

Poly(vinyl chloride)-supported triazoles grafted onto calix[4]arene for chromium ions extraction

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Abstract: A new suitable material was synthesized using click reaction between dialkynyl-*p*-tert-butylcalix[4]arene and poly(vinyl chloride) azide (PVC-N₃). This novel dialkynyl-*p*-tert-butylcalix[4]arene with triazole groups grafted onto PVC polymer (PVC-0.75CX[4]) has an excellent extraction capability for chromium ions from aqueous solutions. It shows a unique ability to extract chromium (VI) ions from aqueous solutions. The soft cavity, the presence of π -triazole rings and hydrogen bonds play all essential roles in the removal of chromium species. Cr (VI) ion sorption capacity is 95.5% at pH = 3.

Keywords: calix[4]arene, poly(vinyl chloride), triazole, chromium(VI) extraction.

Ekstrakcja jonów chromu z użyciem kaliks[4]arenu modyfikowanego triazolami szczepionego poli(chlorkiem winylu)

Streszczenie: W wyniku reakcji typu *click* między dialkyniło-*p*-tert-butylokaliks[4]arenem a azydkiem poli(chlorku winylu) (PVC-N₃) otrzymano nowy związek – dialkyniło-*p*-tert-butylokaliks[4]aren z grupami triazolowymi szczepiony na poli(chlorku winylu) (PVC-0.75CX[4]). Wykazuje on wyjątkową zdolność do ekstrakcji jonów chromu(VI) z roztworów wodnych, dzięki sprężystej wnęce, obecności pierścieni π -triazolowych i wiązań wodorowych. Zdolność do sorpcji jonów Cr(VI) wynosi 95,5% przy pH = 3.

Słowa kluczowe: kaliks[4]aren, poli(chlorek winylu), triazole, ekstrakcja jonów chromu(VI).

Calix[n]arenes are the third generation of supramolecular chemistry following crown ethers and cyclodextrines as first and second generations respectively [1]. However, calixarenes can be easily functionalized at one or both of its rims in order to exploit the potential of these macrocyclic compounds family and its derivatives for the removal of pollutants from environment [2–4]. As well known, the use of poly(vinyl chloride) (PVC) as an adsorbent material in the adsorption process in solutions is very scanty [5]. In addition, the chemical modification of PVC generates an opportunity to produce a novel material with interesting features. PVC containing chelating moieties and triazoles had the capacity to separate heavy

metals from aqueous solutions [6]. Recently, chromate and dichromate anions have been attracted a lot of attention, because of their bioaccumulation and non-biodegradability in the environment as well as high toxicity and persistent character in ground water and soil. As a consequence, several studies have invented some technologies for the removal of toxic metal ions from waste water before releasing into our environment. Moreover, they have applications in host-guest chemistry [7] as sensors [8], calixarene derivatives as biosensors [9], catalysts [10], solid-liquid extractants that can provide a selective separation and recovery of pollutants from the effluent mixtures. In addition, the studies on using calixarenes based covalent polymers are rare, however the covalent polymers functionalized with calixarenes have the capacity for removal of metal ions and several toxins. Therefore, many studies developed some new polymeric adsorbents for removal of heavy metals from aqueous media, several of them have been reported in literature. For example, Chen *et al.* synthesized a novel biopolymeric adsorbent based on the starch grafted *p*-tert-butylcalix[n]arenes (SGC4, SGC6, SGC8) as a potential extractant used for dyes and organic wastewater [11]. Besides, Kitano *et al.* studied the complexation of Bisphenol A with calix[6]

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arene–polymer conjugates [12]. Then, Trivedi *et al.* prepared a novel material calix[6]hydroxyamide-based polymer for complexing uranium, thorium, and cerium [13]. Also, Tabakci *et al.* studied the adsorption properties of calix[4]arene–chitosan polymers towards particular heavy metals cations (Co^{2+} , Hg^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , Ni^{2+} and $\text{Cr}_2\text{O}_7^{2-}$), exceeding chitosan [14]. Moreover, Prabawati *et al.* synthesized three novel polymers [poly(monoallyloxy calix[6]arene), monoallyloxy penta-ester calix[6]arene and poly(monoallyloxy penta-acid calix[6]arene)] as heavy metal cations [Cd(II), Cu(II), and Cr(III)] extractants. Then the presence of hydroxyl group in polymer structure caused an increased area for better separation of heavy metals [15]. Chromium as an ecotoxic pollutant is very dangerous because of its accumulative and persistent character in the environment so it needs to be removed from water. Thereby, Khan *et al.* synthesized an effective calix[4]arene functionalized XAD-4 resin used in the sorption of Cr(VI) from water [16].

