

Preparation of copolymers of *p*-Isopropenylcalix[8]arene and Styrene

Stojan Miloshev (✉), Petia Petrova

Department of Polymer Engineering, Faculty of Chemistry Technology, University of Chemical Technology and Metallurgy, Kliment Ohridsky Boulevard 8, 1756 Sofia, Bulgaria
E-mail: stmiloshev@yahoo.com

Received: 10 March 2005 / Revised version: 20 December 2005 / Accepted: 20 December 2005
Published online: 11 January 2006 – © Springer-Verlag 2006

Summary

p-Isopropenylcalix[*n*]arenes are useful building blocks for the design of novel polymer architectures. This paper is the first report on copolymerization of *p*-isopropenylcalix[8]arene and styrene by free radical polymerization. An extensive study on the optimization of the reaction conditions (especially monomer to initiator ratio, initiator concentration, and duration of the process) was performed in order to prepare high molecular weight copolymers in good yield. Homopolymerizations were also carried out for comparison. The products obtained by homopolymerization of the monomers and their copolymerization were fractionated and each fraction was characterized by chromatographic (GPC and HLPC) and spectroscopic methods as UV, IR and ¹H NMR and analytical methods. Considering the molecular weight, spectroscopic and analytical data the most probable structure of the copolymer was proposed. Extraction of metal picrates from water into organic solvent was used to evaluate the ion binding capabilities of *p*-isopropenylcalix[8]arenestyrene and *O*-acetylated *p*-isopropenylcalix[8]arenestyrene copolymers.

Introduction

Calixarenes are cyclic oligomers composed of phenol units. Because of their cavity shaped architecture, they have been widely employed as building blocks in the design of novel host molecules [1, 2]. Calixarenes are easily and often selectively functionalized and therefore they can be combined in various ways to produce larger molecules containing several calixarene substructures. However, only a few calixarene containing polymers have been reported in the literature. For example, Blanda and Adou [3] copolymerized terephthaloyl chloride with calix[4]arene monomers containing a hydroxyl and an amino group at 1,3-positions attached via spacer. Dondoni and co-workers [4] reported on the copolymerization of 1,3-dimethylcalix[4]arene with bisphenol-A as using dibromomethane as chain extender. Kim and co-workers [5] synthesized poly(amino acids) containing calixarene moieties along the polymer backbone. Harris and co-workers [6] reported on the polymerization and Na⁺ complexation of calix[4]arene methylacrylate. Gravett and Guillet [7] synthesized a water-soluble calixarene-containing polymer and

demonstrated its photophysical properties. Telomers based on calix[4]arene have been synthesized and used for extraction of alkali and transition metal cations [8, 9]. Copolymers containing pendant calix[4]arene units have been synthesized via nucleophilic substitution reactions involving bis(cyanomethoxy)-dihydroxy-calix[4]arenes with 1,5-dibromopentane and bisphenol-A [10]. Polymers containing pendant calix[4]crown-4 units have been synthesized via radical initiated reactions involving calix[4]crown-4 based vinylic monomer and styrene [11]. A calixarene monomer containing a methacryloyloxy group at the phenolic rim has been copolymerized with methyl methacrylate, yielding linear polymers with pendant calixarene groups in the cone conformation [12]. Blanda and Adou [13] prepared three vinyl copolymers containing pendant-calix[4]arene. Cross-linked polymers have been formed from monomeric calixarenes bearing vinyl groups [14, 15] and during the reaction between calixarenes bearing chloromethyl groups and poly(ethyleneimine) [16]. Another way of introducing calixarenes into polymer structures is their immobilization. Immobilized lipophilic tetraesters of calix[6]arene [17] and triesters of calix[4]arene [18] have been investigated as sodium ion-selective ionophores in poly(vinyl chloride) membrane electrodes. Calix[4]arene have been immobilized onto cross-linked polystyrene beads [19] through an etherification reaction. Via copolymerization with acrylic comonomers a calixarene macromonomer containing chromophoric receptor groups and polymerizable allyl groups gets covalently bonded to the polymeric matrix [20]. Zhong and co-workers [21] have reported a silica-gel immobilized calixarene as a liquid chromatography stationary phase.

