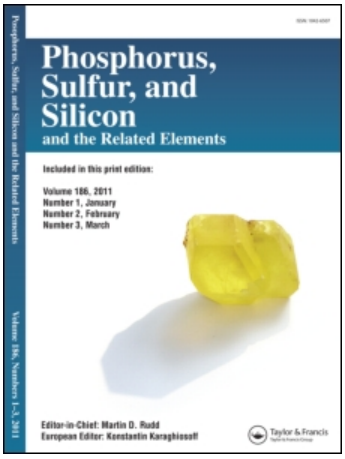

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Synthesis and Characterization of Poly(carbonates) and Poly(thiocarbonates) Derived from Diphenols Containing Silicon as Central Atom

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Synthesis and Characterization of Poly(carbonates) and Poly(thiocarbonates) Derived from Diphenols Containing Silicon as Central Atom

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Poly(carbonates) and poly(thiocarbonates) containing silicon in the main chain and derived from the diphenols bis(4-hydroxyphenyl)-dimethylsilane, bis(4-hydroxyphenyl)-ethylmethylsilane, and bis(4-hydroxyphenyl)-diethylsilane with phosgene or thiophosgene, respectively, were synthesized under phase transfer conditions, using several phase transfer catalysts. Polymers were characterized by spectroscopic methods (IR and ^{1}H, ^{13}C, ^{29}Si NMR) and the results were evaluated by the yields and the η_{inh} values. In general the effectiveness of the phase transfer process was low, the best results being obtained when the NaOH concentration was increased from the stoichiometric due to a salting-out effect. However, at higher concentrations hydrolytic process were observed. Poly(carbonates) and poly(thiocarbonates) showed, in general, the same trend with the catalysts.

Keywords Poly(carbonates); poly(thiocarbonates); phase transfer catalysis; silicon containing polymers

INTRODUCTION

Silicon-containing condensation polymers have been studied widely, because they present scientific and technological interest due to the potential applications for the production of optical and electronic materials. In this sense, several kinds of condensation polymers containing Si as part of the main chain have been described, such as poly(esters), poly(carbonates), poly(amides), and others. Normally the Si atom is bonded to two aromatic rings and two other aliphatic or aromatic ones,

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with the poly(silylene) moities having the general form -Ar-Si(R_1R_2)-Ar- R_1 and R_2 being aromatic or aliphatic groups.[1–3]

In our research group we have focussed our attention on the synthesis of condensation polymers using the phase transfer catalysis technique. This technique permits the transfer of a diphenolate dianion as an ionic pair with the catalyst from the aqueous phase to the organic one, in which the reaction takes place. In this sense we have synthesized several kinds of condensation polymers such as poly(carbonates), poly(thiocarbonates), and poly(esters) and studied the effect of the nature of the catalyst in the yields and inherent viscosity (η_{inh}). We have shown that this technique is a very useful tool for the synthesis of these polymers.[4]

In the last years we have applied the phase transfer catalysis to the synthesis of condensation polymers derived from monomers, diphenols, or acid dichlorides, containing Si or Ge, in order to obtain poly(carbonates), poly(thiocarbonates), and poly(esters) containing one or two of these heteroatoms.[5,6] We have observed that when the NaOH concentration is increased in the aqueous phase, it is possible to see a salting-out effect of the diphenolate to the organic phase, which has, as a consequence, an increase of the yields and in some cases of the molecular weights. This is due to the increase of the concentration that can displace the equilibrium to the diphenolate formation. On the other hand, it was also possible to see hydrolytic effects of both the monomer and the polymeric chains. In addition, we have synthesized poly(urethanes) containing Si or Ge by interphasial condensation.[7]

In this work we describe the synthesis and characterization of poly(carbonates) and poly(thiocarbonates) derived from diphenols containing Si as the central atom bonded to two aliphatic groups and phosgene or thiophosgene, respectively. We studied the qualitative behavior of the phase transfer catalysts and the increase of the NaOH concentration through the yields and the (η_{inh}) of the obtained polymers.