The aim of our studies is to present the preparation, characterization and removal properties of polymeric material towards Cr(VI) ions from aqueous solutions. The synthesized polymeric material was synthesized in two steps. In the first step calix[4]arene was transformed into dipropargylcalix[4]arene. The second step associated a coupling reaction between the derivative dipropargylcalix[4]arene and the azide functionalized poly(vinyl chloride) (PVC- N_3) via click chemistry based on the CuAAC or copper(I)-catalyzed Huisgen's reaction. Synthesized materials were characterized using FT-IR, elemental analysis (EA), GPC, and TGA/DSC thermal analysis.

EXPERIMENTAL PART

Materials

Poly(vinyl chloride) (PVC) powder ($M_w = 43\,000$) was purchased from Fluka, NaN_3 powder ($\geq 99.5\%$), tetrahydrofuran (THF, $\geq 99.0\%$), formaldehyde (HCHO, 37 wt% in H_2O), *p*-tert-butylphenol (99%), ethyl acetate (EtOAc, 99.8%), acetic acid and acetone ($\geq 99.9\%$), toluene (99.8%), potassium carbonate (K_2CO_3 , $\geq 99.0\%$), acetonitrile (99.8%), hexane ($\geq 99\%$), dichloromethane ($\geq 99.5\%$), methanol ($\geq 99.9\%$), *N,N*-diisopropylethylamine (99.5%), copper(I) iodide ($\geq 99.5\%$) were bought from Sigma Aldrich and used without further purification. Deionized water was used in some synthesis.

Methods

Synthesis of PVC- N_3

5 g of poly(vinyl chloride) (16 mmol Cl) was dissolved in 200 ml of dimethylformamide (DMF). Then, 8 g of NaN_3 (123 mmol, 7.7 eq) was added. After cooling down at room temperature, the product precipitated in a mixture of water and methanol (v/v), and was filtered on sintered glass and dried in vacuum oven. The weight of obtained polymer was 4.85 g and its form was a white powder. It had low solubility in THF and was practically insoluble in the other organic solvents [6]. The identification of its chemical structure was conducted by FT-IR and elemental analysis, for the IR spectra the characteristic peaks were: $\nu_{\text{N}_3} = 2100$, $\nu_{\text{OH}} = 3316$, $\nu_{\text{N=N}} = 1655\text{ cm}^{-1}$. The elemental

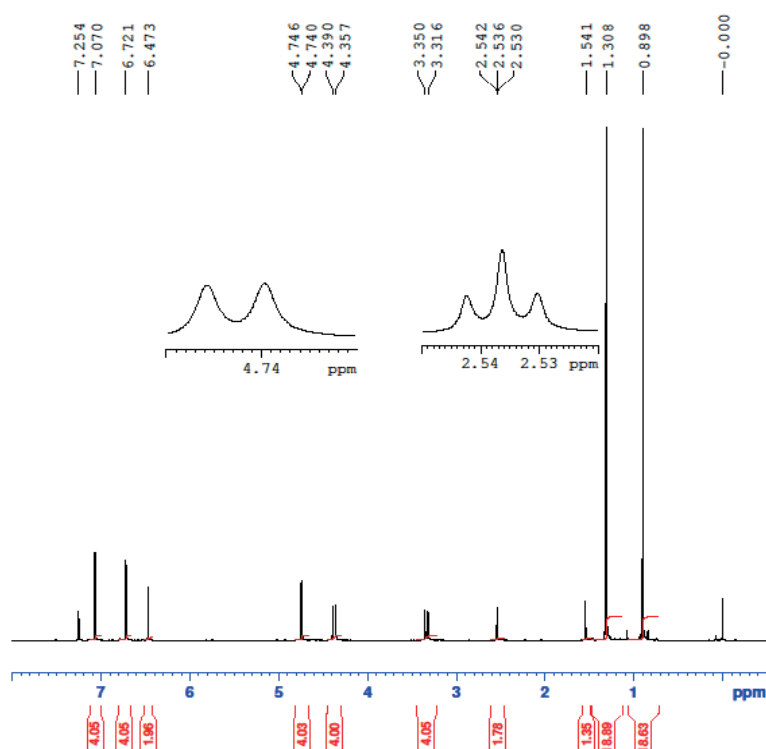


Fig. 1. $^1\text{H-NMR}$ spectrum of cone-5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-dipropargylcalix[4]arene

analysis allowed us to determine the number of moles of chlorine substituted by the azide group (N_3) in the polymer mass, the result was 27.35 mmol N/g or 9.11 mmol N_3 /g fixed on the polymer mass. The percentage of the elements was: %C = 39.15, %H = 4.39, %N = 38.31.

