

Synthesis and physical studies of polycarbonate of *p*-*tert*-butylcalix[4]arene: a highly selective receptor for Na⁺

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The synthesis and characterization of a polycarbonate of *p*-*tert*-butylcalix[4]arene **4** are reported. It was synthesized by condensation of *p*-*tert*-butylcalix[4]arenetetraol derivative **3** with ethyl chloroformate. This new polymer possesses a hydrolyzable backbone and tunable hydrophobic/hydrophilic properties. The experimental results indicate that the polycarbonate was successfully synthesized with average molecular weight \overline{M}_w , (2.328×10^4 g/mol), which was determined by static light scattering method using a Berry plot. The structure of this polymer was determined by IR spectroscopy. The thermal properties were investigated using differential scanning calorimetry (DSC). The degree of crystallinity was measured by means of XRD. The extraction ability of compounds **3** and **4** toward alkali metal cations was studied using conductometry. It was observed that compound **4** had the highest extractability and selectivity toward Na⁺.

Key Words: *p*-*tert*-butylcalixarene, *p*-*tert*-butylcalixarenetetraol, polymer, carbonate, polycarbonate, conductivity.

Introduction

Calix[n]arenes and their derivatives continue to be the focus of considerable research activity since they are easily accessible compounds with a wide range of applications as a result of their unique conformational,

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physiochemical, and complexation properties. In particular, the calix[4]arene macrocyclic structural framework has been shown to be an attractive building block. It can be selectively functionalized either at the upper rim (hydrophobic side) or at the lower rim (hydrophilic side) in order to assess and potentially enhance its selectivity toward supramolecular complexation of ionic or neutral species.^{1–6}

However, calix[4]arene based polymers recently began to receive considerable attention, as these new polymers may then be processed into materials suitable for chemical sensor devices and filtration/extraction membranes.^{7,8} This polymerization of calix[4]arenes can be done either as copolymers containing pendent calix[4]arene derivative monomers or polymerization of monomer of calix[4]arene derivatives.^{9,10}

Several groups have reported some polymeric calixarene derivatives and investigated their extraction properties toward metal cations and anions.^{11–13}