EXPERIMENTAL

Reagents and solvents (from Aldrich or Riedel de Haen) were used without purification. The following catalysts (from Fluka) were used: Tetrabutylammonium Bromide (TBAB), Benziltriethylammonium Chloride (BTEAC), and Methyltrioctylammonium Chloride (ALIQUAT 336). The IR spectra were recorded on a Perkin-Elmer 1310 spectrophotometer and the ^{1}H, ^{13}C, and ^{29}Si NMR were recorded on a 400 MHz instrument (Bruker), using $CDCl_3$, acetone-d_6, or DMSO-d_6 as solvents and TMS as the internal standard. Viscometric measurements were made in a Desreux–Bischoff[8] type dilution viscosimeter at 25°C.

Diphenols

The diphenols bis(4-hydroxyphenyl)-dimethylsilane, bis(4-hydroxyphenyl)-ethylmethylsilane, and bis(4-hydroxyphenyl)-diethylsilane, were synthesized from p-bromo-phenol and dimethyl-, ethylmethyl- or diethyl-dichlorosilane, according to the procedure described by Davidson et al.,[9] in which 14.1 g (0.08 mol) of p-bromophenol in THF were added under N_2 to 75 mL of n-butyllithium (2.5 N solution in n-hexane) at –70°C. Then, the temperature was increased slowly until 5°C and the mixture was stirred for 1 h. The temperature was decreased to –50°C and 0.025 mol of dimethyl-, ethylmethyl-, or diethyl-dichlorosilane were added in THF, and the temperature increased until 10°C and was stirred for 2 h. The mixture was hydrolyzed by adding 5% HCl until obtaining a yellow mixture (pH 1). The organic layer was dried under $MgSO_4$ and the solvent evaporated. The brown oil was poured into n-hexane obtaining a white solid, which was recrystallized from toluene and characterized.

Bis(4-hydroxyphenyl)-dimethylsilane: m.p: 170–171°C (Lit.[8] 173–174°C). I.R. (KBr) (cm^{-1}): 3319 (OH), 3020 (H arom.), 2958, 2871 (CH_3), 1598, 1500 (C=C arom.), 1457 (CH_3), 829 (arom. p-subst.). ^{1}H NMR (δ) (ppm) (acetone-d_6) 0.45 (s, 6H, CH_3), 6.84 (d, 4H, arom), 7.35 (d, 4H, arom), 8.41 (s, 2H, OH). ^{13}C NMR (δ) (ppm) (acetone-d_6): −1.36 (CH_3-Si), 116.2, 129.2, 136.8, 159.6 (arom.) ^{29}Si NMR (δ) (ppm) ($CDCl_3$): −9.36.

Bis(4-hydroxyphenyl)-ethylmethylsilane: m.p.: 138–140°C. I.R. (KBr) (cm^{-1}): 3314 (OH), 3026 (H arom.), 2954, 2874 (CH_3), 2912 (CH_2), 1600, 1503 (C=C arom.), 1459 (CH_3), 831 (arom. p-subst.). ^{1}H NMR (δ) (ppm) (acetone-d_6): 0.51 (s, 3H, CH_3-Si), 1.47 (m, 5H, CH_2-CH_3), 6.92 (d, 4H, arom.), 7.42 (d, 4H, arom.), 8.47 (s, 2H, OH). ^{13}C NMR (δ) (ppm) (acetone-d_6): -4.00 (Si-CH_3), 7.40 ($\underline{C}H_2$-CH_3), 8.25 (CH_2-$\underline{C}H_3$), 116.3, 128, 137.1, 159.6 (C arom.). ^{29}Si NMR (δ) (ppm) ($CDCl_3$): -6.93.

Bis(4-hydroxyphenyl)-diethylsilane: m.p.: 77–78°C. I.R. (KBr) (cm^{-1}): 3330 (OH), 3055 (H arom.), 2960, 2878 (CH_3), 2935 (CH_2), 1599, 1502 (C=C arom.), 1456 (CH_3), 821 (arom. p-subst.). ^{1}H NMR (δ) (ppm) ($CDCl_3$): 0.97–1.03 (m, 10H, CH_2-CH_3), 4.64 (s, 2H, OH), 6.84 (d, 4H, arom.), 7.38 (d, 4H, arom.). ^{13}C NMR (δ) (ppm) ($CDCl_3$): 4.23 (CH_3), 7.42 (CH_2), 114.9, 127.6, 136.6, 156.4 (C arom.). ^{29}Si NMR (δ) (ppm) ($CDCl_3$): −4.83.

