

A Molecularly Imprinted Polymer via a Salicylaldiminato-Based Cobalt(III) Complex: A Highly Selective Solid-Phase Extractant for Anionic Reactive Dyes

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ABSTRACT: A novel molecularly imprinted polymer based on *tert*-butyl acrylate (MIP-BA) was fabricated with the assistance of a cobalt(III)-based catalyst bearing an *N*-salicylidene isopropylamine ligand [(SPA)₂CoCl]. After initiation with methyl aluminoxane, the catalyst system was found to be active toward the polymerization of *tert*-butyl acrylate (*t*-BA) in the presence of a polar template (Cibacron reactive red dye) and divinylbenzene (DVB) as a crosslinker. Polymerization experiments, including those of *t*-BA, *t*-BA, and DVB and *t*-BA and dye, were also carried out. Isolated blank polymers and MIP-BA were analyzed with a variety of techniques, including differential scanning calorimetry, thermogravimetric analysis, gel permeation chromatography, infrared spectroscopy, nuclear magnetic resonance, and ultraviolet–visible spectroscopy. In general, the complex showed moderate polymerization activity and produced high-molar-mass poly(*tert*-butyl acrylate); how-

ever, a decrease in the monomer conversion was observed upon the addition of the dye and/or the crosslinker. The effect of imprinting was obvious when the adsorption capacity of MIP-BA measured at pH 6 for red dye (the imprinted molecule) was increased from 9.2 to 90.4 mg/g after imprinting. Competitive adsorption studies revealed that the dye-imprinted polymer enabled the efficient uptake of red dye, even in the presence of blue and yellow dyes that had similar chemical structures to the imprinted molecule. The selectivity coefficients were 43 and 36 with respect to the blue and yellow dyes, respectively. The proposed polymerization procedure could be extended to other anionic polar reactive dyes and polar reactive polymers. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 2316–2323, 2010

Key words: catalysis; molecular imprinting; thermogravimetric analysis (TGA)

INTRODUCTION

Salen-based complexes are a fundamental class of compounds in coordination chemistry, and they have been known since 1933.¹ Interest in these complexes intensified in 1990 when Jacobsen et al.² and Katsuki et al.³ discovered the enantioselective epoxidation of unfunctionalized alkenes with chiral Mn(salen) complexes as catalysts. Since then, a wide variety of reactions catalyzed by salicylaldiminato complexes has been investigated. These include the epoxidation of alkene,⁴ hydrolytic kinetic resolution of epoxides,⁵ intermolecular hydroamination of allenes,⁶ oxidation of amino acids,⁷ and polymerization of α -olefins.⁸

The polymerization of acrylates is classically carried out with anionic,⁹ radical,¹⁰ or group-transfer polymerization.¹¹ Recently, late-transition-metal-complex-based polymerization methods, including atom-transfer radical polymerization¹² and methyl aluminoxane (MAO)-activated transition-metal com-

plexes, have also been developed.^{13–15} Although the actual mechanism for the MAO-activated late-transition-metal-complex-assisted polymerization of acrylate monomers is still unclear (ionic vs radical), the advantage of those methods is that they function under mild polymerization conditions with low metal-complex concentrations. In addition, they produce polymers with high molar masses and controlled molar mass distributions.^{13,15}

Lately, research on the development of selective adsorbents has been directed to imprinted polymers.¹⁶ Molecular imprinting is a methodology used for the creation of selective recognition sites in synthetic polymers. In this process, functional and crosslinking monomers are copolymerized in the presence of the target analyte.¹⁷ The use of molecularly imprinted polymers (MIPs) as stationary phases in chromatographic separation, chiral separation, and preconcentration solid-phase extraction has been reported in many research articles.¹⁸ Both covalent and noncovalent pathways are used for MIP preparation.¹⁹ The noncovalent imprinting seems to be a more efficient system for mimicking the interactions present in nature (hydrogen bonding, electrostatic interactions, etc.).²⁰ The successful preparation of MIPs depends on the monomers, the crosslinkers, and the appropriate polymerization conditions for a