Synthesis of *p*-tert-butylcalix[4]arene

p-tert-butylcalix[4]arene is a macrocyclic compound formed from *p*-tert-butylphenol and formaldehyde condensations. The preparation of *p*-tert-butylcalix[4]arene was a several-step sequence which followed a well developed literature procedure as was reported by Gutsche and Iqbal [17]. The 1H NMR spectra (400 MHz, $CDCl_3$, Me_4Si) showed 4.23 and 4.27 ppm (d, 4H, $ArCH_2Ar$), 3.47 and 3.50 ppm (d, 4H, $ArCH_2Ar$), 10.33 ppm (s, 4H, ArOH), 7.04 ppm (s, 8H, ArH), 1.21 ppm [s, 18H, $C(CH_3)_3$]. ^{13}C NMR spectra (400 MHz, $CDCl_3$, Me_4Si) showed: 31.41 ppm [$C(CH_3)_3$], 32.62 and 34.01 ppm (CH_2Ar), 146.68 and 144.38 ppm (CMe_3Ar), and 129.05, 128.24, 127.70, 125.94 and 125.31 ppm (Ar). Yield was 49%, for $C_{44}H_{56}O_4$, $M^+ H_2O = 666.21$ m/z. FT-IR (ATR) analysis showed phenolic-OH stretching at around 3163 cm^{-1} ; 2953 and 2867 cm^{-1} were assigned to $C-H(sp^3)$ and $C-H(sp^2)$ stretching respectively. 1594 and 1466 cm^{-1} were assigned for $C=C$ stretching.

Synthesis of cone-5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-dipropargylcalix[4]arene

8 g (12.32 mmol) of *p*-tert-butylcalix[4]arene and 4.12 g (29.28 mmol) of potassium carbonate were suspended in acetonitrile (150 ml) and refluxed under inert atmo-

sphere for about one hour until the most of reagents were dissolved. Afterwards, to this stirred mixture 5.04 g (42.38 mmol, 3.77 ml) of propargyl bromide (80 wt% solution in toluene) in acetonitrile (30 ml) was added dropwise for one hour and the reaction mixture was refluxed for 36 hours [18]. The yield of the synthesis was 80%, ESI-MS result was $M_w = 725.02$, calculated for $C_{50}H_{60}O_4$, $M^+ H_2O = 742.45$ m/z. 1H NMR ($CDCl_3$), Fig. 1, showed: $\delta = 7.25$ ppm (s, 2H, ArOH), 7.07 ppm (s, 4H, ArH), 6.72 ppm (s, 4H, ArH), 6.47 ppm (s, 2H, CCH), 4.74 ppm (d, 4H, OCH_2C), 4.39 ppm (d, 4H, $ArCH_2Ar$), 3.35 ppm (d, 4H, $ArCH_2Ar$), 1.30 ppm [s, 18H, $C(CH_3)_3$], 0.89 ppm [s, 18H, $C(CH_3)_3$]. ^{13}C NMR spectra ($CDCl_3$), Fig. 2, showed: $\delta = 150.37, 147.24, 141.63, 132.57$ ppm (Ar), 128.04 ppm (CMe_3), 125.54–125.03 ppm (ArH), 78.80 ppm ($-C\equiv$), 63.27 ppm ($ArCH_2Ar$), 33.85–33.88 ppm (OCH_2C), 30.95, 31.72 and 32.03 ppm (CMe_3).

The DEPT-135 spectrum (Fig. 3) is in similarity with ^{13}C and 1H which proved the obtained molecular structure.

Synthesis of azide-PVC/dialkylated-*p*-tert-butylcalix[4]arene material

2 g of PVC- N_3 (18.22 mmol of N_3), 1.5 g (2.068 mmol) of dipropargylcalix[4]arene, 1.26 g (8.79 mmol) of cuprous bromide and 2.76 g (17.7 mmol) of 2,2'-dipyridine in 40 ml of DMF were mixed together and the mixture was stirred and kept at a temperature of $30\text{--}40^\circ C$ for 24 hours. After cooling down, the product was precipitated in water and methanol (v/v). Thereafter, it was filtered in order to remove copper salts. After that it was dried overnight in an oven vacuum at $50^\circ C$ to afford PVC-0.75CX[4] as purified and final material (Scheme 1).

