so an accurate determination of crystallinity was not possible.

Acknowledgment. The authors are grateful to Dr. J. B. Lando for X-ray determinations. This research was supported by the U.S. Army Research Office, Durham, N.C., and the National Science Foundation. Special thanks are extended by W. Beever to the Phillips Petroleum Co. for a research fellowship.

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Synthesis and Ion Binding Properties of Epoxy Polymers with Diazacrown Ethers

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Received April 5, 1979

ABSTRACT: The synthesis of polymers obtained by polycondensation of two macrocyclic diamines [21] and [22] (1,4,10-trioxa-7,13-diazacyclopentadecane and 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane) with the diglycidic ether of 2,2-bis(4-hydroxyphenyl)propane (Epikote 815) is described. The polymers strongly chelate with cations, and their efficiency and selectivities in binding cations are compared with those of their monomeric analogues by using data obtained from water–chloroform extraction measurements. The stability constants for the polymeric complexes are comparable to those of the analogues whatever the ratio of complexation, indicating that the polymeric structure has no influence on the structure of the complexes. With all of the cations studied (alkali, alkaline earth, and Cu^{2+}, Cd^{2+}, and Pb^{2+}), the stoichiometry 1:1 was observed in chloroform. With alkali and alkaline earth cations, the selectivity is governed by the respective size of the cations and of the internal cavity of the cycles. With Cu^{2+}, Cd^{2+}, and Pb^{2+} cations, higher stabilities are obtained with the larger cycle. Experiments with mixtures of cations indicate that complexation properties are additive. The stability constants obtained with picrate and perchlorate anions are very comparable, showing that both anions lead to complexes with comparable binding energies. These results, in addition to results obtained by UV spectroscopy, are interpreted in terms of interactions of the anions with the protons of the hydroxylic groups present near the cycles. Aging experiments with oxygen and carbon dioxide indicate that the binding properties are not affected by the aging of the polymers.

Since the discovery by Pedersen[1,2] and Lehn[3] that synthetic macrocycles can form stable complexes with cations, relatively little has been published concerning the synthesis and the study of polymers containing such macrocyclic ligands. Most of these works concern the preparation and study of cross-linked resins[4-6] or membranes.[7,8] The only published investigation of linear soluble polymers or copolymers was by Smid et al.,[9] who synthesized and studied various poly(vinylcrown ethers).

In a previous article, we reported the synthesis of some polymers obtained by polycondensation of diazacrown ethers.[10] In this paper, the synthesis and binding properties of one type of these polymers are discussed. They are obtained by the polycondensation of a diepoxy monomer with the cyclic diamines 1,4,10-trioxa-7,13-diazacyclopentadecane (diamine [21]H) or 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (diamine [22]H). Their ion binding properties are studied by extration equilibria obtained in a water–chloroform system and compared to those of the monomeric analogues which have recently been studied.[11]

Experimental Section

Reagents and Solvents. All of the solvents used are purified and distilled by classical methods. The diamines [21]H and [22]H (Kryptofix 21- and 22-Merck) are purified as previously reported.[11] The diglycidic ether of 2,2-bis(4-hydroxyphenyl)propane (Epikote 815 from Shell Chimie) is purified by dissolution in chloroform, filtration, and precipitation in heptane. The soluble part is recovered after evaporation and drying. The content of the epoxide groups, determined by HCl in dioxan,[12] is found to be 8.74% compared with the theoretical value of 9.40%. Anal. Calcd for $C_{21}H_{24}O_4$: C, 74.12; H, 7.06; O, 18.82; Cl, 0. Found: C, 73.53; H, 7.02; O, 18.88; Cl, 0.53.

Polymerizations. The polycondensations of the diamines [21]H or [22]H with the diepoxy leading to the polymers P-[21]EpiDPP or P[22]EpiDPP are carried out as described below.

Purified Epikote 815 (4.8 mmol) with 5 mL of tetrahydrofuran are placed in a 100-mL flask equipped with a magnetic stirrer, a drying tube, and a nitrogen inlet. [21]H (4.8 mmol) dissolved in 15 mL of dry methanol is added to the flask. The mixture is heated under reflux for 72 h. The polymer is recovered by evaporation of the solvents in a rotary evaporator. It is then dissolved in 10 mL of chloroform, precipitated in 1 L of dry methanol, and dried under low pressure at 40°C for 1 week. The

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yield is about 83%. GPC analysis gives $M_n = 5000$ with $M_w/M_n = 1.42$ indicating an average of nine ligand units in the polymeric chain. Elemental analysis of the polymers is in accordance with the calculated values except for the presence of 0.12 and 0.21% of Cl for [21] and [22] polymers, respectively.