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particular analyte. Many selective adsorbents with high adsorption capacities for organic and inorganic solutes have been fabricated with MIP technology.¹⁶ A very limited number of studies have considered the preparation of MIPs for the selective removal or pre-concentration of anionic reactive dyes.²¹ Natural and synthetic dyes are used heavily in many industries, including the food, pharmaceutical, cosmetic, textile, and leather industries. The effluents of these industries are highly colored, and the disposal of these wastes into natural waters causes damage to the environment.²¹ It has been pointed out that a dye content of less than 1.0 mg/L causes obvious water coloration.²² After dyes are mixed with other water streams, the concentration of the dyes is further diluted. The concentration of dyes could be in the microgram-per-liter level in textile wastewater.²³ Because of their strong interactions with many surfaces, reactive dyes are used to dye wool, cotton, nylon, silk, and modified acrylics. Generally speaking, the adsorption of reactive dyes is modest on most surfaces, except expensive activated carbons. Accordingly, finding other less expensive adsorbents for the extraction of reactive dyes is an essential task for environmental chemists.

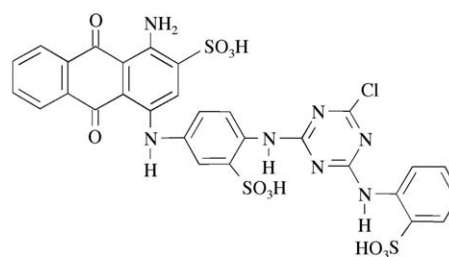
In a previous article, we reported on the synthesis of new pentacoordinated salicylaldiminato-based transition-metal complexes and their application for the first time, after activation with MAO, as catalysts for the polymerization of *tert*-butyl acrylate (*t*-BA). The influence of the metal center, the type of the auxiliary groups, and the substituents in the backbone of the ligands on the polymerization of *t*-BA was evaluated.²⁴ In addition, we developed a very selective MIP prepared via the free-radical polymerization of methacrylic acid and methyl methacrylate in the presence of ethylene glycol dimethacrylate (as a cross-linker) and Cibacron reactive red dye.²⁵ The isolated materials were used to remove the anionic and highly polar Cibacron red dye. The polymers were tested for selective adsorption and pre-concentration of the imprinted dye from water and wastewater. The molecularly imprinted polymer based on methacrylic acid (MIP-MA) adsorbent was selective for the red dye with an adsorption capacity of about 71 mg/g at pH 6.0.

In this article, we report a novel methodology for the fabrication of Cibacron-reactive-dye-imprinted polymers based on the functional monomer *t*-BA by the aid of a salicylaldiminato cobalt(III) based catalyst system. The isolated materials were tested for selective rebinding and pre-concentration of the reactive dye from water.

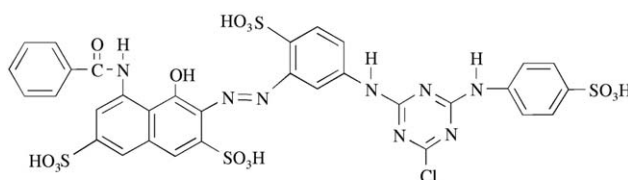
EXPERIMENTAL

Materials

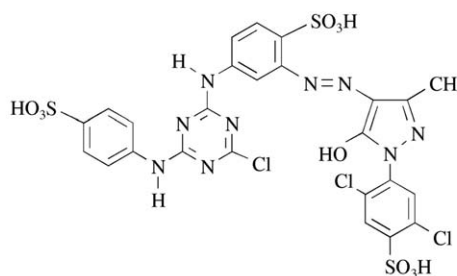
All polymerization experiments were performed under a nitrogen atmosphere with standard Schlenk



a) Cibacron Reactive Blue



b) Cibacron Reactive Red (the imprinted molecule)



c) Cibacron Reactive Yellow

Figure 1 Chemical structures of the Cibacron reactive dyes.

techniques. We carefully purified the monomer (*t*-BA) and the crosslinker, divinylbenzene (DVB), before polymerization by passing them through an activated basic alumina column to remove inhibitors.²⁵ They were then stored under an inert atmosphere. Other reagents were purchased from commercial suppliers with high purity grades and were used as received. The catalyst, chlorobis(*N*-salicylidene-2-isopropylaniline)cobalt(III), was prepared according to a previously published procedure.²⁴ Three reactive dyes (Fig. 1) with wide industrial applications were selected: CI reactive blue 2, CI reactive red 4, and CI reactive yellow 2 (Aldrich Chemical Company, Inc., Milwaukee, WI, USA). As a template for the preparation of MIPs, CI reactive red 4 was selected.

