Polyamides containing dibenzo-18-crown-6 moieties in the backbone: nuclear magnetic resonance studies of their K^+ and Cs^+ complexes in dimethylsulphoxide

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Complexation of potassium and caesium salts by polyamides containing dibenzo-18-crown-6 in the chain was investigated by ^{13}C and ^{133}Cs n.m.r. in dimethylsulphoxide. A study of the chemical shift as a function of crown/cation mole ratio shows that the mechanism of complexation of caesium by the macrocycle involves two equilibria with formation of a 1/1 complex and a sandwich complex, Cs^+ being bound to two macrocyclic moieties: the formation constant thus depends on the polymer structure.

(Keywords: complexation; complexing polymer; dibenzo-18-crown-6; ^{13}C nuclear magnetic resonance; ^{133}Cs nuclear magnetic resonance)

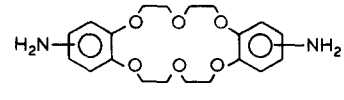
INTRODUCTION

Selective complexation of alkali and alkaline-earth ions by crown ethers in nonaqueous solvents has received much attention and has become an important field of research. Applications have been reported in organic synthesis, polymer chemistry and analytical chemistry[1].

The extent of complexation is strongly dependent on the nature of the solvent and on the dimensions of both cation and crown ether. For example K^+ cation, which fits the 18-crown-6 cavity, forms a more stable complex than Na^+. However, Gokel has recently pointed out that this relationship between cation diameter and crown ether hole size is not always valid[2]. When the cation diameter exceeds that of the crown cavity, the cation is not generally located inside the cavity but slightly outside. Therefore, these cation–crown systems can form 1/1 and 2/1 crown to cation complexes. In the 2/1 type complex, the cation is sandwiched between two macrocycles.

Crown ethers and cryptands have been incorporated in polymeric structures as part of the backbone or pendant. The complexing ability of these polymers was effective but in several cases the binding constants were somewhat lower than for the corresponding monomeric compound. Smid *et al.*[3] have made a valuable contribution in this field; they prepared polymers and copolymers from vinylbenzo-crown ether and reported extensive data on the complexation of alkali picrate salts in various solvents. The complexation constant was generally similar or even higher than the monomeric analogue and evidence for a cooperative effect of the polymer macrocyclic moieties in the complexation of ionic solutes has been given.

The complexation of these ligands has been studied by numerous techniques: potentiometry, conductance, distribution equilibria, calorimetry and n.m.r. The stability of the complexes is highly affected by the nature of the solvent in which the complexation takes place. For example, in a solvent of good solvating ability, a drastic decrease in weak complex formation is generally observed. Popov *et al.*[4–6] have clearly shown that n.m.r. techniques are very useful to study the interaction of macrocyclic polyethers with alkali-metal ions in various organic solvents. The complexation process changes the environment of both metal and ligand, so n.m.r. of the metal or ligand nuclei is particularly sensitive to detect any modification and very useful for structural, kinetic and thermodynamic studies of these complexes[7]. Several authors incorporated the macrocycle, diamino-2,3,11,12-dibenzo-1,4,7,10,13,16-hexacyclooctadeca-2,11-diene (DADB18C6)



1 DADB18C6

into the backbone of the polyamide, and films were prepared by casting from solution[8–10].

Complexation with several alkali ions was reported but few physicochemical studies have been made on these polymers. In particular, nothing can be found in the literature on the influence of chain flexibility on the complexation with alkali ions and on the interaction with Cs^+, a cation whose ionic diameter is larger than the cavity. So we prepared polyamides by polycondensation of diamine **1** with various diacid chlorides.

This paper describes an n.m.r. study of solutions of polyamides containing 18-crown-6 rings in the backbone and K^+ or Cs^+ cations in dimethylsulphoxide (DMSO), a solvent with a high dielectric constant ($\varepsilon = 45$) and strong electron donor properties ($DN_{SbCl_5} = 29.8$). Polymers were characterized by viscometry and ^{13}C n.m.r.; the ionic interactions with the polymers were studied by viscometry, ^{13}C n.m.r. and ^{133}Cs n.m.r.