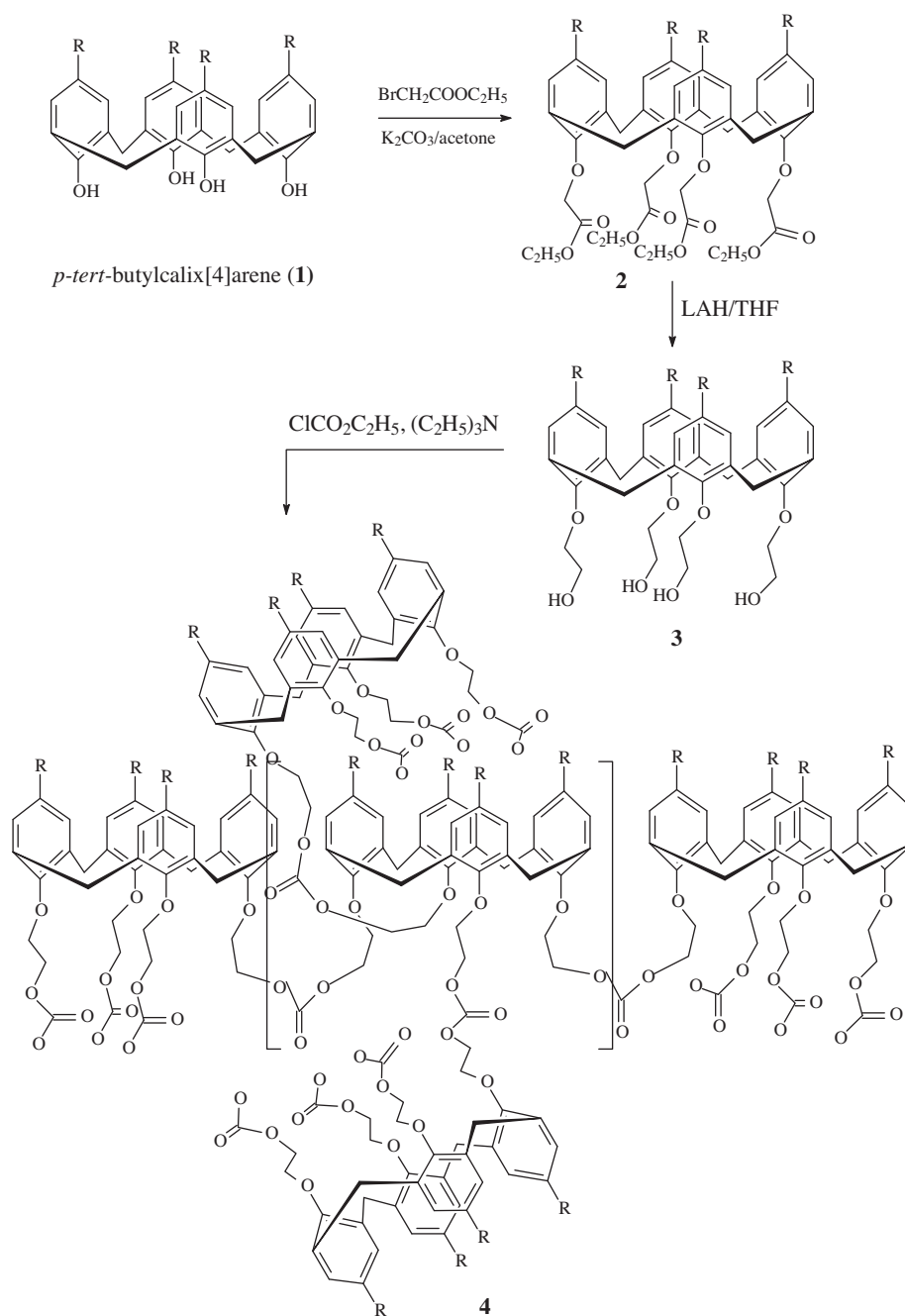
Their complexation studies were performed using liquid-liquid and/or solid-liquid extraction procedures.¹⁴

Some types of polymers find extensive use as medical materials.^{15–17} Several notable examples of functionalizable or biologically polymers are reported. These include linear polyesters,^{18–21} polyester-amides,^{22–24} poly(ether-ester), polyester-dendrimers, and polycarbonates.^{25–27} In recent years; polycarbonates have attracted attention as bioresorbable, biomedical materials²⁶ and are of interest in the design of drug delivery systems.²⁹

Herein, we report the synthesis, characterization, and some physical properties of polycarbonate of calix[4]arene **4** (Scheme), which was synthesized by condensation of *p-tert*-butylcalix[4]arenetetraol derivative **3** with ethyl chloroformate. We think that this polymer possesses a hydrolyzable backbone, and tunable hydrophobic/hydrophilic and chelating properties.

Experimental

¹H- and ¹³C-NMR spectra were recorded on a Bruker spectrometer at 200 and 50 MHz, respectively. Chemical shifts (ppm) are reported downfield from 0.0 ppm using TMS as internal standard using CDCl₃. The shape and surface morphology of the polymer were examined using a Shimadzu-SEM SUPER SCAN SSX Series. The crystallinity measurements of the polymer were obtained using a Shimadzu XRD-6000. The glass transition temperature (T_g) of the polymer was studied by 204 F1 NETZCH differential Scanning Calorimeter (DSC). The thermal stability of the polymer was studied by thermogravimetric analysis (TGA) using a NETZCH STA 409 PG/PC thermal analyzer. Average molecular weight (\overline{M}_w) data of the polymer were obtained by static light scattering using a Malvern CGS-3 compact Goniometer system equipped with a He-Ne laser at $\lambda_o = 633$ nm in conjunction with a fiber-optic detection method. The data are evaluated by Berry plot, which is the square root of the Zimm plot. For static light scattering, light scattered from all dilutions was detected at scattering angles between 30° and 150° at room temperature. The data were analyzed using the refractive index of toluene ($n = 1.4960$) and the refractive index of polycalix **4** ($n = 1.6190$), which was prepared as a film at $\lambda = 590$ nm using an ABBE refractometer (Model 2 WA-J). The average molecular weight was obtained by preparing 4 different concentrations of polymer in toluene. Entering the values of concentration by the 4 injected solutions and the above measured refractive index, the software automatically evaluated the average molecular weight of polymer. Compound **2** and **3** were prepared according to the procedure described in the literature.^{30,31}