Methods

¹H-NMR and ¹³C-NMR spectra (CDCl₃) were recorded on a Varian Gemini 200 spectrometer

TABLE I
Polymerization Experiments with *t*-BA and the Cobalt(III)/MAO Catalyst System

Entry	Polymer	Activity (g of polymer/ mol of catalyst h)	$M_w \times 10^3$ (g/mol)/ M_w/M_n^a	T_g (°C) ^b	T_m (°C) ^b	Physical appearance
1	BP-1	80,500	43.2/1.09	52	NO	Colorless and elastic
2	BP-2	8,930	45.8/1.06	60	NO	Red and elastic
3	BP-3	6,430	ND	76	NO	White powder
4	MIP-BA	5,360	ND	101	127, 158	Reddish powder

The polymerization conditions were as follows: monomer = *t*-BA, catalyst amount = 7.0 μ mol, monomer concentration = 2.0 mol/L, MAO/monomer ratio = 2300 : 1, polymerization temperature = 60°C, solvent = toluene (40 mL), polymerization time = 12 h, dye = Cibacron (red dye; 2.5 mmol), and crosslinker = DVB (1.0 mL). ND = not determined (the material was insoluble in most organic solvents); NO = not observed; T_g = glass-transition temperature; T_m = melting temperature.

^a Determined by GPC with respect to polystyrene standards.

^b Determined by DSC.

(California, USA). Infrared (IR) spectra (KBr) were measured on a Nicolet Magna-IR 560 spectrophotometer. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA 409 PC LUX instrument at a heating rate of 10 K/min. The molecular weight and molecular weight distributions were measured by gel permeation chromatography (GPC) with respect to polystyrene standards. Dyes contents were measured with a double-beam spectrophotometer (Cary 50 ultraviolet-visible spectrophotometer). A digital pH meter (WTW, Inolab, Germany) was used for pH measurements. All spectral measurements were made in triplicate.

Experimental procedures

Synthesis of blank polymer 1 (BP-1)

To a suspension of the complex (7 μ mol) in toluene (40 mL), MAO (Table I) was added. After a short initiation time, the monomer (2.0 mol/L) was injected into the solution; then, the mixture was stirred at room temperature for 12 h. The polymerization reaction was terminated by the addition of acidic MeOH (60 mL). The polymer was collected, rinsed with water to remove traces of acid, and dried in an oven at 60°C until a constant weight was obtained.

Synthesis of blank polymer 2 (BP-2)

Polymerization was carried out with the previous procedure. Reactive red dye (2.5 g, 2.5 mmol) was added directly after the insertion of the monomer.

Synthesis of blank polymer 3 (BP-3)

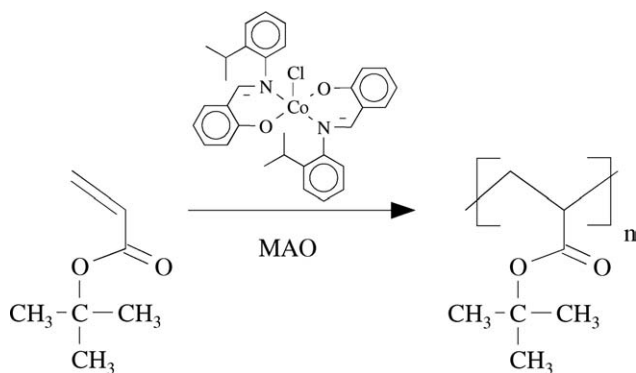
Polymerization was carried out with the previous procedure; however, DVB (1.0 mL) was added directly after the insertion of the monomer.

Synthesis of the red-dye-imprinted polymer [Molecularly imprinted polymer based on tert-butyl acrylate (MIP-BA)]

