

Surface Selectivity Competition of Newly Synthesized Polyarylidene(keto amine) Polymers Toward Different Metal Ions

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ABSTRACT: A new series of polyarylidene(keto amine)s (PAKAs) **3_a**–**3_e** based on thiophene moieties in polymer main chains were synthesized with the solution polycondensation technique. The polymers were synthesized by the reaction of the new monomer 1,1'-(1*E*,1'*E*)-(2-oxocyclohexane-1,3-diylidene)bis(methanylylidene)bis(thiophene-5,2-diyl)bis(2-chloroethanone) (**2**) with different diamines. The new monomer was first synthesized under the normal conditions of the Friedel–Crafts reaction. The results obtained from both elemental and spectral analyses were consistent with the chemical structure of the new monomers and the polymers. Moreover, the identification of the polymers was carried out with different characterization techniques. The analytical competition of the newly synthesized PAKA polymers as selected examples (**3_d** and **3_e**) was also evaluated for a selective extraction of metal ions, including Cd(II), Co(II), Cu(II), Cr(III), Fe(III), Ni(II), and Zn(II), before their determination by inductively coupled plasma–optical emission spectrometry. The results of the selectivity study demonstrated that the **3_d** and **3_e** polymers was the most selective toward Co(II) and Fe(III), respectively. However, the adsorption capacity of **3_d** for Co(II) was improved by 10.10% in comparison to that of **3_e** for Fe(III) after only 1 h of contact time. Moreover, the adsorption isotherm data also showed that the adsorption process was mainly monolayer on the homogeneous adsorbent surfaces of both polymers. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40873.

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INTRODUCTION

Polyarylidene(keto amine)s (PAKAs) are considered a hybrid class of polymers that poses variable and very attractive properties, which can collect the properties of polyketones, polyamine, and arylidene polymers. When we browsed the Internet, we found that there was no available literature for this kind of hybrid polymer so far. In the past decades, arylidene monomers and premonomers were considered a cornerstone for different types of interesting polymers. According to the literature, there is much interest and effort in the development of newly designed polyarylidenes via well-known synthetic routes. They have been incorporated into nearly almost every kind of polymer architecture via the solution polycondensation technique from polyester to polyimide, even hybrid poly(keto amine) polymers.

Diarylidene cycloalkanone derivatives, as an important class of organic molecules, have both mesogenic and photoactive prop-

erties; these can soon be named as versatile photoactive molecules. Such compounds have already shown their potential for several applications in chemistry, biology, materials science, and technology. They have also been studied for medical applications by their incorporation into polymer architectures to harness their properties as photoactive compounds and mesogenic units. The photoactive molecule was first introduced into a macromolecular architecture by Borden et al.^{1,2} in 1969. Arylidene polymers have widely been used in various areas of interest. These kind of polymers have special features, such as a high thermal stability, photocuring ability (for adhesives, photore-sists, and holography), fluorescence, and electronic conductivity. In addition, variable studies on the synthesis and properties of new polymers based on diarylidene cycloalkanones possessing interesting properties, an attractive morphology, a higher thermal stability, liquid-crystalline behavior, corrosion protection, conducting properties, antimicrobial activity, and many other properties, have been presented in the literature.^{3–10}

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Furthermore, the development of simple, rapid, and efficient methods has continued to be of interest in the monitoring of metal ions in the environment. Several analytical methods have been applied to analyze metal ions in aqueous solutions; these include atomic absorption spectrometry,¹¹ inductively coupled plasma (ICP)–optical emission spectrometry (OES),¹² anodic stripping voltammetry,¹³ and ion chromatography.¹⁴ However, analytical methods cannot directly measure metal ions, in particular at ultratrace concentrations, in aqueous systems because of the lack of sensitivity and selectivity of these methods. Therefore, an efficient separation procedure is usually required before the determination of metal ions for sensitive, accurate, and interference-free determination of noble metals.¹⁵

Several analytical methods can be used for the separation of analytes of interest, including liquid–liquid extraction,¹⁶ ion exchange,¹⁷ coprecipitation,¹⁸ cloud-point extraction,¹⁹ and solid-phase extraction (SPE).²⁰ SPE has been reported as one of the most powerful techniques because it minimizes solvent usage and exposure, disposal costs, and extraction time for sample preparation. Several adsorbents have appeared because of the popularity of SPE for the selective extraction of analytes, such as alumina,²¹ C18,²² molecular imprinted polymers,¹² cellulose,²³ silica gel,^{24,25} activated carbon,^{26,27} and carbon nanotubes.^{28,29}

In this study, we aimed to synthesize and characterize a new category of PAKA polymers as adsorbents to explore their analytical potential and competition on the selectivity and adsorption capacity of Co(II) and Fe(III) before their determination by ICP–OES. Several characterization tools have been used to evaluate the properties of the new polymers, including the solubility measurement, thermal analyses [thermogravimetric analysis (TGA), DTG, and differential thermal analysis (DTA)], gel permeation chromatography (GPC), and scanning electron microscopy (SEM). Furthermore, the selectivity of polymers **3_d** and **3_e** as selected adsorbents toward different metal ions, including Cd(II), Co(II), Cu(II), Cr(III), Fe(III), Ni(II), and Zn(II), was studied. Other parameters controlling the maximum uptake of Co(II) and Fe(III) on the **3_d** and **3_e** polymers phases, respectively, were evaluated under batch conditions. The adsorption isotherm data of Co(II) and Fe(III) were modeled with a Langmuir classical adsorption isotherm.

EXPERIMENTAL

Chemicals and Reagents

Cyclohexanone (BDH, 99%), chloroacetylchloride (Merck, 97%), ethanol (BDH, 99.7–100%), thiophencarbaldehyde (Fluka, 95%), benzene (BDH, 99.5%), and anhydrous aluminum chloride were ordered from Sigma-Aldrich (Milwaukee, WI) and were used without purification. Different aliphatic and aromatic diamines, including 1,2-diaminoethane (Fluka), 1,6-diaminohexane (PDH), *p*-phenylenediamine (PDH), *m*-phenylenediamine (Acros), and 1,2-diaminocyclohexane (Fluka), were also purchased from Sigma-Aldrich and were used without purification. Stock standard solutions of 1000 mg/L Cd(II), Co(II), Cu(II), Cr(III), Fe(III), Ni(II), and Zn(II) were obtained from Sigma-Aldrich. Most of the reagents and chemicals we used were ultrapure grade and spectral purity grade. Other

reagents were high purity and were further purified according to a procedure previously reported in the literature.³⁰ Doubly distilled deionized water was used throughout the experimental studies.