Scheme

Synthesis

Polycarbonate of *t*-butyl-calix[4]arenetetraol (4). To a stirred solution of compound 3 (1.25 g, 1.52 mmol) and ethyl chloroformate (0.58 ml, 6.1 mmol) in anhydrous THF (10 ml) was added triethylamine (TEA) (0.85 mL) dropwise at 0 °C. The reaction mixture was then warmed to ambient temperature with further stirring and kept overnight. Precipitated triethylamine hydrochloride was filtered off, and the filtrate was concentrated

under reduced pressure to afford a colorless solid in 85%; mp 215-220 °C, IR (KBr, cm^{-1}): 1192, 1259, 1365, 1485, 1751, 1807.

Conductance measurements

Solutions of approximately $1.00\text{-}1.10 \times 10^{-4}$ M metal ion concentrations were prepared by dissolving a known amount of each salt in anhydrous acetonitrile. These solutions were also used as solvents for preparing the polymer solutions with concentrations of approximately $1.0\text{-}1.1 \times 10^{-3}$ M in order to keep the electrolyte concentration constant during the titration. Conductance measurements were carried out with a microprocessor conductivity meter (WTW/LF537). A calibrated cell (WTW/Tetracon 96) having a cell constant of 0.609 cm^{-1} was used. The cell was calibrated using analytical grade KCl (Merck) in triply distilled deionized water. The temperature of the solution was maintained at 25 ± 0.1 °C using a thermostated circulator water bath (HAAKE D1) equipped with a refrigeration unit. In order to determine the ligand:metal ratio, 50 mL of the desired salt solution was placed in a specially designed water-jacketed cell (150 mL, Pyrex[®]) which was equipped with a magnetic stirrer and was connected to the thermostated circulator water bath at 25 °C. Known amounts (0.5 mL of solutions of polymer **4**) were added in a stepwise manner using a calibrated micro-pipette. The conductivity of the mixture was then measured after stirring and temperature equilibration. This procedure was repeated in the same manner for each addition. Addition of the polymer continued until the desired ligand-to-cation mole ratio was achieved.

Results and discussion

The preparation of calix[4]arene carbonate polymer is presented in the Scheme. Reduction of tetraester derivative **2** with LiAlH_4 in THF at room temperature for a short period of time produced the tetraol derivative **3** as colorless solid in almost 100% yield. The ^1H -, ^{13}C -NMR, and IR spectra of the calix[4]arene tetraol **3** are identical to those described in the literature.³²

Polymer synthesis and characterization

As shown in the Scheme, the calix[4]arene polycarbonate **4** was synthesized via condensation of tetraol **3** with ethyl chloroformate in THF using TEA as catalyst. In the infrared spectrum, the polymer showed characteristic absorption bands at 1807.4, 1751.3, and 1259.6 cm^{-1} corresponding to the residual COCl, carbonate linkage, and ether linkage, respectively. Moreover, there was an evident intensity reduction of the band centered at 3433 cm^{-1} corresponding to the stretching vibration of hydroxyl groups of the tetraol **3**, which reacted during the synthesis. The disappearance of the OH groups can be therefore considered an evidence of the fact that the polymerization reaction took place.