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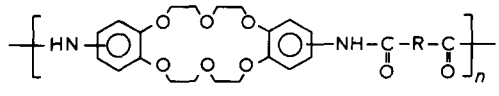
EXPERIMENTAL

The macrocycle **1** was a gift of Dr M. Hiraoka (Nippon Soda). It is a mixture of isomers, which were not separated. Isomers could be detected on high-resolution spectra of compound **1** but not in the case of polymers. The polymers **2–6** were prepared by condensation of the diamino derivative **1** with diacid chlorides (Fluka) in hexamethylphosphorotriamide (HMPT) as described by E. Shchori and J. Jagur-Grodzinsky[10], who reported the synthesis of polymer **2**. HMPT (Fluka) was previously dried over 4 Å molecular sieves before use. All polymers were precipitated in MeOH and purified by Soxhlet extraction with acetone.



R = **2**

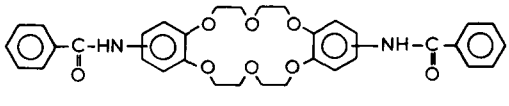
R = **3**

R = **4**

R = $-(CH_2)_2-$ **5**

R = $-(CH_2)_6-$ **6**

For an easier assignment of n.m.r. spectra, a model compound **7** was prepared from condensation of **1** with benzoyl chloride.



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DMSO and all inorganic salts were reagent grade. They were used without any further purification.

^{13}C n.m.r. spectra were run at 62.9 MHz on a Bruker 250 instrument for the characterization of the polymers and the determination of their stability constants with potassium. Spectra of 0.05 M solutions of the various polymers were recorded in d_6-DMSO with increasing amounts of potassium thiocyanate. The chemical shift variations with salt concentration for the most sensitive signals (C(2) or C(3)) were then used in order to calculate the stability constants.

^{13}C chemical shifts were referenced to TMS. Positive values indicate a downfield shift. ^{133}Cs n.m.r. spectra were run at 10.45 MHz on a Varian FT 80 or at 32.87 MHz on a Bruker 250 instrument.

The high kinetic lability of the complexes of Cs^+ leads to rapid cation exchange between complexed and free (or solvated) forms in solution. ^{133}Cs chemical shift measurements were made with reference to an infinitely dilute DMSO Cs^+ solution.

Stability constants can be calculated from the variation of the Cs^+ chemical shift with the addition of polymer.

Intrinsic viscosities were determined with a FICA automatic capillary viscometer. Pure DMSO was filtered on 0.45 μm Millipore filters. The solvent flow time was greater than 180 s. Concentration of polymer solutions was 1%.

DATA TREATMENT

Several numerical methods have appeared in the literature for the calculation of the stability constants[11–16], but for our own problem, two programs were written.

For K^+ ion, we assumed that only one complex is formed and we used a program with two parameters (K_1 and Δ_1^L), additive variations of K_1 and a least-squares fit. We have already calculated crown ether complexation constants by a similar treatment reported in a previous paper[17].

When both complexes with ligand/metal mole ratio 1/1 and 2/1 can form (i.e. Cs^+ complex), an analysis with four parameters (K_1, K_2, Δ_1^L and Δ_2^L) has been developed, where Δ_1^L represents the chemical shift variation for the Cs^+ (crown) complex and Δ_2^L the chemical shift variation for the Cs^+ $(crown)_2$ complex.

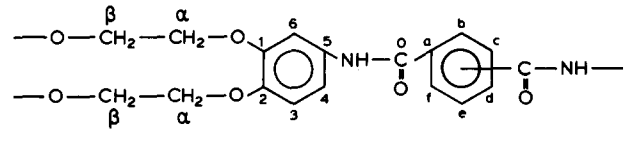
The last program has been corrected by inserting the ion pair formation constant K_{ip} of $CsNO_3$ in DMSO.