The synthesis was carried out with the previous procedure. DVB (1.0 mL) and reactive red dye (2.5 g, 2.5 mmol) were added directly after the insertion of the monomer. Then, the mixture was stirred at room temperature for 12 h. The polymerization reaction was terminated by the addition of acidic MeOH (60 mL). The polymer was collected, rinsed with water to remove traces of acid, and dried in an oven at 60°C until a constant weight was obtained. The resulting solid polymer was crushed into powder and sieved into small and homogeneous particle sizes with the aid of a mechanical grinder and a standard sieve apparatus (Endecotts, London, United Kingdom). To leach the template molecule from the polymer, the polymer particles were subjected to Soxhlet extraction with 200 mL of an acetic acid/ethanol mixture (1 : 1 volume ratio) for 48 h. The polymer particles were removed from solution, washed several times with ethanol, dried at 80°C for 24 h, and sieved before characterization analyses and adsorption tests. The obtained polymer from this procedure was referred to as MIP-BA. The Soxhlet extraction was necessary to leach out the imprinted red dye from the polymer matrix. Under the best leaching conditions, about 90% of the imprinted dye was removed from the polymer matrix. The earlier Soxhlet extraction was repeated for BP-1, BP-2, and BP-3.

Adsorption and selectivity investigation

The selective adsorption of reactive red dye in the presence of other reactive dyes was tested as following: a 100-mL solution containing 100 mg/L of each dye was added to 100 mg of the blank and imprinted polymer (particle size range = 50–74 μ m) in a 250 mL volumetric flask; the mixture was sealed and agitated in a temperature-controlled shaker

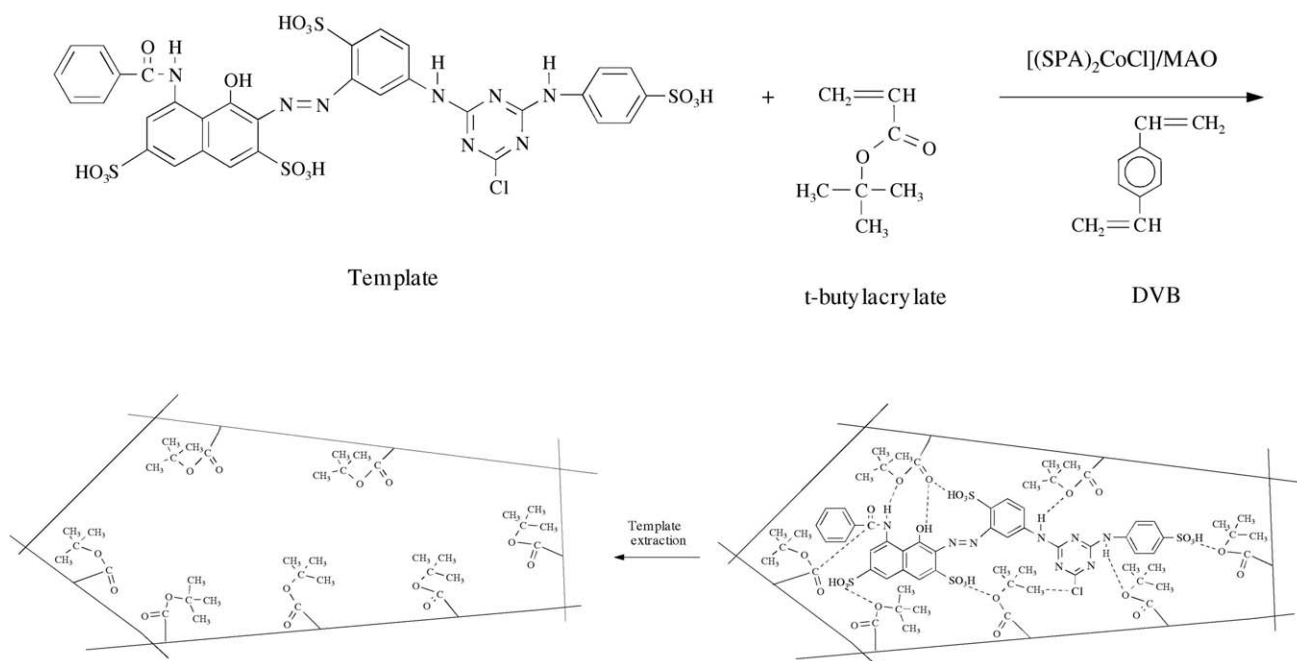


Scheme 1 Polymerization of *t*-BA by the cobalt(III)/MAO catalyst system.

(GFL 1083, Gesellschaft für Labortechnik, mbH, Burgwedel, Germany) for 24 h. The equilibrium time (24 h) for dye adsorption by polymers was determined from earlier kinetic studies. The pH of solutions was adjusted to 6.0 before the adsorption studies with a buffer solution because the adsorption of anionic dyes is favorable at this pH. At the end of the equilibrium time, the mixtures were carefully filtered to separate solid particles and the content of the reactive dyes was determined with Beer's law²⁵ after the absorbances of the dye solution were recorded at 604, 520, and 406 nm, which corresponded to the maximum wavelength of each dye.