Aging Experiments. Aging experiments are carried out in sealed tubes charged with 1 g of polymer in the presence of O_2 or CO_2 or under vacuum. They are kept at 25 °C in a dark box. After 2 years the polymers are dissolved in chloroform, treated with 3 vol of 0.1 M HCl, 1 vol of water, and finally 3 vol of a solution of NEt_4OH in water (pH 12). The solvent is evaporated, and the polymer thus obtained is dried and studied by liquid–liquid extraction.

Measurements. The experimental procedure used for the water–chloroform extraction and for the synthesis of picrate salts is similar to those recently reported.[11] Perchlorate salts were obtained from Merck. The chloroform (Normapur Prolabo) is distilled after being dried for 24 h over $CaCl_2$. Experiments at pH 10 are conducted by adding the necessary quantity of NMe_4OH to the aqueous phase. Contents of salts in the chloroform phase are determined by UV spectroscopy in the case of picrates and by atomic absorption in other cases. A minimum of three independent determinations is made in each case. For the experiments with picrates, in many cases, the UV determinations are confirmed by atomic absorption. The maximum observed difference between the two methods is less than 10%.

The experimental determination of K_c includes two extractions. For each, we have previously determined that in our experimental conditions, 24 h is quite sufficient to obtain equilibrium.

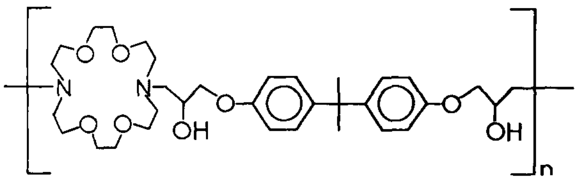
Salt Extraction without Ligand. In a 2 L volumetric flask, 2 L of a salt solution of known concentration and controlled pH is mixed with 1 L of chloroform. The flask is slowly shaken in a dark room with a constant temperature of 25 °C for 24 h. After decantation, the chloroform phase is separated and filtered on cotton-wool, and a known quantity is evaporated in a rotary evaporator. The residue is dissolved in 5 mL of water, and the salt concentration is determined.

Salt Extraction in the Presence of Ligand. In this case, the ligand is dissolved (10^{-3} M) in 50 mL of chloroform and mixed with 50 mL of salt solution. It was ascertained that no polymeric ligand is present in the water phase. Salt concentration is directly determined in the chloroform phase by UV spectroscopy. In the case of determination by atomic absorption, it is necessary to extract the complexed salt by an aqueous acid solution at pH 1.

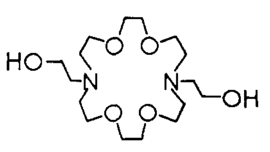
For the liquid/solid extractions, the solid salts are put into contact with the chloroform containing the polymer. After 3 weeks in a dark room at 25 °C (time sufficiently long to obtain equilibrium), the dissolved salt concentration is determined.

Results and Discussion

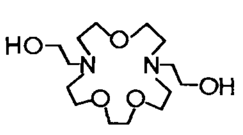
Synthesis and Characterization. The polycondensation of the diamines [21]H or [22]H with the diglycidic ether of 2,2-bis(4-hydroxyphenyl)propane leads to polymers whose repeat unit structures are depicted below together with the structures of the monomeric ligand analogues [22]EtOH or [21]EtOH. Aging experiments carried out in the presence of oxygen or carbon dioxide lead to yellowing of the polymers. However, as will be seen below, this does not seem to affect the binding properties of the polymers.