Numerical calculations were run on an IBM 34 computer.

RESULTS AND DISCUSSION

Assignment of ^{13}C n.m.r. spectra

Spectral assignments of the seven compounds are given in *Table 1*, indexation of the different ^{13}C nuclei being as follows:



Spectra were interpreted with the help of chemical shift increments in the benzene series combined with off-resonance ^1H decoupled spectral information. Substituent effects of methoxy groups[18,19] and secondary amide groups[20] were used to approximate chemical shift evaluations. As expected, the greatest disagreement was displayed for *ortho* substituents.

When further data were required for unambiguous assignment, these were completed by mutual comparison of the spectra of the seven compounds and of their evolutions with potassium salt addition.

As compound **3** was not soluble in pure DMSO, its spectra had to be recorded in the presence of K^+. Therefore, only those chemical shift values corresponding with nuclei unaffected by the occurrence of K^+ in other compounds were reported for compound **3** in *Table 1*.

Equilibrium studies; determination of the formation constants

18-Crown-6 is a macrocycle specific for K^+ ion and we will therefore only consider the formation of the complex with 1/1 stoichiometry.

Table 1 ^{13}C chemical shifts of compounds **1** to **7** (values in brackets are related to calculated shifts[18–20])

Compound	C(0)	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(a)	C(b)	C(c)	C(d)	C(e)	C(f)	C(β)	C(α)
1	–	139	149.1	115.7	105.2	143.4	100.7	–	–	–	–	–	–	69.1	67.6
		(135.7)	146.4)	(116)	(108.5)	(139.8)	(101.8)								
2	164.5	147.7	144.5	112.9	112.5	132.6	106.5	135.2	126.6	135.2	130.3	128.4	130.3	68.2	67.9
		(145.5)	(139.5)	(115.1)	(111.8)	(132.8)	(105.1)	(133.8)	(126.5)	(133.8)	(130.4)	(128.1)	(130.5)		
3[a]	164.3	–	–	–	–	132.5	–	137.3	127.5	127.5	137.3	127.5	127.5	–	–
								(136.9)	(127.3)	(127.3)	(136.9)	(127.3)	(127.3)		
4	166.3	147.5	144.1	112.6	111.7	132.9	105.5	136.6	127.7	129.5	129.5	127.7	136.6	68.8	67.9
								(133)	(127.3)	(131.2)	(131.2)	(127.3)	(133)		
5	169.8	147.6	143.6	112.6	110.8	132.9	–	31.1	–	–	–	–	–	–	–
6	170.7	147.6	143.6	112.5	110.9	132.9	104.8	28.6	25.1	–	–	–	–	–	–
7	165.1	147.6	144.3	112.6	112.5	132.6	106.3	134.9	127.4	128.3	131.3	128.3	127.4	68.9	67.8
								(134)	(127.5)	(128.3)	(131.4)	(128.3)	(127.5)		

[a] Values given in excess of K^+ for ^{13}C signals unaffected by complexation

The diameter of the Cs^+ ion is larger than the cavity of the macrocycle and the interaction between the ligand L and the metal ion M^+ is defined, taking into account both 1/1 and 2/1 complexes.

The strong influence of complexing on the environment of ^{13}C nuclei or ^{133}Cs nucleus permits the determination of the formation constants by observing either the ^{13}C n.m.r. lines of the ligand or the ^{133}Cs n.m.r. line of the metal. If the exchange rate between the different environments of the ligand or the metal ions is fast, the observed chemical shift δ_{obs} represents a weighted average:

$$\delta_{obs} = \sum pi\delta_i \qquad \sum pi = 1$$

Taking into account all equilibria, the system is defined by equations (1)–(11):

$$M^+ + L \rightleftharpoons ML^+ \qquad K_1 = \frac{[ML^+]}{[M^+][L]} \tag{1}$$

$$ML^+ + L \rightleftharpoons ML_2^+ \qquad K_2 = \frac{[ML_2^+]}{[ML^+][L]} \tag{2}$$

$$M^+ + A^- \rightleftharpoons M^+A^- \qquad K_{ip} = \frac{[M^+A^-]}{[M^+][A^-]} \tag{3}$$

where $[A^-]$ is the free anion concentration and $[M^+A^-]$ the ion pair concentration.