There are few studies on calixarene-containing polymers that may be transformed into materials suitable for chemical sensor devices [22], membranes [23], and antioxidant additives [5].

Recently, we described the synthesis of a new class of *p*-isopropenylcalix[*n*]arenes which possess a double bond conjugated to the aromatic ring [24, 25]. In the present work we report on the radical copolymerization of *p*-isopropenylcalix[8]arene and of its acetylated derivative with styrene, and on the thorough characterization of the products obtained. The ion binding properties of the copolymers are demonstrated by extraction of metal picrates from water into organic phase.

Experimental

Materials

All chemicals were of reagent grade and were commercially available. Solvents were purified according to standard procedures and stored over molecular sieves.

Analysis

¹H NMR spectra were recorded in DMSO-*d*₆ solutions at 25°C using a Bruker 300 MHz spectrometer. The Fourier transform infrared spectra (FTIR) were taken in KBr pellets. High performance liquid chromatography (HPLC) analyses were performed using a Waters 991 UV detector on "LiChrospher - C18" column (250x4 mm) with pore size of 5 μm at 22°C. The mobile phase eluting with 0.4 ml/min flow rate was a mixture of methanol (solvent B) and acetate buffer (2.5 mmol/l sodium acetate with pH=3.4 adjusted by glacial acetic acid) (solvent A), and tetrahydrofuran (solvent C) with gradient steps presented in Table 1. The preparative fractionation was performed

on a LC system equipped with Waters 510 pump, U6K injector, Waters 404 differential refractometer, and Waters 730 data processing station and fraction collector. A " μ -BondaPak C18" chromatographic column (19x150 mm) with pore size 5 μ m was used. A mixture of methanol, tetrahydrofuran and water containing 3% acetic acid in ratio 76:12:12 (v/v/v) was used as eluent at 2 ml/min flow rate. 2 ml of 15% solution of the product in THF was injected several times and the fractions were collected at an interval equal to the semiwidth of the chromatographic peak. The collected fractions were dried by rotary evaporation and analyzed by GPC.

Table 1. Scheme of gradient steps of elution.

Time, min	A, % v.	B, % v.	C, % v.
0	80	20	0
4	100	0	0
16	80	0	20
20	80	0	20
30	80	20	0

Gel permeation chromatography (GPC) was carried out on a Waters System using an UV Waters 448 detector, a Waters 410 differential refractometer and a data station. The chromatographic separation was performed on two 300x6.9 mm "Plgel" (Polymer Laboratories) columns with 500 Å pore size, calibrated with polystyrene standards. The eluent was THF at a flow rate of 0.5 ml/min at 45°C.

Details of picrate extractions experiments have been reported elsewhere [26]. Stock solutions of metal picrates (1.0×10^{-4} M) were prepared in deionized water. The solutions of *p*-isopropenylcalix[8]arenes and calixarene-styrene copolymers (8.57×10^{-4} M) were prepared in trichloromethane and trichlorometane/DMF (19:1), respectively. Equal volumes (5.0 ml) of the aqueous and organic solutions were placed in a centrifuge tube equipped with a screw cap and equilibrated for an hour in a thermostat at 25°C. After equilibration, the whole mixture was extracted with a Vortex-Genie for 1 min. The procedure was repeated twice to ensure complete extraction. The mixture was then centrifuged for 10 min to complete phase separation. The concentration of the metal picrate salt remaining in the aqueous phase was determined spectrophotometrically at 355 nm. Blank experiments showed that no picrate extraction occurred in the absence of calixarene or its copolymers.

