Synthesis and characterization of novel optically active, poly(ester-imide)s bearing calix[4]arene and amino acid moieties: ionophoric properties and extraction abilities towards alkali-metal cations

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(Received: 30 November, 2008; published: 07 February, 2010)

Abstract: Optically active poly(ester-imide)s (PEIs) containing upper rim calix[4]arene were prepared in good yield by polycondensation reactions of distal calix[4]arene diol with some optically active diacid chlorides. Pyromellitic dianhydride (3) was reacted with chiral amino acids (4a-4e) to obtain the resulting imide-acids (6a-6e). The compounds (6a-6e) were converted into the corresponding diacid chlorides (7a-7e). The polycondensation reactions of calixarene diol with optically active compounds 7a-7e were carried out by two methods: bulk polycondensation under microwave irradiation and solution polycondensation in a system of triethyl amine (TEA)/dichloromethane (CH₂Cl₂). The optically active PEIs had good yield and moderate inherent viscosity ranging between 0.18-0.38 dL/g. The extraction ability measurements of PEIs towards alkali metal cations (Na⁺, K⁺, Cs⁺) and Ag⁺ showed a remarkable efficiency and selectivity toward Ag⁺.

Keywords: Calixarenes, Condensation polymerization, Ionophores, Optically active, Poly(ester-imide)s

Introduction

Amino acids are constituents of proteins, typical biological polymers, and not only biologically important but also useful as chiral auxiliaries and building blocks in organic synthesis [1, 2]. Amino acid-based synthetic polymers are expected to show biocompatibility and biodegradability similar to polypeptides [3, 4].

Chiral polymers including those bearing main- or side chain amino acid units are used widely in the pharmaceutical industry for enantio-selective separation of drugs. This is achieved mainly via the use of chiral polymers as the stationary phase in chromatography or electrophoresis. Apart from chiral separation, biocompatible amino acid containing polymers are used in drug delivery systems [5].

The interest in calix[4]arene chemistry is rapidly increasing because its derivatives can form inclusion complexes with cations or with neutral molecules [6]. The parent *p*-tert-butyl calix[4]arene (1) contains two interesting substructures [7]. At lower rim four hydroxyl groups are present in very close proximity; these can be used for cation

binding and transport [8, 9]. The upper rim contains hydrophobic cavity that is potentially able to complex neutral substrates.

Calix[4]arenes can undergo chemical modifications either by reaction at the hydroxyl groups (lower rim) or by replacement of the tert-butyl groups (upper rim) by the other substituents [10]. Modified Calix[4]arenes have been found to be extremely useful in host-guest chemistry due to their tendency to form complexes with metal cations and neutral molecules. Based on this property, specific ligands for analytical chemistry [11], membranes [12], decontaminating agents for waste water [13], dendrimers and star polymers from calixarene core [14] have been prepared. Chemical modifications of Calix[4]arenes can also be exploited to keep macrocycle into a fixed conformation and at the same time to provide a special reactivity [15]. For instance the higher reactivity of one hydroxyl group with respect to the others is important for the construction of larger molecular assemblies such as functional polymers [16]. Thus polyacrylates [17], polyamides [18], and polysiloxanes [19] carrying calix[4]arenes derivatives as side group linked to the macromolecular chains have been described.

The introduction of suitably derivatized calixarene units in a polymer backbone can be a substantial advancement for the practical application of the intrinsic receptor properties of the macrocyclic system in a solid support. Calixarene containing polymers have been scarcely investigated. While some reports were dealing with the introduction of calixarene moieties as appendages of polymer chains [20], others described the preparation of polymers containing calixarenes in the backbone [21].

Poly(ester-imide)s (PEI)s possess desirable characteristics with the moieties of both polyimides and polyesters such as high thermal stability and good mechanical properties as well as easy processability [22-27].

In the last decades, many examples in the literature have reported the successful application of microwave (MW) energy leading to accelerated synthesis of different classes of organic compounds [28, 29] as well as macromolecules [30].

Nowadays, the use of MWs to improve classic organic syntheses has become very popular because it very often leads to higher yields, high selective activation of compounds, shorter reaction times, as well as the promotion of a new reaction [31].

Because of the importance of optically active polymers with amino acid moieties and calixarene based polymers, in this paper a new series of optically active PEIs were synthesized using an equimolar amount of calix[4]arene diol in a fixed cone conformation and optically active diacid chlorides 7a-7e by bulk polycondensation using microwave irradiation and solution polymerization in the presence of TEA as a catalyst and CH_2Cl_2 as a solvent. It is worth noting that the retention of the cone conformation along the polymer chain has been reported to impart specific ionophoric properties to the calix[4]arene moieties towards alkali metal cations [32].

These novel polymers containing calix[4]arene moieties in their backbone are useful in the development of artificial membranes for the selective extraction of alkali metal cations from aqueous media into organic solvents and chiral stationary phases for separation of chiral natural ionic materials.

Results and Discussion

The lower rim calix[4]arene diol (**2**) was designed as a suitably derivatized calix[4]arene existing in the fixed cone conformation owing to the extensive O-alkylation of the phenolic oxygens [33]. The different acidity of the phenolic hydroxyl

groups is a well known special feature of calix[4]arenes [34] allowing the selective 1,3-derivatization at either the lower or upper rim (Scheme 1).