We designate respectively L_T and M_T as the total concentrations of the ligand and the metal ion:

$$L_T = [L] + [ML^+] + 2[ML_2^+] \tag{4}$$

$$M_T = [M^+] + [M^+A^-] + [ML]^+ + [ML_2^+] \tag{5}$$

Combining equations (1)–(15) and assuming that

$$M_T = [A_T^-] = [A^-] + [A_{ip}^-] \simeq [A^-] \tag{6}$$

the following equation is derived:

$$K_1K_2[L]^3 + K_1\{1 + K_2(2M_T - L_T)\}[L]^2 + \{1 + K_1(M_T - L_T) + K_{ip}M_T\}[L] - L_T - K_{ip}M_TL_T = 0 \tag{7}$$

and can be solved iteratively.

The observed ^{13}C chemical shifts of the ligand are a weighted average and are given by the equation:

$$\delta_{obs}^L = \frac{[L]}{L_T}\delta_0^L + \frac{[ML^+]}{L_T}\delta_1^L + 2\frac{[ML_2^+]}{L_T}\delta_2^L \tag{8}$$

Using equations (1) and (2) and writing:

$$\Delta_{obs} = \delta_{obs} - \delta_0$$

$$\Delta_1 = \delta_1 - \delta_0$$

$$\Delta_2 = \delta_2 - \delta_0$$

equation (8) becomes:

$$\Delta_{obs}^L = \frac{M_T(K_1[L]\Delta_1 + 2K_1K_2[L]^2\Delta_2)}{L_T(1 + K_1[L] + K_1K_2[L]^2)} \tag{9}$$

Δ_{obs}^L is measured for different values of M_T, L_T being kept constant.

When the resonance line of ^{133}Cs is observed:

$$\Delta_{obs}^M = \frac{K_1[L]\Delta_1^M + K_1K_2[L]^2\Delta_2^M + K_{ip}[A^-]\Delta_{ip}}{1 + K_1[L] + K_1K_2[L]^2 + K_{ip}[A^-]} \tag{10}$$

with $CsNO_3$, this expression, which takes into account the formation of both 1/1 and 2/1 complexes and the formation of the ion pair, was used. With KSCN, we assumed that $K_2 = 0$ and that there is no ion pair in DMSO[21]. Therefore modifications of equations (7) and (8) give:

$$K_1[L]^2 + \{1 + K_1(M_T - L_T)\}[L] - L_T = 0 \tag{11}$$

and

$$\Delta_{obs}^L = \frac{M_TK_1[L]\Delta_1^L}{L_T(1 + K_1[L])} \tag{12}$$

COMPLEXATION OF POLYMER 2

^{13}C *n.m.r. spectra*

K^+ complexes. ^{13}C chemical shifts (δ) of the macrocycle in the presence of K^+ ion were measured in DMSO as a function of the salt concentration at constant polymer concentration. The variation is displayed in *Figure 1*. An upfield shift results with addition of salt. The initial slope

suggests the formation of a 1/1 ligand/metal complex. Data for C(1), C(2), C(3), C(6) and C(α) provide the same constant. Lower induced complexation shifts are observed with the polymer compared to compound **1**. Since this effect occurred also with compound **7**, we think that it is not due to the polymeric nature of the ligand but to the substitution of amine groups by amide groups. Such a substituent effect has been pointed out by Jagur-Grodzinski *et al.*, who reported that the basicity of four oxygens in the macrocyclic ring of dibenzo-18-crown-6 is affected by electron-withdrawing or electron-donating substituents in its aromatic ring[22]. In DMF the complexation constant follows the order dibenzo-18C6 > diaminodibenzo-18C6 ≃ nitrodibenzo-18C6. The value for the latter ligand is one-sixth of the former. The SCN^- counterion was chosen because no ion pair could be detected. *Table 2* gives the formation constant of the complex of stoichiometry 1/1 with K^+.