Poly(carbonates) and Poly(thiocarbonates)

The poly(carbonates) and poly(thiocarbonates) were synthesized according to the following general procedure: the diphenol (1 mmol) was dissolved in 0.5 M NaOH and water (total volume 15 mL), and then

15 mL of CH_2Cl_2 and the catalyst (5% in mol) were added. To this mixture, 1 mmol of phosgene (from a toluene solution) or thiophosgene was added and the mixture stirred at 20°C for 1 h. After this time, the organic layer was poured into 300 mL of methanol and the polymer was filtered, washed with methanol, dried until constant weight, and characterized.

Poly(carbonate) Ia

I.R. (KBr) (cm^{-1}): 3020 (H arom.), 2958, 2871 (CH_3), 1774 (C=O), 1598, 1500 (C=C arom.), 1457 (CH_3), 829 (arom. p-subst.). ^{1}H NMR ($CDCl_3$) (δ): 0.57 (s, 6H, CH_3), 7.29 (d, 4H, arom.), 7.57 (d, 4H, arom). ^{13}C NMR ($CDCl_3$) (δ): -2.19 (Si-CH_3), 115.0, 120.0, 135.6, 136.0 (arom.), 151.9 (C=O). ^{29}Si NMR ($CDCl_3$) (δ): −7.46.

Poly(thiocarbonate) Ib

I.R. (KBr) (cm^{-1}): 3022 (H arom.), 2957, 2873 (CH_3), 1598, 1501 (C=C arom.), 1457 (CH_3), 829 (arom. p-subst.). ^{1}H NMR ($CDCl_3$) (δ): 0.59 (s, 6H, CH_3), 7.22 (d, 4H, arom.), 7.61 (d, 4H, arom.). ^{13}C NMR ($CDCl_3$) (δ): -2.24 (Si-CH_3), 120.6, 121.3, 135.6, 136.6 (arom.), 194.1 (C=S). ^{29}Si NMR ($CDCl_3$) (δ): −7.34.

Poly(carbonate) IIa

I.R. (KBr) (cm^{-1}): 3027 (H arom.), 2956, 2875 (CH_3), 2910 (CH_2), 1775 (C−O), 1590, 1497 (C=C arom.), 812 (arom. p-subst.). ^{1}H NMR ($CDCl_3$) (δ): 0.5 (s, 3H, CH_3), 0.97–1.01 (m, 5H, CH_2-CH_3), 7.23 (d, 4H, arom.), 7.50 (d, 4H, arom). ^{13}C NMR ($CDCl_3$) (δ): -4.77 (Si-CH_3), 6.01 (Si-CH_2), 7.37 (CH_2-$\underline{C}H_3$), 120.4, 135.1, 135.9, 151.7 (arom.), 151.7 (C=O). ^{29}Si NMR ($CDCl_3$) (δ): −5.11.

Poly(thiocarbonate) IIb

I.R. (KBr) (cm^{-1}): 3029 (H arom.), 2955, 2875 (CH_3), 2910 (CH_2), 1586, 1494 (C=C arom.), 811 (arom. p-subst.). ^{1}H NMR ($CDCl_3$) (δ): 0.63 (s, 3H, CH_3), 1.08–1.14 (m, 5H, CH_2-CH_3), 7.28 (d, 4H, arom.), 7.65 (d, 4H, arom). ^{13}C NMR ($CDCl_3$) (δ): -4.77 (Si-CH_3), 6.00 (Si-CH_2), 7.37 (CH_2-$\underline{C}H_3$), 120.4, 135.1, 135.9, 151.8 (arom.), 194.1 (C=S). ^{29}Si NMR ($CDCl_3$) (δ): −5.28.