The distribution ratio (K_d) and selectivity coefficient (S) of the dyes were estimated as follows:

$$K_d = \frac{Q_{\text{ads}}}{C_{\text{dye}}} \quad (1)$$



Scheme 2 Scheme for the synthesis of the red-dye-imprinted polymer.

where Q_{ads} and C_{dye} are the amount of dye taken by the polymer at equilibrium and the amount of dye left over in solution after extraction. $K_d > 1.0$ indicates the favorability of the extraction or adsorption process, and

$$S_{\text{red dye/dye}} = \frac{(K_d)_{\text{red dye}}}{(K_d)_{\text{dye}}} \quad (2)$$

Higher values of $S_{\text{red dye/dye}}$ (selective coefficient of dyes) indicate that the adsorbent was very selective for red-dye removal and that the imprinting process was successful.

RESULTS AND DISCUSSION

Polymer synthesis and characterization

A salicylaldiminato cobalt(III) complex $[(\text{SPA})_2\text{CoCl}]$ was used for the polymerization reactions of *t*-BA in the presence of MAO as an initiator (Scheme 1). After a short initiation time, desired amounts of the monomer, crosslinker, and Cibacron reactive red dye (Scheme 2) were added. The polymerizations reaction was terminated by the addition of an MeOH/HCl solution.

With the same polymerization procedure, three blank polymers were also prepared by the incorporation of the monomer only (BP-1), the monomer and the red dye (BP-2), and the monomer and the crosslinker (BP-3). The polymerization results are summarized in Table I. The isolated materials were characterized by means of GPC, NMR, Fourier transform infrared (FTIR) spectroscopy, TGA, and differential scanning calorimetry (DSC). As shown later, the MIP-BA polymer exhibited a high extraction

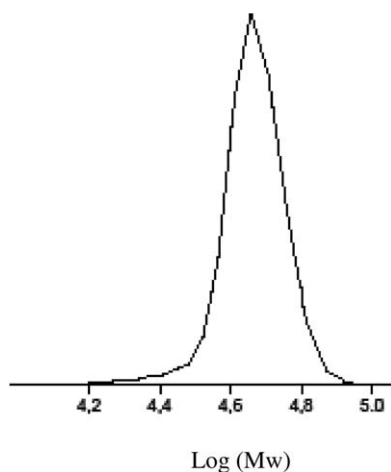


Figure 2 GPC curve of poly(*t*-BA)/dye (BP-2).

power and excellent selectivity for red dye compared to the remaining blank polymers.

In general, the catalyst system possessed moderate activity in the absence of the crosslinker or the reactive red dye [80.5×10^3 g of polymer (mol of catalyst) $^{-1}$ h $^{-1}$]. However, a decrease in the monomer conversion was observed upon the addition of the polar dye or the crosslinker (DVB). This could have been due to the sensitivity of the transition-metal catalyst to electron-donating functional groups.²⁶

GPC

According to the GPC measurements, the catalyst produced high-molar-mass polymers with very low molecular weight distributions, even in the presence of the polar dye [45.9×10^3 g/mol, weight-average molecular weight (M_w)/number-average molecular weight (M_n) = 1.06; Fig. 2]. The low molecular weight distributions could have been an indication of the presence of one catalytically active species with this specific MAO/salicylaldiminato-based transition-metal system (Scheme 1). These unique values for M_w/M_n could mainly have been due to the N–O ligand framework because a minor influence on the molecular weight distribution was observed with variation of the metal center.²⁴

Other iron and cobalt complexes with tridentate or tetradentate nitrogen donors produced poly(*tert*-butyl acrylate) [poly(*t*-BA)] materials with molecular weight distributions in the range 1.8 to 2.6.¹⁴ The molar mass of the materials BP-2 and MIP-BA (Table I, entries 3 and 4) could not be determined because they were insoluble in organic solvents.

