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Synthesis and cation complexation properties of crown ether polyamic acids/imides

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Abstract

The preparation and characterisation of the cation complexation properties of a series of polyamic acid and polyimides containing crown ether units are presented. It is found that the complexing power of the amic acid form of the polymers is significantly higher than that of the imide form; implying the ability of the carboxylic acid grouping to exhibit lariat behaviour. The carboxylic acid group enters into co-ordination with the cation, increasing the binding energy and hence the binding constant. Computer modelling has been used to provide insight into the various factors that influence the binding energy of the cation to the crown ether segment of the polymer chain. The complexation characteristics in aqueous and non-aqueous media are examined and the results are discussed in the context of changes in the contribution of the solvent to solvation sheath of the cation. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Benzo crown ethers; Cation complexation; Lariat effects

1. Introduction

The ability of crown ethers to complex with cations is well known [1–3]. Changes in the ring size and the polarizability of the ring oxygens can be correlated with the complexing power of crown ether ring molecules. In the case of the benzo and dibenzo crown ether systems, a good correlation exists between the effects of variation of substituents in the aromatic ring and their ability to complex cations. Detailed analysis of the complexation data indicates that in general two factors influence the binding power of the ether ring; the polarizability of the electrons on the ring oxygen and the constraints on the conformational changes which are required to occur for the ring to achieve a minimum conformation around the solvated cation. Incorporation of aromatic entities into the crown ether structure allows the electron density and the rigidity of the ring to be influenced in a controlled manner.

Diamino dibenzo 18-crown-6 has been used previously in the preparation of amide linked polymers [4–7]. Michel and Feigenbaum [4] prepared polyamide systems, by reaction with isophthaloyl chloride and Igawa and co-workers [5] have prepared from diamino dibenzo18-crown-6, as a coating on silica. Crown ether polyamic acids, were originally developed by Lawrence [6] for applications in desalination processes. Shono and co-workers [7] have prepared polyamic acids in membrane form, by reaction with pyromellitic acid dianhydride (PDA). The resulting polymers were found to act as proton driven cation exchange membranes, where the ionisable amic acid groups, under basic conditions, aided cation transport through to an aqueous acid phase. A crown ether polyamic acid system was also explored by Anufrieva and co-workers [8], where the cationic binding process was probed by measuring the displacement of fluorescing guest molecules within the host polymers.

Despite the apparent interest in these materials, data on the fundamental binding constants towards alkali metals do not exist. In this paper, the complexation constants for a series of polymers containing crown ethers are determined and the molecular design factors which influence the complexing ability are evaluated. To fully assess the role of polyamic acid/polyimide incorporation, in the binding activity of the macrocycles, the crown ether amines were polymerised with a number of carboxylic acid dianhydrides, Fig. 1. These materials ranged from the highly reactive PDA, which would give a highly aromatic and inflexible polymer backbone, through to the less reactive EDTA dianhydride, whose aliphatic nature should present a more

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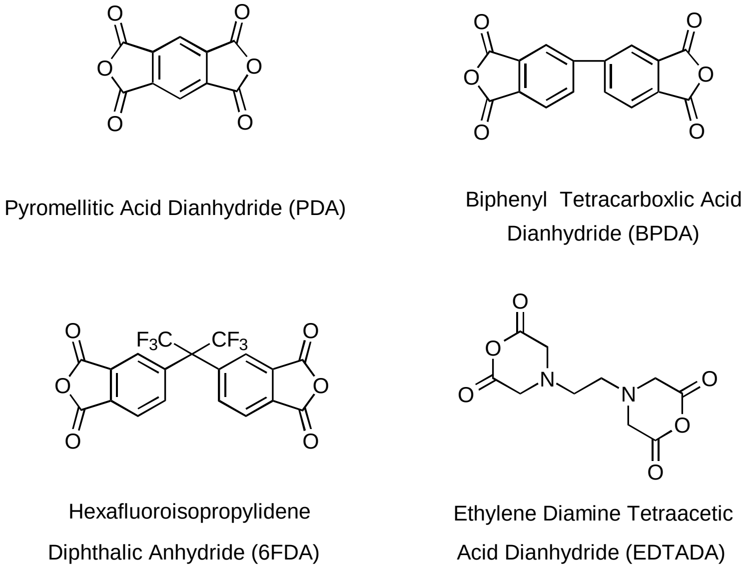


Fig. 1. Dianhydrides used in polyamic/polyimide synthesis.

flexible polymer chain. To increase the understanding of the factors involved in cation binding, diamino dibenzo 15-crown-5 and 4,13 diaza 18-crown-6 were also investigated to a limited extent.

2. Experimental

2.1. Materials

Four anhydrides; PDA, ethylene diamine tetraacetic acid anhydride (EDTADA), biphenyltetracarboxylic acid dianhydride (BPDA), and hexafluoroisopropylidene diphenyl anhydride (6FDA), were purchased from Fluka, and dried under vacuum before use. Dimethylacetamide (DMAC) which was used as a solvent was obtained from Aldrich and dried over anhydrous magnesium sulphate. The 4,13 diaza 18-crown-6 was supplied by Fluka and used as received.

2.2. Monomer and polymer synthesis

The diamino dibenzo crown ethers were prepared by the nitration of dibenzo 18-crown-6 followed by the hydrazine reduction of the dinitro dibenzo 18-crown-6, Fig. 2. The *cis* and *trans* isomers were isolated at the nitration stage prior to the reduction to amine being carried out. Diamino dibenzo 15-crown-5 was supplied by Fluka and purified by contact with carbon black in a chloroform solution.