Scheme 1. Synthesis of p-tert-butyl calix[4]arene diol (**2**).

Diol (**2**) has a fixed cone conformation, as proved by its ^1H NMR spectrum which exhibited the signals for the equatorial and axial protons of the methylene bridges as doublets at 3 and 4 ppm, respectively [35]. FTIR and ^1H NMR spectra of calix[4]arene diol (**2**) has been shown in Figures 1 and 2.

Fig. 1. FTIR spectrum of calix[4]arene diol (**2**).

While some polymeric calixarene derivatives have been reported over the years, quite surprisingly there are very few examples of optically active polymers bearing the calixarene moiety. Given the high chemical, mechanical and thermal character of the imide groups along with biodegradability of amino acids and their biological

properties we envisioned the introduction of imide moieties in distal calix[4]arenes diol (**2**) as an entry to a new class of optically active receptors for metal cations. Hence, condensation reactions of pyromellitic dianhydride (**3**) with two moles of optically active amino acids L-alanine (**4a**), L-phenyl alanine (**4b**), L-leucine (**4c**), L-isoleucine (**4d**) and L-methionine (**4e**) in acetic acid afforded the corresponding optically active imide-diacids **6a-6e** (Scheme 2) in 81-96% isolated yields. FTIR spectrum of diacid (**6b**) has been shown in Figure 3 as an example.

Fig. 2. ^1H NMR spectrum (500 MHz) of calix[4]arene diol (**2**).

The symmetric diacids (**6a-6e**) were converted to the corresponding diacid chlorides (**7a-7e**) by reaction with thionyl chloride. The monomers (**7a-7e**) were purified by washing with n-hexane. For synthesis of N,N'-(pyromellitoyl)-bis-L-methionine diacid chloride (**7e**) less amount of thionyl chloride (5/1 molar ratio of thionyl chloride to diacid) was used and diluted with dry dichloromethane to perform the reflux under mild conditions. Chemical structure and purity of the optically active monomers (**7a-7e**) were proved using FTIR spectroscopy and melting point. FTIR spectrum of diacid chloride (**7b**) is shown in Fig. 3 and compared with the spectrum of diacid (**6b**).

PEIs (**8a-9e**) were synthesized by solution and bulk polycondensation reactions of an equimolar mixture of monomers (**7a-7e**) with calix diol (**2**) (Scheme 3).

Amino acid	L-Alanine	L-Phenyl alanine	L-Leucine	L-Isoleucine	L-Methionine
R	CH_3	CH_2 -	$\text{CH}_2\text{CH}(\text{CH}_3)_2$	CHCH_2CH_3 CH_3	$\text{CH}_2\text{CH}_2\text{SCH}_3$
	a	b	c	d	e

Scheme 2. Synthesis of optically active diacid chlorides (**7a-7e**).

Fig. 3. FTIR spectrum of (a) diacid (**6b**) and (b) diacid chloride (**7b**).

Scheme 3. Synthesis of PEIs (**8a-9e**).

In first method the bulk polymerization of optically active monomers (**7a-7e**) and calix[4]arene diol (**2**) was carried out using microwave irradiation with a controlled time and temperature schedule. We used a Milestone microwave apparatus for polymerization reactions. The best conditions for this method was 5 min at rt-50 °C (1000 W), 5 min at 50-100 °C (1000 W) and 5 min at 100-110 °C (1000 W). The reaction was at constant power with varying temperature. With lower irradiation powers the polymers had low molecular weights, and at higher temperatures and times there were no longer polymer chain growth and decomposition of polymers occurred.

Tab. 1. Some physical properties of PEIs (**8a-8e**) prepared by method 1.

Monomer	polymer					
	Polymer code	Yield (%)	$\eta_{inh}(\text{dL/g})^a$	$[\alpha]_D^{25}{}^b$	m.p. (°C) ^c	Color ^d
7a	8a	80.1	0.31	-10.6	148	B
7b	8b	75.2	0.25	-25.0	180	PY
7c	8c	85.3	0.38	-2.8	186	Y
7d	8d	85.1	0.36	-8.9	172	PY
7e	8e	80.0	0.31	-45.9	240	PB

^a Measured at a concentration of 0.5 g/dL in CHCl_3 at 25 °C.

^b Measured at a concentration of 0.5 g/dL in CHCl_3 at 25 °C

^c Started to melt at this temperature, complete melting at higher temperature.

^d Y=Yellow, PY=Pale Yellow, PB=Pale Brown, B= Brown.

The PEIs (**8a-8e**) were obtained in good yields (75-85%) and moderate inherent viscosities (0.25-0.38 dL/g). Also they were optically active and soluble in organic solvents such as CHCl₃, CH₂Cl₂, THF, DMF and polar aprotic solvents but insoluble in water, CH₃OH and nonpolar solvents. Some physical properties of PEIs (**8a-8e**) is shown in Table 1. Elemental analysis data of PEIs (**8a-8e**) is shown in Table 2.

Tab. 2. Elemental analysis data of PEIs (**8a-8e**).

