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Synthesis and properties of MQ resins with phenyl groups in monofunctional units

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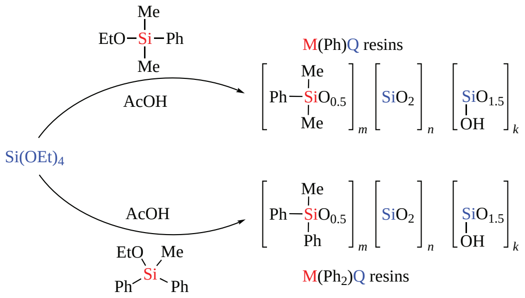
MQ resins have been prepared in acetic acid as an active medium from dimethylphenyl- or methyldiphenylethoxysilane as the M-components and tetraethoxysilane as the Q-component. All prepared samples with M/Q ratios of 1 : 1, 1 : 1.5, 1 : 2, 1 : 3, and 1 : 4 were well soluble in organic solvents like toluene and THF. Compared to MQ resins with trimethylsilyl group as the M-component, the new MQ resins with phenyl substituents may possess improved compatibility to thermoplastic polymers, rubbers and coating formulations.



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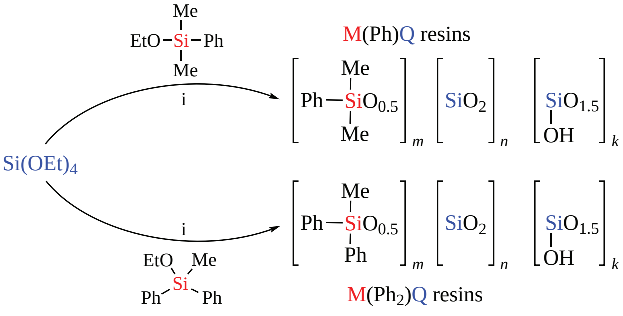
Currently MQ copolymers, often called MQ resins,[1] are produced in many countries around the world and are an important component of modern composite materials with improved physical and mechanical properties, thermal stability, and adhesive properties.[2–6] MQ stands for the co-condensation of M[$R_3SiO_{0.5}$] and Q[SiO_2] units in the structure of the polymer. Such copolymers are obtained by co-condensation of tetraethoxysilane (TEOS) and monofunctional triorganoalkoxysilane. Although their average functionality is usually higher than 2.5, it is a peculiar feature of the co-condensation, that polycyclic and highly branched structures are formed with finite growth even during prolonged high-temperature condensation. Because of their small size in the range of less than a few nanometers, their rather well-defined molecular weight, and their solubility in organic solvents, it is justified to describe MQ resins as globular macromolecules. Hence, they present a macromolecular inorganic/organic hybrid structure constituted by both silica and organic building units.

Methyl-substituted MQ copolymers have been studied rather broadly.[7–11] They have a wide range of practical applications, mainly as modifying additives, regulating the properties of polymer compositions,[12–14] mostly taking advantage of the high molecular miscibility of the MQ copolymer with the respective polymer. However, there is a significant number of macromolecular compounds which are not compatible with methyl-substituted MQ copolymers. Replacing the methyl substituents in the MQ copolymers by other organic groups offers the prospect for new compatibilities of this class of globular copolymers and broadens their field of applications. Literature references on phenyl containing MQ copolymers are fragmentary.[7,15] This raises the need for a systematic study of the structure–property relationship when the methyl groups in MQ copolymers are replaced by other substituents with a focus on the formation of alike globular macromolecules. The aim of this work was to synthesize and to study the properties of MQ resins containing phenyl and diphenyl substituents at the silicon atom in M-units.

The synthesis of MQ resins was carried out by hydrolytic co-polycondensation of tetraethoxysilane and dimethylphenyl- or methyldiphenylsilane in acetic acid as an active medium.[16] We reported the scope and versatility of the synthesis of polyorganosiloxanes of various composition and structure in acetic acid[7,17,18] as one of the chlorine-free approaches.[19–26] The synthesis of MQ copolymers in general is outlined in Scheme 1. For more synthetic details including a description of optimized methods for the synthesis of dimethylphenyl- and methyldiphenylethoxysilanes by the Grignard reaction, see Online Supplementary Materials.

Table 1 lists a series of MQ copolymers which we synthesized either with dimethylphenylsiloxane [M(Ph)Q] or with methyldiphenylsiloxane [M(Ph_2)Q] as the M-units. Both phenyl and diphenyl containing MQ resins with the M/Q ratio of 1 : 1 and



Scheme 1 *Reagents and conditions*: i, AcOH, 120 °C, 10–20 h.

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Table 1 Composition and properties of MQ resins samples.

