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Small-Angle Neutron-Scattering Studies of Cobalt(II) Organophosphorus Polymers in Deuteriobenzene[†]

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Bis(2,4,4-trimethylpentyl)phosphinic acid, an extractant used to separate cobalt from nickel by solvent extraction, can form polymers when bound to large amounts of cobalt(II). The size and shape of these polymers have been measured by small-angle neutron scattering. The polymers form long thin chains, approximately 550 Å long and about 9 Å in radius. In some preparations, although the lengths were similar, the measured average cross-sectional radii were slightly larger, implying some cross-linking. The Co(II) polymers formed from the homologous series phosphoric acid bis(2-ethylhexyl) ester, (2-ethylhexyl)phosphonic acid 2-ethylhexyl ester, and bis(2-ethylhexyl)phosphinic acid were also measured. The first member of this series produced long thin rodlike polymers of constant cross-sectional radius (10 Å) and variable lengths; the phosphonic and phosphinic extractants produced smaller polymers whose neutron scattering did not conform to a cylindrical model.

Introduction

Monoacidic organophosphorus acids in organic solvents can be used to selectively extract Co(II) from aqueous solutions by using techniques such as liquid-liquid extraction or supported liquid membranes (SLM).[1-7] During the extraction process, depending on the particular extractant and the conditions used, a variety of polymeric structures are formed. The formation of such polymers can affect the procedure used for solvent extraction. For example, in SLM separations where the rate of cobalt diffusion through a thin film is of paramount importance, polymer formation can be most influential. When liquid–liquid extraction is used, viscosity changes caused by polymer formation can influence extractor performance. A basic understanding of the structural properties of the polymers formed in the cobalt–organophosphorus systems may then be useful in optimizing separation processes.

Co(II)–organophosphinate polymer structures have been postulated from X-ray diffraction[8,9] and from solubility and infrared studies.[10] A polymer formed by solvent extraction of Co(II) with phosphoric acid bis(2-ethylhexyl) ester (HDEHP) was identified rheologically;[7] the viscosity increased markedly as the cobalt:HDEHP ratio approached 1:2. Each of the proposed structures (and those reported here) involves tetragonal Co(II) bonded to one of the oxygens of the phosphorus acid; the other oxygen of the acid is bonded to another cobalt atom, and so on.

The small-angle neutron-scattering (SANS) technique is one of the powerful techniques for deriving structural information on macromolecular and colloidal systems.[11-17] This technique has been extensively applied to study the structural aspects of polymers, biopolymers, micelles, and microemulsion systems. Depending on the SANS instrument, one can probe dimensions ranging from 5 to 1000 Å. Although small-angle X-ray-scattering (SAXS) and dynamic light-scattering (DLS) techniques are also capable of yielding structural information on systems with similar dimensions, SANS is more powerful due to the ease with which one can vary the contrast for scattering by utilizing the large difference in the neutron-scattering power of the deuteriated system and its hydrogeneous counterpart. The contrast for neutron scattering can be varied by deuteriating either the solute or solvent or both.

In this paper we report SANS studies of deuteriobenzene solutions of Co–organophosphorus polymers. The names, acronyms, and structures of the four extractants used are given in Table I.

Small-Angle Neutron-Scattering Technique. Neutrons are scattered by the atomic nuclei and the extent of scattering is determined by the characteristic scattering length of the individual atoms. Table II lists the neutron-scattering parameters of a few elements relevant to this work. Neutron-scattering parameters of other atoms can be found in ref 18. The scattering properties of the hydrogen and deuterium are quite different; while hydrogen has a negative scattering length and large incoherent scattering cross-section, deuterium has a positive scattering length and very low incoherent cross-section. This difference in the scattering

Table I. Monoacidic Organophosphorus Extractants Considered

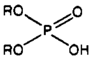
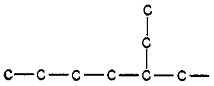
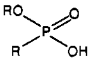
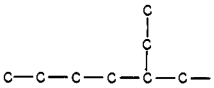
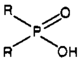
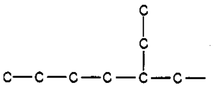
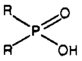
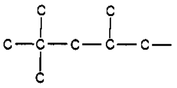
name/abbreviation	formula	R group
phosphoric acid bis(2-ethylhexyl) ester, HDEHP		
phosphonic acid 2-ethylhexyl (2-ethylhexyl) ester, HEH[EHP]		
bis(2-ethylhexyl)phosphinic acid, H[DEHP]		
bis(2,4,4-trimethylpentyl)phosphinic acid, H[DTMPeP]		

Table II[a]

element	scattering length, 10^{-12} cm	σ_{coherent}, barns	$\sigma_{\text{incoherent}}$, barns
hydrogen	−0.374	1.758	79.7
deuterium	0.667	5.597	2.0
carbon	0.665	5.6	<0.02
nitrogen	0.936	11.0	0.46
oxygen	0.583	4.23	<0.02
phosphorus	0.513	3.31	0.0

[a] Data from ref 18.