Synthesis

Synthesis of *p*-isopropenylcalix[*n*]arenes

p-Isopropenylcalix[*n*]arenes were synthesized by reaction of *p*-isopropenylphenol and paraformaldehyde at molar ratio 1:2.40 as already described [24]. *p*-Isopropenylcalix[8]arene was isolated from the reaction mixture by fractional precipitation and preparative HPLC. The yield of *p*-isopropenylcalix[8]arene was 32 % [25], and has the following spectral characteristics: IR (KBr): $\nu = 3369$ (OH), 1645 cm^{-1} (C=C conjugated double bond with aromatic ring); $^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 9.23 (s, 8H, OH), 6.7 (s, 16H, ArH), 4.6 (m, 16H, -C=CH₂), 3.48 (d, 16H, ArCH₂Ar), 2.2 ppm (t, 24H, CH₃-C=); UV-Vis (CH₃OH): 232, 256, 262, 280, 283 nm; Anal. calculated for C₈₀H₈₀O₈: C, 82.16%; H, 6.89%; found: C, 81.52%, H, 6.24%.

Synthesis of O-acetylated p-isopropenylcalix[8]arene

10.0 g of p-isopropenylcalix[8]arene were dissolved in 100 ml of pyridine, and 10 ml of acetic anhydride were added. The mixture was stirred for 2 h at 75°C, and then poured into 1 l of water. The precipitate was filtrated, washed with water and dried to yield 9.5 of O-acetylated p-isopropenylcalix[8]arene. The spectral characteristics of O-acetylated p-isopropenylcalix[8]arene were as follows: IR (KBr): $\nu = 1740 \text{ cm}^{-1}$ (O-C=O stretching); $^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 7.06 (s, 16H, ArH), 3.5 (s, 16H, ArCH₂Ar), 4.4 (m, 16H, -C=CH₂), 1.98-2.25 (d, 24H, COCH₃), 1.6 ppm (t, 24H, CH₃-C=). UV-Vis (CH₃OH): 233, 258, 262, 274, 283 nm; Anal. calculated for C₉₆H₉₆O₁₆: C, 76.57 % H, 6.43% found: C, 76.26 %, H, 6.12 %.

Copolymerization of p-isopropenylcalix[8]arene and of O-acetylated p-isopropenylcalix[8]arene with styrene

All polymerizations were carried out in a 100 ml flask equipped with a reflux condenser, magnetic stirrer and nitrogen inlet tube. The p-isopropenylcalix[8]arene to styrene molar ratio was varied as follows: 20/80; 40/60; 50/50; 60/40; 80/20. In the copolymerization of O-acetylated p-isopropenylcalix[8]arene with styrene the molar ratio of the comonomers was kept constant and equal to 50:50. The reaction was carried out in a mixture of dioxane and water ($v/v=2/1$) to dissolve the reagents. In a typical example, the mixture of styrene (0.208 g, 0.002 mol) and p-isopropenylcalix[8]arene (2.34 g, 0.002 mol) or O-acetylated p-isopropenylcalix[8]arene (3.01 g, 0.002 mol), and 0.018 g of ammonium persulfate (4 mol%), dissolved in 25 ml of dioxane/water was carefully degassed. The polymerization was allowed to continue for 8 h at reflux. The copolymer was precipitated into methanol, filtered and dried at 40°C under vacuum 0.08 MPa. The methanol soluble products were isolated by rotary evaporation. The yield of the methanol insoluble and soluble fractions was 50% and 40%, respectively. The spectral characteristics of copolymer of p-isopropenylcalix[8]arene with styrene were as follows: IR (KBr): $\nu = 3369, 3083, 3058, 3023, 2924, 1718, 1646, 1066, 855, 819, 756, 698 \text{ cm}^{-1}$; $^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 9.23 (OH), 6.6-7.4 (ArH), 3.5 (ArCH₂Ar), 4.6 (-C=CH₂), 1.97 (CH₃-C=), 1.8 (-CH-), 1.48 (-CH₂-), 1.2 (CH₃-) ppm. The spectral characteristics of the copolymer of O-acetylated p-isopropenylcalix[8]arene with styrene were as follows: IR (KBr): $\nu = 1740 \text{ cm}^{-1}$ (O-C=O stretching); $^1\text{H NMR}$ (300 MHz, DMSO- d_6): δ 6.5-7.5 (ArH), 3.56 (ArCH₂Ar), 4.45 (-C=CH₂), 2.09-2.21 (COCH₃), 1.9 (CH₃-C=), 1.8 (-CH-), 1.41 (-CH₂-), 1.3 (CH₃-) ppm.