2.2.1. Preparation of 4,4′(5) dinitro dibenzo 18-crown-6

Into a round bottomed 500 ml flask fitted with a reflux condenser and a dropping funnel, 20 g of dibenzo 18-crown-6 (0.0555 mol) dissolved in 350 cm^3 of chloroform was added. After complete dissolution, 300 cm^3 of glacial acetic acid was also added. A nitrating mixture of 14.0 cm^3 conc. nitric acid ($d = 1.42$) in 40 cm^3 of acetic acid was made up and added to the crown solution slowly over a 30–60 min period. After refluxing for 3 h, the solution was filtered and set aside. The filter residue containing the previously ascribed [4] *trans* isomer (4,5) was set aside for purification by recrystallisation from hot DMF (10.59 g, 42.4% yield).

The filtrate was placed in a refrigerator overnight, where the *cis* isomer (4,4′) was observed to precipitate out of solution. The precipitate was washed with methanol and purified by recrystallisation from DMF (11.5 g, 46.0% yield).

2.2.2. Preparation of 4,4′(5) diamino dibenzo 18-crown-6

The dinitro isomers (2 g) were dispersed in 220 ml of 2-methoxyethanol and 0.1 g of 10% Pd/C was added. After 5 min, 1.3 ml of hydrazine monohydrate was added. The solution was refluxed (–124°C) for 30 min and then allowed to cool. The reaction mixture was filtered and the solvent removed under vacuum to yield the light yellow crude product. Purification by recrystallisation from hot DMF revealed the final product, which existed as white crystalline solids for both the *cis* and the *trans* isomers (1.47 g, 84.6% yield).

2.2.3. Preparation of polymers

The polymers were prepared by firstly dispersing the diamino crown ether in DMAC and then adding an appropriate quantity of the anhydride and stirring under a blanket of nitrogen for about 24 h. The solutions were then used to cast films, which were dried in vacuum at 40°C for 24 h. Details of the quantities of materials used are presented in Table 1. The polyimides were prepared by thermal dehydration (imidisation) in an oven at 225°C for 30 min of the previously prepared aromatic polyamic acids. The extent of the imidisation process was determined using infrared spectroscopy of the final films.

Table 1
Abbreviations prepared in this paper (the reactions were carried out at room temperature (∼300 K), the molecular weight standards used in the calibration of the instrument was polystyrene)

Polyamic acid/polyamide	Polymer systems	Diamino isomer (g)	Volume of DMAC (cm^3)	Dianhydride (g)	M_w	M_n
1	*Cis* diamino dibenzo 18-crown-6/PDA	0.976	10	0.550	4545	2085
2	*Trans* diamino dibenzo 18-crown-6/PDA	0.976	10	0.550	5930	2555
3	*Cis* diamino dibenzo 18-crown-6/BPDA	0.976	12	0.7355	40,850	6380
4	*Trans* diamino dibenzo 18-crown-6/BPDA	0.976	12	0.7355	43,050	7050
5	*Cis* diamino dibenzo 18-crown-6/6FDA	0.976	14	1.1106	7595	3270
6	*Trans* diamino dibenzo 18-crown-6/6FDA	0.976	14	1.1106	9835	3675
7	*Cis* diamino dibenzo 18-crown-6/EDTADA	0.976	10	0.641	3185	1835
8	*Trans* diamino dibenzo 18-crown-6/EDTADA	0.976	10	0.641	3270	1750
9	*Cis*/*Trans* diamino dibenzo 15-crown-5/BPDA	0.866	10	0.550	–	–
10	4,13 Diaza 18-crown-6/BPDA	0.656	8	0.736	–	–

2.3. Appearance of polymer films

The polyamic acid films produced using biphenyl dianhydride were transparent, light yellow in colour and flexible. The films were relatively strong and easily recast from dilute solution to give 10 μm thick films. The polymer films produced with 6FDA were strong and flexible when first prepared, but became inflexible and cracked when allowed to age. An aged dilute solution produced immediately a brittle film, which was postulated as being indicative of a phase change that excludes plasticising solvent from the polymer molecules in the solution phase. The EDTADA polymers produced very brittle films that could not readily be detached from the casting substrate. In general, the polymers made from the *cis* diamino dibenzo 18-crown-6 precursor appeared to be slightly more flexible than their *trans* analogues, with reduced fracturing of the films being observed, possibly due to reduced close packing of the

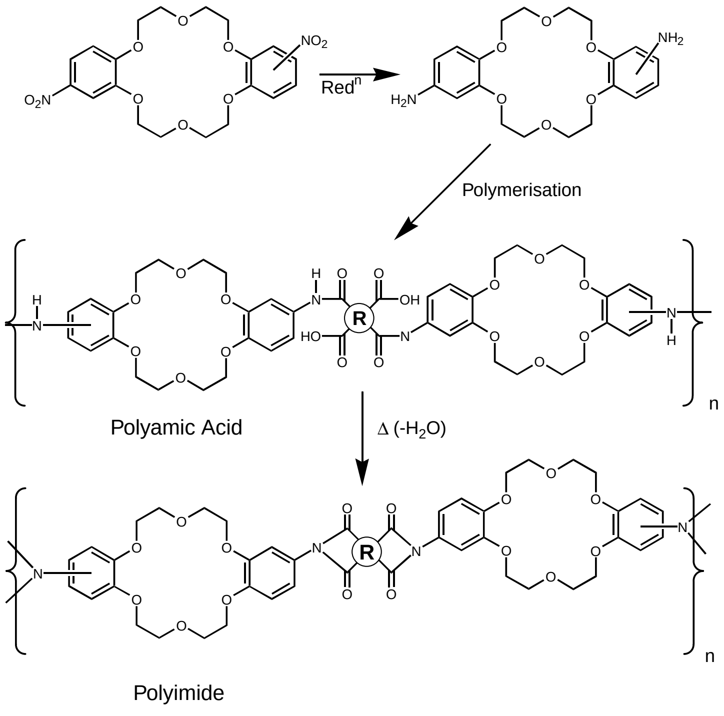


Fig. 2. Polymerisation route to polyamic acids and polyimides.

polymer chains and crystallinity in these films. The polyamic acid derived from BPDA and 4,13 diaza 18-crown-6 was observed to form a colourless film that was too brittle to remove from the casting substrate. The absence of colour was indicative of a lower level of conjugation as a result of using the aliphatic aza crown ether. The polyimides were darker in colour than their corresponding polyamic acids, because of the enhanced conjugation due to the imidisation in the former. The films were generally more brittle than their precursors and prone to cracking. During thermal imidisation of the EDTADA based polymers, considerable decomposition occurred resulting in heavily charred materials.