Preparation of the Monomers and Polymers

Monomer Synthesis. (2E,6E)–2,6-Bis(thiophen-2-ylmethylene)-cyclohexanone (1).³¹ A mixture of cyclohexanone (1.037 mL, 10 mmol) and 2-thiophencarbaldehyde (2.01 mL, 22 mmol) was dissolved in 50 mL of absolute ethanol in the presence of a freshly prepared KOH alcoholic solution (3 mL). The reaction mixture was stirred for 6 h at 25°C. The solid product separated out during stirring was filtered off and dried. Recrystallization of the product was carried out with methanol, and this resulted in yellow needles.

Yield: 82%. mp = 150°C. Anal. Calcd. for C₁₆H₁₄OS₂: C, 67.10%; H, 4.93%; S, 22.39%. Found: C, 66.88%; H, 4.99%; S, 22.43%. IR (KBr, cm⁻¹, ν) = 1600 (s, C=C arylidene linkage), 1660 (s, carbonyl group), 2930 (w, CH stretching of aliphatic), 3074 (w, CH stretching of aromatic). ¹H-NMR (CDCl₃, δ): 2.01 (m, 2H, CH₂ middle of cyclohexanone), 2.94 (t, 4H, 2CH₂ of cyclohexanone), 7.17 (dd, 2H, 2Ar–H), 7.39 (d, 2H, 2Ar–H), 7.49 (d, 2H, 2Ar–H), 8.01 (s, 2H, 2CH=C). Matrix-assisted laser desorption/ionization time-of-flight mass spectroscopy (MALDI-TOF MS): *m/z* = 287.10 [M + 1]⁺.

1,1'-(1E,1'E)-(2-oxocyclohexane-1,3-diylidene)bis(methanylylidene)bis(thiophene-5,2-diyl)bis(2-chloroethanone) (2). The new monomer was synthesized according to normal conditions of the Friedel–Crafts reaction. A mixture of premonomer **1** (2.86 g, 10 mmol) and chloroacetylchloride (2.26 g, 20 mmol) was dissolved in 60 mL of carbon disulfide; this was followed by the addition of anhydrous aluminum chloride (5.34 g, 40 mmol) in small portions. The reaction mixture was stirred in an ice bath for 6 h. The carbon disulfide was evaporated, and the residue was poured into cold hydrochloric acid. The yellow precipitate was collected by filtration, washed with excess water, dried, and recrystallized from ethanol.

Yield: 86%. mp = 153°C. Anal. Calcd. for C₂₀H₁₆O₃Cl₂S₂: C, 54.67%; H, 3.64%; Cl, 16.17%; S, 14.58%. Found: C, 54.20%; H, 4.06%; Cl, 16.45%; S, 14.66%. Fourier transform infrared (FTIR) spectroscopy (KBr, cm⁻¹, ν): 1590 (s, C=C arylidene linkage), 1673 (s, carbonyl of chloroacetyl), 1630 (s, carbonyl of cyclohexanone), 2936 (m, CH stretching of aliphatic), 3098 (m, CH stretching of aromatic). ¹H-NMR (CDCl₃, δ): 7.91–7.26 (m, 2H 2CH=C of arylidene and 4H, two thiazole moieties), 4.62 (s, 4H 2CH₂ chloroacetyl), 2.99 (t, 4H 2CH₂ cyclohexanone), 1.98 (m, 2H, CH₂ middle of cyclohexanone).

Polymer Syntheses. Generally, a mixture of 1 mmol of the new monomer **2** was dissolved in 30–40 mL of dry benzene, and a few drops of pyridine were introduced in a three-necked flask equipped with a condenser (with a dry nitrogen inlet, outlet, and dropper). The aliphatic and aromatic diamines, including 1,2-diaminoethane, 1,6-diaminohexane, *p*-phenylenediamine, *m*-phenylenediamine, and 1,2-diaminocyclohexane (1 mmol) were dissolved in 15 mL of dry benzene and added in a dropwise manner during the stirring. After the complete addition of the

diamines, the stirring was continued for 6–8 h at about 80°C, and a yellowish brown solid polymer separated out. The solid polymer was filtered off; washed with water, hot alcohol, and acetone; and dried under reduced pressure at 80°C for 3 days.

PAKA 3_a. The title compound was synthesized according to a general procedure reported previously of the polymerization with monomer **2** (0.439 g, 1.00 mmol), 1,2-diaminoethane (0.0601 g, 1.00 mmol), and a few drops of piperidine as a catalyst in benzene for 6 h at 80°C, to produce a yellowish precipitate (72%).

Anal. Calcd. for C₂₂H₂₂N₂O₃S₂: C, 61.97%; H, 5.16%; N, 6.57%; S, 15.02%. Found: C, 62.74%; H, 5.32%; N, 6.49%; S, 15.38%. FTIR (KBr, cm⁻¹, ν): 3365 (w, NH, secondary amino group), 3126 (w, CH stretching of aromatic), 2931 (w, CH stretching of aliphatic), 1678 (s, carbonyl of chloroacetyl), 1645 (s, carbonyl of cyclohexanone), 1600 (s, C=C arylidene linkage).

PAKA 3_b. This compound was also prepared according to a general procedure of polymerization with monomer **2** (0.439 g, 1.00 mmol), 1,6-diaminohexane (0.1162 g, 1.00 mmol), and a few drops of piperidine as a catalyst in benzene for 6 h at 80°C; this resulted in a yellowish precipitate (76%).

Anal. Calcd. for C₂₆H₃₀N₂O₃S₂: C, 64.73%; H, 6.22%; N, 5.81%; S, 13.28%. Found: C, 64.21%; H, 5.91%; N, 5.97%; S, 13.46%. FTIR (KBr, cm⁻¹, ν): 3372 (w, NH, secondary amino group), 3034 (w, CH stretching of aromatic), 2930 (m, CH stretching of aliphatic), 1685 (s, carbonyl of chloroacetyl), 1648 (s, carbonyl of cyclohexanone), 1600 (s, C=C arylidene linkage).

