraction percentages of the majority of the cations increased significantly, probably because of electron pumping from the carboxylate group to the triazole moiety through the benzene ring.

Colorimetric Sensing of Fe^{3+} in Water Media

During the extraction experiments, the material $\mathbf{III_{COOH}}$ appeared to behave as a cation-sensor for Fe^{3+}. This polymeric material was initially colorless, but became reddish upon soaking in aqueous solutions containing Fe^{3+}. In contrast, the polymer remained completely colorless in the presence of the other cations tested in the extraction experiments.

To test the colorimetric cation-sensing ability of the polymer, increasing quantities of Fe^{3+} were added to a quartz UV/vis cell containing the $\mathbf{III_{COOH}}$ polymer film. As shown in Figure 5, the absorbance of the 455 nm band gradually increased as

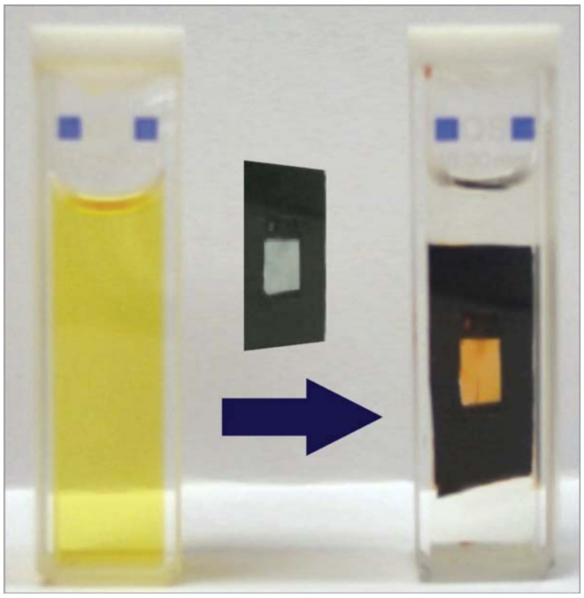


FIGURE 6 A cuvette containing 8 × 10^{-3} M aqueous $Fe(NO_3)_3$ before (left) and after (right) introducing the $\mathbf{III_{COOH}}$ membrane, which is immobilized on a black support.

the concentration of Fe^{3+} rose. A titration could thus be performed, which resulted in a detection limit below 6 ppb, much lower than 300 ppb limit for iron established by the United States Environmetal Protection Agency (EPA) in the National Secondary Drinking Water Regulation.[50] The binding isotherm plateaued at a Fe^{3+} concentration of 4 × 10^{-3} M^{-1} because of the saturation of the receptor motifs within the membrane, an upper limit to the concentration of iron that can be measured. The film remained colorless upon addition of any of the other cations used in the solid–liquid extraction experiments, indicating a high selectivity toward Fe^{3+} in aqueous solution. The different behavior of Fe^{3+}, compared with other cations regarding the host/guest interaction with hosts containing nitrogen atoms, was attributed by Cui et al.[31] to two facts: (a) the smaller size of Fe^{3+}, resulting in a higher charge density; therefore, having a higher electron-accepting capability and consequently leading to more stable complexes and (b) the d^5 structure, where the five electrons may be present as two orbitals occupied by pairs of electrons and one having single occupancy, so it could form an inner-orbital complex, which is more stable than the other host/metal complexes. Thomann et al.[51] and Kolnaar et al.[52] demonstrated the capability of 1,2,4-triazole-containing compounds to give stable bonds with Fe^{3+} by means of characterizing the complexes structures using X-ray diffraction technique. The authors reported N–Fe^{3+} distances of about 2.2 Å for the complexes in the solid state, forming each two nitrogens of each heterocycle two bonds with two different Fe^{3+}.

The colorimetric detection of aqueous Fe^{3+} by the $\mathbf{III_{COOH}}$ membrane can be seen by the naked eye in two ways, as shown in Figure 6. Placing the colorless membrane, in a black support, in a UV–vis cuvette containing the yellow aqueous Fe^{3+} solution caused the membrane to become brownish and the solution to become colorless, a clear indication that the concentration of Fe^{3+} in the water had diminished because of the interaction of the cations with the host motifs of the membrane.

Deprotonating the $\mathbf{III_{COOH}}$ membrane produced the $\mathbf{III_{COO^-}}$ membrane. The colorimetric response of this membrane to aqueous cations was very similar to that of the protonated form, albeit somewhat less sensitive toward Fe^{3+}. The titration curve shown in Figure 7 shows a measurable colorimetric response above 3 × 10^{-4} M, or 16 ppm. Like the protonated membrane, it displayed a clear range of measurable Fe^{3+} concentrations, with one plateau below the detection limit and another at the highest measurable concentration.

We made a comment regarding the detection limits and measurable regions of this kind of system. These can be easily modified and tuned to fit situational needs by increasing or decreasing the molar ratio of the sensing monomer (**3**) to the other comonomers (**4** and the cross-linking agent). These highly interesting parameters may also be modified by increasing or decreasing the hydrophilic character, or the gel behavior, of the membrane using other comonomers or by varying the cross-linking ratio.