Polymer	Formula		C (%)	H (%)	N (%)
8a	(C ₇₄ H ₇₆ N ₂ O ₁₀) _n	Calcd	77.06	6.64	2.43
	(1153) _n	Found	76.33	6.63	2.15
8c	(C ₈₀ H ₈₈ N ₂ O ₁₀) _n	Calcd	77.64	7.17	2.26
	(1237) _n	Found	76.84	6.90	1.89
8d	(C ₈₀ H ₈₈ N ₂ O ₁₀) _n	Calcd	77.64	7.17	2.26
	(1237) _n	Found	77.46	6.95	1.99
8e	(C ₇₆ H ₈₀ N ₂ O ₁₀ S ₂) _n	Calcd	73.28	6.47	2.25
	(1246) _n	Found	74.09	6.18	1.55

Tab. 3. Some physical properties of PEIs (**9a-9e**) prepared by method 2.

Monomer	polymer					
	Polymer code	Yield (%)	η_{inh} (dL/g) ^a	$[\alpha]_D^{25}$ ^b	m.p. (°C) ^c	Color ^d
7a	9a	72.1	0.18	-1.4	195	B
7b	9b	77.6	0.21	-0.6	226	PY
7c	9c	71.5	0.25	-0.7	236	Y
7d	9d	75.2	0.22	-7.9	215	PY
7e	9e	70.8	0.24	-0.3	249	PB

^a Measured at a concentration of 0.5 g/dL in DMF at 25°C.

^b Measured at a concentration of 0.5 g/dL in DMF at 25°C.

^c Started to melt at this temperature, complete melting at higher temperature.

^d Y=Yellow, PY=Pale Yellow, PB=Pale Brown, B= Brown.

Also we investigated the solution polycondensation of monomers (**7a-7e**) and (**2**) as second method. Due to good solubility of both monomers in CH₂Cl₂ we performed the reaction in this solvent in the presence of triethyl amine as a catalyst and acid scavenger. The solution of monomers (**7a-7e**) in dry CH₂Cl₂ was added drop wise to a solution of calix[4]arene diol (**2**) in CH₂Cl₂ in the presence of TEA and the reaction mixture was stirred for 30 min and refluxing conditions for 1 h. During refluxing the polymer was precipitated in the reaction mixture. It is interesting that these polymers were insoluble in CH₂Cl₂, CHCl₃ but soluble in polar aprotic solvents like DMF. The PEIs (**9a-9e**) obtained in the yields of 70-85% and inherent viscosities of 0.18-0.25 dL/g. The optical activity and molecular weight of these polymers were lower than method 1. Some physical properties of PEIs **9a-9e** is shown in Table 3. The solubility of all PEIs is shown in Table 4.

All polymers were fully characterized by FTIR, ¹H NMR and elemental analysis. The FTIR and ¹H NMR spectra of polymers (**8a**) and (**8e**) are shown in Figures 4 and 5, respectively.

Tab. 4. The solubility properties of PEIs (**8a-9e**).

Polymer										
	H ₂ O	MeOH	CH ₂ Cl ₂	CHCl ₃	Acetone	THF	DMF	DMSO	DMAc	H ₂ SO ₄
8a	-	-	+	+	+	+	+	+	+	+
8b	-	-	+	+	+	+	+	+	+	+
8c	-	-	+	+	+	+	+	+	+	+
8d	-	-	+	+	+	+	+	+	+	+
8e	-	-	+	+	+	+	+	+	+	+
9a	-	-	-	-	-	-	+	+	+	+
9b	-	-	-	-	-	-	+	+	+	+
9c	-	-	-	-	-	-	+	+	+	+
9d	-	-	-	-	-	-	+	+	+	+
9e	-	-	-	-	-	-	+	+	+	+

^a Concentration: 5 mg ml⁻¹; +: Soluble at room temperature, -: Insoluble

Fig. 4. FTIR spectrum of PEI (**8a**).

Fig. 5. ^1H NMR (500 MHz) spectrum of PEI (**8a**).

Fig. 6. (a) TGA thermogram and (b) DSC thermogram of PEI **9c**.

The ^1H NMR spectra of these PEIs showed typical signal patterns (two doublets) at 3.3 and 4.3 ppm, which were assigned to the equatorial and axial protons of the methylene bridges of the calix[4]arene residue adopting the cone conformation which was retained during the polymerization. Also the characteristic signals of four *t*-butyl groups in calix[4]arene moieties were appeared as two sharp peaks at 0.95 and 1.29 ppm in ^1H NMR spectra of all polymers which is an evidence for introduction of calix[4]arene moieties in the polymer chain.

The thermal properties of PEI (**9c**) were evaluated by means of TGA/DTG and DSC analysis under nitrogen atmosphere. The PEI (**9c**) exhibited good resistance to thermal decomposition up to 200 and 230 °C and began to decompose gradually above those temperatures. TGA thermogram of this polymer showed three thermal decomposition steps: first step with peak temperature of 289.3 °C and end temperature of 315.3 °C with 10.3% weight loss, second step with peak temperature of 497.3 °C and end temperature of 540.7 °C with 47.8% weight loss and third step with peak temperature of 640.3 °C and end temperature of 709.7 °C with 46.2%. In DSC thermogram of polymer (**9c**) two endothermic regions were observed at around 200 and 250 °C which corresponded to T_g and T_m respectively. TGA and DSC thermogram of PEI (**9c**) is shown in Figure 6.