PAKA 3_c. The title compound was synthesized according to a general procedure mentioned previously of polymerization with monomer **2** (0.439 g, 1.00 mmol), *p*-phenylenediamine (0.108 g, 1.00 mmol), and a few drops of piperidine as a catalyst in benzene for 8 h at 80°C as a brownish precipitate (83%).

Anal. Calcd. for C₂₆H₂₈N₂O₃S₂: C, 65.00%; H, 5.83%; N, 5.83%; S, 13.33%. Found: C, 65.66%; H, 6.13%; N, 5.66%; S, 13.85%. FTIR (KBr, cm⁻¹, ν): 3348 (w, NH, secondary amino group), 3052 (w, CH stretching of aromatic), 2929 (m, CH stretching of aliphatic), 1676 (s, carbonyl of chloroacetyl), 1652 (s, carbonyl of cyclohexanone), 1594 (s, C=C arylidene linkage).

PAKA 3_d. The title compound was prepared according to a general procedure of polymerization with monomer **2** (0.439 g, 1.00 mmol), *m*-phenylenediamine (0.108 g, 1.00 mmol), and a few drops of piperidine as a catalyst in benzene for 8 h at 80°C as a brown precipitate (80%).

Anal. Calcd. for C₂₆H₂₂N₂O₃S₂: C, 65.82%; H, 4.64%; N, 5.91%; S, 13.50%. Found: C, 65.58%; H, 4.67%; N, 6.37%; S, 14.05%. FTIR (KBr, cm⁻¹, ν): 3380 (w, NH, secondary amino group), 3055 (w, CH stretching of aromatic), 2932 (w, CH stretching of aliphatic), 1680 (s, carbonyl of chloroacetyl), 1640 (s, carbonyl of cyclohexanone), 1590 (s, C=C arylidene linkage).

PAKA 3_e. This compound was prepared on the basis of a previous procedure of polymerization with monomer **2** (0.439 g,

1.00 mmol), 1,2-diaminocyclohexane (0.1142 g, 1.00 mmol), and a few drops of piperidine as a catalyst in benzene for 8 h at 80°C as a brown precipitate (77%).

Anal. Calcd. for C₂₆H₂₂N₂O₃S₂: C, 65.82%; H, 4.64%; N, 5.91%; S, 13.50%. Found: C, 65.74%; H, 4.36%; N, 5.74%; S, 13.76%. FTIR (KBr, cm⁻¹, ν): 3365 (w, NH, secondary amino group), 3045 (w, CH stretching of aromatic), 2931 (w, CH stretching of aliphatic), 1676 (s, carbonyl of chloroacetyl), 1645 (s, carbonyl of cyclohexanone), 1590 (s, C=C arylidene linkage).

Metal-Ion Uptake

Sample Preparation and Procedure. Stock solutions of Cd(II), Co(II), Cu(II), Cr(III), Fe(III), Ni(II), and Zn(II) were prepared in 18.2 M Ω -cm distilled deionized water and stored in the dark at 4°C. For the selectivity study of polymers **3_d** and **3_e** as selected examples, standard solutions of each metal ion (with concentrations of 5 mg/L) were prepared and adjusted to a pH value of 5.0 with acetate buffer. Each standard solution was individually mixed with 25 mg of polymer **3_d** (or polymer **3_e**). In this study, a fixed pH value of 5.0 was chosen for all metal ions to prevent any precipitation of other species, in particular, Fe(III). For example, Fe(III) usually forms a precipitate of Fe(OH)₃ with buffer solutions at a pH value of greater than 5.0. For the study of the Fe(III) static adsorption capacity, standard solutions of 0, 5, 10, 15, 20, 25, 30, 50, 75, 125, and 150 mg/L were prepared as previously, adjusted to the optimum pH value of 5.0, and individually mixed with 25 mg of polymer **3_d** (or polymer **3_e**). All of the mixtures were mechanically shaken for 1 h at room temperature.

Apparatus

Monomer and Polymer Identification. The melting points reported for the monomer and premonomer were determined on a Gallen–Kamp melting point apparatus with a digital thermometer. Elemental analyses (C, H, and N) were performed on a CHN rapid analyzer. The new monomer and polymers gave C, H, and N analyses within the range $\pm 0.03\%$ of the theoretical values. FTIR spectra were recorded on a Nicolet 6700 Thermo Fisher Scientific, with the KBr pellet technique. ¹H-NMR was recorded on a Bruker AM 300 (¹H: 300 MHz) and on Bruker Advance 600 MHz with CDCl₃ as solvents with tetramethylsilane (TMS) as the internal reference. The mass spectrum for premonomer **1** was recorded on a high-resolution MALDI-TOF MS. Dithranol and *trans*-2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene]malononitrile were used as matrices. GPC measurements were carried out with GPC with an instrument from Agilent-GPC Agilent technologies. The refractive-index detector was model G-1362A with 100–104–105 Å Ultrastaygel columns connected in series. Tetrahydrofuran (THF) was used as the eluent with a flow rate of 1 mL/min. Commercially available linear poly(methyl methacrylate) and polystyrene standards were used to calibrate the columns. The GPC apparatus was run under the following conditions: flow rate = 2.000 mL/min, injection volume = 100.000 μ L, and sample concentration = 1.000 g/L.