Ca^{2+}. Addition of calcium chloride to a solution of polymer **2** did not shift ^{13}C signals in the same way as did potassium thiocyanate (see *Figure 2*). Thus, with the Ca^{2+} cation, whose diameter is smaller than the crown hole size, complexation mainly occurs with the amide function rather than with the macrocycle, rotation around the C–N bond becoming hindered in the complex as emphasized by the splitting of C(0) and C(5) signals. Such behaviour has been observed for carrier ligands of the ether amide type with $CaCl_2$ (ref. 23) and complexation of polyamides with calcium salts is a well known phenomenon[24]. In this case a formation constant could not be determined

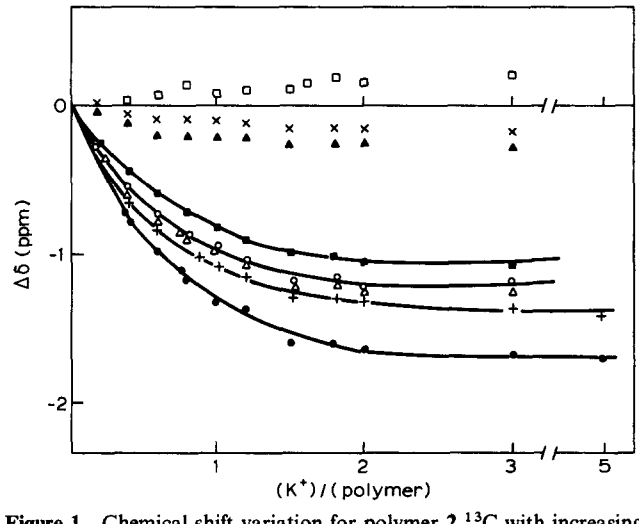


Figure 1 Chemical shift variation for polymer **2** ^{13}C with increasing $[K^+]/[polymer]$ ratios: +, C(1); ○, C(2); ●, C(3); △, C(6); ×, C(a+c); □, C(b); ■, C(α); ▲, C(β); other ^{13}C gave $\Delta\delta < 0.2$ ppm for $[K^+]/[polymer] = 2$

Table 2 Formation constants of 1/1 and 2/1 (L/M) complexes with compounds **1–6**

Compound	Ion	K_1 (M^{-1})	K_2 (M^{-1})
1	Cs^+	80±4	6±0.4
2	K^+	240±12	
2	Cs^+	40±2	6±0.4
3	Cs^+	gel	
4	Cs^+	80±2	10±0.6
5	Cs^+	30±3	8±0.5
6	Cs^+	60	8±0.5

