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EDTA-type Polymer Based on Diazacrown Ether as the Solubilizer of Barium Sulfate to Water

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Abstract: The EDTA dianhydride reacted with diazacrown ethers to obtain the water-soluble EDTA-diazacrown ether polymers **1~3**. The effects of crown ether ring in the polymer chains including its cavity size on the solubilization of barium sulfate to water were investigated by comparison with the crown ring-free analogue **4**. The result shows that the polymer **2** is the efficient solubilizer of $BaSO_4$ and the highest solubilization efficiency of the $BaSO_4$ to water is up to 72.5%.

Keywords: EDTA-diazacrown ether polymers, barium sulfate, solubilization.

The formation and the elimination of barium sulfate-scale have attracted increasing attention for a long time. For example, the use of seawater as injection fluid in oil-producing locations often leads to clogging of wells as a result of $BaSO_4$-scale formation[1]. There are some reports on the eliminating of $BaSO_4$-scale of injection water pipe in oil-producing process, but the most of solubilizers used are difficultly to prepared or their solubilization efficiency is low[2, 3]. For instance, the dissolution efficiency of $BaSO_4$ by [2, 2, 2] cryptand is 100%, however, the rate of dissolution equilibrium is very slow due to its insolubility[4]. In order to improve the hydrophilic capacity of the compelexants of barium cation and its solubility rate, we designed and prepared EDTA–type diazacrown ether polymers **1~3**, which possess good solubility in water, by the reaction of EDTA dianhydride with diazacrown ether. The effects of crown ether in the polymer chains on the solubilization of $BaSO_4$ to water were investigated as compared with the crown ring-free analogue, EDTA-ethylenediamine polymer **4**. The synthetic route of **1~3** and the structure of analogue **4** are shown in **Scheme 1**.

Compounds EDTA dianhydride[5]and diazacrown ethers[6] were prepared according to the published procedures, the EDTA-ethylenediamine polymer **4** was supplied by our laboratory. The infrared spectra were recorded on a Nicolet-1705X spectrometer. ^{1}H NMR spectra were recorded on a Bruker AC-200MHz spectrometer using $(CH_3)_4Si$ as internal standard.

A solution of equal mole diazacrown ethers in dry DMSO was added to a solution of EDTA dianhydride in dry DMSO with vigorous stirring and under N_2 atmosphere. The mixture was stirred at 70℃ for 12 h. Then the reaction mixture was cooled and poured into

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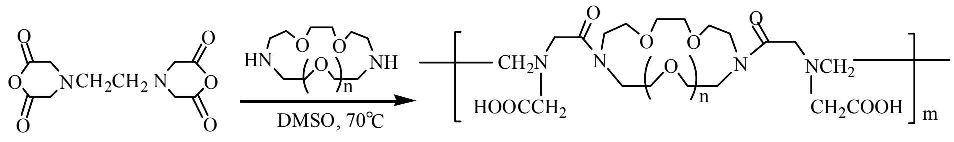
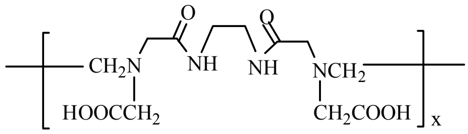
Scheme 1



n =1, **1**
n =2, **2**
n =3, **3**



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acetone to separate the precipitate. The precipitate was filtrated and washed with cold DMSO and acetone, dried in vacuum to give **1~3**.

1: light brown solid; softening point 106℃, yield 92.9%. [η] 0.11 (H_2O; 25℃). IR (KBr, cm^{-1}): 3430 (OH), 1725 (COOH), 1632 (NC=O), 1129 (C-O-C). ^{1}HNMR (D_2O, δ ppm) 2.55~2.79 (m, 12H, NCH_2), 3.21 (s, 4H, NCH_2COOH), 3.46~3.60 (m, 16H, OCH_2 and $COCH_2N$).

2: light brown solid; softening point 97.5℃, yield 90.0%. [η] 0.12(H_2O; 25℃). IR (KBr, cm^{-1}): 3412(OH), 1727(COOH), 1640(NC=O), 1120(C-O-C). ^{1}HNMR (D_2O, δ ppm) 2.69~2.85(m, 12H, NCH_2), 3.25(s, 4H, NCH_2COOH), 3.46~3.53(m, 20H, OCH_2 and $COCH_2N$).