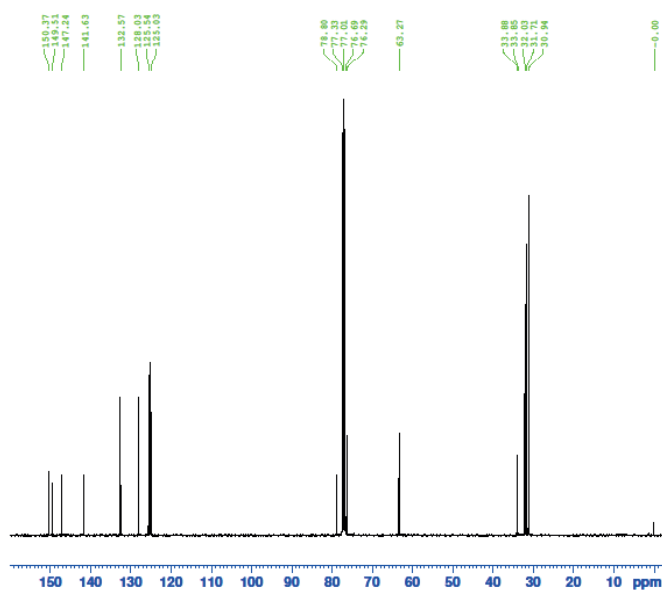


Fig. 2. ^{13}C -NMR spectrum of cone-5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-dipropargylcalix[4]arene

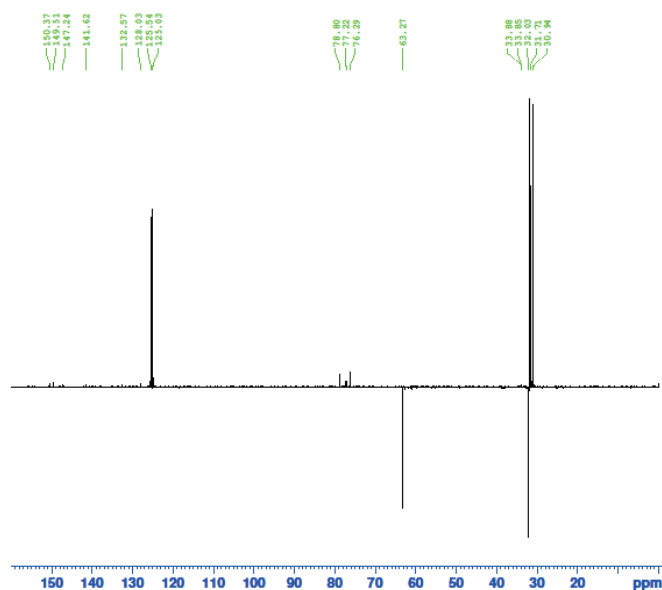
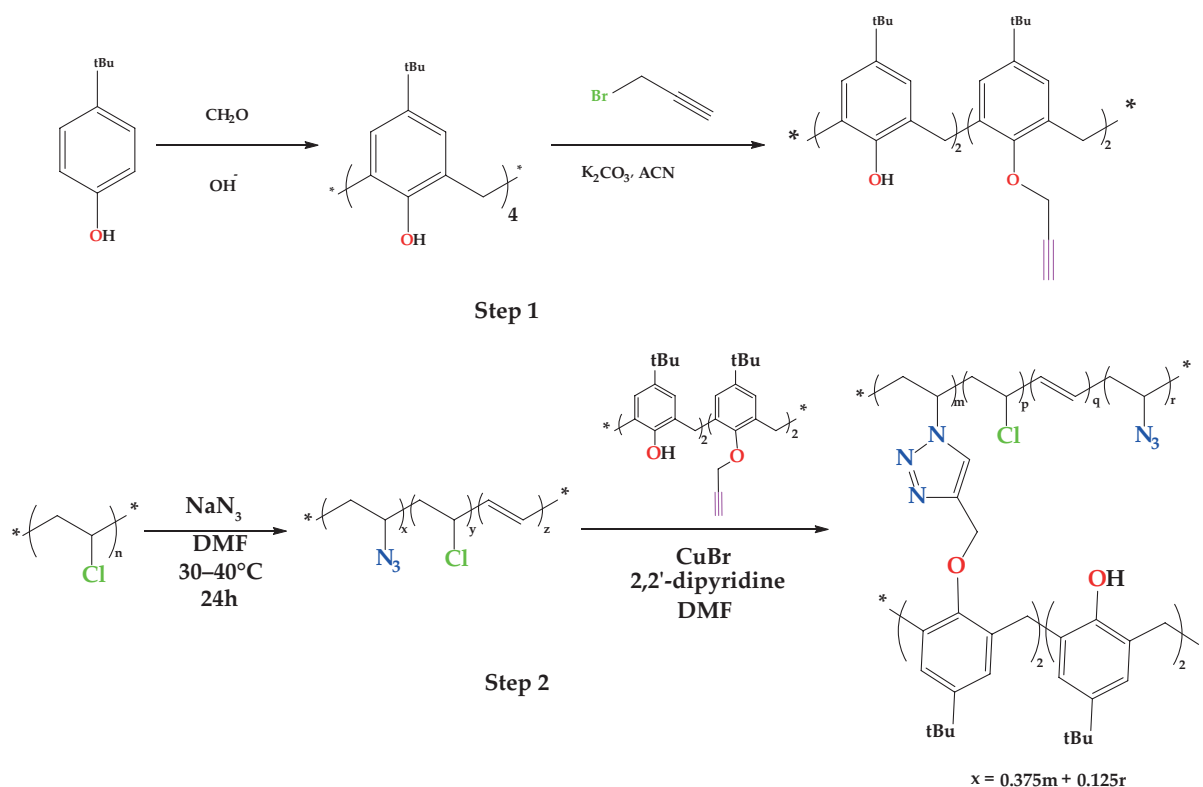