2.4. Polymer characterisation

The molar mass of the polymers were determined by gel permeation chromatography using Polymer Laboratories gel, mixed bead-B, 30 cm, 10 μm columns operating at 120°C, with *m*-cresol as solvent and using a refractive index detector. The average molar masses are summarised in Table 1. The polymers derived from the *trans* diamino dibenzo 18-crown-6 gave higher molecular weights than its *cis* analogue. The 6FDA polymers had higher molecular weights than those obtained from EDTADA, whilst polymers derived from the BPDA had the highest molecular weight and the greatest strength and flexibility.

2.5. Binding constant measurements

The method used was that described by Frensdorf [9] which involves determination of the concentration or activity of the free uncomplexed metal ions in a solution, as a function of the concentration of the added ligand. The degree to which the activity of the cation is reduced, is a direct measure of the amount of cation complexed and can be used to calculate the binding constant. This decrease in cationic activity can be measured in terms of the cell voltage using an appropriate ion selective electrode and related to the binding coefficient through the Nernst equation. The fraction of the cation left uncomplexed, can be expressed as:

$$U = 10^{-\Delta V/S} \tag{1}$$

where U is the fraction of the cation left uncomplexed, V the change in cell voltage on introduction of the ligand and S is the slope of the log of the cation concentration versus EMF plot. The value (U) can be used to calculate the complexed and uncomplexed cation concentrations. For a 1:1 complexation, the equilibrium constant Ks is obtained from:

$$K_s = \frac{(1-U)\,[\mathrm{M}^{n+}]}{(U[\mathrm{M}^{n+}])([\mathrm{crown}]-[\mathrm{M}^{n+}](1-U))} \tag{2}$$

where $(1-U)[\mathrm{M}^{n+}]$ is the concentration of metal and crown in complex, $U[\mathrm{M}^{n+}]$ is the concentration of uncomplexed metal and [crown]—$(1-U)[\mathrm{M}^{n+}]$ is the concentration of uncomplexed crown. Frensdorf [9] has shown that Eq. (2) can be rewritten in the form:

$$K_s = \frac{1-U}{DU([\mathrm{crown}]-[\mathrm{M}^{n+}](1-U))} \tag{3}$$

where K_s is the binding constant, with [crown] equal to the crown ether concentration, $[\mathrm{M}^{n+}]$ equal to the initial metal ion concentration and D equal to the dilution factor. The ion concentration was measured in solution using an ion selective electrode with a thermostated cell to provide a constant temperature of 25°C (±0.5°C). The voltmeter used was capable of measurement down to 0.1 mV. A silver/silver chloride electrode was used as a reference. The ion selective electrode was a sodium glass electrode supplied by Unicam (IS-Na).

The binding constants for sodium of the previously prepared polymers were analysed by the ISE method with methanol as solvent and buffered with (0.02 M tetraethylammonium hydroxide—TEAH). The basic nature of the 0.02 M TEAH solution not only alleviated any hydrogen ion interferences to the Sodium ISE but it also greatly assisted in the dissolution of the polymers in the methanolic medium. The non-film forming polymers, derived from PDA and EDTA dianhydride, were observed to dissolve quickly and this mirrored the rate of ion uptake, which was found to be essentially complete after a few minutes. The polymers derived from the BPDA and 6FDA did not dissolve as readily and the speed of cation uptake was slower, taking around 10 min to reach equilibrium, Fig. 3. The polymer binding strengths could only be calculated for sodium as the polymers were found to interfere with the operation of other available electrodes (e.g. potassium ISE). These interferences mainly manifested themselves in the formation of a gel around the plastic membrane of the potassium ISE, which produced erratic electrode responses and even to the destruction of the electrode's membrane. The molecular weight of the polymer repeat unit was used in the calculation of the association constants.

2.6. Atomic emission (ICP-OES)

This technique was used for the determination of the selectivity of the polymer membranes for various cations. The instrument used was a Thermoelectron Iris System, located at the Analytical Services Department at ICI Explosives. Unfortunately rhodium could not be analysed due its lack of parameterisation within the instrument's software. The first stage in the analysis of these materials was digestion by wet oxidation, using a sulphuric and nitric acid mixture. After the complete digestion of the polymers, the solutions were diluted with deionised water and analysed by ICP-OES. The standards and blanks used in the determination of these metals was matrix matched with the appropriate amounts of the digestion acids used in the sample preparations. From the resulting emission intensities the cation loadings were then compiled.