Table III

solvent system	scattering length density, 10^{10}/cm^2	$\sigma_{\text{incoherent}}$, barns
H_2O	−0.56	159
D_2O	6.34	4
C_6H_6	1.13	480
C_6D_6	5.35	13
Co([DTMPeP])$_2$	−0.10	3830
Co(DEHP)$_2$	0.10	3830
Co(EH[EHP])$_2$	0.055	3830
Co([DEHP])$_2$	−0.047	3830

[†] Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under Contract No. W-31-109-ENG-38.

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properties of hydrogen and deuterium is exploited in neutron structural studies of polymers and micelles.

The generalized equation for small-angle neutron scattering from particles in volume V in a matrix of scattering length density ρ_s (the sum of the scattering lengths of the solvent atoms divided by the solvent molecular volume) is given by[12]

$$I(Q) = K\left\langle \int_v (\rho_r - \rho_s) \exp(iQr)\, d^3r \right\rangle^2 + I_{\text{inc}} \qquad (1)$$

where ρ_r is the scattering length density of the rth volume element in the particle, K includes all experimental constants, Q, the scattering vector, is defined as $4\pi(\sin\theta)/\lambda$, θ is half the scattering angle, λ is the neutron wavelength, and I_{inc} is the incoherent scattering background. The neutron-scattering parameters for the systems of interest here are listed in Table III. Equation 1 shows that the intensity of scattered neutrons is proportional to the square of the difference in the scattering length densities of the particle and the surrounding matrix.

Experimental Section

Reagents. Phosphoric acid bis(2-ethylhexyl) ester (HDEHP, Kodak) and 99+% deuteriobenzene (C_6D_6, Sigma), were used as purchased. HEH[EHP] and H[DEHP] (see Table I) were synthesized as described in ref 19. Bis(2,4,4-trimethylpentyl)phosphinic acid, H[DTMPeP], (CYANEX-272, Cyanamid Canada Inc.) was purified by using the procedure described in ref 20.

The samples for SANS measurements were prepared in two ways, resulting in (I) excess extractant and (II) a stoichiometric equivalent ratio of extractant to cobalt (2:1) in the organic phase.

I. An aqueous solution containing cobalt was brought to pH 7 by addition of small portions of NaOH while alternately mixing the solution for 10–15 min with a deuteriobenzene solution containing the extractant. Analysis of one of these solutions gave an extractant to cobalt ratio of 2.5:1.

II. A three-phase system consisting of freshly precipitated cobalt hydroxide/water/deuteriobenzene containing H[DTMPeP] was equilibrated by shaking for 3 h or more. The extractant to cobalt ratio in the organic phase was 2.0:1 in this case. Preparations by method II produced more viscous samples than those prepared by using method I at the same H[DTMPeP] concentrations. In both preparations the organic phase was blue, indicating tetragonal coordination of the Co(II) ion. The concentration of the solute was varied by dilution with deuteriobenzene, rather than by separate preparations with different extractant concentrations. The concentrations of the polymers are expressed in terms of the formula weight, F, of the organophosphorus extractant.

The extractant to cobalt ratio was determined by measuring the cobalt by inductively coupled plasma atomic emission spectroscopy and the phosphorus by spectrophotometric absorption measurement after treatment with nitric acid in a Carius tube at 275 °C.