Fig. 3. DEPT-135 spectrum of cone-5,11,17,23-tetra-tert-butyl-25,27-dihydroxy-26,28-dipropargylcalix[4]arene



Scheme 1. Mechanism of the formation of the PVC/calixarene derivatives

Methods of testing

Fourier transform infrared spectrometry (FT-IR) was recorded on a Nicolet iS10 FT-IR for different polymers spectra in the range of 500–4000 $^{\circ}$ C.

The ^1H , ^{13}C and DEPT-135 NMR data of *p*-tert-butylcalix[4]arene and dipropargylcalix[4]arene were processed using 500 MHz NMR spectrometer Bruker and with CDCl_3 as a solvent and TMS as an internal standard.

CHN elemental analysis was performed using an Exeter CE-440 Elemental Analyzer.

Gel Permeation Chromatography (GPC) measurement (Agilent GPC/SEC Software Version 1.2.3182.29519) at RT (flow rate: 1 ml/min, column: mixed PL gel 300 \times 718 mm, 25 μm) with HPLC-grade THF as solvent was used for performing average molar weight and dispersity of PVC and PVC functionalized calixarene.

TGA/DSC simultaneous thermogravimetric analysis with differential scanning calorimetry was carried out using a TA instruments SDT Q600 unit. In a standard analysis, a sample of 6 mg was heated up in a temperature range of 20–800 $^{\circ}$ C at a heating rate of 5 $^{\circ}$ C/min under nitrogen.

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (Agilent 5110 ICP-OES) was used for the quantification of ion concentration in aqueous solutions. The results were reported in parts per million (ppm).

RESULTS AND DISCUSSION

FT-IR analysis

The IR spectra of PVC- N_3 and its derivative supported 1,2,3-triazole (PVC-0.75CX[4]) are shown in Fig. 4. A progressive decrease in the peak intensity of azide functional group at 2111 cm^{-1} with the loading amount of calix[4]arene onto the PVC chain [6] can be observed. The FT-IR

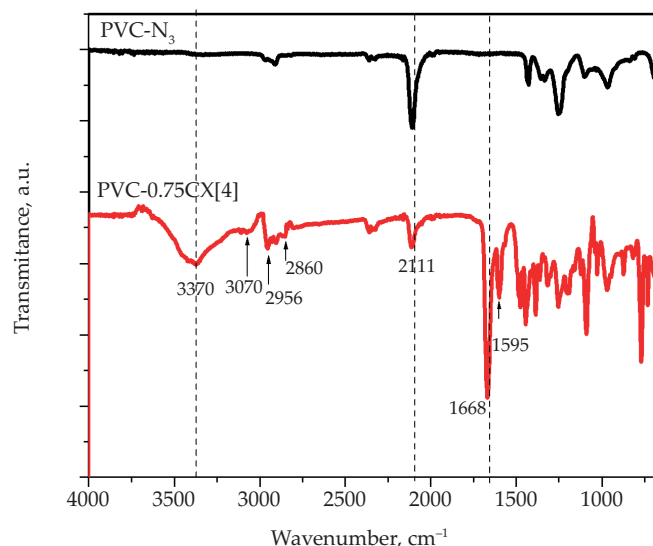


Fig. 4. FT-IR spectra of PVC- N_3 and PVC-0.75CX[4]