Metal picrates

Metal picrates were prepared from picric acid (Merck) and the corresponding metal hydroxide or chloride in ethanol as already described [27]. They were dried *in vacuo* and purified by recrystallisation from absolute ethanol.

Results and Discussion

The homopolymerization of styrene and p-isopropenylcalix[8]arene as well as their copolymerization at a [p-isopropenylcalix[8]arene]: [styrene] relative molar ratio of 20:80 were performed under the same conditions (2 mol% ammonium persulfate). The main characteristics of the products obtained are summarized in Table 2.

Table 2. Main characteristics of the products prepared by homopolymerization of styrene and copolymerization of styrene and p-isopropenylcalix[8]arene. Conditions: monomers concentration 1.07 mol/l; [p-isopropenylcalix[8]arene]:[styrene] molar ratio = 20:80; ammonium persulfate 2 mol%.

Monomers:	High molecular weight fraction		Olygmeric fraction	
	M_w , Da	Amount, %	M_w , Da	Amount, %
Styrene	12000	3.6	300-400 monomer	35.6 60.8
Styrene and p-isopropenyl- calix[8]arene	43000	70.0	200-400 1400-2000 monomers	3.4 26.6 -

The data in Table 2 show that the copolymerization of styrene with p-isopropenylcalix[8]arene, performed under the selected conditions, provided high molecular weight product in good yield (70%). The homopolymerization of styrene under the same conditions resulted in the formation of oligomeric products in 40% yield, while isopropenylcalix[8]arene hardly polymerized (yield 0.08 %). One can assume that the initiation by ammonium persulfate generates a higher concentration of styrene radicals in the early stages of the copolymerization. Subsequently the attack of the styrene radicals on the p-isopropenylcalix[8]arene molecules results in the formation of p-isopropenylcalix[8]arenestyrene macroradicals, which are involved in heteroaddition to styrene.

The effect of the initiator concentration on the copolymerization process was studied by GPC analyses of the products obtained. The experiments were performed at a constant [p-isopropenylcalix[8]arene]: [styrene] relative molar ratio of 20:80 and monomers concentration of 1.07 mol/l. The initiator concentration was varied from 0.5 to 12 mol %. It has been found that increasing the initiator concentration above 4 mol% leads predominantly to the formation of styrene oligomers. These results confirm the assumption that the initiation of the copolymerization proceeds mainly on styrene.

The time dependence of the amount of both the high molecular weight fraction and of the oligomeric fraction obtained during the homopolymerization of styrene and its copolymerization with p-isopropenylcalix[8]arene is presented in Fig.1

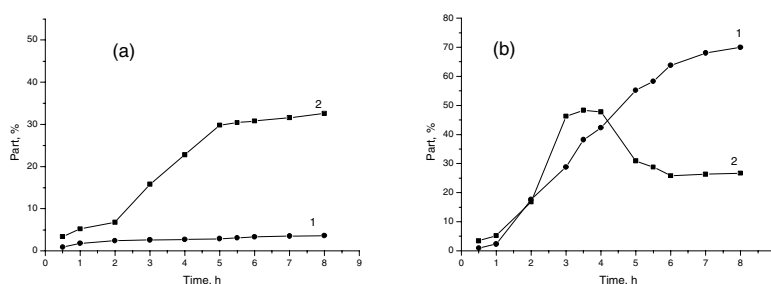


Figure 1. Time dependence of the amount of: (1) polymeric fraction, and (2) oligomeric fraction during: a) styrene homopolymerization, and b) copolymerization of p-isopropenylcalix[8]arene with styrene at 20:80 molar ratio. Monomer concentration - 1.07 mol/l; initiator concentration - 4 mol%.

Fig. 1a shows that during the homopolymerization of styrene the amount of the oligomeric fraction increased up to the 4th hour. At the same time the amount of the polymeric fraction remained low. Quite distinct are the results obtained during the copolymerization of styrene with p-isopropenylcalix[8]arene (Fig. 1b). Fig. 1b shows that during the first 3 hours the amount of both the oligomeric and the high molecular weight products increased but after the 5th hour the amount of the oligomeric products significantly decreased. One can assume that after consumption of the styrene during the initial stage of the process p-isopropenylcalix[8]arenestyrene is involved in the copolymerization.