Conductivity

To gain insight about the cation–polymer interaction, conductivity measurements were performed on solutions containing $\mathbf{I_{COOH}}$ with a solubilized polymer content corresponding to a 5 × 10^{-4} M concentration of the triazole-containing monomer (**3**), increasing concentrations of Hg^{2+} or Pb^{2+} salts, and 2-[bis(2-hydroxyethyl)amino]-2-(hydroxymethyl)-1,3-propanediol (BIS–TRIS) buffer (pH 7.0).

The variation of the molar conductivity, $\Delta\Lambda = \Lambda_{exp} - \Lambda_0$, of aqueous $Hg(NO_3)_2$ and $Pb(NO_3)_2$ at different salt concentrations in the presence (Λ_{exp}) and the absence (Λ_0) of polymer $\mathbf{I_{COOH}}$ is shown in Figure 8. The negative values of $\Delta\Lambda$ can

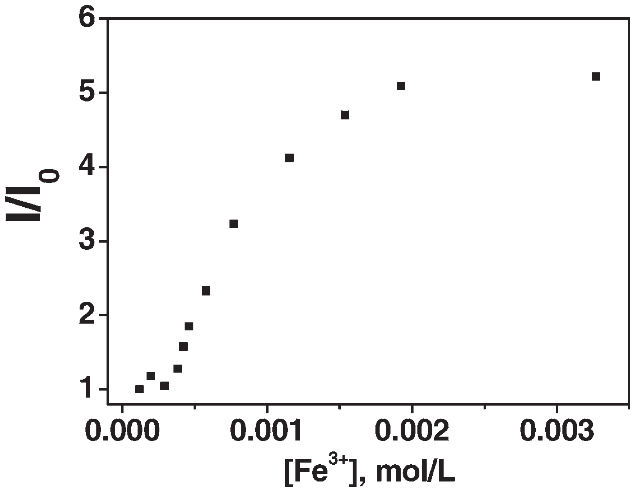


FIGURE 7 UV/vis titration curve of film $\mathbf{III_{COOH}}$ with aqueous Fe^{3+}. I/I_0 versus Fe^{3+} concentration at 457 nm. The reference was an aqueous solution of Fe^{3+} with the same concentration as that of the sample cuvette.

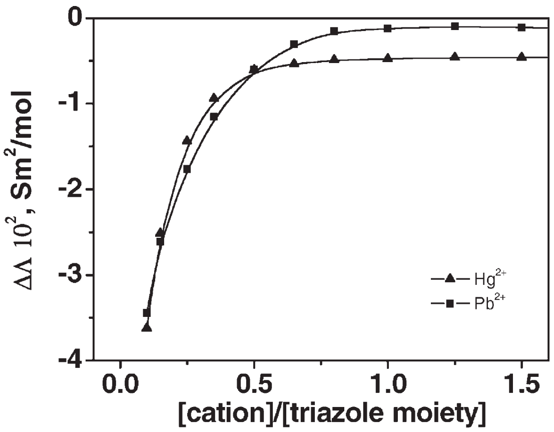


FIGURE 8 Effect of cation concentration on the difference between the molar conductivities of Hg^{2+} and Pb^{2+} in the presence (Λ_{exp}) and the absence (Λ_0) of polymer $\mathbf{I_{COOH}}$. $\Delta\Lambda = \Lambda_{exp} - \Lambda_0$ (solvent: water, buffered at pH = 7.0).

be ascribed to reduced mobility of the cationic species arising from interaction between the cations and the host motifs. The variation in the molar conductivity reaches its maximum, making a plateau, when all of the host motifs are interacting with metal cations. The initial steep slope of the curve suggests that the complexes between the polymer motifs and the cations were very stable. The $\Delta\Lambda$ value plateaued at a cation/host motif ratio of ~0.5 for Hg^{2+} and 1 for Pb^{2+}. This result could be tentatively attributed to cation/host motif interactions with stoichiometries of 1:2 for Hg^{2+} and 1:1 for Pb^{2+}. The stoichiometry corresponding to the Hg^{2+} was also observed by Hung et al. in a chemosensor containing a bis-1,2,3-triazole receptor motif,[38,45] and the interaction of a Hg^{2+}–triazole complex was characterized by different researchers by means of determining its chemical structure using the single crystal X-ray diffraction technique.[39,46] Nevertheless, we are cautious in suggesting this interpretation because of the complexity of the system. Conductivity studies of the deprotonated polymer, $\mathbf{I}_{\mathbf{COO}^-}$, could not be carried out because of precipitation upon the addition of the salts.

CONCLUSIONS

A water-insoluble organic molecule (**3**) with pendant 1,2,4-triazole and acid group moieties as host or receptor motifs was polymerized with hydrophilic acrylic comonomers to yield a water-soluble linear copolymer and two water-insoluble cross-linked materials, a powder and a hydrophilic membrane or film that both exhibited gel behavior. The cross-linked powder was used for the extraction or removal of environmentally deleterious cations from aqueous media. The membrane, in the form of film strips, was used as for the colorimetric detection of aqueous Fe^{3+} by the naked eye. Upon swelling with water, both cross-linked copolymer materials permitted solvated cations to diffuse into the swelled network and reach the highly hydrophobic organic sensing motifs, giving rise to the recognition or extraction phenomena. Following this procedure of anchoring organic sensing molecules to appropriate polymeric nets, these supramolecular phenomena can be easily performed in water.

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