NMR spectroscopy

Various stereospecific polymerizations with Ziegler–Natta,²⁷ metallocene,²⁸ anionic,²⁹ or radical polymer-

izations³⁰ have been reported earlier. Highly isotactic poly(*t*-BA) was synthesized with a chiral zirconocene ([*m*] dyad 83%)²⁸ or *n*-BuLi in the presence of LiOH ([*m*] dyad 85%).³¹ The highest syndiotactic dyad value reported was with [*r*] = 63% for poly(*t*-BA), which was prepared by radical polymerization at low temperature,³² and a triad syndiotacticity [*rr*] of about 40% was reported for anionic polymerization with diphenylmethyl lithium as an initiator.³³ According to the NMR results, the poly(*t*-BA) materials prepared in this study were syndiotactic-rich atactic polymers with [*rr*] dyads around 40% (BP-1). We reported similar results earlier with MAO-activated bis(imino)pyridine based-iron dichloride complexes.¹⁵ The $^1\text{H-NMR}$ spectrum of BP-2 was similar to that of BP-1. The spectrum showed broad peaks at 1.46, 1.85, and 2.24 ppm, which corresponded to $\text{C}(\text{CH}_3)_3$, CH_2 , and CH , respectively (Fig. 3).³⁴ No signals due to the reactive red dye were observed, which indicated that no external dye was attached to the polymer, and the adopted Soxhlet extraction was effective for stripping the dye molecules from the polymer.

DSC

An insignificant difference was observed in glass-transition temperatures of BP-1 (52°C) and BP-2 (60°C); this indicated that the presence of the red dye had a slight influence on the microstructure of poly(*t*-BA). However, the polymerization of *t*-BA in

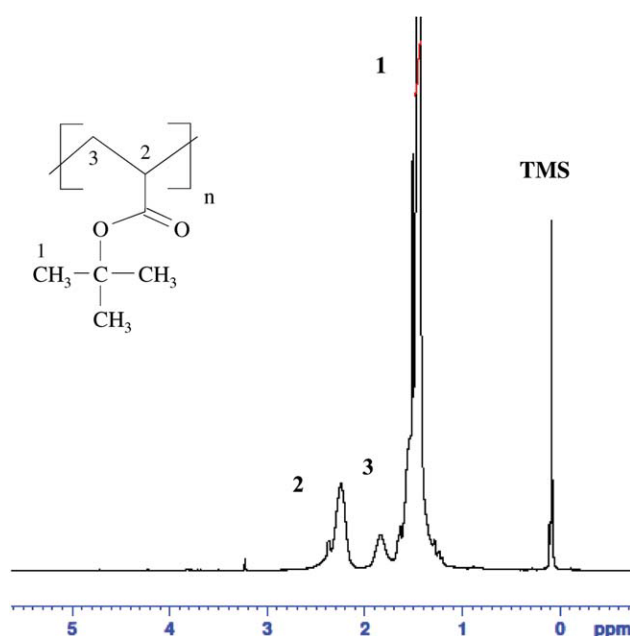


Figure 3 $^1\text{H-NMR}$ spectrum of BP-2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

