Novel Network Polymers Based on Calixresorcinarenes

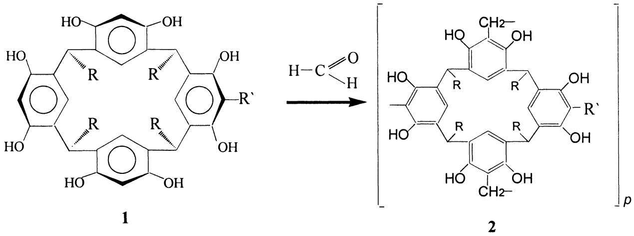
*Henrikh Altshuler, Elena Ostapova, Oksana Fedyaeva, Lidiya Sapozhnikova, Olga Altshuler**

Institute of Coal and Coal Chemistry, Siberian Branch of Russian Academy of Sciences, Sovetsky prosp. 18, 650099 Kemerovo, Russian Federation

Summary: The novel network polymers **2a-2d** based on calix[4]resorcinarene derivatives were obtained with yields **2a**:80%, **2b**:90%, **2c**:70%, **2d**:70%. Polymers **2a** and **2b** containing fragments of tetramethylcalix[4]resorcinarene or tetraphenylcalix[4]resorcinarene as a repeating units were synthesized by condensation cis-tetramethylcalix[4]resorcinarene or cis-tetraphenylcalix[4]resorcinarene with formaldehyde. Polymers **2c** and **2d** containing fragments of furylcalix[4]resorcinarene were obtained by condensation of formaldehyde with products of calix[4]resorcinarene and furfural interaction. The IR spectra and sorption properties of the polymers were researched. It is found out that **2a-2d** can participate in the cation-exchange reaction.

Introduction

The calixarenes have been the focus of interest of many chemists in recent years due to the ability of these synthetic macrocyclic to be selectively linked with various substrates by complementary stereoelectronic interactions. Special attention has been given to C-calix[4]resorcinarenes (**1a**, **1b**) capable of interacting both with neutral molecules[1] and with cations.[2] A few publications on the synthesis of water-soluble linear polymers on the basis of p-tert-butylcalix[4]arene are known.[3,4] The resole polycondensation of calix[4]resorcinarene derivatives with formaldehyde affords a cross-linked polymers possessing ion-exchange ability. But the synthesis of calix[4]arenes immobilized in three-dimensional polymers has not been described so far. We report in the present paper about novel network polymers **2a** – **2d** obtained by the catalytic resol polycondensation of **1a-1d** with formaldehyde (Scheme 1).



1 **2**

Scheme 1 **a: R=CH$_3$, R`=H** **b: R=C$_6$H$_5$, R`=H**
c: R=CH$_3$, R`=CH(OH)Fur** **d: R=C$_6$H$_5$, R`=CH(OH)Fur

CCC 1022-1360/00/$ 17.50+.50/0

Experimental

The compound **1a** in the *cis* conformation was obtained by the condensation of resorcinol with acetaldehyde.[5] To identify this compound its octaacetate was synthesized by the action of the excess acetic anhydride in the presence of pyridine. The properties of the obtained acetate were consistent with the published data.[6] The compound **1b** in the *cis* conformation was obtained by the condensation of resorcinol with benzaldehyde.[7]

The polymer **2a** was synthesized by adding 42 mmol of formaldehyde to 14 mmol of the compound **1a** dissolved in 40 ml of the 10% NaOH solution. The resultant mixture was heated at 90°C for 20 h. Next, the excess alkali was washed out of the gel formed with cold water. The gel was allowed to stand at 100°C for 10 h. Then, the gel was transformed to the H form by treatment with the 0.1 M HCl solution. The yield of **2a** was 80%.

The polymer **2b** was obtained by the catalytic resol polycondensation of 10 mmol of the compound **1b** with 30 mmol of formaldehyde with subsequent curing. The yield of **2b** was 90%.

The polymer **2c** was obtained by the catalytic resol polycondensation of 30 mmol of formaldehyde with the product of the interaction between 10 mmol of the compound **1a** and 40 mmol of furfural. The yield of **2c** was 70%.

The polymer **2d** was obtained by the catalytic resol polycondensation of 30 mmol of formaldehyde with the product of the interaction between 10 mmol of the compound **1b** and 40 mmol of furfural. The yield of **2d** was 70%.

The IR spectra of **2a-2d** (Figure 1) exibit broad bands in the region 3500-3400 cm^{-1} (intramolecular hydrogen bond in diols), bands at 2970, 2920, 2860 cm^{-1} (oscillation of C-H bond of aliphatic hydrocarbons), bands at 1600, 1500 cm^{-1} (oscillation of C-H and C-C bonds in a benzene ring), a band at 1212 cm^{-1} (oscillation of C-OH bond in phenols).The region of "fingers-prints" contains a slightly intensive band at 830 cm^{-1}, which is typical of tetramers.[8] In fact, absorption bands of **2a-2b** and **1a-1b** coincide,[9] but the absorption spectra of **2a-2b** are presented by a smooth curve characteristic of polymeric structures. The spectra of **2c-2d** exhibit the bands of calix[4]resorcinarenes and bands at 3120, 1485, 1015, 885, 745 cm^{-1} (characteristic bands of furan[10]). Hence, polymer **2a-2d** containing fragments of appropriate calix[4]resorcinarenes.