Fig. 7. Complexation of the calix[4]arene derivative (in a fixed cone conformation) with alkali metal and silver cations.

Calix[n]arenes are well known to act as ligands or to host various species including small organic molecules, metal cations, and some anions. For example, compounds bearing four ether groups at lower rim showed good binding properties towards alkali metal cations but were inert towards alkaline earth metal ions, divalent and trivalent metal cations [36-38]. This binding selectivity was related both to the macrocycle ring size and its conformation. However a fine tuning of the cation binding was possible by varying the alkoxy groups at the lower rim [34]. The complexation of transition metals has been reported to be favored by the introduction of functional groups containing soft donor atoms such as nitrogen, sulfur, and phosphorus [39]. Alkoxy lower rim substituted calix[4]arene derivatives have been shown to bind silver cations [36]. In this case, a cation- π interaction appeared to be operative [42] since the silver ion was bound in a sandwich-like manner between two opposite phenyl rings. Quite interestingly the partial-cone conformation of the macrocycle provided the best arrangement for the silver and potassium cation binding [36, 37, 41, 42]. Also it was reported that Ag^+ (and probably K^+ also) is bound to the upper rim through the interaction with one or two oxygens and two benzene rings in these conformers.

These cationic guests are selectively included in the cone cavity and the preorganization of benzene rings is indispensable to the appearance of the “cation- π interaction” (Fig. 7) [42]. The selective Ag^+ recognition is an important requisite for several technological and biomedical applications such as photographic materials and radioimmunotherapy [43].

In this study we synthesized a diol derivative of *p*-tert-butyl calix[4]arene (**2**) and then we immobilized it through the imide and ester chain in the polymeric backbone to check the effectiveness of more than one calix[4]arene moiety together in a liquid-liquid extraction system. We selected the PEIs **8a-8e** for liquid-liquid extraction due to their good solubility in CHCl_3 . The extraction ability of calix[4]arene based PEIs **8a-8e** towards metal cations was measured using the Cram picrate method in a two-phase solvent system (CHCl_3 – H_2O) [44]. The extraction ability data of imide-ester containing calix[4]arene based polymers expressed as percentages of extraction from water to chloroform, are collected in Table 5. First of all it has to be noticed that among the calix[4]arene based PEIs, polymers (**8a**), (**8d**) and (**8e**) exhibited high levels of extraction abilities towards cation Ag^+ . Hence these extraction abilities have to be ascribed to the complexation ability of the calixarene macrocycle along with ester and ether groups. On the other hand, the calix[4]arene based PEIs were good ionophores for Na^+ .

Tab. 5. Cation percentage extraction values of calix diol (**2**) and PEIs (**8a-8e**) containing calix[4]arene moieties.

Host ^a	Cations ^b			
	Ag^+	Na^+	K^+	Cs^+
Calix diol (2)	52.08	64.82	35.25	0.00
8a	53.10	18.45	10.49	0.00
8b	10.00	49.00	63.00	0.00
8c	18.44	19.81	4.17	0.00
8d	50.87	21.75	8.90	0.00
8e	55.70	11.82	7.68	0.00

^a The initial concentration was 2.0×10^{-3} M in CHCl_3 .

^b Concentration 1.0×10^{-3} M of the corresponding nitrate salts in aqueous solution containing 2.0×10^{-5} M of picric acid.

These results demonstrate that PEIs (**8a**), (**8d**) and (**8e**) have the highest selectivity for absorbing Ag^+ , (**8b**) is the most selective for K^+ and all have good extraction ability toward Na^+ . Also we performed liquid-liquid extraction studies of some heavy metal cations (Co^{2+} , Hg^{2+} , Cd^{2+} and Cu^{2+}) but there was demonstrated no absorption ability towards these cations. Also all of the polymers and calix diol (**2**) had no extraction ability towards Cs^+ ion. This result showed that the binding ability of the compound (**2**) and PEIs is related to the macrocycle ring and metal ion size. The UV curves of PEIs for both initial picrate solutions and final solutions containing Ag^+ are demonstrated in Figure 8.

The advantage that can be foreseen with these polymers is their use as new materials for the extraction of alkali cations and silver ion in chiral natural media. On the other hand we can use these compounds both as ion selective polymers for ion separation and as chiral stationary phases for separation of enantiomers in chiral media. Also these polymers are superior to some sorbents such as polyelectrolytes due to their insolubility in water and their ability to use in aqueous ionic media.

Fig. 7. UV curves for initial and final aqueous solutions containing Ag^+ .

Conclusions

We have demonstrated that the macrocycles, such as calix[4]arene diol (**2**) can be polymerized with optically active imide containing diacid chlorides to give optically active PEIs. The main goal of this work is introducing optically active amino acid moiety in the calix[4]arene based polymer chain. Thus we combined the characteristics of ester-imide groups with extraction ability of calix[4]arene. In this design we achieved valuable results: optical activity, good solubility in solvents like chloroform and dichloromethane as well as good inherent viscosity and thermal stability. The different polymerization methods influenced the chemical and physical properties of the corresponding polymers. These PEIs are a new family of useful polymeric materials for ion exchange studies and separation of enantiomers in chiral media.