Neutron-Scattering Measurements. SANS data were measured by using the Small Angle Diffractometer (SAD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. Neutrons produced in pulses by spallation from 450-MeV protons were moderated by solid methane at 12 K to wavelengths of 0.5–14 Å. The moderated neutrons passed through Soller collimators to produce a beam of small divergence. At the sample position, the circular beam, defined by a cadmium aperture, is ~0.9 cm in diameter. The neutrons scattered by the samples were detected by a 17 × 17 cm² position-sensitive multidetector. The neutron wavelengths were determined by time of flight. The scattering data of the samples were corrected by subtracting the scattering from the quartz cell and the solvent and the incoherent scattering. The reduced data were then expressed as a function of the scattering vector, Q. The Q range accessible at SAD at IPNS is 0.005–0.35 Å^{-1}. The scattering intensity was normalized for the incident neutron spectrum and the detector sensitivity by using scattering from a ~0.87 mm thick water sample. All measurements were made at 22 °C.

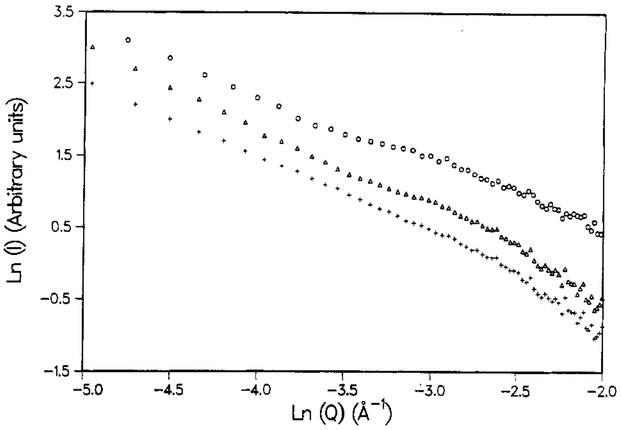

Figure 1. Neutron scattering intensity, $I(Q)$, vs. scattering vector Q, for Co([DTMPeP])$_2$ polymers of varying concentrations in deuteriobenzene. The extractant formalities are (○) 0.20F, (△) 0.165F, and (+) 0.065F.

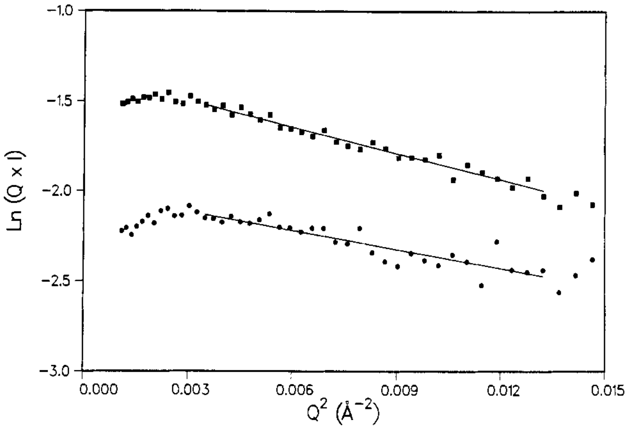

Figure 2. Modified Guinier analyses of Co([DTMPeP])$_2$ polymers whose concentrations are 0.165F and 0.20F. The linearity of the fitted lines supports the model of a long, thin, rodlike shape. The slopes give the cross-sectional radii of gyration.

Polymers of Co([DTMPeP])$_2$ and Co(DEHP)$_2$ were measured at different concentrations in C_6D_6 to study the influence of the amount of diluent on the polymer size and shape and to study the interparticle effects upon the SANS response. The concentration was varied from 0.065F to 0.2F.

Results

Co([DTMPeP])$_2$ Polymer. Figure 1 shows the raw data measured for three concentrations of Co([DTMPeP])$_2$ in deuteriobenzene. The low-Q region has similar slopes at all three concentrations, indicating that the particle sizes are all similar. However, the scattering data show marked differences in the Q region of 0.03–0.1 Å^{-1}, which are due to the interparticle interactions. The interparticle interactions are reduced as the extractant concentration decreases from 0.2F to 0.065F. The Guinier analysis[16] of the data give radii of gyration values close to 150 Å. The radius of gyration, R_g, is a measure of the spatial extension of the particle and for a cylindrical shape $R_g^2 = (R^2/2 + L^2/12)$, where L and R are the length and radius of the cylinder, respectively.

As the scattering patterns showed evidence of elongation, a modified Guinier analysis,[17] ln (QI) vs Q^2, pertinent to long cylinders, was then applied to the data. In Figure 2, the modified Guinier plots for two concentrations of Co([DTMPeP])$_2$ are shown. The slopes of the modified Guinier plots determine the cross-sectional radii of gyration, R_c (where $R^2 = 2R_c^2$), of the rodlike structures.