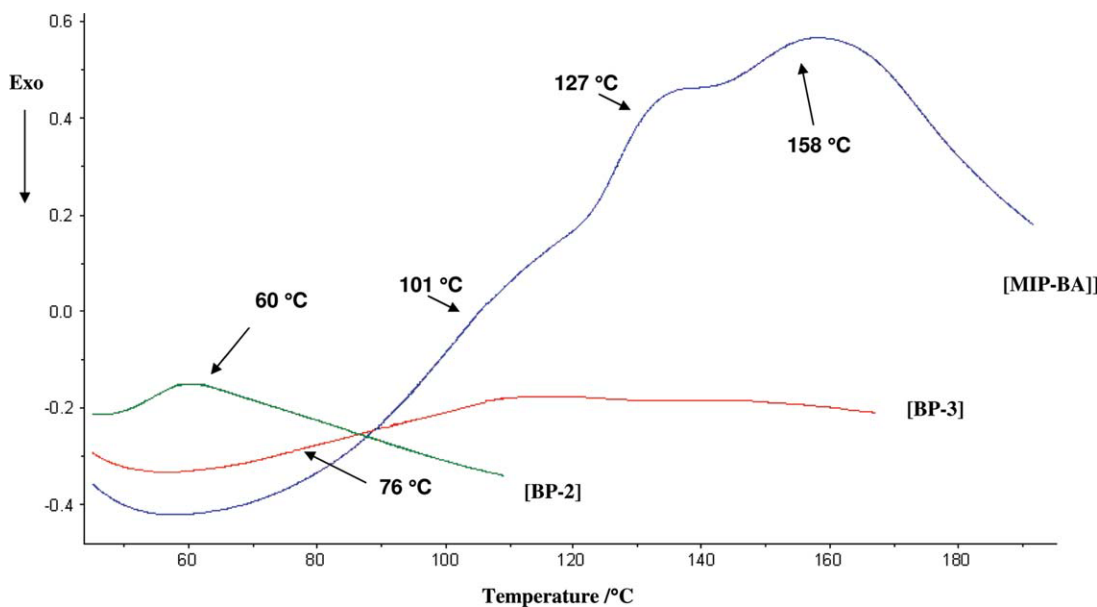


Figure 4 DSC traces of BP-2, BP-3, and MIP-BA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the presence of the crosslinker gave an inflexible material with a higher glass-transition temperature (Table I; 76°C for BP-3). Evidence of molecular imprinting and the effect of imprinting on the structural properties of MIP-BA were investigated by TGA and DSC. The DSC scan of the MIP-BA material was different from those of the blanks. The scan of MIP-BA showed a higher glass-transition temperature (101°C) and new transition peaks at 127 and 158°C (Table I and Fig. 4). This was attributed to the different structure of the dye-MIP. The appearance of these transitions could have been due to the creation

of new ordered segments in the polymer structure upon imprinting.

TGA

The thermal stability of the prepared polymers and the effect of imprinting on polymer stability were studied with TGA. The thermogravimetric curves of the MIP-BA and BP-1 and BP-3 are depicted in Figure 5. Generally, the thermogravimetric plots showed that MIP-BA was more stable than both BP-3 and the pure polymer BP-1. This observation

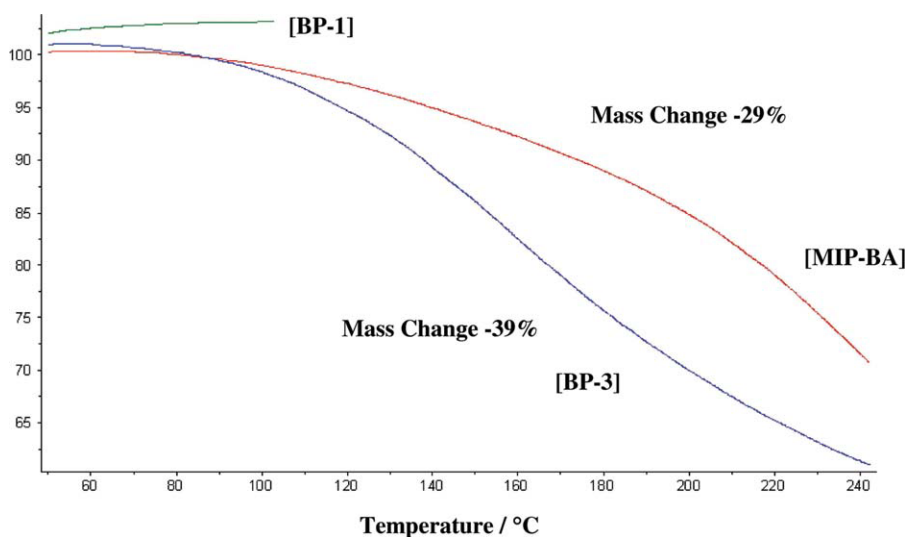


Figure 5 Thermogravimetric plots of BP-1, BP-3, and MIP-BA. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE II
Adsorption, K_d , and S Values of Dye Uptake by the Prepared Polymers

Dye	Adsorption (mg/g)			K_d (L/g)			S		
	BP-1 ^a	MIP-BA ^a	MIP-MA ^b	BP-1 ^a	MIP-BA ^a	MIP-MA ^b	BP-1 ^a	MIP-BA ^a	MIP-MA ^b
Red	9.2	90.4	70.9	0.10	9.40	2.45	—	—	—
Blue	11.6	17.9	16.2	0.13	0.22	0.19	0.8	43	13
Yellow	13.4	20.8	18.3	0.15	0.26	0.22	0.7	36	11

The conditions were as follows: polymer mass = 100 mg, dye level = 100 ppm, solution volume = 100 mL, temperature = 25°C, and agitation time = 24 h. The pH was initially adjusted to 6.0 with a 0.1M phosphate buffer. Adsorption data are reported as averages of three trials (relative standard deviation = 2.4–6.3%).