A systematic study on the copolymerization of p-isopropenyl-calix[8]arene with styrene was performed at different molar ratios of the monomers. Table 3 lists the data for the yield and the total molecular weight of the products obtained. A series of products was obtained by copolymerization of the monomers at various molar ratios in the feed. They were subjected to fractionation according to the following work-up procedure: The reaction mixture was precipitated into methanol and the insoluble fraction, termed “high molecular weighed” fraction, was further subjected to fractionation by semi-preparative liquid chromatography.

Table 3. Molecular weight data and yield of the products obtained by copolymerization of p-isopropenylcalix[8]arene and styrene for 8 hours at reflux.

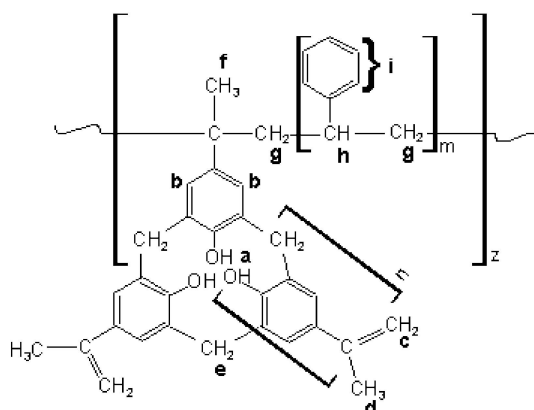
[p-isopropenyl-calix[8]arene]: [styrene] molar ratio	M _w , Da	M _n , Da	ID	Yield, %
0:100	900	400	2.25	39
20:80	23300	9300	2.50	48
40:60	18200	7600	2.39	62
50:50	17500	7500	2.33	78
60:40	8300	4800	1.73	51
80:20	8200	5200	1.58	38
100:0	1170	1230	1.05	98

Table 4. Characteristics of the fractions separated from the products obtained by copolymerization of p-isopropenylcalix[8]arene and styrene monomers at various molar ratios of the monomer.

[p-isopropenyl- calix[8]arene]: [styrene] molar ratio	Fraction 1		Fraction 2		Fraction 3		Fraction 4	
	M _w , Da	Amount, %	M _w , Da	Amount, %	M _w , Da	Amount, %	M _w , Da	Amount, %
0:100	-	-	12500	-	-	-	400	-
20:80	67800	21	16200	36	7800	42	-	-
40:60	76800	16	19600	7	6500	69	-	-
50:50	100900	10	24000	12	5400	83	-	-
60:40	99500	3.2	21600	2,8	7200	55	1400	39
80:20	94400	4	25700	4	8900	26	1660	66
100:0	-	-	-	-	-	-	1170	100

The fraction soluble in methanol, termed “low molecular weight fraction” was isolated after solvent evaporation. The molecular weights of the separated fractions evaluated from by GPC are presented in Table 4. The data summarized in Table 4 suggest that the amount of the fractions and their molecular weight depend on the styrene concentration in the feed. With the increase of the styrene concentration in the feed the amount of the higher molecular weight fractions increased.

It was established that the main product obtained during styrene homopolymerization has molecular weight of about 400 Da, corresponding to oligomer consisting of 2 or 4 styrene units. The product obtained by the copolymerization of p-isopropenylcalix[8]arene with styrene at molar ratio of 80:20 consisted mainly of “low molecular weight” fraction (66%) with molecular weight of about 1600 Da (Table 4, fraction 4).



Scheme 1. The proposed structure of p-isopropenylcalix[8]arene-styrene chain ($m=1\div 10$; $n=6$).

It can be concluded, therefore, that the most probable structure of the oligomer formed consists of four styrene units, connected to p-isopropenylcalix[8]arene (Scheme 1).

The structure of the oligomeric product was confirmed by combining the data from UV, IR and ^1H NMR measurements.