Since the accessible minimum Q in the SAD instrument is 0.005 Å^{-1}, there were not many points in the low-Q region to satisfy the

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Table IV. Co(II)-$(DTMPeP)_2$ Polymers (Excess Extractant Condition; Extractant:Co(II) = 2.5:1)

no.	concn of monomer extractant, *F*	radius $\langle R_c\rangle$, Å	$\langle R\rangle$, Å	$\langle R_g\rangle$, Å	length $\langle L\rangle$, Å
1	0.11	6.3 ± 0.8	8.9 ± 1.1	131 ± 7	454 ± 24
2[a]	0.11	6.5 ± 0.8	9.2 ± 1.1	133 ± 8	461 ± 28
3	0.165	8.5 ± 0.7	12.0 ± 1	138 ± 7	478 ± 24
4	0.165	8.2 ± 0.6	11.6 ± 0.8	129 ± 8	447 ± 28

[a] Sample 1 measured 2 months later.

Table V. Co(II)-$([DTMPeP])_2$ Polymers (Stoichiometric Condition; Extractant:Co(II) = 2.01:1)

no.	concn of monomer extractant, *F*	radius $\langle R_c\rangle$, Å	$\langle R\rangle$, Å	$\langle R_g\rangle$, Å	length $\langle L\rangle$, Å
1	0.065	13.7 ± 0.6	19.4 ± 0.8	168 ± 8	582 ± 28
2	0.165	16.1 ± 0.8	22.8 ± 1.1	169 ± 6	585 ± 21
3	0.165	9.6 ± 0.6	13.6 ± 0.8	164 ± 7	568 ± 24
4	0.200	9.5 ± 0.9	13.4 ± 1.3	160 ± 7	554 ± 24

Guinier condition $QR_g \leq 1$. Hence the scattering data were fitted by using the Fournet function for a cylinder[16]

$$I(Q) = \int_0^{\pi/2} [2J_1(A)(\sin B)/AB]^2 \sin\theta \, d\theta \qquad (2)$$

where $A = QR(\sin\theta)$, $B = QL(\cos\theta)$, and J_1 is the first-order Bessel function. A nonlinear regression analysis was used for obtaining (a) the radius of gyration, (b) the forward scattering, (c) the length-to-diameter ratio, and (d) the incoherent background values. Figure 3 shows the fitted data for the 0.065*F* Co($[DTMPeP])_2$ polymer. All R_g values given below are those obtained from the model-fitting approach only. Since there could be polydispersity in the sizes of the polymers, the measured R_g from SANS represents a *Z*-averaged value defined as

$$\langle R_g^2\rangle_z = \sum_i N_i M_i^2 (R_g)_i^2 / \sum_i N_i M_i^2 \qquad (3)$$

where N_i and M_i are the concentration and mass, respectively, of the polymers of kind *i* and the $(R_g)_i$ is its radius of gyration.

Table IV shows the average R_g and R_c values obtained for the Co($[DTMPeP])_2$ polymers prepared by method I. The R_c values are smaller when the extractant concentration is 0.11*F* than when it is 0.165*F*. The radius of the cylinder corresponding to R_c = 6.3 Å is 9 Å, which is consistent with expectations based on the length of the hydrocarbon chain of the H[DTMPeP] molecule. The higher values of R_c noted at 0.165*F* H[DTMPeP] could be attributed to a small amount of cross-linking. The average R_g values are the same at both concentrations, indicating that the lengths of the polymers are independent of the concentration of the extractant. The R_g and R_c values found for the same 0.11*F* sample measured 2 months apart, did not change, indicating that the structures are quite stable. In Table IV (and in subsequent tables) the stated error comes from the standard deviation of a selected range of data from the fitted curve.

Table V lists the average dimensions of the Co($[DTMPeP])_2$ polymers formed under stoichiometric conditions (preparation method II). Here again the R_c values vary with the concentration of the extractant. Also, the R_c values are larger for the preparations in Table V (method II) than for those in Table IV (method I). This indicates more cross-linking in the polymers formed under the stoichiometric condition than in those formed under the excess-extractant condition. The average R_g values (proportional to the length of the cylindrical particles) are shown in Table V. They are independent of the extractant concentration, but they are higher than those measured for the polymers formed under the excess-extractant condition (Table IV). These results are consistent with a suggestion made by Kolarik and Grimm[7] that excess extractant reduces the extent of polymerization in the Co($DEHP)_2$ system as it is involved in chain termination of the polymers.