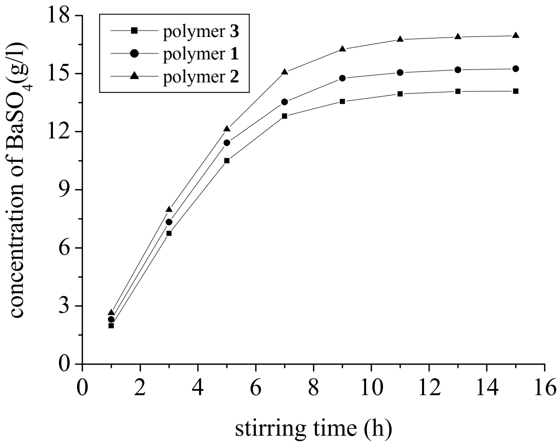
3: light brown solid; softening point 115℃, yield 92.0%. [η]0.13 (H_2O; 25℃). IR (KBr, cm^{-1}): 3440 (OH), 1725 (COOH), 1634 (NC=O), 1117(C-O-C). ^{1}HNMR (D_2O, δ ppm) 2.69~2.81 (m, 12H, NCH_2), 3.23(s, 4H, NCH_2COOH), 3.44~3.50 (m, 24H, OCH_2 and $COCH_2N$).

The characteristic viscosity coefficients([η]) of polymers **1**~**3** are nearly the same and indicate that polymerization reaction can easily proceed and be repeated. As a matter of fact, the polymers **1**~**3** may be water-soluble oligomer. The polymers **1**~**3** possess certain rigidity due to the big molecular size of diazacrown ethers and EDTA dianhydride.

Scheme 1 shows that m represents the polymerization degree of polymer, *i.e.* the polymer containing m chain units bearing aza-crown ring should load m BaSO4 molecules in theory. So the mole of solubilized $BaSO_4$ by per mole chain unit in polymer was regarded as $BaSO_4$ dissolving efficiency. If per chain unit containing aza-crown ring can load one $BaSO_4$, the $BaSO_4$ dissolving efficiency of the polymers is 100%.

The solubilization capabilities of the polymers were determined by known equipment and method[2], 5 mmol $BaSO_4$ was added to a solution of 0.5 mmol chain unit of polymer dissolved in 5 mL water, then the mixture solution was adjusted to pH=10 by the addition of tetrabutyl ammonium hydroxide. The mixture was stirred vigorously at 20℃. After centrifugal separating, the concentration of barium ion in the filtrate containing Ba(II) complexant was determined by ICP. The result was shown in **Figure 1** and **Table 1**.

Figure 1 The plots of the accumulated concentration of Ba^{2+} *versus* the stirring time for the mixture of the polymers and $BaSO_4$



Condition: complexant 0.1 mol/L, pH 10 and temperature 20℃

Figure 1 shows that the accumulated concentration of Ba^{2+} increases with the increase of the stirring time of mixture of the polymers and $BaSO_4$. The result reveals that the longer the stirring time is, the higher the accumulated concentration of Ba^{2+} in water is. However, after stirring for 13 h, the accumulated concentration of Ba^{2+} almost unchanged, and the $BaSO_4$ reached basically dissolution equilibrium. The result shows that the rate of the $BaSO_4$ reached dissolution equilibrium is faster than that of literature[2] reported.

The effect of solution acidity on the solubilization of $BaSO_4$ was investigated with the polymer **3**. When the pH value of **3** is 7.0, 9.0, 10.0, 11.0, the dissolved $BaSO_4$ was 0.03, 10.72, 14.08 and 14.09g/L, respectively. The result shows that the dissolution of $BaSO_4$ by polymer **3** is of high efficiency under pH ⩾10, and that the negative ion of the deprotonated carboxylic group(COO^-) which affords the cooperation with the crown rings and plays a more important role than that of the amido carbonyl group(C=O) on the polymer chain for solubilizing $BaSO_4$.

Table 1 The dissolution efficiency of $BaSO_4$ by aqueous solutions of the complexantes **1-4**[a]

Complexant	Dissolved $BaSO_4$(g/L)	Efficiency [b] (%)
None	0.0019	
EDTA	6.21	26.6
1	15.19	65.2
2	16.89	72.5
3	14.08	60.4
4	5.83	25.0

[a] condition: complexant 0.1 mol/L, stirring 13 h, pH 10 and temperature 20℃
[b] efficiency: mole of dissolved $BaSO_4$ to per mole of chain unit of polymer

Table 1 shows that the solubilizing $BaSO_4$ efficiencies of EDTA-diazacrown ether polymers **1**~**3** are much higher than that of crown ring-free analogue **4**. The highest solubilization efficiency of polymer **2** is up to 72.5%. It may be due to the cavity size of the crown ring in polymer **2** matches well with the diameter of barium ion. The poor efficiency of polymer **4** for solubilizing $BaSO_4$ may be for that the acyclic polymer **4** only contains EDTA structure unit.

In conclusion, the investigated result shows that the crown rings in polymers **1**~**3** play a major role for the solubilizing $BaSO_4$ to water.

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