The average molecular weight determination

Static light scattering measures light intensity as a function of scattering angle and solute concentration. This allows the determination of average molecular weight (\overline{M}_w) for the solute. The measurement is carried out in

a light scattering cell without prior separation of the polymer solution. The average molecular weight (\overline{M}_w) was determined as (2.328×10^4 g/mol) by static light scattering measurements using the Berry plot shown in Figure 1. Thus the average chain length is about 28 calixarene units of **3**. The solubility of the polymers was evaluated in various solvents such as ethyl ether, ethyl acetate, acetone, methylene chloride, 1,4-dioxane, benzene, DMF, toluene, acetonitrile, hexane, and tetrahydrofuran at 5 mg/mL. The incorporation of carbonate linkage into the polymer backbone enhances the solubility in common organic solvents to a high degree. The polymer shows good solubility in all the above common organic solvents except hexane, which displays partial solubility in it.

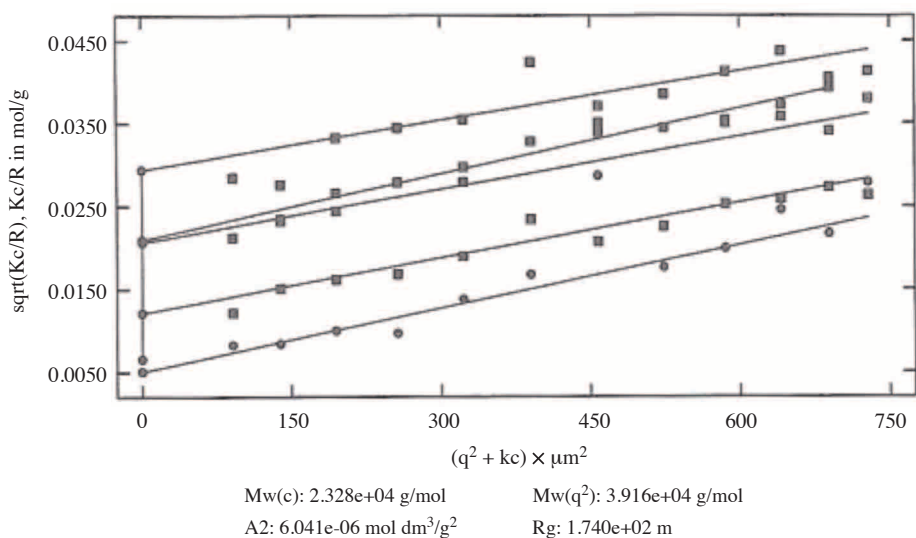


Figure 1. Static light scattering measurements using a Berry plot.

SEM observations

To observe the surface morphology of the polymer, scanning electron microscopy (SEM) of the gold-coated sample was performed under liquid nitrogen. The images are shown in Figure 2. The SEM micrographs show 2-dimensional textural morphology with sharp edges that enhance the minor crystallinity. Moreover, irregular-shaped amorphous satellite particles appear to adhere to these 2-D structures. It seems that these small particles are strongly attached as they do not disturb the continuity of the surface at the point of attachment.

XRD data

The PXRD pattern and crystallinity measurement of the synthesized polymer were obtained and are presented in Figure 3. The PXRD pattern revealed that the percent of crystallinity was about 13%, whereas the percent of amorphism was 87%, which implies that the polymer structure is considered amorphous and has a relatively low regular packed crystal system within its molecules, which is in compliance with the SEM observations.

