METHOD FOR PRODUCTION OF MQ RESINS BEARING ALCOHOL GROUPS

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Abstract

The reaction of bis(β-oxyethoxymethyl)tetramethyldisiloxane with tetraethoxysilane in an active medium affords MQ resins bearing $MeC(O)OCH_2CH_2OCH_2SiMe_2O$ ester groups. Their analogs with (acetoxymethyl)dimethylsiloxane M units are derived from (acetoxymethyl)(ethoxy)dimethylsilane, acetoxy(acetoxymethyl)dimethylsilane, and bis(acetoxymethyl)-tetramethyldisiloxane. The methanolysis of these resins affords polyols with SiO_2 and $OSiMe_2ROH$ moieties, where R = CH_2, $CH_2OCH_2CH_2$.

Key words: MQ resins with ester groups, metanolysis, polyols.
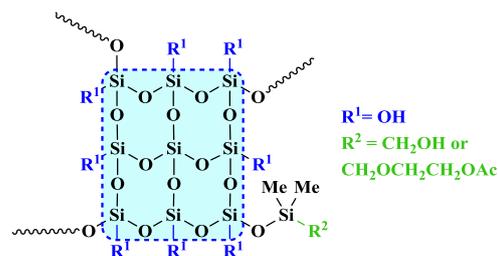
Introduction

MQ resins that consist of mono- (M) and quad-functional (Q) siloxane units attract continuous attention of researchers [1]. A peculiarity of these systems is the complete absence of insoluble cross-linked structures even after prolonged high-temperature condensation, although their average functionality is usually above 2.5 and they are soluble in both organic solvents and polydimethylsiloxanes [2–6]. MQ resins can serve as versatile modifiers for organosilicon polymers and improve the properties of all compositions [7–9]. Their additives can play different roles, varying from strengthening of elastomers to regulation of adhesiveness and creation of glues and antiadhesive coatings sensitive to pressure. Most of the investigations in this field are devoted to methyl-substituted MQ resins [10, 11]. However, of particular interest are functionalized polymers of this type. Nowadays, the copolymers bearing vinyl and hydride functional groups in M units are known [12–14]. The introduction of a new type of functional groups into the composition of MQ resins may extend their application scope owing to both the appearance of new properties and the possibility of their application as intermediate products for further transformations and in the compositions based on organic polymers. The goal of this work was to study the possibility of production of MQ resins having alcohol groups in M units as potential semiproducts for further interaction with organic compounds. It was assumed that an efficient synthetic approach to these compounds could be based on the polycondensation of alkoxy-functionalized precursors in an active medium of anhydrous acetic acid [15].

Results and discussion

At the first step, bis(β-oxyethoxymcethyl)tetramethyl-disiloxane, $HOCH_2CH_2OCH_2SiMe_2OSiMe_2CH_2OCH_2CH_2OH$, was used as a source of M units at the M:Q ratio equal to 1:1. The reaction was carried out in the presence of a catalytic amount of hydrochloric acid.

The preliminary experiments showed that a viscous transparent oligomer, obtained after the removal of acetic acid, contains ester groups. Its ^1H NMR spectrum displays the signals in the range of glycolic group methylene units that can be attributed to both $CH_2OC\underline{H}_2C\underline{H}_2OH$ (3.53, 3.70 ppm) and $CH_2OC\underline{H}_2C\underline{H}_2OC(O)Me$ (3.60, 4.20 ppm) [16] with 1:4 approximate ratio of these groups. This means that the reaction in the active medium leads to esterification of most of the hydroxy groups.

$$Si(OEt)_4 + [HOCH_2CH_2OCH_2SiMe_2]_2O \xrightarrow{MeCOOH}$$
$$\longrightarrow [SiO_2]O_{0.5}SiMe_2CH_2OCH_2CH_2OC(O)Me$$
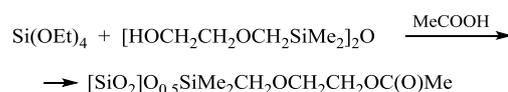
The content of acetoxy groups defined by saponification composed 20.94%, which is in agreement with the NMR spectroscopic data.

As a rule, MQ resins are tested for the content of residual ethoxy and silanol groups. A typical content of silanol groups in MQ resins, ranging within 2.0–2.5%, means for the resin of a general formula $\{[Me_3SiO_{0.5}][SiO_2]\}$ that 5 M units are accounted for one silanol group [17, 18].

The MQ resin with SiOH:M = 8:1000 was obtained by the hydrolytic condensation of tetraethoxysilane with trimethylchlorosilane [6], Note that the content of trimethylchlorosilane was equivalent to 8% of HCl. However, in our case, an increase in the catalyst loading to the same values did not lead to the desired effect (see Table 1). Along with the signals of $OC\underline{H}_2SiMe_2$ groups (δ = 3.2 ppm), the spectra of the

resulting oligomers demonstrated also the signals at *ca.* 2.8 ppm which correspond to the protons of ClCH$_2$SiMe$_2$O units [19].