The data from the UV spectra of the fractions recorded during the HPLC analysis are listed in Table 5.

Table 5. The UV- spectra of the starting monomers and separated fraction.

Compound	Absorptions maximum , nm
Oligomer fraction from homopolymerization of styrene with molecular weight about 400 Da	223, 232, 244, 260*
Oligomeric fraction from copolymerization of styrene and p-isopropenylcalix[8]arene with molecular weight about 1600 Da	241, 256, 271, 283*, (296**)
Oligomeric fraction from copolymerization of styrene and p-isopropenylcalix[8]arene with molecular weight about 4000-8000 Da	244,262,288,296*, (303**)
p-Isopropenylcalix[8]arene	232*, 256, 262, 280 , (283**)
O-acetylated p-isopropenylcalic[8]arene	233,258, 262, 274*, (283**)

* the strongest absorption ; ** shoulder in UV-spectra

The oligomeric fraction from the styrene homopolymerization shows absorption maximum at about 260 nm. In the UV-spectrum of p-isopropenylcalix[8]arene the most intensive absorption is that at 232 nm, whereas at O-acetylated p-isopropenylcalix[8]arene is at 274 nm. The plateau typical for the calixarenes appeared in the interval from 240 to 280 nm. Besides, a shoulder at 280-283 nm was also observed [1].

The UV-spectrum of the copolymerization oligomeric product showed the characteristic absorptions for the starting monomers. But with the augmentation of its molecular weight the shoulder typical for calixarenes is shifted toward 290-300 nm.

The IR spectra of calixarene-co-styrene oligomers are almost identical. There is a difference in the intensity of some characteristic bands depending on the ratio of comonomers in the resulting copolymer.

Isopropenylcalixarene-co-styrene copolymers exhibit the following typical vibration bands: The band at 3369cm^{-1} is attributed to the $-\text{OH}$ groups from the calixarene structure. The bands at 3083, 3058, 3023 cm^{-1} are characteristic of the monosubstituted ring of styrene.

The double bonds of p-isopropenylcalix[8]arene molecule are partially involved in the copolymer chain construction. Therefore, the absorption peaks at 1718, 1646 and 617 cm^{-1} , attributed to the double bonds in the pendent chain, are clearly observed in the IR spectrum of the oligomeric product. When the copolymer contains a greater amount of calixarene moieties the absorptions at 1066, 855 and 819 cm^{-1} , assigned to four substituted aromatic rings, are more pronounced.

In the IR spectrum of the acetylated product the stretching band at $3400\text{-}3300\text{ cm}^{-1}$ is not observed and a new absorption band at 1740 cm^{-1} appeared due to the presence of an ester bond.

The structure of the p-isopropenylcalixarene-co-styrene copolymers was also confirmed by ^1H NMR spectra. The data for the chemical shifts in the ^1H NMR spectra of p-isopropenylcalix[8]arene and of p-isopropenylcalixarene-co-styrene copolymers are presented in Table 6. The assignment of the peaks is presented in Scheme 1.

The ^1H NMR spectra of p-isopropenylcalixarene-co-styrene copolymers confirmed the proposed structure. The integral ratio of $=\text{CH}_2$ protons (c) to CH_3 protons (d) is consistent with number of double bonds in the side calixarene unit equal to 7. The analytical method for determination of the amount of double bonds by treatment the product with mercury diacetate [28] gave the same result.

Table 6. ^1H NMR data of p-Isopropenylcalix[8]arene (Scheme 3a), p-Isopropenylcalixarene-styrene copolymers (Scheme 3b) and O-acetylated-p-isopropenyl-calixarene-styrene copolymers.

Compound	Chemical shift δ in ppm									
	a	b and i	c	d	e	f	g	h	-OCOCH ₃	
p-Isopropenylcalix[8]arene	9.23	6.7	4.6	2.2	3.48					
O-acetylated p-isopropenylcalix[8]arene	-	7.06	4.4	1.6	3.5					1.98- 2.25
p-Isopropenylcalixarene-styrene copolymers	9.23	6.6÷7.4	4.6	1.97	3.5	1.2	1.48	1.8		
O-acetylated p-isopropenylcalixarene-styrene copolymer	-	6.5÷7.5	4.45	1.9	3.56	1.3	1.41	1.8	2.09 - 2.21	

The integral ratio of the aromatic protons of styrene (i) and those of calixarene cycles (b) reveal the formation of copolymers with one calixarene ring per two or three styrene units independent of the monomer ratio in the feed.