Table 2
Polymeric binding constant and electronic charge densities for the various polymer systems

Polymer	Diamine conform	Log K_s (Na in methanol)	Phenolic oxygen charge
Dibenzo 18-crown-6	–	4.18	−0.212420
Polydibenzo 18-crown-6	–	2.85	–
Polyamic acid 1	*Cis*	4.66	−0.208877
Polyimide 1	*Cis*	2.45	−0.206815
Polyamic acid 2	*Trans*	4.78	−0.208877
Polyimide 2	*Trans*	2.54	−0.206815
Polyamic acid 3	*Cis*	4.92	−0.210695
Polyimide 3	*Cis*	2.70	−0.207661
Polyamic acid 4	*Trans*	4.96	−0.210695
Polyimide 4	*Trans*	2.70	−0.207661
Polyamic acid 5	*Cis*	5.07	−0.209167
Polyimide 5	*Cis*	2.90	−0.207189
Polyamic acid 6	*Trans*	5.12	−0.209167
Polyimide 6	Trans	2.85	−0.207189
Polyamic acid 7	*Cis*	4.83	−0.209295
Polyimide 7	*Cis*	–	−0.208697
Polyamic acid 8	*Trans*	4.90	−0.209295
Polyimide 8	*Trans*	–	−0.208697
Polyamic acid 9	Mixed	3.37	−0.196211
Polyimide 9	Mixed	< 1	−0.194310
Polyamic acid 10	–	2.97	–
Diamino dibenzo 18-crown-6	*Cis* or *trans*	4.55	−0.213620
Diamino dibenzo 15-crown-5	*Cis* or *trans*	2.71	−0.201941
4,13 Diaza 18-crown-6	–	2.77	–

3. Results and discussion

3.1. Binding constant measurements for the polymeric crown ethers

Comparison of the polydibenzo 18-crown-6 system and the parent crown indicate that a decrease in the binding constant has occurred on incorporation of the crown ether ring into the polymer, Table 2 and Figs. 2 and 4. This effect may be attributed to the cation accessibility to the crown ethers being reduced when it is part of the backbone of the polymer. Once the crown ether is locked into the polymer framework, it will be less able to undergo conformational adjustments to achieve closer co-ordination with the cation. The trend of reduced binding strength on polymerisation was also observed for the polyimides, which had binding constants, an order of magnitude lower than their diamino dibenzo 18-crown-6 precursors. However, the opposite

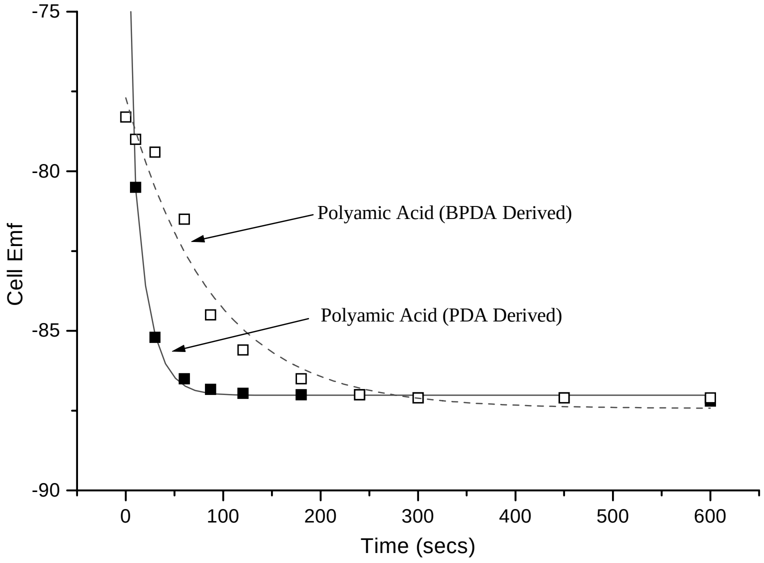


Fig. 3. Time response for the cell EMF after introduction of the crown polymer.

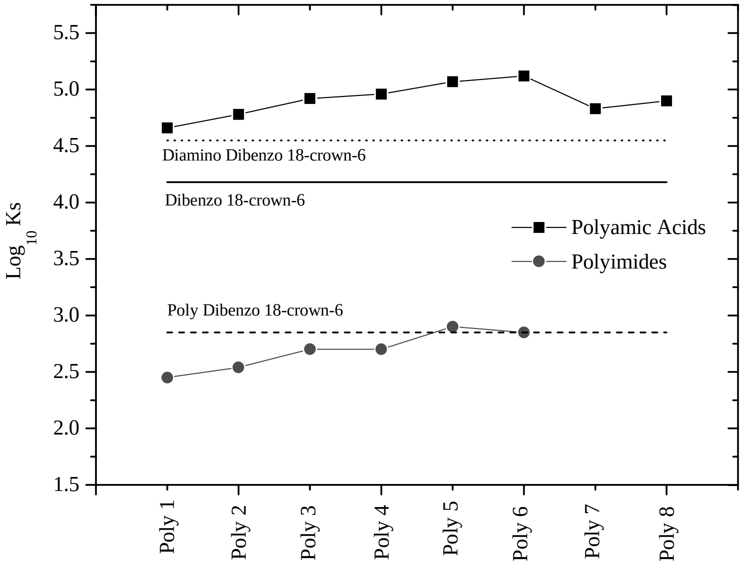
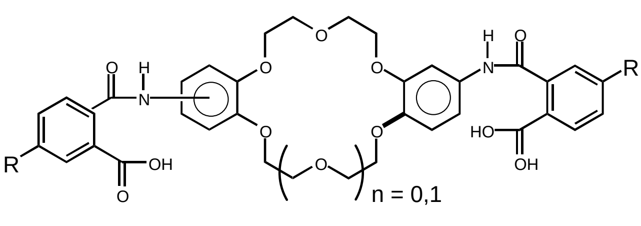


Fig. 4. Polymer binding constants across the dibenzo-18-crown-6 series.

trend was found with their polyamic acid precursors. In these systems, the binding constants were found to be an order of magnitude higher than their polyimide analogues, with binding strengths that even exceeded those of their monomeric parent compounds. The relatively high binding constant values observed for the crown ether polyamic acids for both aromatic crown ethers as well as the diaza-derived polymer. In some instances, the binding enhancements over the monomeric parent compounds were large, up to 0.6 log units. The selectivity of the polyamic acids towards sodium complexation was found to be similar to that observed for their monomeric parent compounds, i.e. for the monomer, log K_s (Na) is in the order; DB18C6 > DB15C5 > Diaza18-crown-6 and the corresponding values for the polymer are Polyam 3,4 > Polyam 9 > Polyam 10. This implies that the macrocycles are exerting the major influence on the cationic binding behaviour of the polymer as a whole.