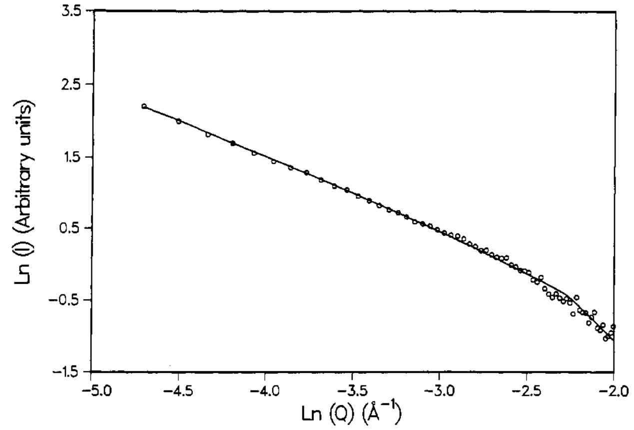

Figure 3. Model fitting of scattering from 0.065*F* Co($[DTMPeP])_2$ polymer using a cylindrical model with a length of 582 ± 28 Å and radius of 15±6 Å. The solid line is calculated from (2).

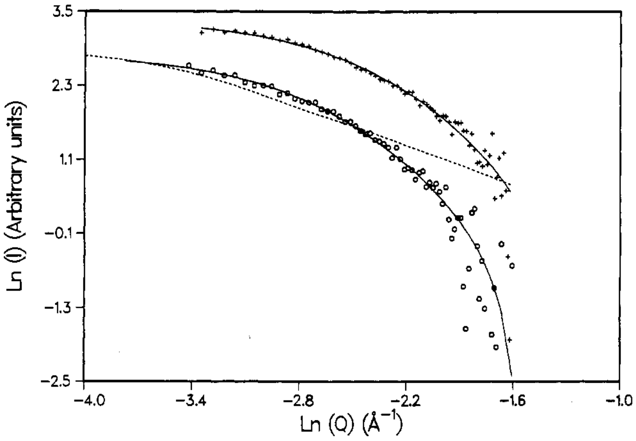

Figure 4. Debye function (solid line) fitted to scattering data for Co(II) polymers with HEH[EHP] (○) and H[DEHP] (+). The extractant concentrations are 0.11*F* in deuteriobenzene. The scattering data could not be adequately fitted with a cylindrical model (- - -).

Polymers of the Homologous Series. The first three extractants in Table I are identical except for having 2, 1, or no oxygen atoms between the 2-ethylhexyl groups and the phosphorus. They form a homologous series, phosphoric, phosphonic, and phosphinic acids, of decreasing acid strength (increasing bonding strength to cobalt). Their polymers were made so that excess extractant was present (method I). Table VI shows a marked change in polymer size and shape as the acid strength of this series decreases: Co($DEHP)_2$ polymer is rod-shaped; the weaker acids form smaller polymers that do not conform to the cylindrical model (Figure 4). As seen above, the phosphinic acid H([DTMPeP]) forms linear polymers also. These results show that the acid strength is not the sole factor

Table VI. Comparison of the Sizes for Polymers of Organophosphorus-Co(II) Complexes (Excess Extractant Condition)

no.	extractant	concn of monomer extractant, *F*	radius $\langle R_c\rangle$, Å	$\langle R\rangle$, Å	$\langle R_g\rangle$, Å	length $\langle L\rangle$, Å
1	H[DTMPeP]	0.11	6.5 ± 0.8	9.2 ± 1.1	133 ± 8	461 ± 28
2	HDEHP	0.20	7.0 ± 0.8	9.9 ± 1.1	66 ± 3	229 ± 10
3	HDEHP	0.11	7.1 ± 0.7	10.0 ± 1.0	42 ± 3	145 ± 10
4	HEH[EHP]	0.11			23 ± 1	
5	H[DEHP]	0.11			18 ± 1	