Table 1. The content of C, H, N in PVC-N₃ and PVC-0.75CX[4]

Samples	C, %	H, %	N, %	N, mmol/g
PVC-N ₃	39.15	4.39	38.31	27.35
PVC-0.75CX[4]	53.53	5.86	9.20	6.57

Table 2. Relative molecular weight and distribution of PVC and its derivatives

PVC derivatives	Average relative molecular weight M_n , g/mol	Average molecular weight M_w , g/mol	Dispersity M_w/M_n , g/mol
Pristine PVC	11 172	28 787	2.5
PVC-N ₃	17 707	34 668	2
PVC-0.75CX[4]	32 989	46 449	1.4

spectrum confirmed that the conversion of azide groups to triazole rings is a partial process. The appearance of a new strong band at 1668 cm⁻¹ indicates the C=C ring stretch, and a very small N=N band is visible at 1595 cm⁻¹. The IR spectra showed also a broad absorbance band at 3370 cm⁻¹ which was assigned to the OH stretching of phenols, the absorbance bands at 2956–2860 cm⁻¹ due to the CH₂ stretching modes, and the band at 3070 cm⁻¹ for unreacted =CH function. These IR results suggested that the conversion to the triazole groups was still partial. Whereas the FT-IR spectra materials presented a similarity due to the same triazole calix[4]arenes linked on PVC chain.

Elemental analysis (EA)

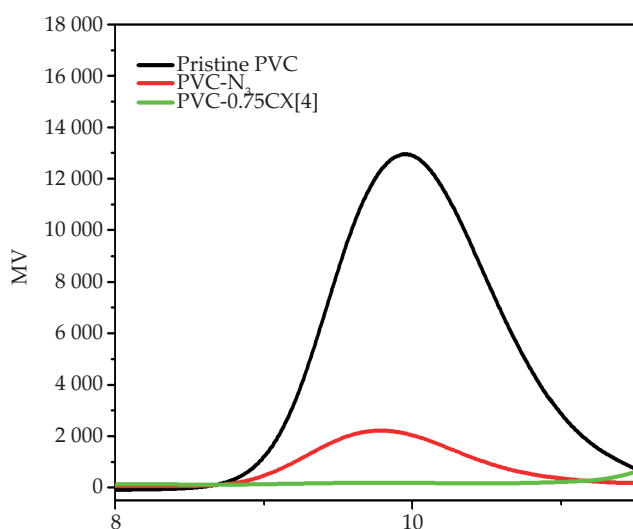
Table 1 summarizes the percentages of carbon, hydrogen and nitrogen of different synthesized materials. The results of the elemental analysis showed that the nitrogen content in the two resins PVC-N₃ and PVC-0.75CX[4] was, respectively, 38.31 and 9.2%. Furthermore, their molar nitrogen content calculated from the elemental analysis was 27.35 and 6.57 mmol/g respectively. The results suggested that the structure of the resin, particularly the

amount ratio of the calixarenes, influenced the nitrogen content.

GPC spectra of PVC and its derivatives, shown in Fig. 5 and Table 2, outlined data of relative molecular weight and distribution of PVC derivatives. However, a single broad peak in GPC chromatogram of PVC materials with a clear shift to a higher molecular weight region indicated the monodispersity of these polymeric materials. Moreover, the decrease in the peak area with the increase of loaded calixarene unities occurred due to the filtration of highly branched polymers. The data collected in Table 2 indicated that the increase of calixarene units covalently bonded to PVC-N₃ structure using click chemistry reaction increased the M_n of PVC derivatives (from 11 172 to 32 989 g/mol) and M_w (from 28 787 to 46 449 g/mol).

TGA/DSC thermal analysis

The TGA/DSC thermograms of pristine PVC and PVC functionalized calixarene recorded for 6 mg sample with a heating rate of 5°C/min under nitrogen in the temperature range of 20 to 800°C are shown in Fig. 6. The DSC curve showed broad endothermic peak in the range from 20 to 180°C corresponding to a loss of moisture of a sample, and three endothermic peaks, respectively at 280°C, 325°C, 454°C, indicating the polymer decomposition which took place in stages. The endothermic peak at 280°C, accompanied by a significant loss weight of 23.86% in the temperature range 220–350°C, occurred probably due to the dehydrochlorination of poly(vinyl chloride) [19]. Then the small sharp endothermic peak at 325°C, followed with a significant loss weight of 56.7% in the range temperature of 310–360°C, possibly was due to the water molecule release. The other endothermic peak at 454°C, accompanied with an important loss weight of ~77% in the range temperature of 400–535°C [20], was attributed to the PVC major degradation. The TGA/DSC curves for PVC functionalized calixarene were similar. However, a broad endothermic peak due to the moisture desorption in the temperature range of 20–100°C and three sharp important endothermic peaks at 130 and 216°C could be observed. The latter endothermic peaks are attributed to the major polymers degradation which consequence was a gradual decrease of PVC derivatives weight loss in