Poly(carbonate) IIIa

I.R. (KBr) (cm^{-1}): 3027 (H arom.), 2956, 2875 (CH_3), 2910 (CH_2), 1775 (C=O), 1589, 1497 (C=C arom.), 813 (arom. p-subst.). ^{1}H NMR ($CDCl_3$) (δ): 0.98–1.02 (m, 6H, CH_3), 1.06–1.11 (m, 4H, CH_2), 7.27 (d, 4H, arom.), 7.53 (d, 4H, arom). ^{13}C NMR ($CDCl_3$) (δ): 4.0 (CH_2), 7.3

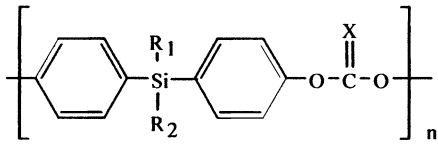
(CH_3), 120.3, 134, 136.3, 152.4 (arom.), 152.4 (C=O). ^{29}Si NMR ($CDCl_3$) (δ): -3.55.

Poly(thiocarbonate) IIIb

I.R. (KBr) (cm^{-1}): 3029 (H arom.), 2955, 2874 (CH_3), 2934 (CH_2), 1586, 1494 (C=C arom.), 828 (arom. p-subst.). ^{1}H NMR ($CDCl_3$) (δ): 1.00–1.04 (m, 6H, CH_3), 1.09–1.12 (m, 4H, CH_2) 7.22 (d, 4H, arom), 7.58 (d, 4H, arom). ^{13}C NMR ($CDCl_3$) (δ): 3.97 (CH_2), 7.38 (CH_3), 121.2, 134.61, 136.2, 154.8 (arom.), 194 (C=S). ^{29}Si NMR ($CDCl_3$) (δ): -3.55.

RESULTS AND DISCUSSION

Poly(carbonates) and poly(thiocarbonates) derived from the diphenols bis(4-hydroxyphenyl)-dimethylsilane, bis(4-hydroxyphenyl)-ethylmethylsilane and bis(4-hydroxyphenyl)-diethylsilane with phosgene or thiophosgene, respectively, were synthesized under phase transfer conditions using several phase transfer catalysts in CH_2Cl_2 as a solvent at 20°C. Polymers were characterized by I.R. and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy, and the results agreed with the following proposed structures (Scheme 1):



Ia: $R_1 = R_2 = -CH_3$, X = O
Ib: $R_1 = R_2 = -CH_3$, X = S
IIa: $R_1 = -CH_3$, $R_2 = -CH_2\text{-}CH_3$; X = O
IIb: $R_1 = -CH_3$, $R_2 = -CH_2\text{-}CH_3$; X = S
IIIa: $R_1 = R_2 = -CH_2\text{-}CH_3$, X = O
IIIb: $R_1 = R_2 = -CH_2\text{-}CH_3$, X = S

SCHEME 1

In all polymers it was possible to see the disappearance of the OH band. In poly(carbonates) it was possible to see a new band at 1775 cm^{-1} corresponding to the C=O of the carbonate group, and for the poly(thiocarbonates) the increase of the intensity of the band at 1185 cm^{-1} corresponded to the C=S group.

In this study the catalyst concentration, solvent, reaction time, and temperature remained constant. Three base concentrations were studied, the molar ratios of NaOH/phenol being 2/1, 3/1, and 4/1, respectively. The volume of the aqueous phase was the same in all cases (15 mL). The efficiency of the catalysts was studied by measuring the yields and inherent viscosity values (η_{inh}) of the obtained polymers.

The reaction took place when the diphenolate dissolved in the aqueous phase was transferred to the organic one as an ionic pair due to the

action of the catalyst. For all the polymers, comparison experiments without catalyst were made in order to evaluate the behavior of the interphase of the system, with the observation that in some cases polymers were obtained due to an interphasial polycondensation process between the diphenolate dissolved in the aqueous phase and the phosgene or thiophosgene dissolved in the organic one. Three phase transfer catalysts were used: TBAB, BTEAC, and ALIQUAT 336.

The choice of the catalysts was according to their structure. TBAB has a symmetrical structure and has been described as adequate for the synthesis of poly(carbonates) derived from analogous diphenols.[10] BTEAC is a hydrophilic catalyst[11] and adequate for the transportation of more lypophilic diphenolates or with high organic content. On the other hand, ALIQUAT 336 is a lypophilic catalyst due to the three n-octyl chains bonded to the N atom, and is adequate for transporting more hydrophilic diphenols or with a less organic content. In this study the organic content of the diphenols is increased.