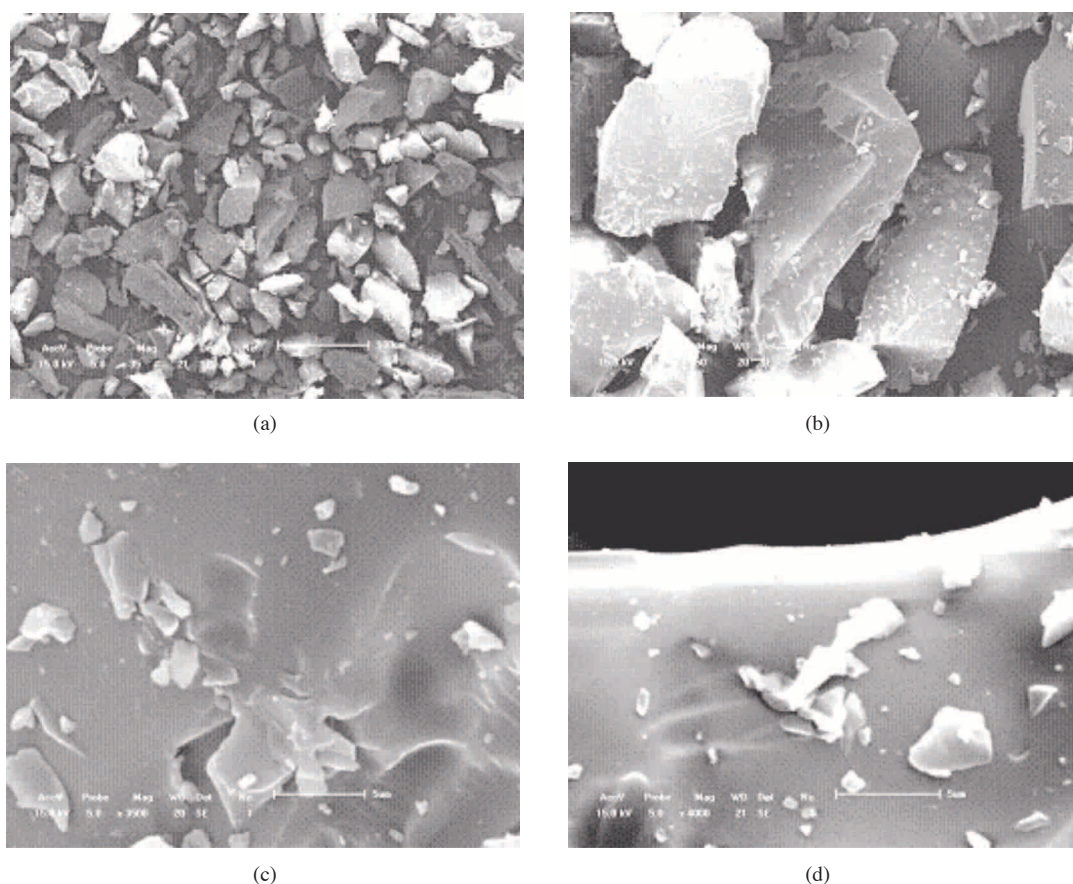


Figure 2. Scanning electron microscopy (SEM) of polymer 4 (magnification **a** = 600 ×, **b** = 1200 ×, **c** = 12,000 ×, **d** = 24,000 ×).

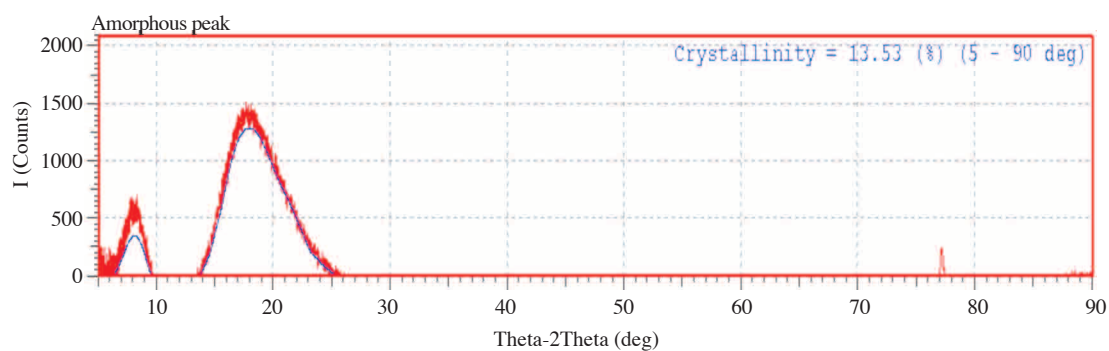


Figure 3. PXRD plot for the polycalix[4]carbonate 4.