In previous studies, it was found that in benzo and dibenzo crown ethers [14], changes in the charge on the aromatic oxygen in the macrocycle, brought about by change in the nature of the substituent, produced profound effects on the binding constants. To explore these effects, molecular models of each of the polymer systems were constructed using the HyperCHEM [10] software package. The models constructed were composed of a crown ether unit joined to two of the anhydride units, as shown in Figs. 5 and 6. The large size of these molecules necessitated that the geometry optimisation was carried out using the molecular mechanics method (MM +). The electronic charges of the optimised molecules were then recalculated by single point calculations under the semi-empirical AM1 method and are presented in Table 2. Through investigation of these molecular models, it was found that the addition of the polyamic acid and polyimide functionalities reduced the electronic charge density of the aromatic oxygens in the polymers compared with the values for the parent diamino compounds. The decrease in the aromatic oxygen charge within the macrocycle will reduce the available electron density for cation complexation. The calculations suggest that the binding constants of the polymers should be decreased compared to the values for the parent compounds, even if the reduced access to the crown ether ring on polymerisation is ignored.

However, in practice it was observed [11] that in the polyamic acid systems, the binding constant rather than decreasing was found to increase, which indicated that the high value of the cationic binding coefficient is due to "additional factors" other than the binding power and accessibility of the



R= remainder of dianhydride.

Fig. 5. Polyamic acid analogue.

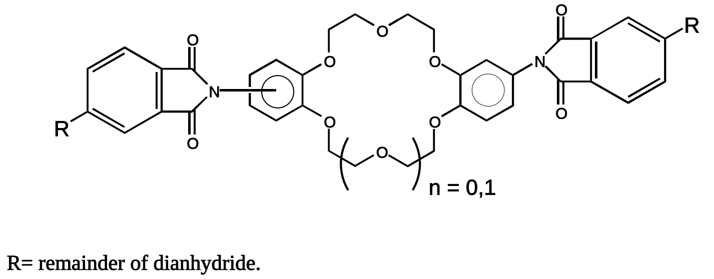


Fig. 6. Polyimide analogue.

macrocycle alone. In addition, the binding coefficient in the polyimides decreased sharply compared with the parent macrocycle, indicating that these "additional factors" were not in operation in the completely imidised systems. The greater than expected binding of the polyamic acids is attributed to the presence of the carboxylic acid residues which can influence the complexation process in a number of ways. The carboxylic acid can:

- Prevent chain close packing and increase the free volume of the polymer. This could make the crown ether moieties more easily accessible to the cations than in the polyimides.
- Act as a lure for the cation and possibly behave as a pseudo lariat group by becoming involved in the binding site and in the complexation process.
- On ionisation, generate a negatively charged polymer, which could provide more beneficial electrostatic interactions with the positively charged cations.

The possibility of lariat binding effect has been demonstrated in the molecular modelling of the polyamic acid analogues. In the geometry optimised structures, the carboxylic acid groups were found to be within reach of the macrocycle and so were regarded as being capable of assisting in the binding of the cation. The effect can be seen in Fig. 7, where a sodium ion has been placed in the cavity of the macrocycle. Within the polyamic acid series, the binding constants were observed to conform to the following order:

6FDA derivative > BPDA derivative > EDTADA derivative > PDA derivative

The differences were reasonably small but beyond the error limit of the method and the origin of the phenomenon is unclear at present. Close inspection of the binding constants revealed that the polymers derived from the *trans* diamino dibenzo 18-crown-6 isomer were slightly better binding agents than their *cis* counterparts. However, these binding constant differences are approaching the limit of the error in the binding coefficient determination and have to be treated with some caution.

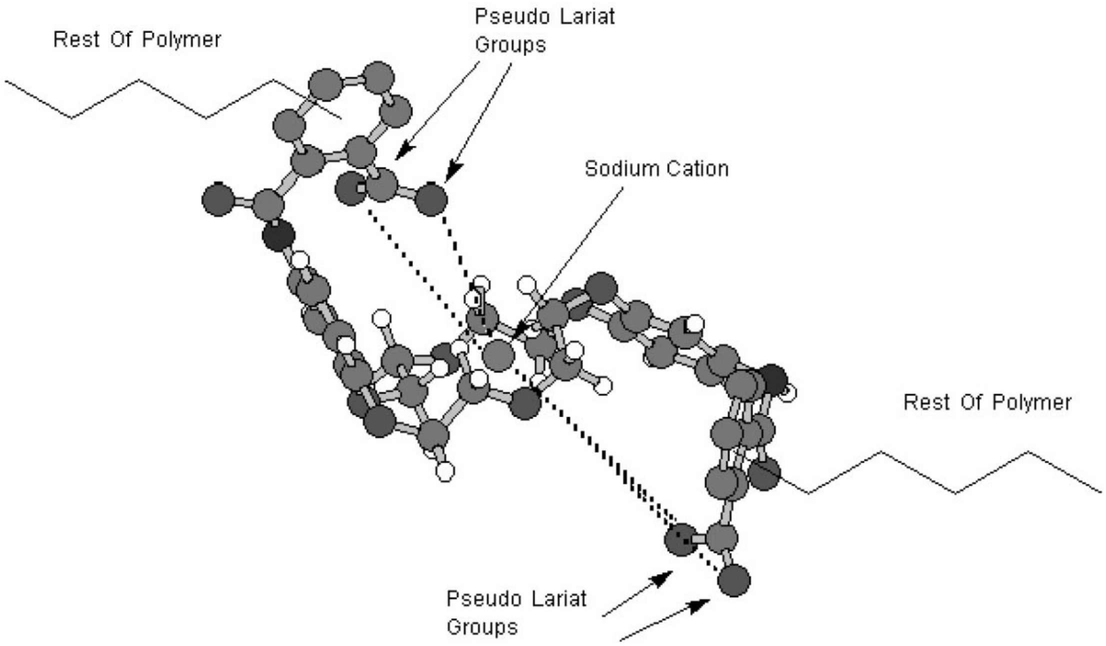


Fig. 7. Possible lariating behaviour of crown ether polyamic acid (polyamic acid 1,2 analogue).

