



SYNTHESIS OF CYCLIC OLIGOMETHYLPHENYLSILOXANES IN AN ACTIVE MEDIUM

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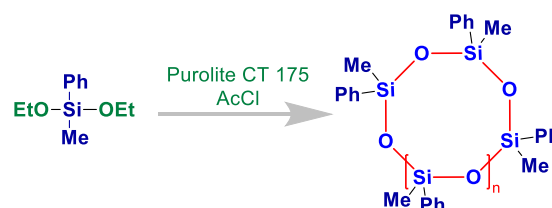
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Abstract

The polycondensation of diethoxy(methyl)phenylsilane in an active medium in the presence of acetyl chloride or cation exchanger Purolite CT 175 has been studied, and their effect on the rate and selectivity of the process has been evaluated. It is shown that the use of the sulfonic cation exchanger allows for achieving 100% yields of methylphenylcyclosiloxanes.

Key words: active medium, polycondensation, oligomethylphenylcyclosiloxanes.



Introduction

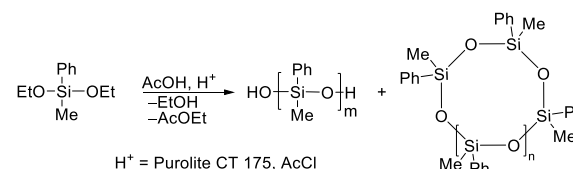
Nowadays, cyclic oligomethylphenylsiloxanes are widely used as monomers for the production of rubbers and oligomethylphenylsiloxane fluids by the catalytic rearrangement [1].

One of the modern ecologically friendly methods for obtaining polyorganosiloxanes with controlled composition and structure is the polycondensation of alkoxy silanes in an active medium. The latter traditionally refers to an excess of anhydrous acetic acid, which simultaneously acts as a solvent, reagent, and catalyst [2]. Therefore, it seemed interesting to evaluate the applicability of this approach as a one-step method for obtaining cyclic oligomethylphenylsiloxanes.

It is known that the main factor determining the selectivity of the formation of linear and cyclic oligomers during the polycondensation of dialkoxydiorganosilanes in an active medium is the rate of water formation, and its rapid release contributes to the synthesis of oligosiloxanes of a predominantly cyclic structure. In particular, the polycondensation of diethoxy(methyl)phenylsilane in excess anhydrous acetic acid affords a mixture of linear and cyclic oligomers with the relative contents of 70% and 30%, respectively [3]. However, this approach is characterized by a long duration: the complete conversion of alkoxy groups is achieved in 6–8 h of refluxing. Earlier, using diethoxy(dimethyl)silane as an example, it was shown that the application of acetyl chloride and sulfonic cation exchanger as catalysts allows for a significant reduction in the process duration down to 1 h with high yields of cyclic products [4]. Therefore, of particular interest was the investigation of the possibility of intensifying the polycondensation process of diethoxy(methyl)phenylsilane in an active medium, while maintaining the high selectivity towards the formation of cyclosiloxanes in a minimum time and at room temperature.

Results and discussion

The polycondensation of diethoxy(methyl)phenylsilane in the presence of acetyl chloride was carried out at room temperature and under reflux, in the case of sulfonic cation exchanger Purolite CT 175—at room temperature and 50 °C (Scheme 1).



Scheme 1. Polycondensation of diethoxy(methyl)phenylsilane in an active medium in the presence of the catalysts.

The process was carried out until the complete conversion of alkoxy groups, which was determined by analyzing the ¹H NMR spectra of the evacuated aliquots of the reaction mixture (Fig. 1).

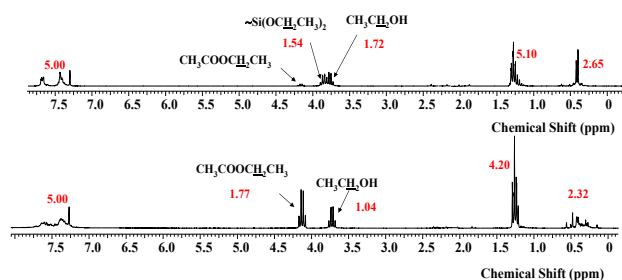


Figure 1. ¹H NMR spectra of the reaction mixture in 15 min and 3 h after the reaction beginning.

The crude products were isolated by rinsing the reaction mixtures to neutral pH; the solvent was removed, and the

siloxane portion was analyzed by gel permeation chromatography (GPC) to determine the ratio of linear and cyclic components (Fig. 2, Table 1, entries 1 and 2). The products obtained were distilled to analyze the composition of the volatile components by gas liquid chromatography (GLC). The results are presented in Table 1.