The increase of the NaOH concentration would displace the equilibrium to the diphenolate formation and also positively affect the transfer process. However, the higher concentration of NaOH would increase the possibility of hydrolysis of the phosgene or thiophosgene and of the polymeric chains, with a consequence of a decrease in the yields in the first case, and in the molecular weights (η_{inh}) in the second.

Table I shows the results obtained for the poly(carbonate) **Ia** and poly(thiocarbonate) **Ib** derived from the diphenol bis(4-hydroxyphenyl)-dimethylsilane. For poly(carbonate) **Ia** the best results were surprisingly obtained with BTEAC, which showed an increase of the yields and the η_{inh} values when the NaOH concentration was increased. This catalyst has been described as ineffective for the synthesis of the poly(carbonate) derived from bisphenol A, which is analogous with this diphenol, but when using a stoichiometric NaOH concentration.[12] In this case, the effectivity can be due to two factors. The first is the salting-out effect of the diphenolate from the aqueous phase to the organic one due to the increase of the NaOH concentration. The second can be the absence of the hydrolysis of both the phosgene and the polymeric chains, due to the effect of the catalyst. This catalyst has been described as hydrophilic[11] and consequently does not promote hydrolysis, which has been described in the synthesis of other poly(carbonates).[13] With TBAB it is possible to see only a slight increase of the yields when the NaOH concentration is increased to a 3:1 ratio, but at a ratio of 4:1, the poly(carbonate) was not obtained. Probably in these cases there is hydrolysis of the phosgene and the polymeric chains. ALIQUAT 336, which is a more lypophilic catalyst, hardly was effective at a stoichiometric amount of NaOH due to the hydrolytic process. Without a catalyst, the

TABLE I Yields and Inherent Viscosities Obtained for Poly(carbonate) Ia and Poly(thiocarbonate) Ib Derived From the Diphenol Bis(4-hydroxyphenyl)-dimethylsilane I, Poly(carbonate) IIa, and Poly(thiocarbonate) IIb Derived From the Diphenol Bis(4-hydroxyphenyl)-ethylmethylsilane II, and Poly(carbonate) IIIa, and Poly (thiocarbonate) IIIb Derived From the Diphenol Bis(4-hydroxyphenyl)-diethylsilane III

		Catalyst							
		—		TBAB		ALIQUAT		BTEAC	
Polymer	NaOH:phenol*	%**	η***	%**	η***	%**	η***	%**	η***
Ia	2:1	—	—	38	0.16	17	0.13	35	0.16
Ia	3:1	59	0.25	59	0.16	—	—	79	0.44
Ia	4:1	5	—	—	—	—	—	79	0.50
Ib	2:1	—	—	14	0.08	16	0.08	7	0.04
Ib	3:1	31	0.18	73	0.28	73	0.21	—	—
Ib	4:1	57	0.13	30	0.13	56	0.13	—	—
IIa	2:1	—	—	—	—	—	—	44	0.11
IIa	3:1	27	0.11	53	0.12	43	0.16	39	0.10
IIa	4:1	20	0.14	21	0.12	—	—	—	—
IIb	2:1	—	—	—	—	—	—	42	0.10
IIb	3:1	41	0.14	73	0.08	83	0.10	12	0.07
IIb	4:1	47	0.14	73	0.14	84	0.12	6	0.09
IIIa	2:1	2	—	9	—	4	—	68	0.14
IIIa	3:1	—	—	15	0.12	2	—	71	0.15
IIIa	4:1	—	—	21	0.09	2	—	46	0.10
IIIb	2:1	—	—	—	—	—	—	71	0.11
IIIb	3:1	20	0.08	32	0.09	15	0.09	61	0.16
IIIb	4:1	2	—	6	—	10	0.09	54	0.16

*Molar ratio.

**Yields.

***Inherent viscosity, in $CHCl_3$ at 25 °C (c = 0.3 g/dL).

poly(carbonate) was obtained only at a 3:1 NaOH/phenol ratio, which showed the relative effectivity of the transfer process, when the catalysts were used.