3.2. Solid phase cation uptake

The solid phase cation uptake can be defined as the quantity of a cation that will be extracted from solution by a solid phase absorbent. This value is an indicator of the complexation strength for cations whose binding constants may otherwise be difficult to analyse, and in addition, provides a realistic account of how the polymers could behave in cation extraction applications, indicating their possible use as chromatographic supports for cation chromatography. The degree of binding or cationic loading for the polyamic acids 3 and 9 which formed good flexible films were investigated as indicated below. The two different ring systems were studied so that any selectivity changes, between the cavity sizes of the crown ethers, could be explored.

3.3. Aqueous cation uptake

The procedure involved in exposing a segment of the polymer film ($2 \times 2\ \mathrm{cm}^2$, 0.1 mm film thickness) to a range of aqueous based 1 M solutions of alkali metal and alkaline earth chlorides. The films were exposed for 24 h and then washed in deionised water before drying in a vacuum for an additional 24 h at 50°C. Blank samples were also analysed, the polymers being immersed in deionised water for 24 h. The metal salts used in this experiment were: alkali metal (MCl); Li, Na, K, Rb and Cs and alkaline earth ($\mathrm{MCl_2}$); Mg, Ca, Sr and Ba. After exposure, rinsing and drying, the cationic loading of the polymers were determined by measurement of the chloride anion concentrations by microanalysis. From the values, quoted in % (w/w), the cationic loading was calculated using the relations:

No. of moles MCl_x in 1 g of polymer complex

$$= \frac{(\%\mathrm{Cl})}{100(\mathrm{Mwt\ Cl}_x)} = X$$

Total weight of salt in 1 g of polymer complex

$$= X(\mathrm{Mwt\ MCl}_x) = Y$$

Weight of polymer in 1 g of polymer complex $= 1 - Y$

No. of moles crown 1 g of polymer complex

$$= \frac{1 - Y}{\text{Mwt polymer rpt unit}} = Z$$

$$\text{Mole \% crown ether units complexed} = \frac{100X}{Z}$$

The mass analyses results from the polymer blanks were very close to the theoretical values for the polymers without the co-ordinated solvent. This implied that during the extended immersion in water, the DMAC was replaced by water, which was then more easily removed under the vacuum conditions applied. The molecular weight of the repeat unit was, therefore, calculated from the theoretical repeat unit mass on a dry basis.

Table 3
Alkaline and alkaline earth metal cation uptake (aqueous)

Cation	Ionic radius (Å)[a]	Mol% complexed polyam 3 (18C6)[b]	Mol% complexed polyam 9 (15C5)[c]	Mol% complexed polyamide (18C6)
Li	0.78	39.0	28.0	24
Na	0.98	56.3	38.3	54
K	1.33	67.4	36.6	64
Rb	1.49	55.2	24.0	–
Cs	1.65	32.1	16.7	0
Mg	0.78	5.0	12.6	–
Ca	1.06	22.2	14.1	0
Sr	1.27	19.4	5.6	–
Ba	1.43	14.4	< 1	0

[a] Cation radii taken from Ref. [2].
[b] Cavity radius of 18-crown-6 = 1.45 Å.
[c] Cavity radius of 15-crown-5 = 0.92 Å.

Using the above equations, the cation loadings were calculated and are presented in Table 3. The values are compared with the cation uptake values from the literature results [12, pp. 9, 18–20, 138/139] for a polyamide crown polymer, derived from diamino dibenzo 18-crown-6. These measurements were carried out by Michel et al. [4] and were calculated using the same anion determination method employed in the present polyamic acid systems. The polyamic acid crown ether polymers showed a considerable level of cation uptake across the range of metals, Figs. 8 and 9. The polymer derived from diamino dibenzo 18-crown-6 displayed its optimum cation uptake for potassium and the selectivities of this polymer system generally parallel the order found for the ring size effect determined from studies of the crown ether rings; i.e. $\mathrm{K} > \mathrm{Rb}$, $\mathrm{Na} > \mathrm{Cs} > \mathrm{Li}$. The degree of uptake of the cations was observed to be higher for the polyamic acid than the corresponding polyamide. As both of these polymers were derived from the same precursor (diamino dibenzo 18-crown-6), then the additional uptake present on the polyamic acids was attributed to the effects of the carboxylic acid residue in this polymer. The polyamic acid polymer is able to take up alkaline earth cations, which is in contrast to the polyamide polymer and once more is attributed to the effect of the carboxylic acid residues.

The dibenzo 15-crown-5 derived polyamic acid also displayed efficient cationic binding, where the optimum uptake was found to occur for the sodium system. As with the larger dibenzo 18-crown-6 system, the selectivity of this polymer was consistent with the ring size effect, i.e. $\mathrm{Na} > \mathrm{K} > \mathrm{Li}$, $\mathrm{Rb} > \mathrm{Cs}$. This polymer was also capable of alkaline earth metal uptake, but the level of cation incorporation was less than the dibenzo 18-crown-6 derived material. The degree of alkaline earth uptake was consistent with the ring size relationship, i.e. $\mathrm{Ca} > \mathrm{Mg} > \mathrm{Sr} > \mathrm{Ba}$.