Sample	M/Q, theor.[a]	Elemental analysis data (calc./found)			M/Q, found[b]	OH groups (wt%)[c]	M_W (SEC)	Yield (%)	T_g/°C
		Si (%)	C (%)	H (%)					
M(Ph)Q resin									
1	1:1	27.5/27.3	47.3/47.1	5.4/5.5	1:1.0	3.3	1500	90	–50
2	1:1.5	30.0/29.6	41.2/41.3	4.7/4.7	1:1.5	4.3	2000	87	0
3	1:2	31.9/31.6	36.5/36.2	4.2/4.3	1:1.72	4.3	2800	77	100
4	1:3	34.6/34.2	29.7/29.2	3.4/3.6	1:2.73	6.1	10000	70	$>T_d$[d]
5	1:4	36.5/32.3	25.0/25.2	2.8/3.5	1:4.6	8.4	53000	51	$>T_d$
$M(Ph_2)Q$ resin									
6	1:1	21.1/21.1	58.9/58.4	4.9/5.1	1:1.0	3.6	2000	86	–20
7	1:1.5	23.7/23.2	52.8/52.2	4.4/4.6	1:1.28	8.2	3300	80	–5
8	1:2	25.8/25.4	48.0/47.9	4.0/4.2	1:2.45	4.3	4400	85	0
9	1:3	29.1/25.3	40.5/41.2	3.4/4.6	1:2.7	7.3	7000	65	$>T_d$
10	1:4	32.5/29.3	33.0/33.3	2.3/3.4	1:4.9	13.2	25000	55	$>T_d$

[a] From the ratio of starting components. [b] From ^{29}Si NMR. [c] From ^{1}H NMR for dimethylvinylsilane-blocked samples. [d] T_d is decomposition temperature.

1:1.5 were viscous liquids. With an increase in the silica component, the copolymers turned out to be solids (white glassy powders) except sample **8** being a soft and sticky material.

Most importantly, in the course of preparations with larger fraction of Q (1:2 to 1:4) gels were not formed but soluble substances were obtained. In contrast to the preparation with the phenylsilanes, trimethylsilyl-MQ resin synthesis at such M/Q ratios always leads to macroscopic gelation. The phenyl MQ resins with M/Q units ratio of 1:3 and 1:4 remained completely soluble in organic solvents like toluene, THF and others. Elemental analysis as well as the ratio of ^{29}Si-NMR signal intensities for M and Q-units in the condensation products were in agreement with the feed ratios of the reagents. Together with the observed solubility, this indicates that intermolecular linking of the growing molecules got sterically limited by the incorporation of the M-units in the late stages of the condensation reaction. This restriction is the cause of a finite growth of the molecular particles. Only for increased Q-unit content, we observed larger deviations in favor to the Q-content, indicating some incomplete conversion of the M-monomer product and corresponding to losses upon washing (see yields in Table 1).

Finite growth and the resulting molecular character of the MQ condensates are confirmed by size exclusion gel permeation chromatography (GPC) of different samples. Increase in the Q-unit content affords copolymers with higher molecular weight and broader molecular weight distribution (Figure 1, Table 1). For the $\langle M_w \rangle$ values listed in Table 1, we employed calibration by linear polystyrene standards. Taking into account a globular structure of the MQ condensates, their absolute molecular weights should be higher. Thus, reported molecular weight values can only demonstrate their relative changes within this particular set of samples.

So far, we demonstrated that the replacement of methyl groups by phenyl groups within the M-units can limit the growth reaction and screen the Q-units against intermolecular condensation at high conversion, the former get enriched in the shell of the growing globular molecules and, thus screen silanol groups inside from intermolecular condensation. Such a core–shell growth, however, requires a rather controlled nucleation and growth mechanism by which a fast nucleation phase is followed by a slowed down growth phase, which means the kinetic control. We achieved such a kinetic control by two factors: (i) improved steric screening by phenyl groups in place of methyl groups, and (ii) the active media approach of alkoxysilane synthesis providing equalization of reactivity of M and Q monomers.[7,16,27] The latter slows down the rates of the condensation reactions compared to acid catalyzed hydrolytic condensation.

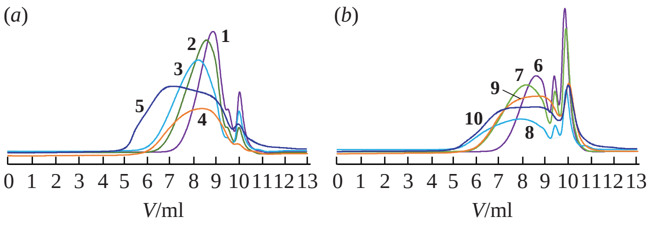

Figure 1 GPC curves of (*a*) M(Ph)Q resins **1**–**5** and (*b*) $M(Ph_2)Q$ resins **6**–**10**, respectively, with different M/Q ratios.