**Fig. 5.** GPC spectra of pristine PVC and PVC functionalized calixarene

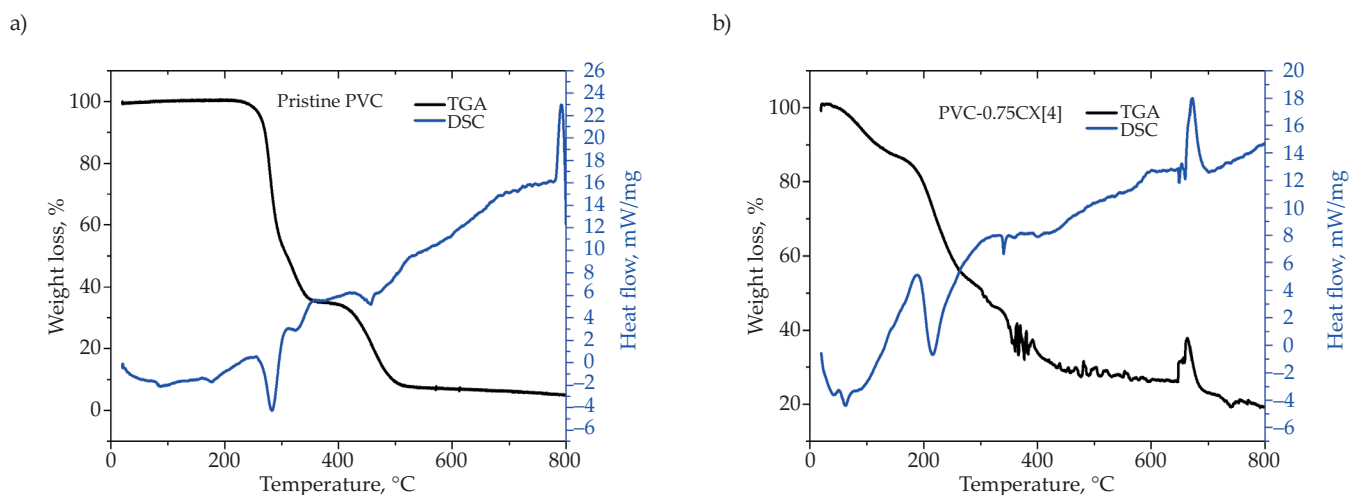


Fig. 6. TGA/DSC curves of: a) pristine PVC and b) PVC-0.75CX[4]

temperature range ~280–454°C, possibly due to the PVC peak displacement.

Cr(VI) extraction experiments

In order to explore the effect of pH on the sorption of chromate ions from aqueous solutions onto PVC-0.75CX[4] at 25°C in the pH range of 1–10, KOH and HCl (1 mol/l) were added to the aqueous solutions to adjust the pH values to the desired one from given pH range. All batch adsorption experiments were carried out to determine concentration by exploiting the same adsorption process as that reported in [21]. The examined 10^{-4} M solutions were prepared with potassium dichromate ($K_2Cr_2O_7$). 25 mg of PVC-0.75CX[4] and 10 ml of dichromate solution at given pH were mixed in batches for solid-liquid extraction. Then the prepared mixtures were stirred at 1700 rpm for 1 hour at room temperature and filtered using 0.2 μ m syringe filters to separate the polymers. The chromate concentration was measured before and after sorption process by ICP-OES. Dichromate sorption percentages (% Sorption) were calculated using the following equation (1):

$$\% \text{ Sorption} = \frac{(C_i - C_e)}{C_e} \cdot 100 \quad (1)$$

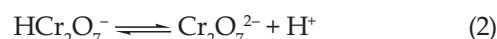
where: C_i – initial concentration of chromate(VI) in aqueous solution,

C_e – equilibrium concentration of chromate(VI) in aqueous solution.

pH effect on the sorption of Cr(VI)

The effectiveness of the synthesized material as an extractant of Cr(VI) from aqueous solutions depended on pH of the sorption medium. The mechanism of the sorption process of Cr(VI) onto the adsorbent polymer was the protonation/deprotonation of the different nitrogen atoms in triazole ring (Fig. 8). A static method at a pH range