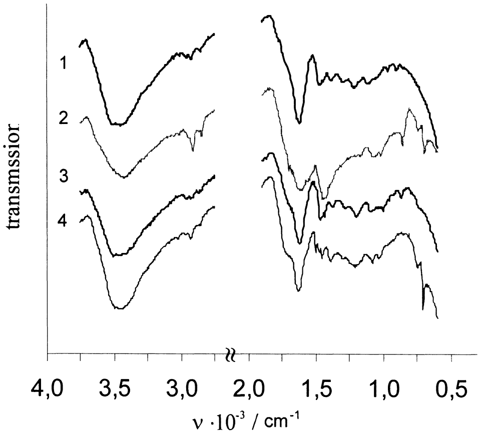


Figure 1. IR spectra of the polymers **2a** (1), **2b** (2), **2c** (3), **2d** (4).

Technological Properties

Polymers **2a-2d** can participate in the cation-exchange reaction, because the OH groups capable of dissociating with formation of mobile protons are present in its repeating units. The material balance data of the sorption of sodium, potassium, tetramethylammonium, tetraethylammonium and tetrabuthylammonium hydroxides from aqueous solutions show that the interaction of synthesized polymers with electrolytes proceeds by an ion-exchange reaction. The dynamic ion-exchange capacity of network polymers on a basis calix[4]resorcinarenes with respect to Na $^+$, K^+, Me_4N^+, Et_4N^+, and Bu_4N^+ cations is in an interval 2.9-4.6 mol of cations per one kilogram of dry polymer in the H form. The total dynamic ion-exchange capacity of **2a-2d** with respect to 0.1 M NaOH and 0.1 M $(CH_3)_4NOH$ are presented in Table 1.

Table 1. The characteristics of polymers based on calix[4]resorcinarene derivatives.

Polymer	The dynamic ion-exchange capacity to cations mol/kg		Content of calixresorcinarene fragments mol/·kg
	Na^+	$(CH_3)_4N^+$	
2a	5.0 ± 0.2		1.25±0.10
2b	3.8 ± 0.1	3.8 ± 0.2	0.95±0.10
2c	3.80 ± 0.15	3.86 ± 0.15	0.95±0.10
2d	3.38 ± 0.15	3.32 ± 0.15	0.84±0.10

Taking into account that, under the conditions studied, four protons of eight hydroxyl groups participate in the ion-exchange reaction, we calculated the content of calixresorcinarene fragments in polymers (Table 1). As it follows from Table 1 the content of calixresorcinarene fragments in polymers **2a-2d** is in the 0.84-1.25 mol·kg^{-1} range.

Acknowledgements

The authors would like to thank the Russian Foundation for Basic Research for financial supporting of this work (project No. 00-03-32589).

[1] L.R. MacGillivray, J.L. Atwood, *J. Am. Chem. Soc.* **1997**, *119*, 6931.

[2] A.R. Mustafina, R.R. Galimov, L.V. Ermolaeva, N.N. Sarvarova, A.R. Burilov, V.S. Reznik, *Russ. Chem. Bull.* **1996**, *45,* 1170.

[3] M.T. Blanda, E. Adou, *Chem. Commun.* **1998,** 139.

[4] A. Dondoni, C. Ghiglione, A. Marra, M., Scoponi, *Chem. Commun.* **1997,** 673.

[5] D.J. Cram, S. Karbach, H.-E. Kim, C.B. Knobler, E.F. Maverick, J.L. Ericson, R.C. Helgeson, *J. Am. Chem. Soc.* **1988**, *110*, 2229.

[6] S. Hogberg, *J. Org. Chem.* **1980**, *45*, 4498.

[7] S. Hogberg, J. Am. Chem. Soc. **1980**, *102*, 6046.

[8] C. Gutsche, in "*Host Guest Complex Chemistry Macrocycles: Synthesis, Structures, Application*", F. Vogtle and E.Weber, Eds., Springer-Verlag, Berlin 1985, p. 445.

[9] G.N. Al'tshuler, O.N. Fedyaeva, L.A.Sapozhnikova, and E.V.Ostapova, *Polymer Science* **2001**, *43*, 112.

[10] A.R. Katritzky, A.P. Ambler, in "*Physical Methods in Heterocyclic Chemistry",* A.R. Katritzky, Ed., Academic Press, New York and London 1963, p.460.