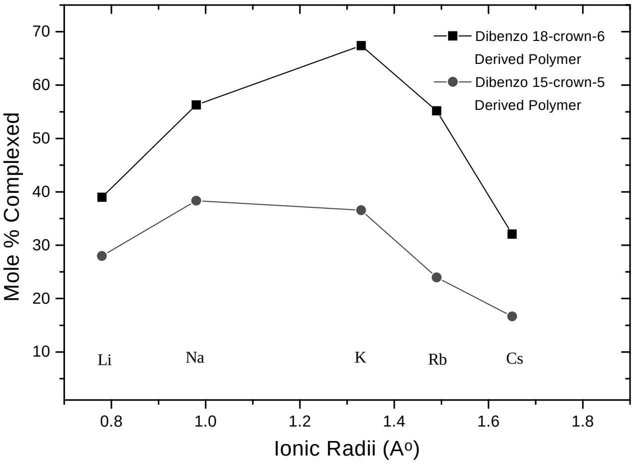


Fig. 8. Alkali metal cation uptake (aqueous).

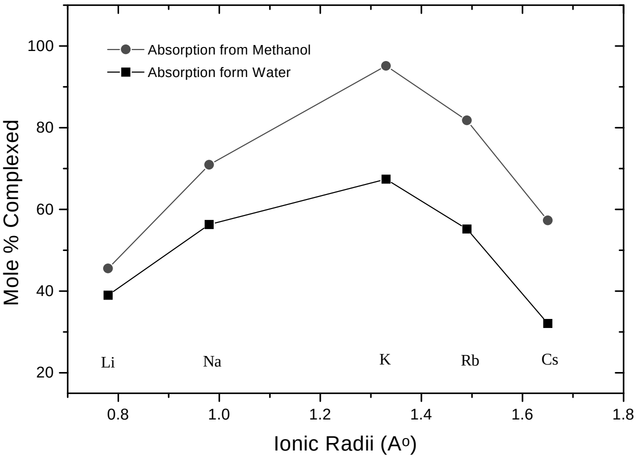


Fig. 10. Effect of solvent on alkali metal cation uptake (polyamic acid 3—dibenzo 18-crown-6 polymer).

3.4. Cationic uptake from methanol

The study was extended to investigate the effect of change from an aqueous to a methanolic media on the binding coefficients. The iodide salts were used, as they are much more soluble than the corresponding chlorides in the less polar organic methanol solutions. The polymers were exposed to a solution of the alkali metal salts (0.7 M) and after drying they were analysed for anion content by microanalysis. The cation uptake values were calculated from the iodine concentrations using the equations for the chloride study, Figs. 10 and 11. The move from an aqueous system to an organic based system resulted in an increased capacity of the polymer to bind cations. The solubility of the polymers is slightly higher in methanol than in aqueous media and this may in part influence the ability of the polymer to take up ions. The degree of swelling of the polymer films was, however, imperceptible during the period of the ion uptake experiments. The level of cation incorporation was quite remarkable, with in some cases >80% of the crown ether units accommodating a metal ion. The values obtained appeared from measurements performed as a function of exposure time to be equilibrium quantities. These values are all the more remarkable in view of the fact that solid polymer membranes were being used. The flexibility of these complexed polymers was not observed to be noticeably different from the uncomplexed blank materials.

The enhancement in cation uptake in methanol may be the result of a number of factors:

- The crown having a stronger affinity for the cation. This has been found in conventional monomeric studies of crown ethers, where the macrocycles provide enhanced binding in organic media due to the less effective co-ordinating power of the solvent to the metal ion.
- The organic solvent allows the polymer to swell more and provide an increase in the accessibility of the binding sites.

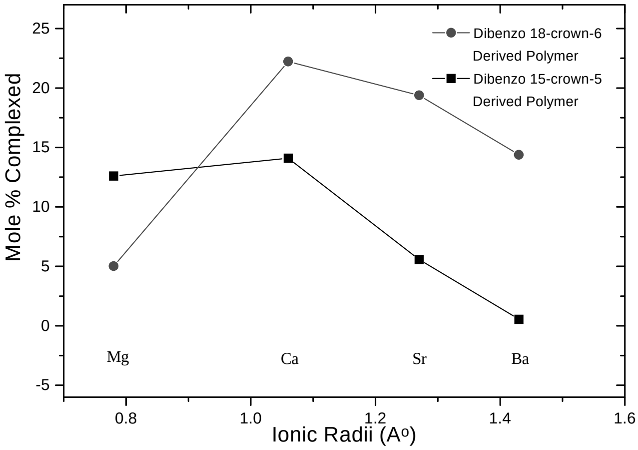


Fig. 9. Alkaline earth metal cation uptake (aqueous).

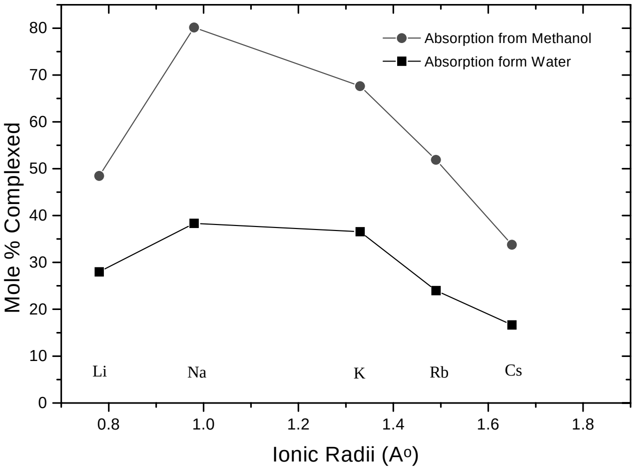


Fig. 11. Effect of solvent on alkali metal cation uptake (polyamic acid 9—dibenzo 15-crown-5 polymer).