^a See Table I for the preparation procedure.

^b See Al-DeGS et al.²⁵ for the preparation procedure.

indicated that, with imprinting, the stability of the polymer particles was increased.

FTIR analysis

The IR spectra of MIP-BA and its corresponding blanks were recorded over the range 4000–400 cm^{-1} . In fact, FTIR analysis can provide much useful information regarding the nature of surface functional groups created on a polymer surface. The characteristic band of the carbonyl group (1732 cm^{-1}) and the aliphatic C–H stretching bands (2996 and 2954 cm^{-1}) appeared clearly in the spectrum of MIP-BA. It seemed that there was no external dye attached to the polymer because the main FTIR bands of the dye (1137, 1051, and 616 cm^{-1}), which contributed to the strong vibrations of the $-\text{SO}_3\text{H}$ group, were not detected in the MIP-BA spectrum. In addition, the IR spectrum of BP-3 lacked any peaks due to unreacted vinyl groups; this indicated that DVB acted as a crosslinker and not as a comonomer.

Adsorption and selectivity analysis

The adsorption capacity (milligrams/gram), K_d (liters/gram), and S values are summarized in Table II. The adsorption behavior of the polymers in this study was compared with those reported in an earlier study.²⁵

As noted, the new MIP material (MIP-BA) outperformed the other polymers in removing the red dye. The effect of imprinting was obvious from the data; the adsorption capacity increased from 9.2 to 90.4 mg/g at pH 6 after imprinting; that is, the original adsorption capacity increased by 880 times after imprinting. The effect of imprinting was also obvious when the K_d values were compared. The K_d value of the red dye increased from 0.1 to 9.4 and improved slightly for the rest of dyes. Relatively speaking, the blank polymers showed a modest reactivity for all of the dyes, including the red dye. For the red dye, the adsorption capacities were 9.2, 15.6, and 19.3 mg/g for BP-1, BP-2, and BP-3, respec-

tively. Moreover, it was interesting to observe the high performance of the new polymer (MIP-BA) toward the red dye (a polar molecule) compared to MIP-MA (entry 5), which was fabricated with a classical radical procedure. The obtained selectivity values also reflected the unusual performance of Co(III)/MIP-BA, which were 43 and 34 relative to the blue and yellow dyes. However, we report 71.1 and 13.9 relative to the blue and yellow dyes for the MIP-MA polymer. It seemed that the new method of preparation created many more active sites that fit the red dye molecules compared to radical-based methods.²⁵ In fact, more characterization of the prepared adsorbent should be carried out in the future to explain the interaction mechanisms between the dye molecules and MIP. The application of the new MIP could be evaluated for the removal of red dye from rather complex matrices.

CONCLUSIONS

A novel methodology using a transition-metal-based catalyst was used for the preparation of a new Cibacron reactive red-dye-based MIP with *t*-BA as a monomer and DVB as a crosslinker. Four different polymers were prepared to assess the preparation conditions on the uptake capacity of the adsorbent. Preliminary adsorption and selectivity studies on the new MIP showed that the material was highly selective toward the removal of the anionic and highly polar Cibacron reactive red dye from tap water and treated textiles. The adsorption capacity measured at pH 6 for the red dye (the imprinted molecule) increased from 9.2 to 90.4 mg/g after imprinting. It seemed that this novel approach created many more active sites that fit the red dye molecule compared to traditional radical-based methods. These unusual results could have been due to the presence of both hydrophobic and hydrophilic sites on the surface of the imprinted polymer and/or due to the higher regularity in the microstructure of the poly(*t*-BA) due to the application of the transition-metal-based catalyst system. In fact, more characterization of the

prepared adsorbent should be carried out in the future to explain the interaction mechanisms between the dye molecules and MIP. We do believe that the MIP prepared with the transition-metal catalyst was structurally different from the one prepared via the common radical pathway. Because of the bulkiness of the used catalyst, it was not able to connect monomers around the template, but the living polymer chain attracted the template from its different sites forming, therefore envelopes around it via different coordination modes. These holes were then fixed by crosslinking.

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