Polymer Characterization and Applications. Solubility. The solubility characteristics of the polymers were inspected with the same solvents under the same conditions with 50 mg of

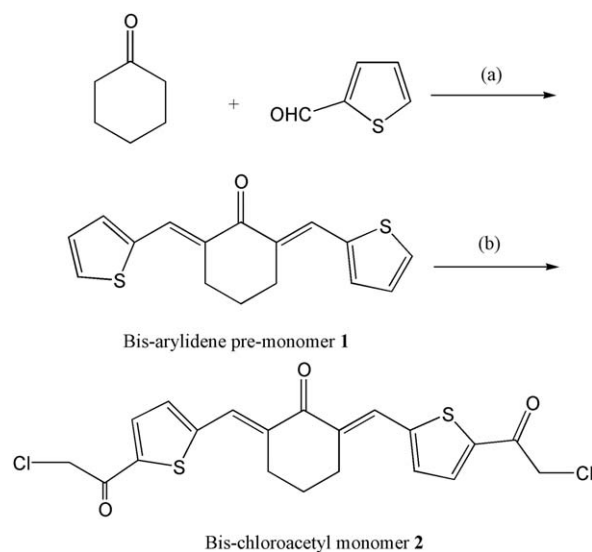


Figure 1. Synthesis procedure for premonomer 1 and monomer 2. The reagents and conditions were as follows: (a) absolute ethanol, KOH alcoholic solution, and stirring at 25°C for 6 h and (b) Friedel–Crafts conditions (chloroacetylchloride, carbon disulfide, and anhydrous aluminum chloride) and stirring in an ice bath for 6 h.

polymer in 1 mL of solvent. Solubility measurement was done for the powdery samples in excess solvent, including formic acid, chloroform, *n*-hexane, acetonitrile, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO).

Thermal analyses. TGA, derivative thermogravimetry (DTG), and DTA measurements were performed on a TA 2000 thermal analyzer. All of the measurements were carried out in an air stream under the same conditions with a heating rate of 10°C/min. The mass loss was plotted against increasing temperature and its first derivative (DTG), which represented the change in the decomposition rate.

SEM. The morphological behavior of the obtained PAKAs was examined by SEM with a JEOL JSM-5400 LV instrument. We prepared the SEM sample by putting a smooth part of the polymer powder on a copper holder and then coating it with a gold–palladium alloy. SEM images were taken with a Penta Z Z-50P camera with an Ilford film at an accelerating voltage of 15 kV with a low-dose technique.³²

ICP–OES. ICP–OES measurements were acquired with the use of a PerkinElmer ICP–OES model Optima 4100 DV. The ICP–OES instrument was optimized daily before measurement and operated as recommended by the manufacturers. The ICP–OES spectrometer was used with the following parameters: Force regular (FR) power = 1300 kW, frequency = 27.12 MHz, demountable Ar/Ar/Ar quartz torch, plasma gas (Ar) flow = 15.0 L/min, auxiliary gas (Ar) flow = 0.2 L/min, nebulizer gas (Ar) flow = 0.8 L/min, nebulizer pressure = 2.4 bar, glass spray chamber according to Scott (Ryton), sample pump flow rate = 1.5 mL/min, integration time = 3 s, replicates = 3, and wavelength range of the monochromator = 165–460 nm. Selected metal ions were measured at wavelengths of 228.80 nm for Cd(II), 238.90 nm for Co(II), 327.39 nm for Cu(II), 267.72 nm for Cr(III), 259.94 nm for Fe(III), 221.65 nm for Ni(II), and 206.20 nm for Zn(II).

RESULTS AND DISCUSSION

Syntheses of PAKAs 3_a–3_e

As a continuation of our study on the synthesis and characterization of different new polymers containing arylidenecycloalkanone moieties possessing interesting properties, it was, therefore, thought appropriate to synthesize new PAKA 3_a–3_e hybrid polymers with the solution polycondensation method. These polymers mainly consisted of thiophene–arylidene–thiophene as building units with different aromatic and aliphatic spacers in the main chains. The new polymers necessitated the synthesis of new monomers. (2E,6E)-2,6-bis(thiophen-2-ylmethylene)cyclohexanone premonomer 1 was prepared by the basic catalyzed condensation of 2 mol of 2-thiophenecarbaldehyde with 1 mol of cyclohexanone in ethanol. A new thiophene-based monomer, namely, 1,1'-(1E,1'E)-(2-oxocyclohexane-1,3-diylidene)bis(methanylylidene)bis(thiophene-5,2-diyl)bis(2-chloroethanone) 2, was synthesized in high yield, depending on the electrophilic Friedel–Crafts condensation reaction. The reaction was carried out by the interaction of premonomer 1 with chloroacetylchloride in the presence of carbon disulfide and anhydrous aluminum chloride, as illustrated in Figure 1. The structure of premonomer 1 was confirmed as described in our previous study (see the Experimental section).³¹ The structure of the new monomer 2 was also confirmed by elemental and spectral data, with fully assignable FTIR and ¹H-NMR spectra, as presented in the Experimental section.

A solution polycondensation technique^{7,9} was used to synthesize a new interesting class of PAKA 3_a–3_e containing a thiophene moiety in the polymer main chains by the interaction of monomer 2 with different aliphatic, cyclic, and aromatic diamines. The synthetic procedure is given in Figure 2. The reaction yield was high and ranged between 72 and 83% as long as the thiophenes could easily be incorporated into the polymer chains. Elemental analyses and spectral data were consistent with the chemical structures of the new polymers and the characteristic repeating units of each polymer. The spectral data also supported the structural assignments for the new polymers (the data were included in the Experimental section). The FTIR spectral data for the PAKA displayed bands at 3400–3300 cm⁻¹, which were attributed to N–H of the secondary amino group; 1685–1670 cm⁻¹ due to the carbonyl of the chloroacetyl group; 1640–1660 cm⁻¹, which represented the carbonyl of the cyclohexanone moiety; and 1200–1300 cm⁻¹ for C–N. The elemental and spectral data were given in the Experimental section.

Polymer Characterization

The resulting polymers were inspected with various characterization tools, including solubility, thermal analyses (TGA, DTG, and DTA), GPC molecular weight determinations, and SEM measurements.