Thermal properties

The thermal properties of the polymer were investigated with DSC and TGA. The glass transition temperature (T_g) was 81.0 °C. These T_g values of aromatic polycarbonate 4 are due to the existence of the aromatic

stiffening groups, which restrict the movement of polymer segments and thus increase the glass transition temperature. The DSC thermogram of the polymer is shown in Figure 4. The thermal stability of the polymer **4** was investigated by dynamic TGA under dry nitrogen. The Table summarizes the initial thermal decomposition temperature T_d^i and the $T_d^{5\%}$, $T_d^{10\%}$, and $T_d^{50\%}$ decomposition temperatures, which correspond to the temperatures at which 1%, 5%, 10%, and 50% loss of mass of polymer sample occurs, respectively. The Table also shows the residual mass percent remaining after heating the polymer sample to 500 °C. Residual mass percent remaining at 700 °C was about 12.2%. As shown in Figure 5, the TGA curves of the polymer displayed one-stage characteristics with a slow loss of mass starting from 300-400 °C and a relatively fast loss of mass between 400 and 500 °C, which indicates that the thermogravimetric curves of aromatic-aromatic polymer showed that this polymer has good thermal stability. The fast losses of the polymer may be attributed to further condensation of polymer chains and the elimination of aromatic functionality.^{33–35}

Table. Thermal stability of polymer **4**.

T_d^i	$T_d^{5\%}$	$T_d^{10\%}$	$T_d^{50\%}$	Residual mass % at 500 °C
180.0	275.8	313.2	392.2	12.20

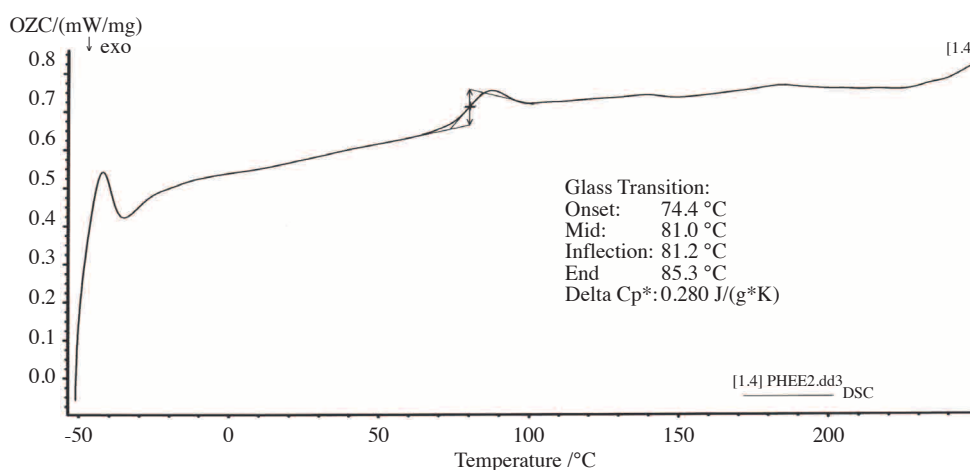


Figure 4. The DSC thermogram of the polymer **4**.

Conductometric titration

In principle, measurements of the variation of electrical conductance with the concentration of metal salts and receptors can be used to determine the strength, stoichiometry, and stability constants of complex formation and to assess the nature of the interactions involved. We employed such measurements to establish the stoichiometry of the complexes formed between several individual alkali metal cations and **4**. The variation in molar conductivity (Λ) with $[L]_T/[M]_T$ for complexation of polymer **4** with Li^+ , Na^+ , K^+ , Pb^+ , and Cs^+ cations in acetonitrile solvent system was studied at 25 ± 1 °C. $[L]_T$ and $[M]_T$ denote total concentrations of polymer and metal cations, respectively. The resulting molar conductance–mole ratio plots are shown in Figure 6.