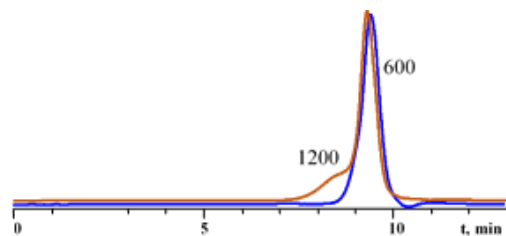


Figure 2. GPC curves of the condensation products (Table 1, entries 2, 4).

The addition of acetyl chloride during the polycondensation of diethoxy(methyl)phenylsilane in an active medium promoted the acceleration of the process, and upon refluxing, the complete conversion of ethoxy groups was achieved in 2 h (entry 2, Table 1). In this case, the predominant cyclization is observed, and the yield of methylphenylcyclosiloxanes increases from 27% for the classical polycondensation in an active medium (entry 8) to 87–90% (entries 1, 2), which is comparable with the reactions promoted by ethanol (entry 9).

Therewith, a mixture of six- (A_3), eight- (A_4), and ten-membered (A_5) cyclosiloxanes is formed with the predominant content (45–60%) of a *trans*-isomer of methylphenylcyclohexasiloxane.

The use of cation exchanger Purolite CT 175, as in the case of diethoxydimethylsilane, appeared to be more effective than the addition of acetyl chloride and led to the complete conversion of alkoxy groups in 5 h at room temperature and in 3 h at 50 °C (entries 3 and 5, respectively). In contrast to diethoxydimethylsilane, an increase in the monomer concentration in the reaction mixture afforded a reduction in the reaction time required for the complete conversion of alkoxy groups from 5 to 3 h and from 3 to 1 h at room temperature and 50 °C, respectively (entries 4 and 6, respectively). Regardless of the reaction conditions, only methylphenylcyclosiloxanes were

formed, with the predominant content of *trans*-isomers of six- and eight-membered rings (~85%).

The use of acetyl chloride leads to an intermediate result: at room temperature, A_3 , A_4 , and A_5 rings are formed with the contents of 23, 50, and 17%, respectively, while upon refluxing their contents compose 8, 66, and 13%, respectively. This result is likely to be associated with a higher rate of hydrolysis of acetoxy groups and promotion of the condensation processes at early stages of chain formation when using the catalysts, which leads to the formation of rings by intramolecular cyclization, in contrast to the reactions with the addition of alcohol, which ensures rapid hydrolysis of the resulting acetoxy groups and stabilization of oligomers with terminal hydroxy groups capable of both intra- and intermolecular condensation. This is supported by the composition of the cyclic products formed during the polycondensation of diethoxy(methyl)phenylsilane in the presence of acetyl chloride.

Conclusions

The effect of catalytic additives of acetyl chloride and sulfonic cation exchanger on the polycondensation of diethoxy(methyl)phenylsilane in an active medium was investigated. The possibility of intensifying the process with the predominant formation of cyclic methylphenylsiloxanes was shown. The results obtained indicate the prospects of using cation exchanger Purolite CT 175 for the directed production of cyclic oligomethylphenylsiloxanes.

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Table 1. Effect of the catalysts on the polycondensation of DEMPS in an active medium

Entry	Ratio of the reagents		T , °C	Time for the complete conversion, h	Contents of the volatile products (GLC), %			Non-volatile products		Ratio of the cyclic/linear products, %
	MePhSi(OEt) ₂ /AcOH, mol/mol	Catalyst, wt %			A_3 <i>cis/trans</i>	A_4 <i>cis/trans</i>	A_5 <i>cis/trans</i>	%	M_p (GPC)	
1	1/10	AcCl, 1	25	72	20/3	4/46	10/7	10	2300	90/10
2	1/10	AcCl, 1	120	2	2/6	7/59	8/5	13	1200	87/13
3	1/10	Purolite, 10	25	5	7/34	6/53	–	–	–	100/0
4	1/3	Purolite, 10	25	3	7/33	6/54	–	–	–	100/0
5	1/10	Purolite, 10	50	3	6/28	7/59	–	–	–	100/0
6	1/3	Purolite, 10	50	1	6/30	7/57	–	–	–	100/0
7	1/3	Purolite, 1	50	3	9/39	5/47	–	–	–	100/0
8 [3]	1/10	–	120	6	11	16	–	73	1600	27/73
9 [3]	1/10/3.25 (EtOH)	–	120	8	–	25	60	15	1300	15/85

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