Prolonging the polymerization process resulted in formation of insoluble products. The GPC chromatograms of the oligomeric fractions separated from the products by extraction with methanol are identical to those for the products obtained at 8h polymerization time (see Table 4, fraction 4).

The ability of p-isopropenylcalixarene-styrene copolymers to extract metal picrates (Li, K, Na, Cs, Rb, Ag, Ni, Ba, Cd, Co) from aqueous solution was studied by liquid-liquid extraction. The results were compared with the behavior of the O-acetylated derivatives. The copolymers were obtained at monomer ratio of 50:50. In the control experiments, without the presence of ligand, no transfer of metal picrate was observed. The results obtained are summarized in Table 7.

Table 7. Results from extraction of metal picrates from aqueous into organic phase. The copolymers used were obtained at p-isopropenylcalix[8]arene:styrene molar ratio of 50:50*.

Ligands ^C	Metal picrate extracted into organic phase (%) ^{a, b}										
	Li ⁺	K ⁺	Na ⁺	Cs ⁺	Rb ⁺	Ag ⁺	Ni ²⁺	Mg ²⁺	Ba ²⁺	Cd ²⁺	Co ³⁺
1 ^C	0.8	0.3	0.4	0.9	4.8	0.9	0.1	0.12	0.2	0.9	0.9
1*	2.9	3.4	3.2	3.1	3.1	2.1	0.2	2.7	4.3	2.3	3.7
2 ^d	0.9	3.8	2.1	3.7	3.5	3.6	0.6	3.4	4.7	3.7	6.14
2*	11.6	9.5	9.8	18.2	19.9	4.0	0.9	9.4	11.3	18.2	24.8
3 ^e	3.6	14.6	8.1	14.3	13.1	14.2	3.1	13.5	18.0	14.2	24.3
3*	44.3	36.2	37.2	66.0	76.2	16.1	3.6	36.0	43.5	69.7	85.1

* Acetylated product; ^a Temperature 25°C; aqueous phase (3ml), [picrate]= 1×10^{-4} M; organic phase (dichloromethane, 3ml), [ligand]= 8.57×10^{-4} M; ^b Average of three independent extraction experiments; ^c p-isopropenylcalix[8]arene; ^d Oligomeric fraction.; ^e unfractionated product

The results suggest that p-isopropenylcalixarene-co-styrene copolymers are more effective as extraction reagents compared with p-isopropenylcalix[8]arenes. They were highly effective for transport of Co, Rb, Cd and Cs ions. The extraction capacity grows up with the molecular weight of copolymers. The o-acetylated p-isopropenylcalix[8]arene-styrene displays significantly greater extraction ability and is especially effective for extraction of Rb, Cs, Cd and Co picrates.

Conclusions

The article reports the first study on the free-radical copolymerization of the recently synthesized p-isopropenyl-calix[8]arene and styrene. They have been copolymerized at different molar ratios and reaction times in order to establish the optimal conditions for the synthesis of high molecular weight copolymers in good yield. The comparison of the homopolymerizations and copolymerizations in terms of the molecular weight data of the products obtained indicates that under certain conditions the copolymerization of the monomers is preferred to their homopolymerization. The parameters essential for the synthesis of high molecular weight copolymers are the monomer molar ratio and the duration of the process. The copolymer chain formed at

the early stages of the copolymerization is rich of styrene monomer units while isopropenylcalixarene units are incorporated at later stages. A long reaction time leads to the formation of cross-linked copolymer network.

The results from transfer of metal picrates from aqueous to organic phase demonstrate that both p-isopropenyl-calix[8]arene styrene and O-acetylated p-isopropenyl-calix[8]arene styrene exhibit significant phase-transfer properties.