Experimental

Materials and methods

Pyromellitic dianhydride (**3**) and amino acids were from Merck Co. and used without further purification. Dichloromethane was dried over CaCl_2 . Reactions were monitored by TLC on silica gel. NaNO_3 , KNO_3 , CsNO_3 , and AgNO_3 were purchased from Merck and were used as received. *p*-Tert-butyl calix[4]arene (**1**) was prepared as described [8].

Characterization

IR spectra were recorded on a FT/IR-680 plus spectrophotometer using KBr pellets. Band intensities are assigned as weak (w), medium (m), and strong (s). Band shapes

assigned as shoulder (sh), sharp (s), and broad (br). Inherent viscosities were measured by a standard procedure using a Cannon Fenske routine viscometer at 25 °C using DMF as solvent. ¹H NMR spectra were recorded on 500 MHz instrument, using CDCl₃ as solvent and tetra methyl silane as shift reference (tube diameter 5 mm). Specific rotations were measured by a JASCO P-1030 Polarimeter. Thermal gravimetric analysis (TGA) was obtained by a Mettler TGA-50 under air atmosphere at a rate of 10 °C/min. Differential scanning calorimetry (DSC) was obtained by a Mettler DSC-30 under nitrogen atmosphere. Melting points were measured in open capillaries with a Gallenkamp instrument. Elemental analysis was performed by Malek-Ashtar University of Technology, Tehran, Iran. The MicroSynth Milestone Microwave apparatus was used for the reactions under microwave irradiation.

Monomer Synthesis

- Synthesis of *p*-t-butyl calix[4]arene diol (distal cone) (**2**)

A suspension of *p*-t-butyl calix[4]arene (5.0 g, 7.7 mmol), anhydrous K₂CO₃ (1.2 g, 8.8 mmol) and benzyl bromide (1.8 ml, 15.4 mmol) in CH₃CN (50 ml) was refluxed for 20 h. The solvent was removed under reduced pressure, the mixture was treated with CH₃Cl (100 ml) and washed with 1N HCl (2×25 ml) and brine (25 ml). The organic layer was dried with MgSO₄ and evaporated under reduced pressure. The pale yellow solid was washed with cold CH₃OH (100 ml) to give compound **2** as a white powder (4.2 g, 71.2%). mp: 194-195 °C. FTIR (KBr, cm⁻¹): 3419 (s, br), 3030 (m), 2957 (s), 2865 (s), 1749 (w), 1599 (m), 1484 (s), 1454 (s), 1392 (m), 1375 (s), 1361 (s), 1301 (s), 1206 (s), 1122 (s), 1096 (m), 1078 (w), 1018 (s), 994 (m), 944 (m), 916 (m), 887 (w), 871 (s), 818 (w), 788 (w), 755 (m), 730 (s), 693 (m). ¹H NMR (500 MHz, CDCl₃, 25°C): δ 0.99 (s, 18H), 1.33 (s, 18H), 3.31 (d, 4H, *J* = 13.1 Hz), 4.33 (d, 4H, *J* = 13.0 Hz), 5.10 (s, 4H), 6.83 (s, 4H), 7.09 (s, 4H), 7.30 (s, 2H), 7.40-7.42 (m, 3H), 7.68-7.70 (m, 2H).

- Synthesis of diacids (**6a-6e**): general procedure

Into a 25-ml, round-bottomed flask 5.61 mmol of pyromellitic dianhydride (**3**), 11.2 mmol of amino acids (**5a-5e**), 15.0 ml of acetic acid and a stirring bar were placed. The mixture was stirred at room temperature overnight then was refluxed for 6 h. The solvent was removed under reduced pressure and 10 ml of cold concentrated HCl was added to the residue. A white precipitate was formed, filtered off, washed with a large amount of water and dried under vacuum at 100 °C to give compounds (**6a-6e**). Recrystallization from methanol/water gave pure crystals.

Diacid (**6a**): White crystals. Yield (%) = 96%. mp: 265-266 °C. $[\alpha]_D^{25} = -29.02^\circ$ [0.050 g in 10 ml acetone]. IR (KBr, cm⁻¹): 2400-3500 (m, br), 1778 (s), 1714 (s, br), 1458 (m), 1383 (s), 1363 (s), 1251 (s), 1170 (m), 1078 (m), 1022 (m), 927 (m), 850 (m), 817 (m), 767 (w), 730 (s), 671 (w), 619 (m), 565 (w) cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆) δ 1.6 (d, 6H), 4.9 (q, 2H), 8.3 (s, 2H), 13.4 (s, 2H) ppm; Elemental analysis: Calculated for C₁₆H₁₂N₂O₈: C (53.34%), H (3.36%), N (7.77%); found C (52.90%), H (3.40%), N (7.30%).