The general observations discussed so far hold for both groups of condensates, *i.e.*, those with diphenyl and those with monophenyl M-groups. A closer look at the data reveals noticeable differences for the two groups of copolymers. In the case of $M(Ph_2)Q$ resins, molecular weights appear to increase less at high fraction of Q-monomers than in the case of the M(Ph)Q resin. At the same time, we also observed a significantly higher amount of residual OH groups for the resin **10** compared to resin **5** despite former's lower molecular weight. Such observation is in agreement with steric shielding by the phenyl substituents, which prevented extensive intermolecular condensation. In the late stages of the reaction even intramolecular condensation was impeded indicated by the observation that the intramolecular network became less dense. This observation is in good agreement with the core–shell growth mechanism discussed above.

To characterize the transition from a liquid to a solid, observed at increasing Q content, we performed indentation thermomechanical analysis (TMA) experiments (Figure 2). Solid samples (M/Q = 1:2, 1:3, 1:4) were prepared by compression under ambient conditions. Liquid samples were first solidified in the device by cooling before recording the indentation upon raising temperatures. The indentation experiments shown in Figure 2 could be reproduced in repeated heating scans as long the sample was not heated above 250 °C and decomposition was excluded.[28]

The data demonstrate the transition from a glassy solid to a viscous fluid for **1** and **2** at –50 and 0 °C, respectively. For **6** and **7** liquid yielding set occurred at –20 and –5 °C. When the M/Q ratio was decreased to 1:2, we observed the onset of flow at higher temperatures (100 °C for **3** and 0 °C for **8**). Indentation, however, ceased at $\varepsilon = 50\%$. Even for the solid products obtained with M/Q ratios of 1:3 and 1:4, we observed some yielding around ambient temperature, which in case of the $M(Ph_2)Q$ resin was followed by a second yielding step at about 100 °C.

The thermomechanical characterization confirms that the MQ resins prepared with a small Q-content are molecular liquids with a defined and reversible glass transition. For the samples with the higher Q content, we may explain the partial yielding by

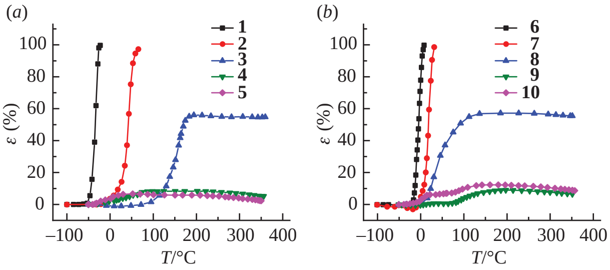

Figure 2 TMA data for (*a*) M(Ph)Q and (*b*) M(Ph_2)Q resins **1**–**10**, respectively; ε denotes the relative penetration of a pin at a constant load of $\sigma = 0.2$ MPa into a disc sample. Measurements were done at increasing temperatures with a heating rate of 5 K min^{-1}.

the broad molecular weight distribution and the corresponding composition of a more liquid and a more solid fraction.[7] Higher molecular weights correspond to globular granules which in combination with the liquefied smaller molecular weight fraction allow partial yielding.

The results so far demonstrated the formation of MQ resin molecules with properties at the borderline between small colloidal particles and macromolecules, whose solubility is mediated by the phenyl substituents. This raises the question whether such MQ resins can be blended into a polymer melt. Figure 3 depicts first blending studies, in which we mixed resins **1**, **5** and **6**, **10** into an injection molding grade polystyrene ($M_w = 250.000$ D, $M_n = 50.000$). The optical micrographs demonstrate homogeneous blend, and improved clarity for the blends with the M(Ph_2)Q resins.

Thus, we demonstrated well controlled formation of MQ resins with one or two phenyl substituents in the M-units. In combination with the improved steric shielding by the phenyl groups compared to methyl units, the active media process, which we employed, allowed a rather rigorous control of the molecular weights, superior to what is known for trimethylsilyl MQ resins. By the choice of the M/Q ratio, we could prepare very small globular macromolecules, but also much larger colloidal particles. Infinite growth leading to gelation could be prevented even for M/Q ratios as high as 1 : 4, which demonstrates rather rigorous steric limitation of the condensation reaction and indicates the formation of core shell colloids with a Q rich core. Further studies on narrow fractions of these samples will provide additional data for more thorough analysis of composite nature of phenyl-substituted MQ resins. First blending studies with polystyrene showed the potential of the phenyl-modified MQ resins for the modification of polymers. Such transparent blends might be of particular interest for the formulation of clear coatings.

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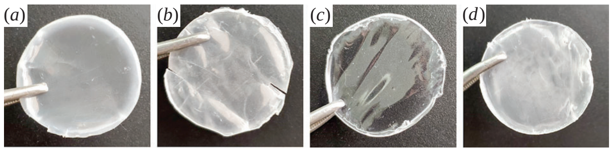

Figure 3 Blends of polystyrene ($M_w = 250.000$ D, $M_n = 50.000$) with 10 wt% of resins (*a*) **1**, (*b*) **5**, (*c*) **6** and (*d*) **10**. Thickness of the films is 0.2 mm.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2022.03.003.

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