The room-temperature solubility was examined, as previously mentioned in the Experimental section. The solubility results for those PAKA in the selected solvents are given in (Table I). All of the polymers were soluble in protonic solvents, such as formic acid, and had yellowish to deep brown colors. However, we found that all of the polymers were completely soluble at room temperature in DMSO and DMF as polar aprotic

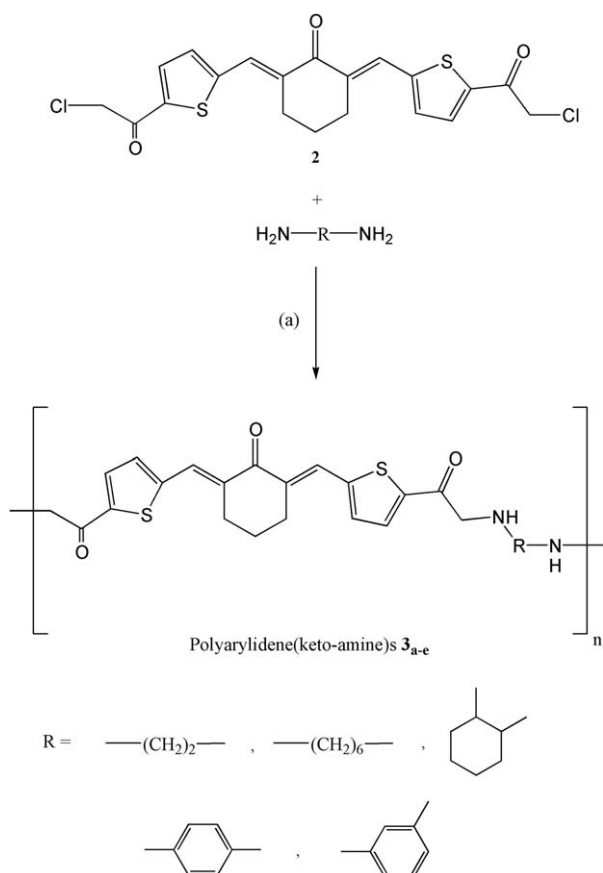


Figure 2. Synthesis procedure for PAKAs **3_a–3_e**. The reagents and conditions were as follows: (a) polycondensation, dry benzene, a few drops of pyridine, and stirring for 6–8 h at about 80°C.

solvents. On the other hand, half of these polymers were partially soluble in *n*-hexane and chloroform, whereas the second half were completely insoluble, except polymer **3_b**, which was completely soluble in *n*-hexane. The majority were partially or completely soluble in acetonitrile, except for polymer **3_c**, which was completely insoluble in the same solvent. Furthermore, polymers based on flexible polymethylene spacers [(CH₂)₆] had slightly more solubility than the other polymers containing aromatic moieties. This observation was also more pronounced for the shorter aliphatic methylene spacers [(CH₂)₂] and appeared clearly in both the *n*-hexane and acetonitrile solvents. The resulting PAKA hybrid polymers acting as analogue polymers were described in our previous study.^{6,33} The higher flexibility of the cyclohexanone moiety gave better solubility for most of the polymers in most of the tested solvents compared to the other moieties described elsewhere.^{4,34} More particularly, the presence of thiophene–arylidene–thiophene triblocks containing two thiophene moieties as heteroaromatic species in the polymer main backbone resulted in an increasing chain packing distance and decreasing interchain interactions, such as hydrogen bonding, and hence, this made solvation easier.³⁵ The results illustrated in Table I clearly indicate that the PAKA-based aliphatic spacers in the polymers main chain had a slightly higher solubility than the PAKA-based aromatic spacers, which clearly appeared in the two solvents *n*-hexane and acetonitrile.

Table I. Solubility Characteristics of PAKAs **3_a–3_e**

Polymer code	DMSO	DMF	<i>n</i> -Hexane	CH ₃ CN	CHCl ₃	HCOOH
3_a	+	+	±	+	–	+
3_b	+	+	+	+	±	+
3_c	+	+	±	+	–	+
3_d	+	+	–	±	±	+
3_e	+	+	–	±	–	+

+, soluble at room temperature; ±, partially soluble; –, insoluble.

Molecular weights were determined by GPC. The value of molecular weight was computed by means of a computer program, results are recorded in Table II. From the data presented in Table II, it was noticed that the weight-average molecular weight (M_w) were from 40,193.7 to 33,578.6 for polymers **3_{b–d}** as selected examples. This average molecular weight is considered as high molecular weight in comparison to that previously reported in the literature for nearly similar thiophene–arylidene–thiophene system.³⁶ In all cases, the linking aliphatic, cyclic, and aromatic units gave nearly the same molecular weight of the polymers. PAKA **3_d** provided the highest molecular weight [$M_w = 40,193.7$, number-average molecular weight (M_n) = 36,314, average number of repeating units (P_w) ≈ 85, and polydispersity index (PDI) = 1.106], whereas PAKA **3_b** resulted in the lowest molecular weight ($M_w = 33,578.6$, $M_n = 29,645$, $P_w = \sim 70$, and PDI = 1.13).

The thermal properties of PAKA **3_a–3_e** were evaluated by TGA, DTG, and DTA at a heating rate of 10°C/min in the presence of an air atmosphere, as shown in Figure 3. The T_{10} , T_{20} , T_{30} , T_{40} , and T_{50} values represent the temperatures for various percentages of weight loss (10, 20, 30, 40, and 50%, respectively; Table III). The thermographs of all of the polymers had the same pattern of decomposition. All of the curves showed a small weight loss in the range 3–5%; this may have been attributed to the loss of moisture and entrapped solvents. It is noteworthy that the decomposition occurred mainly in a two-step process. The first stage ranged from 165 to 384°C, whereas the second stage of degradation of those polymers occurred between 412 and 595°C. The rate of degradation in the first stage was somewhat faster than that in the second stage. The expected nature of the decomposition in the first step was dependent on the nature of arylidene polymers; this may have been due to the pyrolytic oxidation of C=C bonds and the scission of many bonds.³⁷ Similar behavior for the analogues arylidene polymers was also observed, as described in our previous report.^{3–5,9} The expected decomposition in the second step was based on the degradation rate of the keto–amino group, the scission of many bonds, and the formation of char as an end product. This finding was in good agreement with that previously reported by Patel et al.³⁸ The maximum polymer degradation temperature (PDT_{max}) corresponded to the temperature at which the maximum rate of weight loss occurred. PDT_{max} for all of the polymers were nearly the same in the range 475–492°C, as illustrated in Table III. T_{10} , in the range from 247 to 306°C, was considered the polymer