To estimate the content of residual silanol groups, we used the method of trimethylsilylation (treatment of the oligomers with trimethylchlorosilane in the presence of pyridine) [20] according to the following scheme:

$$Me_3SiOH + ClSiMe_3 \xrightarrow{Py} Me_3Si{-}O{-}SiMe_3$$
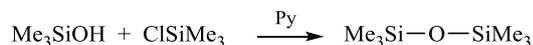
The analysis of the ^{1}H NMR spectra allowed us to define the ratio of M and trimethylsiloxy units (Mt).

It is obvious from Table 1 that an increase in the amount of hydrochloric acid leads to an increase in an integral intensity of the signal with δ = 2.8 ppm, rather than to an increase in a condensation degree. The ratio of intensities of the signals with δ = 2.8 (**A**) and 3.2 (**B**) ppm indicates the degree of ester group cleavage. The analysis of the oligomer obtained in the presence of 8% of hydrochloric acid revealed the presence of 3.4% of chlorine. It was shown earlier [21] that hydrochloric and sulfuric acids almost do not differ in the catalytic activities during the synthesis of MQ resins; therefore, some reactions were carried out in the presence of sulfuric acid.

The results of the performed investigations are summarized in Table 1.

Table 1. Effect of the nature and loading of the catalyst on some characteristics of the MQ resins bearing β-oxyethoxymethyl groups in M units

Cat.	Cat. wt %	Residual EtO groups, % of M	Mt:M	**A:B**
HCl	1.5	0.79	0.46:1	1:18
	8	0.55	0.38:1	1:4.6
H$_2$SO$_4$	1.5	0.70	0.29:1	–
	8	0.5	0.26:1	–

Since the synthesis in the active medium is accompanied by acetylation of alcohol groups, the resin with oxymethyl groups was obtained starting from acetoxymethyl derivatives.

In this case, three compounds can serve as a source of M units: (acetoxymethyl)(ethoxy)dimethylsilane MeC(O)OCH$_2$SiMe$_2$OEt (**1**), acetoxy(acetoxymethyl)-dimethylsilane MeC(O)OCH$_2$SiMe$_2$OC(O)Me (**2**), and bis(acetoxymethyl)tetramethyldisiloxane [MeC(O)OCH$_2$SiMe$_2$]$_2$O (**3**).

To assess the potential of these monomers, the effect of the following parameters on the content of residual ethoxy and silanol groups (Mt:M ratio) in the presence of 1.5% of sulfuric acid was studied: the nature of the M unit source and the excess of acetic acid. The results are presented in Table 2.

The data in Table 2 show that the effects of the excess of acetic acid and the nature of the acetoxy derivative are insignificant, but, with all minuteness of the differences, the use of acetoxy(acetoxymethyl)dimethylsilane seems to be preferential.

The effect of the amount of sulfuric acid on the content of residual ethoxy and silanol groups at different ratios of M and Q units of the oligomers based on acetoxy(acetoxymethyl)-dimethylsilane is presented in Table 3.

Table 2. Effect of the excess of acetic acid on the content of residual ethoxy and silanol groups in the oligomer. Figures **1**, **2**, and **3** correspond to the initial monomers (*vide supra*)

	Excess of acetic acid, %	Residual EtO groups, % of M	Mt:M	Yield, %
1	60	0.9	0.27:1	88
	250	0.7	0.23:1	88
2	60	0.6	0.21:1	95
	250	0.6	0.20:1	90
3	60	0.6	0.24:1	90
	250	0.6	0.21:1	90

Table 3. Dependence of the content of residual silanol groups in the oligomer on the catalyst loading and the ratio of M and Q units

H$_2$SO$_4$, wt %	M:Q	τ, h	Residual EtO groups, % of M	Mt:M	Resulting (M+Mt):Q ratio
0.5	1:1	15	0.85	0.23:1	1:0.81
	1:1.5	15	1.01	0.56:1	1:0.96
1.0	1:1	15	0.7	0.25:1	1:0.8
	1:1.5	15	0.95	0.42:1	1:1.06
2.0	1:1	15	0.3	0.21:1	1:0.83
		7	1.6	0.41:1	1:1.06
	1:1.5	15	1.6	0.37:1	1:1.09
		30	0.6	0.34:1	1:1.12
	1:3	15	5.1	0.87:1	1:1.61
4.0	1:1.5	15	0.9	0.34:1	1:1.12
	1:3	15	0.7	0.71:1	1:1.75

As can be seen from Table 3, the higher the content of Q units, the higher the content of residual silanol groups in the oligomers, other conditions being equal. Their content can be reduced by an increase in the time of heating or an increase in the amount of the catalyst in the system, but the effect of these manipulations is insignificant.

To obtain the target polyols, the oligomers bearing ester groups were treated with methanol in the presence of a catalytic amount of hydrochloric acid. It was shown earlier that in the case of cyclic derivatives of a general formula {PhSiO[OSiMe$_2$CH$_2$OCH$_2$CH$_2$OC(O)Me]}$_n$, where n = 6 or 12, the methanolysis proceeds without affecting a siloxane backbone of the molecule [15].