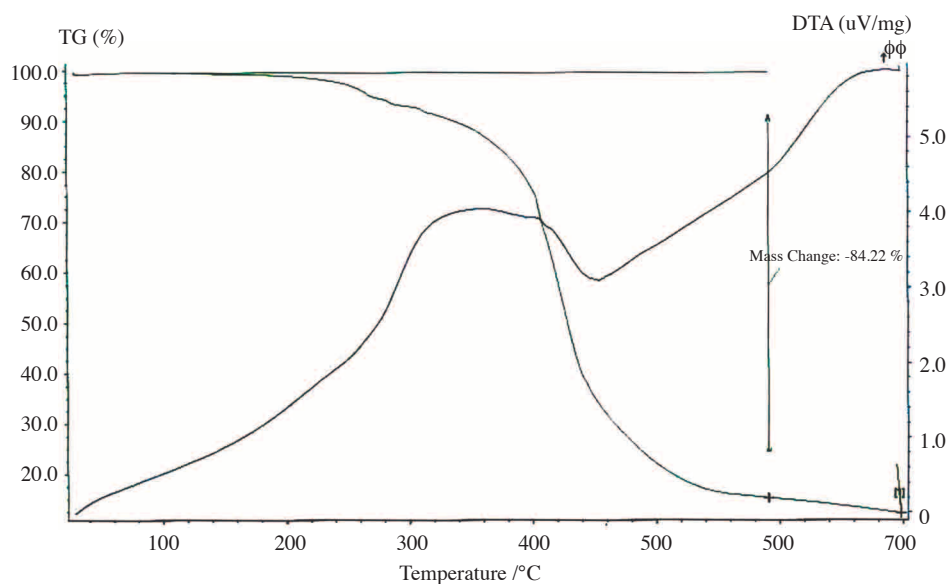


Figure 5. The TGA curves of the polymer 4.

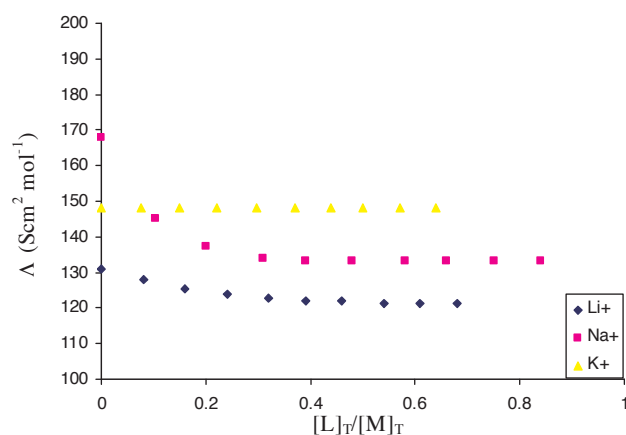


Figure 6. Molar conductance versus $[L]_T/[M]_T$ in CH_3CN at 25°C .

It is obvious from Figure 6 that the addition of polymer 4 to Li^+ or Na^+ perchlorate salt solution causes a decrease in the molar conductivity of the resulting solutions, which begins to level off at a ligand:metal mole ratio of 0.25, indicating the formation of a stable 1:4 complex. This decrease indicates that the complex has lower mobility than the free solvated metal ions. On the other hand, Figure 6 shows that no detectable changes in molar conductance were found when a solution of 4 was added to K^+ or to (Rb^+ and Cs^+ ; not shown in Figure 6) perchlorate salt solutions. This indicates that no complexation is taking place between these metal cations and the polymer.

This shows that the polymer 4 complexes selectively with either Li^+ or Na^+ . It is important to mention that in most cases the degree of the curvature $\Lambda:[L]_T/[M]_T$ plot is related to the strength of the interaction between metals and ligands. As Figure 6 shows, the degree of the curvature of the Na^+ plot is sharper than the degree of the curvature of the Li^+ plot. This shows that the strength of 4- Na^+ complex is larger than the

strength of **4-Li⁺** complex. It is worth noting that when compound **3** was tested toward extraction of alkali metal cations using the conductometric technique, no change in the conductivity of metal solutions was observed. This indicates that the presence of carbonyl functional group in the ligand plays a key role in enhancing its ability to select and complex with a variety of metal cations.¹¹

In conclusion, we were able to synthesize one calix[4]polymer in high yield and simply. It shows high extractability and selectivity toward Na⁺. Use of **4** as a membrane in the separation of some azeotropic liquids with similar boiling points is currently underway. The results will be published in due course.

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