Table II. GPC Results for PAKAs 3_a–3_e

Polymer code	Molecular formula	GPC ^a		
		M_w	P_w	PDI
3 _a	(C ₂₂ H ₂₂ N ₂ O ₃ S ₂) _n	—	—	—
3 _b	(C ₂₆ H ₃₀ N ₂ O ₃ S ₂) _n	33,578.6	~70	1.13
3 _c	(C ₂₆ H ₂₈ N ₂ O ₃ S ₂) _n	37,814.4	~79	1.12
3 _d	(C ₂₆ H ₂₂ N ₂ O ₃ S ₂) _n	40,193.7	~85	1.106
3 _e	(C ₂₆ H ₂₂ N ₂ O ₃ S ₂) _n	—	—	—

^aAll GPC measurements were performed in THF.

decomposition temperature. Therefore, the data in Table III indicate that all of the investigated PAKA polymers had a high thermal stability at T_{10} , except polymer 3_b, which was thermally stable up to 247. The order of higher thermal stability at T_{10} was 3_d > 3_c > 3_a > 3_e > 3_b. Polymer 3_b was the lowest thermally stable polymer at all of the given temperatures for various percentage weight losses (10–50%). This was attributed to the flexible aliphatic spacer (CH₂)₆. The final decomposition temperature (FDT) corresponded to the temperature at which the rate of degradation that could occur was nearly completed. We clarified from the TG curves that the FDT for all of the polymers was nearly completed around 534–560°C. These data indicate that the produced PAKA 3_a had a higher PDT_{max} and FDT than other synthesized PAKA. Furthermore, the decompositions at T_{40} and T_{50} were mainly dependent on the chemical structure of the polymer. The relative thermal stability of polymers was determined from both values. An examination of the data showed that the T_{40} and T_{50} values were in the range 400–420 and 427–448°C, respectively; this indicated their high thermal stability.

The morphological properties for PAKA 3_b, as a selected example, were measured by SEM measurements with a JEOL JSM-5400 LV instrument to show the surface of the polymer, as described in the Experimental section. The study of the polymer 3_b surface magnification (7500×) showed that it consisted of a coflower shape [Figure 4(a)], with higher magnifications

(10,000×) showed a spongy shape [Figure 4(b)], whereas the magnification of 15,000× showed coral reefs with small rodlike aggregates containing microholes. The presented microholes had expansion slots in the range 0.5–1.0 μm [Figure 4(c)].

Selectivity Competition Toward Different Metal Ions

Selectivity Study of the PAKA 3_d and PAKA 3_e Polymers. Selectivity of the newly synthesized PAKA 3_d and PAKA 3_e polymers toward different metal ions was investigated on the basis of the determination of the distribution coefficient of the PAKA 3_d and PAKA 3_e polymers. The distribution coefficient (K_d , mL/g) was obtained with the following equation:³⁹

$$K_d = (C_0 - C_e / C_e) \times (V / m) \quad (1)$$

where C_0 and C_e refer to the initial and final concentrations before and after filtration with PAKA 3_d (or PAKA 3_e), respectively; V is the volume (mL); and m is the weight of the PAKA 3_d (or PAKA 3_e) polymer (g). The distribution coefficient values of all of the metal ions investigated in this study are summarized in Table IV. As clearly shown in Table IV, the greatest distribution coefficient value was obtained for Co(II) with PAKA 3_d and for Fe(III) with PAKA 3_e in comparison to other metal ions. As shown in Table IV, the amounts of Co(II) and Fe(III) were almost all extracted by the PAKA 3_d and PAKA 3_e polymers, respectively. However, the distribution coefficient value obtained for Fe(III) with PAKA 3_e (85,206.90 mL/g) was greater than that obtained for Co(II) with PAKA 3_d (49,505.05 mL/g); this indicated that the PAKA 3_e adsorbent was more selective than PAKA 3_d. Thus, the selectivity study results indicate that the newly synthesized PAKA 3_d and PAKA 3_e polymers were the most selective toward Co(II) and Fe(III), respectively, among all of the metal ions. On the basis of the previous results, negative charge sites and incorporated donor atoms (N, O, and S) present in the PAKA 3_d and PAKA 3_e polymers were able to easily bind with positively charged Co(II) and Fe(III), respectively, ions via electrostatic attraction. In addition, the effects of several ions on the extraction of Co(II) and Fe(III) were investigated. In this study, model standard solutions containing fixed amounts of 1 mg/L Co(II) [or Fe(III)] with mixed-matrix ions were prepared according to the recommended procedure. The results show that the extractions of Co(II) and Fe(III) were not affected by the medium composition containing mixed ions.

Static Adsorption Capacity. For the determination of the static uptake capacities of Co(II) and Fe(III) on the same examples of

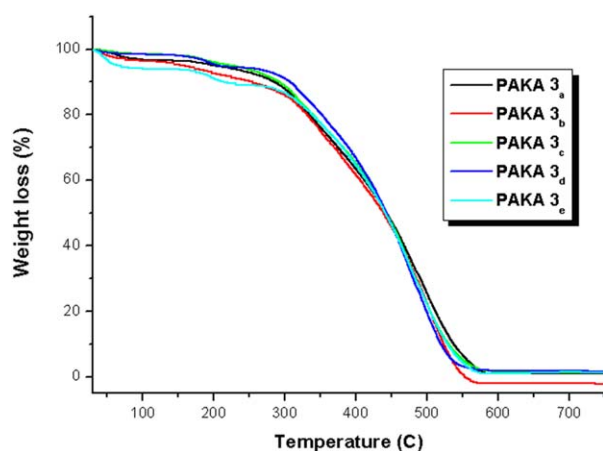


Figure 3. TGA curves of PAKA 3_a–3_e in air at a heating rate of 10°C/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Thermal Properties of PAKAs 3_a–3_e

Polymer code	PDT _{max} (°C) ^a	FDT (°C) ^b	Temperatures at various decomposition percentages (°C) ^b				
			T ₁₀	T ₂₀	T ₃₀	T ₄₀	T ₅₀
3 _a	492	560	282	331	372	410	445
3 _b	475	535	247	329	362	400	427
3 _c	477	542	292	338	376	413	447
3 _d	480	536	306	348	383	420	448
3 _e	475	534	277	331	373	413	446

^aDetermined from differential thermal gravimetry (DrTGA) curves.

^bDetermined by TGA at a heating rate of 10°C/min.