The cation uptake selectivities, shown by these polymers,

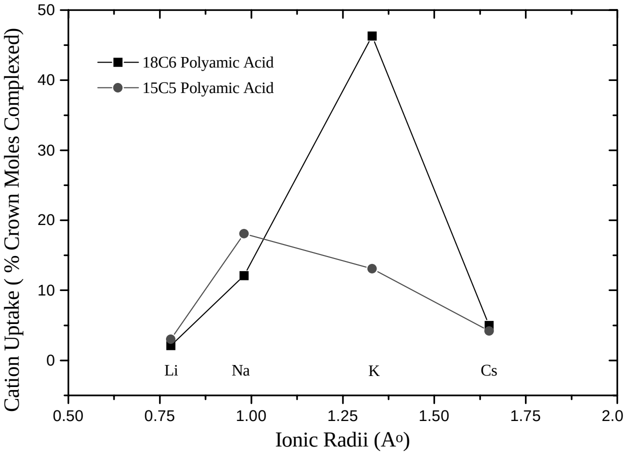


Fig. 12. Competitive alkali metal cation uptake (aqueous).

were in agreement with the aqueous measurements and were generally consistent with what would be expected from the ring size effect.

3.5. Competitive cationic uptake

The degree of cation uptake in ionic mixtures cannot be so easily evaluated, as calculations based on the anion will yield only the total concentration of metal ions absorbed and provide no discrimination about the cation type. To overcome this problem the polymers were analysed by atomic emission (ICP-OES). The treatment of the sample polymers were carried out as indicated above. The films were exposed to mixtures comprising 0.2 M of each of the alkali metal chlorides, then dried and analysed for metals content by ICP-OES. The selectivity observed in the previous separate cation uptake experiments was paralleled in the competitive cation absorption results. In both cases, the selectivity observed was consistent with what could be expected from the ring size effect of the polymers' constituent crown ether, Fig. 12. The potassium selectivity of the diamino dibenzo 18-crown-6 polyamic acid was found to be very pronounced. These solid phase cation uptake studies have indicated the potential of crown ether polyamic acids in cation removal. The size selectivity of the polymers with respect to cation uptake was also indicative of the crown ethers central role in the complexation process.

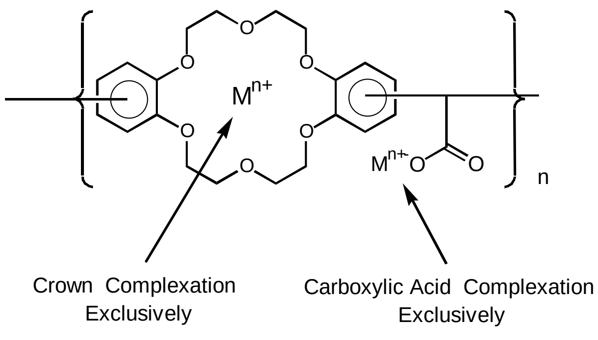


Fig. 13. Alternate cation capture mechanisms.

4. Conclusions

This study has indicated that both the presence of the carboxylic acid residues and the size of the crown ether units in the polyamic acids play important roles in the cationic binding strength of the polymeric materials. Within the polyamic acids, the combination of the ionisable carboxylic acid residues and the co-ordinating crown ether units can lead to at least two different cation capture mechanisms (Fig. 13). The carboxylic acid residues can operate as ion exchange centres or in conjunction with crown ether units provide a neutral co-ordinating cation capture site. Alternatively, the two processes can operate together to give a dual cation capture mechanism.

An analogous dual cationic capture system was studied by Bartsch et al. on polymers derived from acrylic acids and styryl crown ether oxyacetic acids [13]. In purely ion exchange systems (e.g. polyacrylic acid), lithium is preferentially taken up due to its high charge density. Other alkali metal cations were not observed to be selectively absorbed. However, when crown ether units were introduced into the polymers, the selectivity for Li fell and the polymers as a whole displayed the selectivity that would be expected for the monomers.

The observations on the polyamic acids indicate the pivotal role that the crown ether units contributed towards the overall binding behaviour. This is demonstrated by the binding constant selectivity towards sodium for various crown units and the cation uptake measurements across the alkali metal series. The close relationship between the polymeric results and those for the parent monomeric species, indicate that the inclusion of the crown units had conferred a large degree of cationic recognition to the final polymers. From this observation it is concluded that the crown ether plays a dominant role and probably the cation capture mechanism accounts for a major part of the binding to the polymer. If an ion exchange process, through the carboxylic acid residues, had been the single or dominating process these selectivities would not have been observed.

The carboxylic acid residues do, however, play an important role in assisting the binding process, which was most clearly shown by the much larger binding constants of the polyamic acids compared with the corresponding polyimides. The high binding constants observed for these systems, which even exceed their monomeric counterparts, were reflected in their cation uptake values. The molecular models generated indicated that the carboxylic acid residues lie close to the macrocyclic ring and could act as lariating species to assist in the complexing of the cations. The electrostatic interaction of the ionised and negatively charged crown ether polymers should also not be discounted, as previous studies on the effect of sulphonation [15] has demonstrated the importance of these effects on cationic binding.

In conclusion, the crown ether polyamic acids offer scope for their application in the capture of alkali metal cations and are very efficient when used in organic systems. The degree of selectivity observed by alteration of features such as the macrocycle ring size, would also allow these materials to be used in selective cation removal and in chromatographic supports.

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