Diacid (**6b**): White crystals. Yield: 90.3%. mp: 291-293 °C. $[\alpha]_D^{25} = -288.54^\circ$ [0.050 g in 10 ml acetone]. FTIR (KBr, cm⁻¹): 2500-3500 (m, br), 1766 (s), 1722 (s, br), 1498 (w), 1454 (m), 1384 (s), 1280 (m), 1224 (m), 1178 (m), 1109 (m), 1151 (w), 997 (w), 941 (m), 918 (w), 883(w), 827 (m), 756 (m), 733 (m), 700 (m), 673 (w), 630 (w), 567 (w)

cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆) δ 3.32 (dd, 2H), 3.52 (dd, 2H), 5.2 (dd, 2H), 7.2 (m, 10H), 8.23 (s, 2H) ppm; Elemental analysis: Calculated for C₂₈H₂₀N₂O₈: C (65.62%), H (3.93%), N (5.46%); found C (65.30%), H (4.10%), N (5.30%).

Diacid (**6c**): White crystals. Yield: 80.8%. mp: 292-293 °C. [α]_D²⁵ = -48.88° [0.050 g in 10 ml acetone]. FTIR (KBr, cm⁻¹): 3000-3500 (m, br), 2960 (m), 2873 (m), 1759 (s), 1712 (s), 1469 (m), 1392 (s), 1367 (s), 1273 (m), 1246 (m), 1192 (s), 1153 (s), 1091 (s), 1061 (m), 956 (w), 912 (m), 866 (w), 829 (m), 794 (m), 735 (m), 671 (w), 652 (w), 630 (m), 599 (w), 563 (m) cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆) δ 0.9 (d, 12H), 1.52 (m, 2H), 1.9 (td, 2H), 2.2 (td, 2H), 4.88 (dd, 2H), 8.3 (s, 2H), 13.4 (s, 2H) ppm; Elemental analysis: calculated for C₂₂H₂₄N₂O₈: C (59.45%), H (5.44%), N (6.30%); found C (59.10%), H (5.80%), N (6.71%).

Diacid (**6d**): White crystals. Yield: 81.6%. mp: 266-268 °C. [α]_D²⁵ = -79.10° [0.050 g in 10 ml acetone]. FTIR (KBr): 2500- 3500 (m, br), 1774 (s), 1772 (s, br), 1461 (m), 1432 (m), 1384 (s), 1360 (s), 1284 (s), 1153 (m), 1112 (m), 1083 (m), 1012 (w), 895 (m), 835 (w), 814 (w), 779 (w), 734 (m), 701 (w), 634 (m), 565 (w) cm⁻¹. ¹H NMR (300 MHz, DMSO-d₆) δ 0.95 (t, 6H), 1.09 (d, 6H), 1.2 (m, 4H), 2.4 (m, 2H), 4.65 (d, 2H), 8.4 (s, 2H), 13.2 (s, 2H) ppm; Elemental analysis: Calculated for C₂₂H₂₄N₂O₈: C (59.45%), H (5.44%), N (6.30%); found C (59.20%), H (5.70%), N (5.90%).

Diacid (**6e**): Pale yellow crystals. Yield: 85.1%. mp: 292-294 °C. [α]_D²⁵ = -73.52° [0.050 g in 10 ml acetone]. FTIR (KBr, cm⁻¹): 2400-3500 (s, br), 1718 (s, br), 1440 (m), 1384 (s), 1367 (s), 1290 (m), 1360 (s), 1217 (m), 1178 (m), 1105 (m), 1012 (w), 929 (m), 900 (m), 833 (m), 800 (w), 730 (m), 681 (w), 650 (w), 623 (m), 565 (w) cm⁻¹.

- Synthesis of diacid chlorides (**7a-7e**): general procedure

Into a 25 ml round-bottomed flask were placed 0.225 mmol of compounds (**6a-6e**) and 5 ml (an excess amount) of thionyl chloride. The mixture was refluxed for 3h. Unreacted thionyl chloride was removed under reduced pressure and the residue was washed with n-hexane, to leave diacid chlorides (**7a-7e**).

Diacid chloride (**7a**): White powder. Yield: 92.7%. mp: 243-244 °C. [α]_D²⁵ = -91.2 (0.05 g in 10 ml DMF); FTIR (KBr): 3003 (m), 2947 (m), 1780 (s), 1724 (s, br), 1454 (m), 1383 (s), 1363 (s), 1278 (w), 1178 (m), 1157 (m), 1128 (m), 1080 (m), 1016 (m), 943 (s), 900 (w), 879 (m), 839 (m), 769 (w), 732 (m), 696 (w), 603 (m), 559 (w) cm⁻¹. Elemental analysis: Calculated for C₁₆H₁₀N₂O₆Cl₂: C (48.38 %), H (2.54 %), N (7.05 %); Found C (48.29 %), H (2.58 %), N (6.96 %).

Diacid chloride (**7b**): White powder. Yield: 81.6%. mp: 189-190 °C. [α]_D²⁵ = -246.6° [0.050 g in 10 ml acetone]. FTIR (KBr): 3031 (m), 2912 (m), 1803 (s), 1776 (s), 1728 (s), 1496 (w), 1456 (m), 1378 (s), 1361 (s), 1205 (w), 1157 (w), 1132 (m), 1109 (m), 1016 (m), 958 (m), 920 (m), 891 (m), 841 (m), 783 (m), 756 (m), 731 (m), 702 (m), 621 (w), 548 (w), 520 (m) cm⁻¹. Elemental analysis: Calculated for C₂₈H₁₆N₂O₆Cl₂: C (61.22 %), H (3.30 %), N (5.10 %); Found C (60.98 %), H (3.11 %), N (4.87 %).