For the poly(thiocarbonate) **Ib** the best results were obtained at a 3:1 NaOH:phenol ratio. A stoichiometric amount of NaOH the poly(thiocarbonate) was not obtained without a catalyst, but when the catalysts were used, very low yields and η_{inh} values were obtained. When the NaOH concentration was increased, TBAB and ALIQUAT 336 were effective, and an increase of the yields and η_{inh} values was observed principally due to a salting-out effect of the diphenolate to the organic phase in which the reaction takes place. The same occurs without catalyst but the values were lower. But if the NaOH concentration

is increased to twice the stoichiometric, it is possible to see lower values of both parameters, due to a hydrolysis of the thiophosgene and the polymeric chains promoted by these lypophilic catalysts, although TBAB, according to its symmetrical structure, has been described as effective for analogous synthesis.[14] BTEAC was ineffective at all the NaOH concentration according to its hydrophilic nature.

Table I shows the results obtained for the poly(carbonate) **IIa** and poly(thiocarbonate) **IIb** derived from the diphenol bis(4-hydroxyphenyl)-ethylmethylsilane. In general for the poly(carbonate) **IIa**, the best results were obtained at a 3:1 NaOH:phenol ratio, a 50% in excess respect to the stoichiometric, showing a salting-out effect of the diphenolate. But if this concentration was increased, the poly(carbonate) was not obtained or it was possible to see a decrease of both parameters due to hydrolytic effects. BTEAC was effective at stoichiometric NaOH concentration, but the effectivity decreased at a higher concentration. TBAB and ALIQUAT 336, which are more lypophilic catalysts, can promote hydrolytic effects in the phosgene or in the polymeric chains, resulting in a decrease in the yields in the first case and a decrease in the η_{inh} in the second case.

For the poly(thiocarbonate) **IIb**, an analogous situation was observed at a stoichiometric concentration of NaOH. When the NaOH concentration is increased, the poly(thiocarbonate) is obtained without a catalyst when TBAB and ALIQUAT 336 are used. But with these catalysts we obtained higher yields. In these cases we cannot suppose a hydrolytic process because yields and η_{inh} values are very similar for the two NaOH concentrations. It is probably that thiophosgene is more stable toward the hydrolysis than phosgene, which implies obtaining the poly(thiocarbonate) **IIb** at twice the required NaOH concentration. Also, the salting-out effect due to the increase of the NaOH concentration implies the obtaining of this polymer at this concentration.

Table I shows the yields and the η_{inh} values obtained for poly(carbonate) **IIIa** and poly(thiocarbonate) **IIIb** derived from the diphenol bis(4-hydroxyphenyl)-diethylsilane. For both polymers, only BTEAC was effective as a catalyst, due to its hydrophilic character suitable for transporting a diphenolate with a higher organic content such as this. Without a catalyst, polymers practically were not obtained, which showed the effectivity of the phase transfer process with BTEAC. Also with BTEAC, it was possible to see a slow decrease of the yields, probably due to a hydrolytic process. This catalysts of hydrophilic nature is more effective when the organic content of the diphenolate increases.

In general, the effectiveness of the phase transfer process was low. The diphenolates containing Si must show a higher charge dissipation

due to the stringer electron acceptor character of the Si atom, which is at least, relative to the carbon analog. Consequently, the best results were obtained at a 3:1 NaOH:phenol ratio. This effect also was described in analogous polymers but with Ge as a central atom.[6]

On the other hand, although the increase of the NaOH concentration displaces the equilibrium to the diphenolate formation, the higher concentration (4:1 NaOH:diphenol ratio) promotes the hydrolytic process of both the phosgene or thiophosgene, and the polymeric chains if the OH^- anions are transferred to the organic phase with lipophilic catalysts, with the results being poor in general at this NaOH concentration. These results are responsible for the low values of inherent viscosity because this species is of oligomeric nature.

Also, it is possible to see that when the organic groups that are bonded to the Si atom are increased, the results turn poorer, which also was observed in analogous polymers with Ge as the central atom.[6] This effect must be investigated more.

CONCLUSIONS

We can conclude that the phase transfer process was relatively poor in the synthesis of poly(carbonates) and poly(thiocarbonates) derived from diphenols containing Si as a central atom. The increase of the NaOH concentration has influence in the results, in the sense that it displaces the phenol-phenolate equilibrium, but also increases the possibility of hydrolysis of the phosgene or thiophosgene and the polymeric chains, diminishing the yields in the first case and the η_{inh} in the second case. Also it would be necessary in the future to study further the effect of the increase of the organic groups bonded to the heteroatom.

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