PAKA 3_d and PAKA 3_e, 25 mL of the Co(II) [or Fe(III)] sample solutions with different concentrations (0–150 mg/L) were adjusted to pH 5.0 and individually mixed with 25 mg of PAKA 3_d (or PAKA 3_e). These mixtures were mechanically shaken for 1 h at room temperature. The static adsorption capacity was obtained with eq. (2) as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where q_e represents the concentration of metal ions adsorbed by the polymer (mg/g); C_0 and C_e are the initial and equilibrium

concentrations of the metal ions in solution (mg/L), respectively; and m is the weight of polymer (g). Figure 5 displays the metal-uptake capacity of both the PAKA 3_d and PAKA 3_e polymers for Co(II) and Fe(III), respectively, obtained from the experiment of adsorption isotherms. The adsorption capacities of PAKA 3_d and PAKA 3_e for Co(II) and Fe(III) were determined to be 69.00 and 62.67 mg/g, respectively. These results indicate that the adsorption capacity of PAKA 3_d for Co(II) was improved by 10.10% in comparison to that of PAKA 3_e for Fe(III) after only 1 h of contact time. The reported adsorption capacities in this study were comparable with those previously

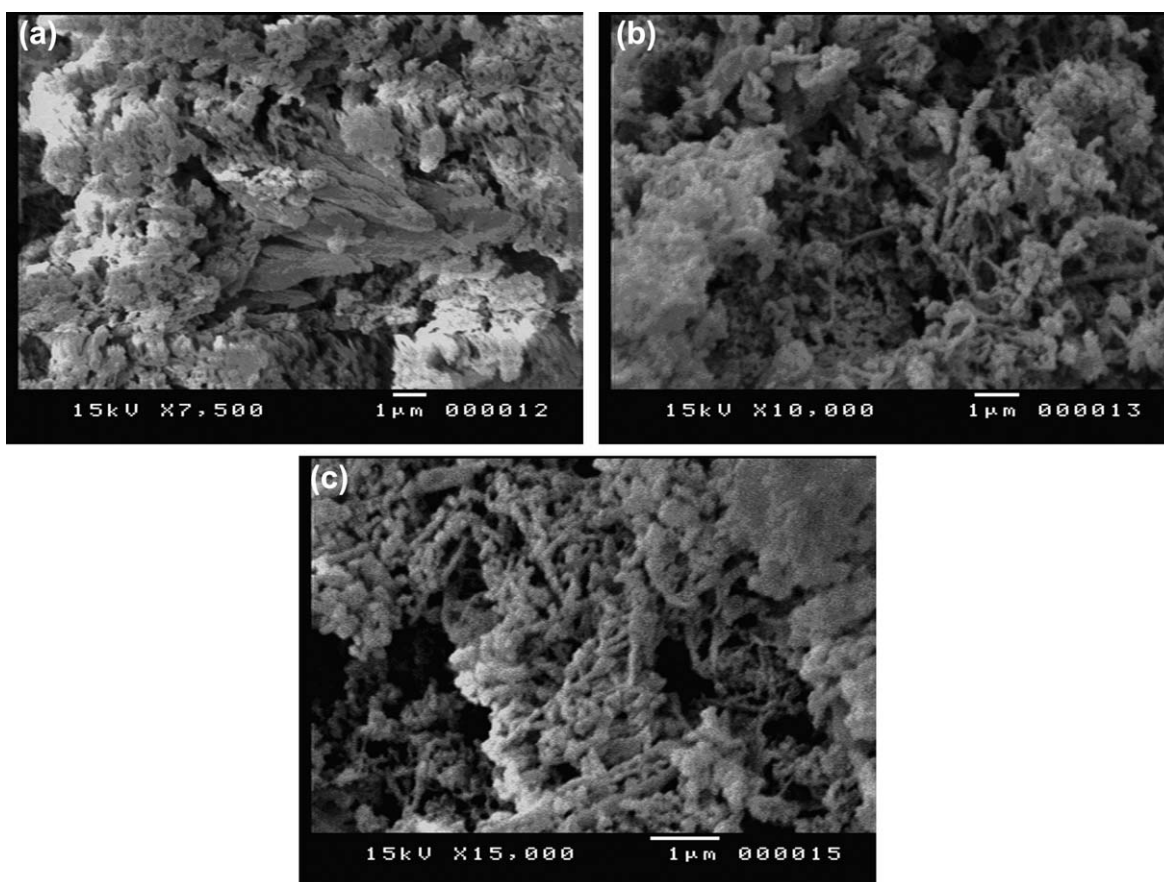


Figure 4. SEM images of the polymer surface of PAKA 3_b at different magnifications: (a) 7500, (b) 10,000, and (c) 15,000×.

Table IV. Selectivity Study of the Adsorption of Polymers **3_d** and **3_e** Toward Different Metal Ions at pH 5.0 and 25°C ($N = 3$)

Metal ion	q_e (mg/g)		K_d (mL/g)	
	3_d	3_e	3_d	3_e
Cd(II)	0.01	0.40	2.00	87.90
Co(II)	4.90	0.74	49,505.05	173.71
Cr(III)	0.60	1.68	137.40	505.57
Cu(II)	0.01	0.49	2.00	108.65
Fe(III)	0.29	4.94	61.35	85,206.90
Ni(II)	3.31	0.49	1960.33	108.40
Zn(II)	0.02	0.03	4.02	6.04

N , number of reading.