Diacid chloride (**7c**): White powder. Yield: 80.8%. mp: 166-167 °C. [α]_D²⁵ = -47.86° [0.050 g in 10 ml acetone]. FTIR (KBr, cm⁻¹): 3106 (m), 2962 (m), 2935 (m), 2873 (m), 1807 (s), 1778 (s), 1724 (s, br), 1468 (m), 1381 (s), 1273 (w), 1232 (w), 1170 (m), 1155 (m), 1118 (m), 1082 (m), 1053 (m), 995 (m), 937 (m), 920 (m), 875 (w), 841 (m), 775 (m), 736 (m), 665 (w), 603 (m), 563 (m) cm⁻¹. Elemental analysis: Calculated

for $C_{22}H_{22}N_2O_6Cl_2$: C (54.90%), H (4.61%), N (5.82%); found C (54.68%), H (4.32%), N (5.68%).

Diacid chloride (**7d**): White powder. Yield: 81.6%. mp: 143-144 °C. $[\alpha]_D^{25} = -91.10^\circ$ [0.050 g in 10 ml acetone]. FTIR (KBr): 3110 (w), 3052 (w), 2973 (s), 2937 (m), 2881 (m), 1797 (s), 1778 (s), 1724 (s, br), 1461 (m), 1381 (s), 1357 (s), 1247 (m), 1172 (m), 1151 (m), 1128 (m), 1084 (s), 1020 (m), 962 (m), 895 (m), 854 (m), 810 (m), 765 (m), 733 (s), 669 (w), 634 (m), 605 (m), 561 (m), 520 (w) cm^{-1} . Elemental analysis: Calculated for $C_{22}H_{22}N_2O_6Cl_2$: C (54.90%), H (4.61%), N (5.82%); found C (54.72%), H (4.31%), N (5.64%).

Diacid chloride (**7e**): White powder. Yield: 92.73%. mp: 128-130 °C. $[\alpha]_D^{25} = -63.96$ (0.05 g in 10 ml DMF); IR (KBr): 2950 (m), 2923 (m), 1790 (s), 1780 (s), 1730 (s), 1485 (m), 1377 (s), 1365 (s), 1104 (m), 837 (m), 796 (w), 729 (m), 628 (w), 563 (w) cm^{-1} . Elemental analysis: Calculated for $C_{20}H_{18}N_2O_6Cl_2S_2$: C (46.43%), H (3.51%), N (5.41%); found C (46.12%), H (3.18%), N (5.11%).

Polymerization

- Bulk polycondensation of diacid chloride (**7a-7e**) with calix[4]arene diol (**2**) under microwave irradiation (Method 1): general procedure

Into a 10 ml round-bottomed flask compounds (**7a-7e**) (0.2 mmol) and calix[4]arene diol (**2**) (0.2 mmol) were added. After mixing thoroughly, the mixture was subjected to microwave irradiation using a power of 1000 W with temperature of 50 °C for 3 min, 50-100 °C for 5 min and 100-110 °C for additional 5 min. The reaction was performed under temperature control. The polymer films were washed with methanol (30 ml) to leave PEIs (**8a-8e**).

PEI (**8a**): FTIR (KBr): 3399 (m, br), 3031 (m), 2959 (s), 2869 (m), 1776 (m), 1729 (s), 1678 (m), 1598 (m), 1484 (s), 1381 (s), 1362 (s), 1295 (m), 1206 (s), 1121 (s), 1100 (s), 1009 (m), 917 (m), 871 (m), 819 (w), 781 (w), 753 (m), 730 (m), 696 (m), 607 (w), 565 (w), cm^{-1} . 1H NMR: δ 0.94 (s, 18H), 1.23 (d, 6H, $J = 15.5$), 1.29 (s, 18H), 3.26 (d, 4H, $J = 13.1$), 4.28 (d, 4H, $J = 13.1$), 4.59-4.76 (m, 2H), 5.05 (s, 4H), 6.78 (s, 4H), 7.04 (s, 4H), 7.33 (s, br, 6H), 7.35-7.37 (m, 4H), 8.26 (s, 2H).

PEI (**8b**): FTIR (KBr): 3338 (m, br), 3031 (m), 2958 (s), 2906 (m), 2867 (m), 1726 (m), 1729 (s), 1680 (m), 1600 (m), 1483 (s), 1460 (s), 1363 (m), 1298 (m), 1203 (s), 1122 (m), 1097 (m), 1012 (m), 991 (m), 945 (w), 914 (w), 871 (m), 817 (w), 783 (w), 754 (s), 696 (m), 634 (w), 590 (w), cm^{-1} . 1H NMR: δ 0.94 (s, 18H), 1.29 (s, 18H), 3.05-3.21 (m, 4H), 3.26 (d, 4H, $J = 13.1$), 4.28 (d, 4H, $J = 13.1$), 4.71-4.80 (m, 2H), 5.05 (s, 4H), 6.78 (s, 4H), 7.04 (s, 4H), 7.29-7.41 (m, 20H), 8.12 (s, 2H).