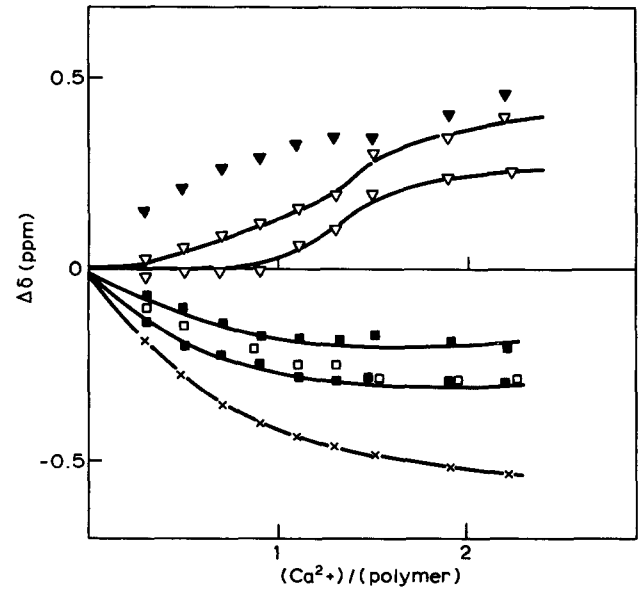


Figure 2 Chemical shift variation for polymer **2** ^{13}C with increasing $[Ca^{2+}]/[polymer]$ ratios: ×, C(a+c); □, C(b); ▽, C(5); ▼, C(d+f); ■, C(0); other ^{13}C gave $\Delta\delta < 0.2$ ppm for $[Ca^{2+}]/[polymer] = 2$

because equations became much more difficult to establish.

Cs^+. Caesium ion, which is larger than the cavity, induced the same complexation pattern as K^+ but, with a given ion/macrocycle molar ratio, ^{13}C chemical shift variations were smaller. Furthermore, the variation displays an obvious change of slope near the 1/1 ratio and suggests that the complexation reaction occurs as expected in two steps: formation of a stable 1/1 complex, followed by the addition of a second ligand molecule forming a sandwich compound.

In such conditions, the most sensitive ^{133}Cs shifts appeared to us a more appropriate method for constant calculations.

^{133}Cs n.m.r. spectra

It has been shown by i.r. spectroscopy[25] that alkali nitrate salts form contact ion pairs in DMSO. The association is generally less than 1, but to investigate the complexation of Cs^+ ion with the polymer in DMSO, we first studied the concentration dependence of the ^{133}Cs chemical shift of $CsNO_3$. The results indicate that there is formation of an ion pair in this solvent:

$$M^+ + A^- \overset{K_{ip}}{\rightleftharpoons} M^+A^-$$

The observed chemical shift is given by:

$$\delta_{obs} = \alpha\delta_{ip} + (1-\alpha)\delta_f \tag{13}$$

where α is the ion pair fraction, δ_{ip} the chemical shift of the ion pair and δ_f the chemical shift of the free ion:

$$\text{as } \alpha \ll 1 \qquad K_{ip} \simeq \frac{\alpha}{C(1-2\alpha)} \tag{14}$$

where C is the concentration of the salt. Combining (13) and (14) we obtain the following equation:

$$\frac{1}{\delta-\delta_f} = \frac{2}{\delta_{ip}-\delta_f} + \frac{1}{K_{ip}}\frac{1}{\delta_{ip}-\delta_f}\frac{1}{C} \tag{15}$$

The curve $1/(\delta-\delta_f)=f(1/C)$ is linear and the best fit for this relation gives $K_{ip}=2.8$.

Several authors[26–32] have studied the complexation of Cs^+ with crown ether. From ^{133}Cs n.m.r., Popov and Dye reported the formation of both 1/1 and 2/1 crown/Cs^+ complexes with 18-crown-6 and dibenzo-18-crown-6 and determined the complexation constants. A decrease in basicity of oxygen atoms and a more rigid cycle decrease the constants. It was suggested that only relatively weak complexes of Cs^+ ion could be formed by the crown ether in a solvent like DMSO which combines a relatively high dielectric constant and a high donicity. ^{133}Cs chemical shifts of caesium salts in the presence of polymer **2** were measured as a function of crown/Cs^+ mole ratio at a fixed concentration of caesium.

As could be expected, the initial slope does not fit with a 1/1 stoichiometry (*Figure 3*). Indeed no fit could be obtained with the two-parameter analysis (K_1,Δ_1^L) but good agreement could be found with four parameters. Results introducing the correction due to the ion pair formation are given in *Table 2*.