Acknowledgements. The authors gratefully acknowledge the financial support from the University of Chemical Technology and Metallurgy, Sofia, Bulgaria (Contract No 10030).

References

- Gutsche CD. (1998) In Calix[4]arenes Revisited; Stoddart, FJ. (ed.); Monographs in Supramolecular Chemistry; The Royal Society of Chemistry: Cambridge
- Calixarenes 2001 (2001), Eds. Asfari Z., Böhmer V., Harrowfield J, Vincen J. Kluwer Academic Publishers: Dordrecht
- Blanda MT, Adou E (1998) Chem. Commun 1:139
- Dondoni A, Ghiglione C, Marra A, Scoponi M (1999) Macromol. Chem. Phys. 200: 77
- Kim SI, Shin TJ, Ree M, Hwang GT, Kim BH, Han H, Seo J (1999) J. Polym. Sci., Part A: Polym. Chem. 37: 2013
- Harris S J, Barrett G, McKervey MA (1991) J. Chem. Soc. Chem. Commun. 17:1224.
- Gravett DM, Guillet JE (1996) Macromolecules 29: 617
- Yilmaz A, Memon S, Yilmaz M (1999) J. Polym. Sci., Part A: Polym. Chem. 37: 4351
- Memon S, Yilmaz M (2000) Reactive & Functional Polymers 44: 228
- Memon S, Oğuz, O, Yilmaz A, Tabakci M, Yilmaz M, Ertul S (2001) J. of Polymers and the Environment 9: 97
- Memon S, Uysal G, Yilmaz M (2001) Reactive & Functional Polymers 47: 165
- Vocanson F, Seigle-Ferrand P, R Lamartine, Fort A, Coleman AW, Shahgaldian P, Mugnier J, Zerroukhi A (2003) J. Mater. Chem. 13:1596
- Blanda MT, Adou E (1998) Polymer 39: 3821
- Parzuchowski P, Malinowska E, Rokicki G, Brzozka Z, Bohmer V, Arnaud-Neu F, Souley B (1999) New J. Chem. 23: 757
- Kawabata H, Aoki M, Murata K, Shinkai S (1993) Supramol. Chem. 2: 33
- Georgiev EM.; Troev K, Roundhill DM (1993) Supramol. Chem. 2: 61
- Oh H, Kwon Lee S, Chun Nam K, Jeon, S (2003) Bull. Korean Chem. Soc. 24: 109
- Kim YD, Jeong H, Kang SO, Nam KC, Jeon S (2001) Bull. Korean Chem. Soc. 22: 405
- Alexandratos SD, Natesan S (2001) Macromolecules 34: 206
- Przygorzewska J, Rakoczy P, Rokicki G (2003) Wiadomości Chemiczne 57: 43
- Zhong ZL, Tang CP, Wu CY, Chen YY (1995) J. Chem. Soc. Chem. Commun. 17:1737
- a) Arrigan WM, Svehla G, Harris SJ, McKervey MA (1995) Electroanalysis 6: 97; b) Diamond D, McKervey MA (1996) Chem. Soc. Rev. 1:15
- Nijenhuis WF, Buitenhuis EG, De Jong, F, Sudhölter EJR, Reinhoudt DN (1991) J. Am. Chem. Soc. 113: 7963
- Novakov P, Miloshev S, Tuleshkov P, Gitsov I, Georgieva M (1998) Angew. Makromol. Chemie (German) 255: 23
- Miloshev S, Petrova P, (2005) unpublished results
- a) Gutsche CD, Nam KC (1988), J. Am. Chem. Soc., 110: 6153; b) Cho YH, Rha SG, Chang SK (1988), J. of Phenomena. and Macrocyclic Chemistry, 31: 119
- a) Wong KH, Ng HL (1981) J. Coord. Chem. 11: 49; b) Coplan MA, Fuoss RM (1964) J. Phys. Chem. 68: 1177
- Luce EN (1959) Monomers and Polymers of Styrene. In: Kline GM (ed) Analytical Chemistry of Polymers, Part I. Interscience Publishers, New York, London