P[22]EpiDPP



[22]EtOH



[21]EtOH

Ion Binding Properties. In order to study the ion binding properties of the polymers, the liquid–liquid extraction process is used. An aqueous solution of picrate or perchlorate salt (MA) is repeatedly shaken with a chloroform solution of the polymeric ligand (L). To avoid the protonation of the ligand, the aqueous phase is buffered at pH 10 with NMe_4OH. After equilibrium, we have in the chloroform phase:

$$\mathrm{MA} + \mathrm{L} \overset{K_c}{\rightleftharpoons} \mathrm{LMA} \qquad (1)$$

where LMA is a complexed ligand in the polymeric chain and where it is assumed that a 1:1 complex is formed and that the ionic species present in the organic phase are in the form of ion pairs.[9c] K_c is calculated from the expression:

$$K_c = \frac{[\mathrm{MA}]_T - [\mathrm{MA}]}{[\mathrm{MA}][[\mathrm{L}]_0 - [\mathrm{MA}]_T + [\mathrm{MA}]]} = \frac{1}{[\mathrm{MA}]}\left(\frac{f}{100 - f}\right)$$

where $[\mathrm{L}]_0$ and $[\mathrm{MA}]_T$ are respectively the total concentration of ligand and of salt in the chloroform, and [MA] is the concentration of uncomplexed salt. Since there is a large excess of salt in the aqueous phase, then [MA] is equal to the solubility of the salt in chloroform in the absence of ligand. We define the percent complexation (% f) as the ratio between the concentration of complexed ligand and the total concentration of ligand. The values of $[\mathrm{MA}]_T$ and [MA] determined by UV spectroscopy and/or atomic absorption are used to calculate K_c and % f. It should be pointed out that K_c is not an extraction constant but a stability or association constant which depends on the solvent and the anion.

This experimental procedure[15] was judged superior to those used by Frensdorff[13] and Smid.[9] These authors assumed that the solubility of the picrate salts in the chloroform phase is given at any concentration by the equilibrium:

$$\mathrm{M}^+ + \mathrm{Pi}^- \overset{K}{\rightleftharpoons} (\mathrm{MPi})_{\mathrm{CHCl_3}} \qquad (2)$$

Our previous investigation of the solubility of picrate salts in chloroform as a function of the concentration of salt in the aqueous phase shows that this is not the case and that probably some associations or interfacial phenomenon disturbs the equilibrium.[2] Some of these previous results are given in Table I.

The interpretation of the experimental data according to equilibrium 1 asssumes that 1:1 complexes of cation with ligand are obtained whatever the concentrations. This has been previously verified for monomeric analogue molecules by NMR spectroscopy. In the case of polymers, the stoichiometry has been determined by liquid–solid extraction experiments. The polymer dissolved in chloroform is placed in contact with a gradually increasing quantity of solid picrate salt. After some weeks, the content of dissolved picrate is determined. In Figure 1, an example of the results obtained with calcium and sodium picrates and [22]EpiDPP polymer is shown. A 1:1 stoichiometry is observed. Analogous results were obtained with all the cations studied. This stoichiometry is confirmed by studies of the stability constants and of the structure of the complexes by UV spectroscopy as discussed below.

(a) Alkali and Alkaline Earth Cations. One major difference between a conventional ligand and a polymeric ligand is the possibility in the latter case of having a variable quantity of complex on the same molecule. This

Table I
Water-Chloroform Extraction of Picrate Salts at 25 °C According to Equilibrium 2[a]

	initial concn of picrates in aqueous phase, M							
	3×10^{-4}		10^{-3}		3×10^{-3}		10^{-2}	
	$[MPi]_{CHCl_3}$, $M \times 10^7$	K, M^{-1}	$[MPi]_{CHCl_3}$, $M \times 10^7$	K, M^{-1}	$[MPi]_{CHCl_3}$, $M \times 10^7$	K, M^{-1}	$[MPi]_{CHCl_3}$, $M \times 10^7$	K, M^{-1}
Na^+	1.6	1.78	3.8	0.38	5.6	0.062	8.3	0.0083
K^+	1.1	1.22	2.0	0.20	4.40	0.049	7.7	0.0077
Rb^+	4.3	4.78	7.0	0.70	17.6	0.196	19.8	0.0198
Sr^{2+}	3.2	3.56	9.0	0.90				
Ca^{2+}	3.8	4.22	10.5	0.11				

[a] $[M^+] = [Pi^-]$ in the water phase adjusted to pH 10 with NMe_4OH.