Viscometry

Complexation of cations to polymeric ligands affects the viscosity of polymers. Smid *et al.*[33] showed that the intrinsic viscosity of poly(vinylbenzo-crown ethers) is enhanced in the presence of salts, due to a chain expansion, and the polymers behave as polyelectrolytes when the binding constant is large. The interaction leads eventually to gelation when a cation can complex simultaneously with two crown moieties. There is a competition between inter and intra 2/1 crown/cation complexes, and intramolecular complexes will be predominant with flexible polymers.

The decrease in viscosity clearly indicates that there is a contraction of the polymer. This behaviour has been reported by Gramain who gave evidence for the formation of a barium sandwich complex with a polymer including the diazatetraoxa macrocycle in the backbone[34].

Whatever the salt concentration, a normal plot of reduced viscosity *versus* polymer concentration is observed. In DMSO the intrinsic viscosity of polymer **2** increases by 60% when KSCN is added to a stoichiometric ratio L/M = 1.

Addition of Cs^+ salt in polymer solution affects the solution viscosity. The intrinsic viscosity dependence with crown/Cs^+ ratio is shown in *Figure 4*. There is no

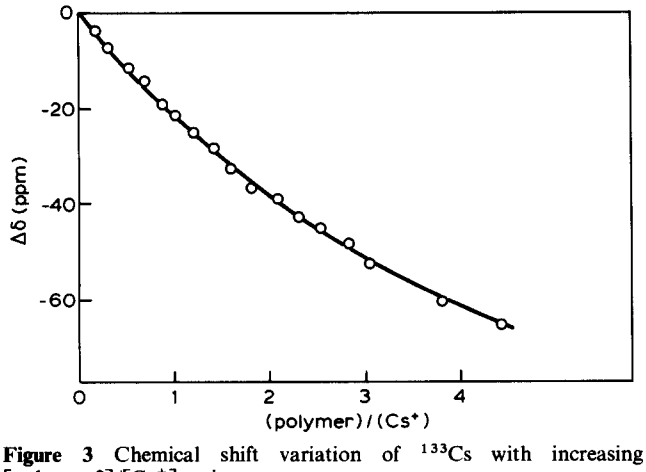


Figure 3 Chemical shift variation of ^{133}Cs with increasing [polymer **2**]/[Cs^+] ratio

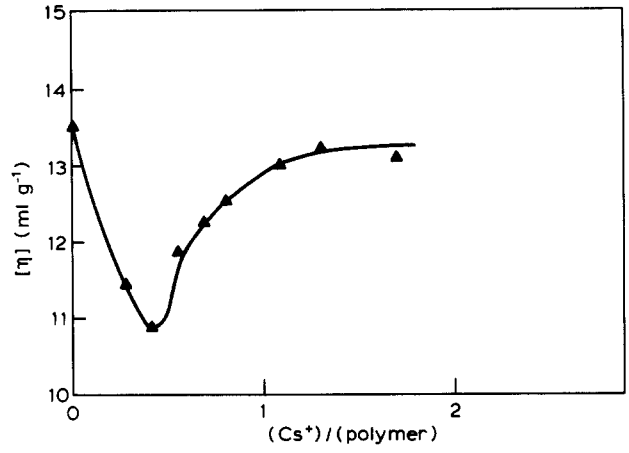


Figure 4 Evolution of polymer **2** intrinsic viscosity against [Cs^+]/[polymer] ratio

polyelectrolyte effect because the formation constant is too low but we observe a minimum [η] value corresponding to a crown/Cs^+ ratio of 2/1. Complexes of 2/1 stoichiometry are formed and in dilute solution the chain tends to coil, which is probably due to a majority of intra *versus* inter crown moiety interactions.

In contrast, in concentrated solutions we observe with time a thermoreversible gelation, a process that depends on intermolecular interactions.