PEI (**8c**): FTIR (KBr): 3418 (m, br), 3031 (m), 2960 (s), 2868 (s), 1776 (s), 1729 (s), 1600 (m), 1485 (s), 1430 (m), 1381 (s), 1362 (s), 1300 (m), 1206 (s), 1122 (s), 1019 (m), 979 (m), 947 (m), 917 (m), 872 (s), 819 (m), 780 (m), 754 (m), 730 (s), 695 (s), 637 (m), 619 (m), 552 (m), 521 (m), cm^{-1} . 1H NMR: δ 0.93 (d, 12H, $J = 10.1$), 0.94 (s, 18H), 1.10-1.28 (m, 6H), 1.29 (s, 18H), 3.26 (d, 4H, $J = 13.1$), 4.28 (d, 4H, $J = 13.1$), 4.91-4.98 (m, 2H), 5.05 (s, 4H), 6.78 (s, 4H), 7.04 (s, 4H), 7.26 (s, 6H), 7.35-7.37 (m, 4H), 8.26 (m, 2H).

PEI (**8d**): FTIR (KBr): 3388 (m, br), 3031 (m), 2961 (s, br), 2870 (s), 1777 (s), 1726 (s), 1638 (m), 1599 (m), 1483 (s), 1462 (s), 1381 (s), 1360 (s), 1298 (s), 1206 (s), 1122 (s), 1081 (m), 1009 (s), 947 (m), 917 (m), 889 (m), 872 (s), 819 (m), 780 (m),

753 (m), 731 (s), 696 (s), 637 (m), 607 (m), 565 (m), 521 (m), cm^{-1} . ^1H NMR: δ 0.81 (t, 6H), 0.94 (s, 18H), 1.16-1.19 (d, 6H), 1.29 (s, 18H), 2.51-2.59 (m, 4H), 3.26 (d, 4H, $J=13.1$), 4.28 (d, 4H, $J=13.1$), 4.71-4.76 (m, 2H), 5.05 (s, 4H), 6.78 (s, 4H), 7.04 (s, 4H), 7.26 (s, 6H), 7.35-7.37 (m, 4H), 8.24 (s, 2H, Ar).

PEI (**8e**): FTIR (KBr): 3398 (m, br), 3031 (m), 2958 (s, br), 2867 (s), 1776 (s), 1728 (s), 1598 (m), 1484 (s), 1462 (m), 1381 (s), 1362 (s), 1300 (s), 1206 (s), 1122 (s), 1104 (s), 1019 (s), 979 (s), 947 (m), 916 (m), 871 (s), 818 (m), 781 (m), 753 (m), 729 (s), 695 (s), 637 (m), 592 (m), 552 (m), 521 (m), cm^{-1} . ^1H NMR: δ 0.83-0.86 (m, 6H), 0.95 (s, 18H), 1.29 (s, 18H), 1.32-1.38 (m, 4H), 2.10-2.14 (m, 4H), 3.26 (d, 4H, $J=13.1$), 4.28 (d, 4H, $J=13.1$), 4.91-4.98 (m, 2H), 5.05 (s, 4H), 6.79 (s, 4H), 7.04 (s, 4H), 7.26 (s, 6H), 7.35-7.37 (m, 4H), 8.01 (s, 2H).

- Solution polycondensation of monomers (**7a-7e**) and calix[4]arene diol (**2**) (Method 2): general procedure

In a solution of diol (**2**) (0.2 mmol) in dry CH_2Cl_2 (5 ml) in the presence of TEA (0.2 ml, 1.4 mmol) was added drop wise the solution of diacid chlorides (**7a-7e**) (0.2 mmol) in dry CH_2Cl_2 (3 ml) at room temperature. The solution was stirred at room temperature for 30 min and then was refluxed for 1 h. During this time the polymer precipitates appeared. The solvent was reduced and methanol (20 ml) was added. The polymer powders (**9a-9e**) were filtered and washed with methanol (20 ml) and dried.

- Picrate extraction procedure

Picrate extraction experiments were performed following the Cram procedure [44]. 5 ml of an aqueous solutions containing 2.5×10^{-4} M of picric acid (2,4,6-trinitrophenol) and 10^{-2} M of an alkali salt M^+NO_3 , were added 5 ml of a 2.0×10^{-3} M solution of calix[4]arene derivative polymers (**8a-8e**) in CHCl_3 . After vigorous stirring at room temperature for 20 h in a stoppered glass flask (10 ml), the picrate concentrations in the two solvents were spectrophotometrically monitored at 355 nm using a Perkin–Elmer Lambda 6 spectrophotometer equipped with integrating sphere. The salts used for the extraction, NaNO_3 , KNO_3 , CsNO_3 and AgNO_3 , were reagent grade. No detectable amounts of picrate anions were observed into the organic layer after the extraction without calix[4]arene based polymers. The percent sorption of ion (S %) has been calculated as

$$S(\%) = \left[\frac{C_i - C_e}{C_i} \right] \times 100 \quad (1)$$

where C_i and C_e are the initial and final concentration of metal picrates before and after sorption, respectively.

Acknowledgements

We gratefully acknowledge the funding support received for this project from Isfahan University of Technology (IUT), IR Iran (ARH). Further financial support from Centre of Excellence in Sensor and Green Chemistry research (IUT) is gratefully acknowledged.

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