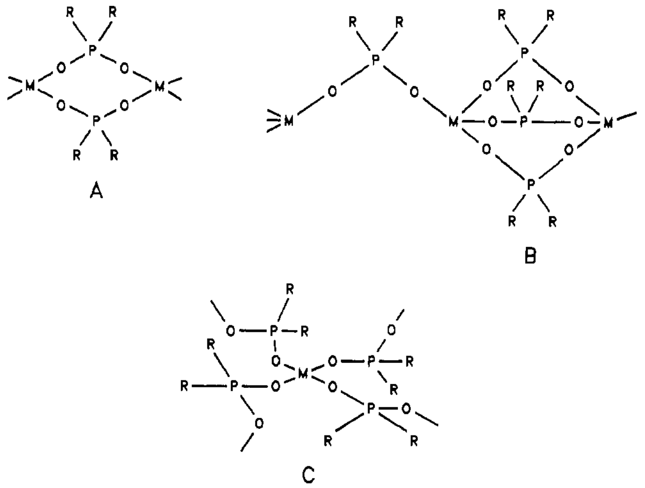

Figure 5. Suggested modes of polymer formation for tetrahedral Co(II) and organophosphorus bridging molecules.[8,10] Modes A and B yield the linear chains observed for Co([DTMeP])$_2$ and Co([DEHP])$_2$; mode C is consistent with the observations made on Co[EH(EHP)]$_2$ and Co([DEHP])$_2$.

determining the polymer conformation.

The nonlinear polymers Co(EH[EHP])$_2$ and Co([DEHP])$_2$ are quite small: they are fitted with the Debye function[21]

$$I(Q) = \frac{2}{Q^2R_g^2}[\exp(-QR_g) + QR_g - 1]$$

with R_g values of 23 and 18 Å, respectively. The Debye function does not invoke any explicit shape, but it does give the average internal spatial distribution of the scattering particle.

The rodlike polymer Co(DEHP)$_2$ (Table VI) exhibits no change in its cross-sectional radius as it is diluted with deuteriobenzene, but its average length is reduced upon dilution.

Discussion and Conclusions

The SANS data described above indicate that Co([DTMPeP])$_2$ polymers have a long cylindrical shape and their shape and size do not change with time. The lengths of the polymer are independent of the concentration of the extractant; however, there is some dependence on the ratio between the extractant and Co(II) in the organic phase. The lengths are greater in the case of the stoichiometric condition than when excess extractant is present. It is possible that the excess extractant influences the chain termination as has been suggested for the case of Co(DEHP)$_2$.[7]

The formation of linear polymers by the metal(II)-bis(phosphinates) has been extensively reported.[7-10] Most of the studies have concerned the solid state. Gillman and Eichelberger,[10] from their combined X-ray powder diffraction, IR, and solubility studies of metal(II)-organophosphorus extractants list three kinds of backbone structures for the polymers formed as shown in Figure 5. A symmetric double-bridged polymeric model (type A) and an alternating single- and triple-bridged phosphinate polymeric model (type B) could account for the linear polymers; type C bonding is consistent with nonlinear structures. All three types invoke tetrahedral coordination of cobalt(II). Both type A and B models have been used to interpret powder diffraction measurements of linear polymers.[8,9] Our SANS studies are consistent with Co([DTMPeP])$_2$ polymers having a backbone of either type A or B but not with type C (Figure 5). The higher cross-sectional radius values obtained for some preparations of this polymer (see Tables IV and V) could be attributed to a small amount of cross-linking, perhaps through inclusion of a small amount of type C bonding.

The Co(DEHP)$_2$ polymers also assume long cylindrical shapes (type A or B backbone) with radius around 10 Å and lengths of about 145 and 229 Å, at 0.11*F* and 0.2*F* extractant concentrations, respectively. The lengths of these polymers are quite small compared to those of the Co([DTMPeP])$_2$ polymers. Further, the polymer lengths become smaller upon dilution with deuteriobenzene. The radius of the polymer is consistent with the size of the HDEHP molecule and the invariance of the radius at different concentrations indicates that there is no apparent crosslinking, as noted in the case of Co([DTMPeP])$_2$ polymers.

The polymers of Co(II) with HEH[EHP] and H[DEHP] form smaller particles whose scattering do not show any evidence of elongated structures. It is likely that these two polymers assume predominantly type C structures (Figure 5).

The acid strength of the extractant in the homologous series that was studied seems to have an effect on the conformation of the polymers. The Co(DEHP)$_2$ polymers are cylindrical, but the phosphonic and phosphinic acids form cobalt polymers that are small and noncylindrical. However, both in this work and in the literature[8,9] Co(II)-phosphinate linear polymers have been identified. Therefore, in addition to the extractant acidity, other factors such as the length of the hydrocarbon chain and the position of the side chains seem to influence the conformation of the polymers.

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