The ^{1}H NMR spectra of the products of methanolysis of β-acetoxyethoxymethyl derivatives revealed the absence of the signals at 3.60 and 4.40 ppm, which correspond to the acetylated glycol moiety, and the lack of the signal at 2.02 ppm, which corresponds to the methyl group of the acetoxy moiety. In turn, the signals at 3.53 and 3.70 ppm relating to CH$_2$OCH$_2$CH$_2$OH fragment were detected. In the case of the oxymethyl derivatives, the signals of SiCH$_2$OC(O)Me (3.73 and 2.02 ppm, respectively) disappeared and the signal at 3.31 ppm arose that corresponds to the protons of the oxymethyl group at the silicon atom.

Based on the MQ resins with [SiO$_2$][O$_{0.5}$SiMe$_2$CH$_2$OCH$_2$CH$_2$OH] elementary units, a series of network polymers were obtained. The linear components in use were 2,4-toluene diisocyanate (2,4-TDI), macrodiisocyanates based on oligobutylene oxide or an organosilicon diol of the following formula HOCH$_2$CH$_2$OCH$_2$SiMe$_2$[OSiMe$_2$]$_9$CH$_2$OCH$_2$CH$_2$OH and 2,4-

TDI. Solution casting at the NCO:OH ratio of 1.1:1 afforded polymer films with gel fractions of 99%, 92%, and 83%, respectively.

Experimental

^{1}H and ^{29}Si NMR spectra were registered with a Bruker Avance 400 spectrometer at 400.13 and 79.49 MHz for ^{1}H and ^{29}Si nuclei, respectively. For the quantitative measurement of the intensities of ^{29}Si signals, the spectra were recorded in a pulse suppression mode with long delays of 25 s, which excludes the nuclear Overhauser effect. The solutions in acetone-d_6 were used. The chemical shifts were measured relative to TMS. The spectra were registered at 298 K.

GPC analysis was carried out using a Shimadzu system (Japan, Germany), a RID-20 A refractive index detector, an SPD-M20A photodiode array detector, a Phenogel 500A column with the sizes of 300×7.8 mm, and THF as a solvent at 40 °C with the flow rate of 1 mL/min.

Synthesis of MQ resins. A stirred mixture of acetic acid, tetraethoxysilane, bis(β-oxyethoxymethyl)tetramethyldisiloxane, acetoxy(acetoxymethyl)dimethylsilane, (acetoxymethyl)(ethoxy)dimethylsilane, or bis(acetoxymethyl)tetramethyldisiloxane, and the catalyst was refluxed for 15 h. After cooling to room temperature, sodium acetate was added, and the resulting solution was stirred for 30 min. After quenching of the catalyst, the target polymer was precipitated with 5-fold excess of water, dissolved in ethyl acetate, and dried over anhydrous sodium sulfate. The resulting solution was filtered and evaporated to the constant mass. Below are two examples of the synthesis of the MQ resins with M:Q = 1:1.

Synthesis of the oligomer bearing β-oxyethoxymethyl substituents in M units. A mixture of bis(β-oxyethoxymethyl)tetramethylsiloxane (5.64 g, 0.02 mol), tetraethoxysilane (8.33 g, 0.04 mol), acetic acid (15 mL, 60% excess), and HCl (0.22 g, 0.5 mL of hydrochloric acid with the density of 1.18 g/mL) was refluxed with a backflow condenser for 15 h. After cooling to room temperature, sodium acetate (0.6 g) was added. In 30 min, the target polymer was precipitated with water (65 mL), dissolved in ethyl acetate, and dried over anhydrous sodium sulfate. The resulting solution was filtered and evaporated to the constant mass to afford a colorless viscous residue. Yield: 8.17 g (88%).

Synthesis of the oligomer bearing acetoxymethyl substituents in M units. A mixture of acetoxy(acetoxymethyl)dimethylsilane (3.52 g, 0.02 mol), tetraethoxysilane (4.16 g, 0.02 mol), acetic acid (17 mL, 250% excess), and concentrated sulfuric acid (0.12 g) was refluxed with a backflow condenser for 15 h. After cooling to room temperature, sodium acetate (0.3 g) was added. In 30 min, the target polymer was precipitated with water (85 mL), dissolved in ethyl acetate, and dried over anhydrous sodium sulfate. The resulting solution was filtered and evaporated to the constant mass to give a colorless viscous residue. Yield: 3.6 g (90%).

Methanolysis was carried out according to the published procedure [12].

Conclusions

The performed investigations showed that during the synthesis of MQ resins based on tetraethoxysilane and bis(β-oxyethoxymethyl)tetramethyldisiloxane in an active medium, acetylation of the major part of hydroxy groups takes place.

The MQ resins with (acetoxymethyl)dimethylsiloxane frameworks were obtained by the interaction of tetraethoxysilane with acetoxy(acetoxymethyl)dimethylsilane, (acetoxymethyl)(ethoxy)dimethylsilane, or bis(acetoxymethyl)tetramethyldisiloxane. The optimal catalyst for these processes appeared to be sulfuric acid.

The methanolysis of the resulting esters afforded polyols bearing alcohol groups in the organic substituents, which interaction with diisocyanates resulted in the network polymers.

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