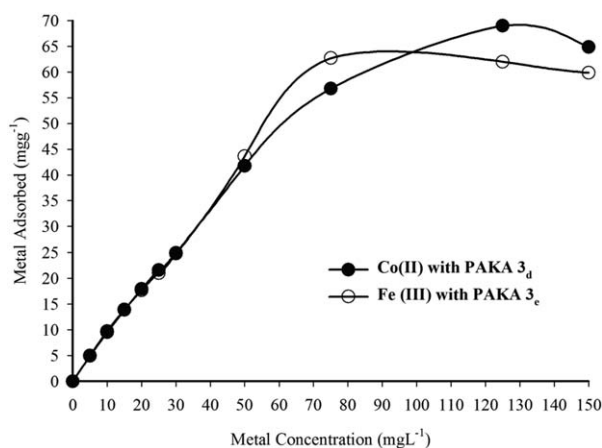
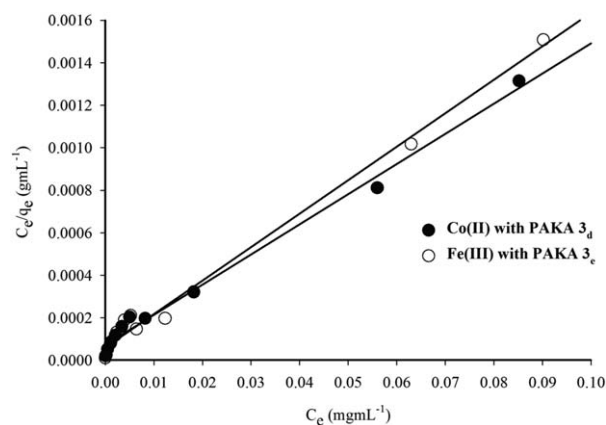
reported for Co(II) (0.92–1.69,⁴⁰ 2.90,⁴¹ 11.53,⁴² 19.75,⁴³ 24.75,⁴⁴ 27.62,⁴³ and 212.80–322.60 mg/g⁴⁰) and Fe(III) (7.00,⁴⁵ 18.30,⁴⁶ 28.90,⁴⁷ and 173.14 mg/g⁴⁸) by other approaches.

Adsorption Isotherm Models

Experimental equilibrium adsorption data were analyzed with different models to develop an equation that accurately represented the results. The Langmuir equation is based on the assumption of a monolayer adsorption onto a completely homogeneous surface with a finite number of identical sites and a negligible interaction between the adsorbed molecules. The Langmuir adsorption isotherm model is governed by the following relation:⁴⁹

$$C_e/q_e = (C_e/Q_o) + 1/Q_o b \quad (3)$$

where C_e corresponds to the equilibrium concentrations of Fe(III) ions in solution (mg/mL) and q_e is the concentration of metal ions adsorbed by the adsorbate (mg/g). The symbols Q_o and b refer to Langmuir constants related to the adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. These constants were determined from a linear plot of C_e/q_e against C_e with a slope and intercept equal to $1/Q_o$ and $1/Q_o b$,

**Figure 5.** Adsorption profiles of Co(II) and Fe(III) on 25 mg of the PAKA **3_d** and PAKA **3_e** polymers, respectively, with respect to the concentration at pH 5.0 and 25°C.**Figure 6.** Langmuir adsorption isotherm model of the Co(III) and Fe(III) adsorption on 25 mg of the PAKA **3_d** and PAKA **3_e** polymers, respectively, at pH 5.0 and 25°C. The adsorption experiments were performed with different concentrations (0–150 mg/L) of Co(II) and Fe(III) under static conditions.

respectively. Moreover, the essential characteristics of the Langmuir adsorption isotherm are represented in terms of a dimensionless constant separation factor, or equilibrium parameter (R_L), which is defined as follows:

$$R_L = 1/(1 + bC_0) \quad (4)$$

where C_0 the initial concentration of the analyte. The R_L value indicates the type of the isotherm, and R_L values between 0 and 1 represent a favorable adsorption.⁵⁰

It can be clarified from Figure 6 that the experimental isotherm data fit well with the Langmuir equation on the basis of the least squares fit; this supported the validity of the Langmuir adsorption isotherm model for the adsorption process. Consequently, the adsorption isotherm data indicated that the adsorption process was mainly a monolayer one on a homogeneous adsorbent surface. The Langmuir isotherm constants for the adsorption of Co(II) and Fe(III) on PAKA **3_d** and PAKA **3_e**, respectively, are tabulated in Table V. As illustrated in Table V, high correlation coefficients were obtained from the Langmuir adsorption model for the adsorption of Co(II) and Fe(III) on PAKA **3_d** and PAKA **3_e**. Furthermore, the static adsorption capacities calculated from the Langmuir equation of the PAKA **3_d** (70.47 mg/g) and PAKA **3_e** (63.49 mg/g) polymers were strongly correlated with those obtained from the experimental isotherm studies (69.00 mg/g for PAKA **3_d** and 62.67 mg/g for PAKA **3_e**). The R_L values of Co(II) and Fe(III) adsorption on the PAKA **3_d** and PAKA **3_e** polymers were also found to be 0.04

Table V. Parameters of the Langmuir Isotherm Constants for the Adsorption of Co(II) and Fe(III) onto **3_d** and **3_e**, Respectively, at pH 5.0 and 25°C ($N = 3$)

Adsorbent	Q_o (mg/g)	b (L/mg)	R^2	R_L
3_d	70.47	0.20	0.99	0.04
3_e	63.49	0.26	0.99	0.05

N , number of reading.

and 0.05, respectively; this showed that highly favorable adsorption processes were based on the Langmuir classical adsorption isotherm model. Thus, the adsorption isotherm data of Co(II) and Fe(III) for PAKA **3_d** and PAKA **3_e**, respectively, fit well with the Langmuir adsorption isotherm. This strongly confirmed that the adsorption process was mainly a monolayer one on the homogeneous adsorbent surfaces.

CONCLUSIONS

New PAKAs containing thiophene moieties in the polymer main chains were synthesized by the interaction of a new monomer, **2**, with different aliphatic, cyclic, and aromatic diamines. All of the polymers showed high solubility characteristics in polar aprotic solvents at room temperature. PAKA polymers **3_b**–**3_d** showed a range of 40,193.7–33,578.6. Polymer **3_b** was the lowest thermally stable polymer at all of the given temperatures for various percentage weight losses. The order of higher thermal stability at T_{10} was $3_d > 3_c > 3_a > 3_e > 3_b$. All of the polymers had similar PDT_{max} values, which appeared in the range 475–492°C. The efficiency of the newly synthesized PAKA **3_d** and PAKA **3_e** polymers for selective adsorption and determination of Co(II) and Fe(III) in aqueous solution was evaluated. Reasonable static adsorption capacities of 69.00 for PAKA **3_d** and 62.67 for PAKA **3_e** were achieved for Co(II) and Fe(III), respectively. The adsorption isotherm results of Co(II) and Fe(III) fit well with the Langmuir classical adsorption isotherm model. Thus, the method may play an important role in its use as an effective approach for the selective adsorption and determination of Co(II) and Fe(III) in complex matrices for a range of several applications.

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