The polymer behaviour should depend on the flexibility of the backbone. It was therefore interesting to study the structure–property relationship and so we prepared several polymers with different structure. Polymer **4** prepared by polycondensation of the diamino macrocyclic derivative with phthaloylchloride has an intrinsic viscosity [η] = 8 ml g^{-1}. Compared to the intrinsic viscosity of polymer **2**, a lower value is obtained. As a consequence, polymer **4** has a fairly low degree of polymerization, which can be explained by steric hindrance when the *ortho* disubstituted benzene reacts with the diaminodibenzo macrocycle. In dilute solution the addition of K^+ salts increases the viscosity but changes with crown/caesium ratio are small.

POLYMER BEHAVIOUR TOWARDS COMPLEXATION: A COMPARATIVE STUDY

Solubility

The polymers dissolve easily in DMSO, except polymers **6** and **3**. Polymer **6** swells and it is difficult to separate the aggregated hydrocarbon chains, but this can be done by complexation. For example, by addition of K^+ the polymer **6** solution becomes fluid as soon as the K^+/crown ratio reaches 0.5.

Polymer **3** is still swollen when the ratio is 0.5, and to achieve dissolution a large excess of salt is needed.

Formation constants

We have studied the dependence of the polymer ^{13}C chemical shifts with K^+/crown ratio. For a fixed ratio, no significant difference in $\Delta\delta$ was observed between the six species, which indicates that the formation constants of the complexes are similar. It seems that there is little influence of the polymer structure on 1/1 K^+ complexation. The solubility of polymer **3** was too weak even in K^+ solution and formation constants could not be derived from n.m.r. spectra.

As caesium can form 1/1 and 2/1 crown/Cs^+ complexes with the dibenzo-18-crown-6 macrocycle, the influence of the polymer structure has been checked with this cation. Addition of polymer to solutions of constant concentration of caesium shifts the caesium resonance line and the dependence on polymer structure can be found in *Table 2*. Two polymers display large differences:

(a) Polymer **3** with *para* disubstituted aromatic ring in the backbone has a low solubility and $\Delta\delta$ variation is lower.

(b) Polymer **4** with the *ortho* disubstituted aromatic ring gives larger chemical shift and forms the more stable complexes with caesium as shown in *Table 2*. From these data, we can point out the behaviour of macrocyclic model *versus* polymer. Larger constants are obtained with the *ortho* derivative and with the flexible polymer **6**.

Polymer **4** has the highest K_1 and K_2 constants. In this case the structure of the backbone enables the complexation of Cs^+ by two close macrocycles incorporated in the chain and the stacking of the macrocycles is facilitated by the chain conformation. By contrast to the other polymers of the series, the solution does not give a gel with time.

To confirm the existence of both complexes with all polymers under investigation, we added potassium malonate salt to a polymer solution and studied the chemical shift variation of ^{13}C nuclei of the macrocycle with increasing malonate concentration. A change in the slope is observed at a malonate/crown ratio of 0.5, that is K^+/crown = 1. This behaviour shows evidence for the participation of the two K^+ ions of malonate in complexation.

Again this salt gives a gelation of the solutions except with polymer **4**.

CONCLUSION

When comparing data provided by ^{133}Cs n.m.r. we noted for all polymers studied the formation of both 1/1 and 2/1 complexes in DMSO. The formation constants are low in that strongly solvating solvent, but values depend on the nature of the polymer.

When Cs^+ cation binds two macrocycles, they can be located on two chains or on the same chain, and the nature of the interaction will depend on the structure of the chain. It seems that when two macrocycles on the same chain are spacially close (polymer **4**), the binding of Cs^+ is higher. In this case the polymer is a better complexing agent than the monomer. It has been reported[35] that the decrease in entropy upon complexation is related, in part, to changes in the conformational entropy of the macrocycle. Although the chain of polymer **4** has a restricted motion, it is reasonable to suggest that Cs^+ ion fits the ordering of the macrocyclic moieties and that interactions lead to the formation of predominant intramolecular 2/1 complexes. Accordingly, gelation is not observed.

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