Table II
Water-Chloroform Extraction of Picrate Salts at 25 °C with the [22]EpiDPP Polymer Percent Complexation (% *f*) and Stability Constants According to Equilibrium 1[a]

	initial concn of picrates in aqueous phase, M							
	3×10^{-4}		10^{-3}		3×10^{-3}		10^{-2}	
	% *f*	$K_c \times 10^{-5}$, M^{-1}	% *f*	$K_c \times 10^{-5}$, M^{-1}	% *f*	$K_c \times 10^{-5}$, M^{-1}	% *f*	$K_c \times 10^{-5}$, M^{-1}
Na^+	3.6	2.3	6.3	1.8	21.7	1.1	49.1	1.2
K^+	15.0	16.1	20.7	13.2	48.2	21.1	56.2	16.6
Rb^+	5.5	1.4	8.1	1.3	26.2	2.0	29.2	2.1
Sr^{2+}	15.2	5.6	30.1	4.8				

[a] $[M^+] = [Pi^-]$ in the water phase adjusted at pH 10 with NMe_4OH and a ligand concentration in chloroform of 10^{-4} M.

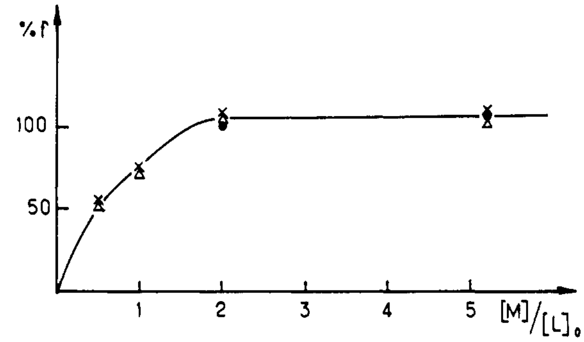


Figure 1. Extraction of solid picrates by the [22]EpiDPP polymer in chloroform at 25 °C. Percent complexation vs. cation-ligand ratio with $[L]_0 = 10^{-3}$ M: Ca^{2+} (▲, 15 days; X, 30 days), Na^+ (●, 20 days).

Table III
Stability Constants in Chloroform of Polymeric Picrate Complexes Compared with the Monomeric Analogues from Water-Chloroform Extraction at 25 °C According to Equilibrium 1[a]

	$K_c \times 10^{-5}$ M^{-1}							
	Li^+	Na^+	K^+	Rb^+	Cs^+	Ca^{2+}	Sr^{2+}	Ba^{2+}
[21]EtOH		5.9	4.4		0.2	8.7	15.7	13.6
P[21]EpiDPP	0.9	2.4	2.5	0.8	0.9	3.0	6.2	5.3
[22]EtOH		4.2	30.3	2.1	2.9	8.3	19.1	14.3
P[22]EpiDPP	0.8	1.8	13.2	1.3	0.8	2.5	4.8	4.4

[a] Picrate concentration 10^{-3} M in the aqueous phase adjusted at pH 10 with NMe_4OH and a ligand concentration of 10^{-4} M in chloroform.

Table IV
Stability Constants and Percent Complexation in Chloroform of Polymeric Picrate Complexes with Three Transition Metals at 25 °C According to Equilibrium 1[a]

	Cu^{2+}	Cd^{2+}	Pb^{2+}
atomic radius	0.72 Å	0.95 Å	1.20 Å
	P[21]EpiDPP		
% *f*[b]	39	17	38
$K_c \times 10^{-5}$ M^{-1}	50	16	50
	P[22]EpiDPP		
% *f*[b]	72	49	89
$K_c \times 10^{-5}$ M^{-1}	200	79	610

[a] Picrate concentration 10^{-3} M in the water phase at pH 5.5 and a ligand concentration of 10^{-4} M in chloroform.
[b] Measured by UV spectrometry and atomic absorption.

can influence not only the configuration of the polymers (with, for example, formation of macromolecular or multimolecular aggregates) but also the structure of the complexes and their stability constants. In a first attempt to detect a possible effect, we have studied the variation of the stability constant with the content of complexed ligands. Such experiments also have the advantage of testing the validity of the experimental procedure used and of justifying the use of equilibrium 1.

In Table II some results are reported for various cations at different concentrations in the case of the polymer [22]EpiDPP. The experimental errors are considerable. Based on the reproductibility of the results, they can be estimated to be of the order of ±30% on K_c. The most reliable values are obtained with a salt concentration of 10^{-3} M. It can be seen that regardless of the stoichiometry, the stability of the complexes is unaffected. Each ligand unit maintains its independence with no apparent interaction with the others, and if, as is probable, there is some change of configuration of the chains, this does not appear to affect the stability of the complexes.