1–10 was performed to examine the sorption process of chromate and dichromate ions using PVC-0.75CX[4] polymer with an initial concentration of solutions 10^{-4} mol/l and after 1 hour of stirring. Once the equilibrium has been reached, the sorption results (Fig. 7) showed a high sorption percentage of about 95.5% of all Cr(VI) species existing in aqueous solutions (H_2CrO_4 , CrO_4^{2-} , $Cr_2O_7^{2-}$, $HCr_2O_7^{2-}$, and $HCrO_4^-$) at an optimal pH = 3 [22–24]. Under the high acidic conditions $K_2Cr_2O_7$ was transformed into the $H_2Cr_2O_7$ form, and after the ionization $HCr_2O_7^-$ and/or $Cr_2O_7^{2-}$ forms existed in aqueous solution as represented by the following equation (2):



In this equation and under acidic conditions the equilibrium moves toward the left in the direction of extracting $HCr_2O_7^-$ [25–26]. The behavior of the adsorption of $HCr_2O_7^-$ ions on PVC-0.75CX[4] polymer in acidic medium was explained by the possible protonation of nitrogen atoms in triazole ring [27]. However, acidic conditions at low pH values may be contributed to the neutraliza-

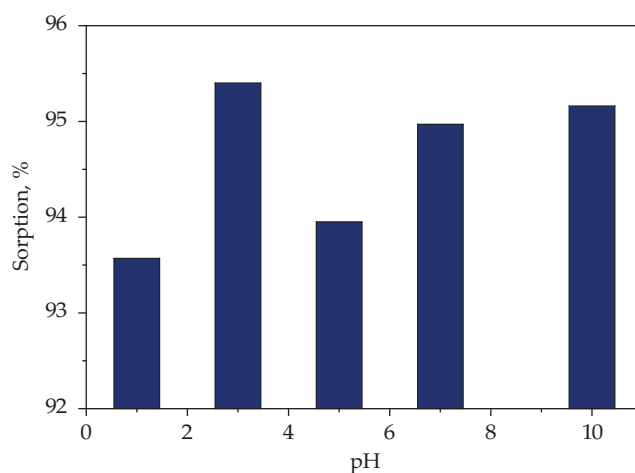


Fig. 7. Effect of pH on the sorption of Cr(VI) onto PVC-0.75CX[4] at 25°C for 1 hour

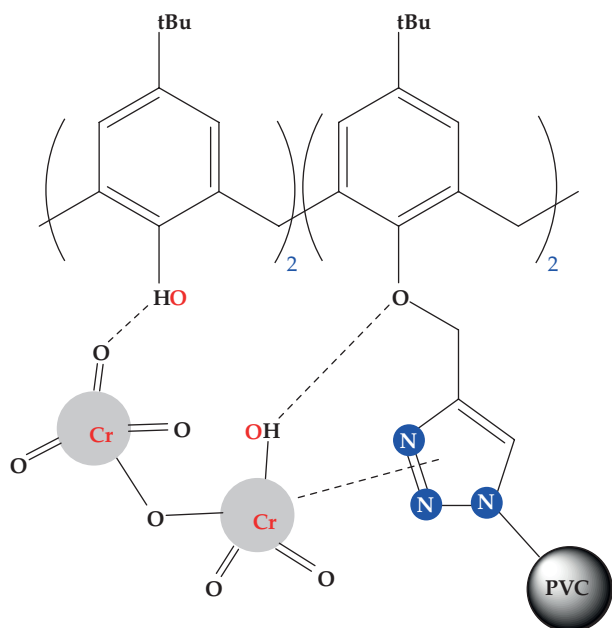


Fig. 8. Suggested Cr(VI) sorption mechanism

tion of the negative charge of adsorbent surface, which means more adsorption of the hydrogen dichromate ions by solid intermolecular attraction forces linking the chromate ion and oxygen functionalities onto the backbone of adsorbent polymer [28].

CONCLUSIONS

In this study, calixarene-based covalent polymers as a new generation of materials with very interesting features were described. The synthesis of a novel polymeric material PVC-0.75CX[4] via click chemistry, by coupling the calixarene terminal alkyne with azide PVC, was presented. The experiments on the removal of Cr(VI) species from aqueous solutions revealed a high sorption percentage of 95.5% at pH = 3 which could be attributed to the adsorbent large surface area. Thermal behavior of the prepared material showed high stability which could be reached at 350°C. Thus, these thermal properties reflected a positive character of this polymer as an adsorbent of metal ions in various industrial processes where high temperature of water purification may be needed.

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