In Table III are collected the values obtained for the constants K_c for the polymers [22]EpiDPP and [21]EpiDPP in the case of alkali and alkaline-earth cations. For comparison, values previously obtained[11] for the analogous molecules [22]EtOH and [21]EtOH are also given.

Stability constants for the polymers are comparable to those of the small-molecule analogues. At best we observe a slight decrease in stability when the ring is included in the polymeric backbone. Since the conformation of the rings leading to the more stable complexes is the endo-endo conformation, it is possible that the polymeric structure does not favor this conformation. It should also

Table V
Water-Chloroform Extraction of a Mixture of Picrates at 25 °C[d] and Stability Constants and Percent Complexation of Polymeric Complexes[d]

	water		chloroform			
	without polymer		with p[21]EpiDPP 10^{-3} M		with P[22]EpiDPP 10^{-3} M	
e	[M],[a] 10^{7} M	$[\mathrm{Pi}]_{\mathrm{total}}$,[b] 10^{7} M	% *f*	K_c,[c] 10^{-5} M^{-1}	% *f*	K_c,[c] 10^{-5} M^{-1}
NaPi 0.5	6.5		6.2	1.1	7.5	1.3
+		7.8				
KPi 0.5	1.1		0.8	0.7	8.2	8.2
NaPi 1	7.1				20.1	3.5
+		9.0				
KPi 1	1.6				21.1	16.5
KPi 1	1.8				20.9	14.9
+		12.8				
RbPi 1	10.8				14.6	1.6
$CaPi_2$ 0.5	6.3		29.2	6.6	38.8	10.1
+		12.0				
$SrPi_2$ 0.5	5.7		17.7	3.8	40.7	12.1

[a] Measured by atomic absorption. [b] Total concentration of picrate measured by UV spectroscopy. [c] Estimated error of K_c, ±50%. [d] The water phase is adjusted at pH 10 with NMe_4OH and the ligand concentration in chloroform is 10^{-3} M. [e] Initial concentration of each salt in the mixture × 10^{3} M.

Table VI
Aging Experiments with [22]EpiDPP Polymer[a]

picrates in water at 10^{-3} M	P[22]EpiDPP in chloroform, 10^{-4} M			
	ref	vacuum	O_2	CO_2
Na^+	1.8	1.7	1.5	1.5
K^+	13.2	12.4	10.9	9.2
Ca^{2+}	2.5	3.1	3.4	3.4
Ba^{2+}	4.4	4.1	4.2	3.6

[a] Water-chloroform extraction after two years in sealed tubes in the presence of oxygen or carbon dioxide or under vacuum.

be noted that the selectivities for the polymers and for the analogous small molecules are the same. The more stable complexes are obtained with cations of size corresponding to the cavity size of the rings, i.e., 1.0 and 1.4 Å respectively for the [21] and [22] rings calculated on the basis of macroscopic models.

(b) Transition Metal Cations. The stability of complexes formed with three transition metal cations Cu^{2+}, Cd^{2+}, and Pb^{2+} has been studied by the same method. In order to avoid precipitation of the hydroxides, the aqueous phase containing the picrates is kept at pH 5.5. Results for the percent complexation and stability constants are collected in Table IV. High values are obtained. In all cases, stabilities are higher with the larger ring independent of the size of the cations. The electronic structure of the transition metals becomes, as expected, the main determinant of stability: the less rigid larger ring can easily adapt its conformation to the electronic structure of the cations.

(c) Mixtures of Cations. Some experiments have been carried out with mixtures of cations in order to evaluate the possible use of such polymers for separation purposes. This has been done by determining the stability constants for the various cations in the mixtures. Our aim was not to determine the best conditions for separation but to see if interactions between the different complexes are able to perturb the respective stabilities. Results are summarized in Table V. Also shown in Table V are the solubilities in chloroform of the various mixtures in the absence of ligand. We note that the interactions between the cations affect the solubilities of the picrates. Comparing these data with the results obtained with only one cation, we observe the well-known phenomenon of solubility depression: the solubility of potassium picrate in chloroform is strongly decreased by the presence of sodium picrate. On the basis of the solubilities obtained for each metal in the presence of another, stability constants for the different polymeric complexes can be calculated. Taking into account the rather large experimental error (±50%), the values obtained are comparable to those with only one cation (Table III). It may be concluded that the selectivities calculated from the ratio of stability constants are in good agreement with the observed values. In our experimental conditions, the interactions between the different cations present on the polymeric chain are either negligible or nonexistent.

(d) Aging Behavior. Such properties make possible the use of these polymers as chelating agents. However, such utilization requires long-term stability with conservation of the complexing properties. In the present study, it has consistently been observed that complex formation

Table VII
Water-Chloroform Extraction with Picrate and Perchlorate Anions at 25 °C Stability Constants and Percent Complexation

		ligands in chloroform at 10^{-4} M					
		$[22]CH_3$		P[21]EpiDPP		P[22]EpiDPP	
salt in water phase[c]		% *f*	$K_c \times 10^{-5}$,[a] M^{-1}	% *f*	$K_c \times 10^{-5}$,[b] M^{-1}	% *f*	$K_c \times 10^{-5}$,[b] M^{-1}
Na^+	Pi^-	38	19	8.5	2.4	6.7	1.8
	ClO_4^-	35	4	30.9	3.2	27	2.6
K^+	Pi^-	19	14	4.7	2.5	20.7	13.2
	ClO_4^-	21	8	14.5	4.2	38.5	15.6

[a] Estimated errors on K_c, ±50%. [b] Estimated errors on K_c, ±20%. [c] pH 10 with $[NMe_4OH] = 10^{-3}$ M.

is completely reversible in acid media (pH 1). However, it is well-known that amines are sensitive to oxygen and carbon dioxide. In order to determine whether exposure to these gases leads to an irreversible loss of properties, further experiments were carried out. After several weeks in sealed tubes in the presence of oxygen or carbon dioxide, the polymers develop a slight yellow color. The complex formation properties of these aged polymers, following treatment with acid, were determined. The results, given in Table VI show that no change in complex formation occurs.

(c) Influence of the Counterion. In low dielectric constant media, the stability of the complexes is determined by the interactions between the ligand, the cation, the anion, and the solvent. If the main factor for stability is the interaction between the ligand and the cations, it may be predicted that the electronic structure of the anion with the possible interactions of the anion with the ligand will contribute to a stabilization or destabilization of the complexes. Thus recently Cram[14] has shown that the substitution of Cl^- for SCN^- in the salt decreases energy. Because the charge is more localized on Cl^- than on SCN^-, greater charge separation takes place. In our study of the binding properties of the ligand [22]EtOH, we have shown that contrary to the results with the diamine [22]CH_3 (λ_{max} 365 nm) no bathochromic shift occurs in the UV spectrum of the complexes with picrate anion. Instead we observe an absorption maximun at 355 nm which corresponds to picric acid itself. This has been interpreted in terms of interactions between the protons of the hydroxylic groups of the ligands and the anion. A similar result is obtained with the diamines [22]H and [21]H (λ_{max} 355 and 350 nm). With the polymers [21]- and [22]EpiDPP, the same phenomenon is observed, except in the case of the sodium cation (the smallest cation studied), where the main absorption band is shifted from 355 to 365 nm. Total acetylation of the OH groups on the polymers leads, for the K^+ complexes, to λ_{max} 365 nm. This compares with λ_{max} 355 nm for the unmodified polymers. Such a result can be interpreted in terms of competitive interactions between the anion, the cation, and the proton of the hydroxyl groups. In the case of sodium, the small size of the cation and the nature of the polymeric structure probably favor the anion–cation interactions.

In Table VII, comparative results obtained with picrate and perchlorate anions are summarized. It can be seen that in spite of the very different ratio of complexation obtained, the stability constants for the two anions are quite similar. The slight differences observed, insofar as they are significant, correspond to a very slight difference in binding energy. It can be concluded that the structures of the complexes are the same in both cases. The trend toward greater stability of the perchlorate complexes, observed with the diamine [22]CH_3, can be considered as additional proof of the participation of hydroxyl groups in the complexes formed with the polymers.

Acknowledgment. Financial support of this research by the Délégation Générale á la Recherche Scientifique et Technique is gratefully acknowledged. The authors wish to thank Dr. J. Simon for helpful discussions and E. Kraeminger for technical assistance in this and the previous[11] work. Thanks are also due to Shell Chimie Co. for gifts of Epikote 815.

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