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One-Pot Synthesis of Hyperbranched Polyethoxysiloxanes

Xiaomin Zhu, Manfred Jaumann, Karin Peter, and Martin Möller*

Deutsches Wollforschungsinstitut an der RWTH Aachen, Pauwelsstrasse 1, D-52074 Aachen, Germany

Claudiu Melian, Alina Adams-Buda, Dan E. Demco, and Bernhard Blümich

Institut für Technische und Makromolekulare Chemie, RWTH Aachen, Worringer Weg 1,
D-52074 Aachen, Germany

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ABSTRACT: Hyperbranched polyethoxysiloxanes were prepared via a one-pot synthetic route based on a condensation reaction of tetraethoxysilane with acetic anhydride in the presence of an organotitanium catalyst. Volatile compounds can be fully removed using a thin-film evaporator. According to size-exclusion chromatography and viscosity measurements, the average molecular weight as well as the molecular weight distribution of the products increased exponentially by increasing the molar ratio of acetic anhydride to tetraethoxysilane from 1.0 to 1.2. At the molar ratio 1.3, a solid gel was formed. The liquid products are stable and hydrophobic; they are miscible with most organic solvents. ^{29}Si NMR spectroscopy and MALDI-ToF mass spectrometry show that they have a hyperbranched structure with additional internal loop formation.

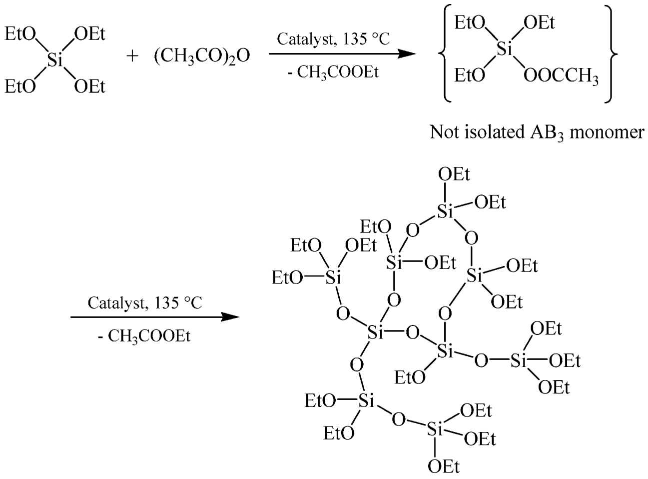
Introduction

Hyperbranched polymers are considered a fast growing field in polymer science. In comparison with their linear analogues, these polymers exhibit lower melt viscosities and much higher solubility. At the same time, they possess a large number of "surface groups" that can readily be functionalized. Furthermore, their preparation is much more economical than the multistep synthesis of flawless branched dendrimers. Because of their unique properties, current research activities in the field of hyperbranched polymers nowadays are broad.[1,2]

The formation of hyperbranched polymers was first described by Flory[3] as a special type of polycondensation when AB_x monomers are condensed, where only the cross-coupling of A and B functionalities is possible. This process has the typical features of a step growth reaction of multifunctional monomers, however, without the danger of cross-linking. Hyperbranched polymers prepared in this way bear a large number of unreacted B functions, but only one A focal function unit. If a "core" molecule B_x is added, mainly for a better control over the molar mass but also for a control of the resulting geometrical shape, no A function will be present.[2,4] Preparation of hyperbranched polymers from a combination of A_2 and B_3 monomers instead of the often commercially not available AB_x has been published;[5] silicon-containing hyperbranched polymers were also prepared by this means.[6] However, these reactions can hardly be controlled; hence, it is difficult to obtain fully soluble or liquid products of high molecular weight.

Silicon is a very important building element for the dendritic polymers due to the versatility of organosilicon chemistry.[7−9] Among various silicon-containing polymers, polyethoxysiloxanes (often named "ethylsilicates" or "condensed ethylsilicates") are of increasing technological interest as processable precursors for silica.[10] Typically they are condensation products of tetraethoxysilane (TEOS) with water, and the products obtained contain silanol groups, which can undergo further condensation and thus cause aging and changes in the properties upon storage.[11] Previously, we have published the controlled synthesis of hyperbranched polyethoxysiloxanes (PEOS) from triethoxysilanol and acetoxytriethoxysilane AB_3 monomers.[12] Compared to "ethylsilicates" synthesized via hydrolytic condensation of TEOS, the polymers synthesized from these AB_3 monomers do not contain any hydroxyl groups. Hence, they are stable upon long-term storage. However, the synthesis of AB_3 monomers required a complicated purification process, which makes these routes unsuitable for a large scale production. We have already demonstrated that condensation of acetoxytriethoxysilane, which was obtained by monoacylation of TEOS using acetic anhydride, led to the formation of PEOS.[12] Yet, the AB_3 monomer acetoxytriethoxysilane was prepared and isolated in the first step at 137 °C, before the hyperbranched PEOS was obtained in the second step. For each step more than 30 h was required to complete the reaction. Here we present a controlled one-pot synthesis of PEOS based on the catalyzed condensation reaction of TEOS with acetic anhydride. It is demonstrated that this reaction allows a distinct molar mass control of the product.

Scheme 1. One-Pot Synthesis of Polyethoxysiloxanes (PEOS) via a Catalytic Condensation Reaction of Tetraethoxysilane (TEOS) with Acetic Anhydride



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* To whom correspondence should be addressed. E-mail: moeller@dwi.rwth-aachen.de.

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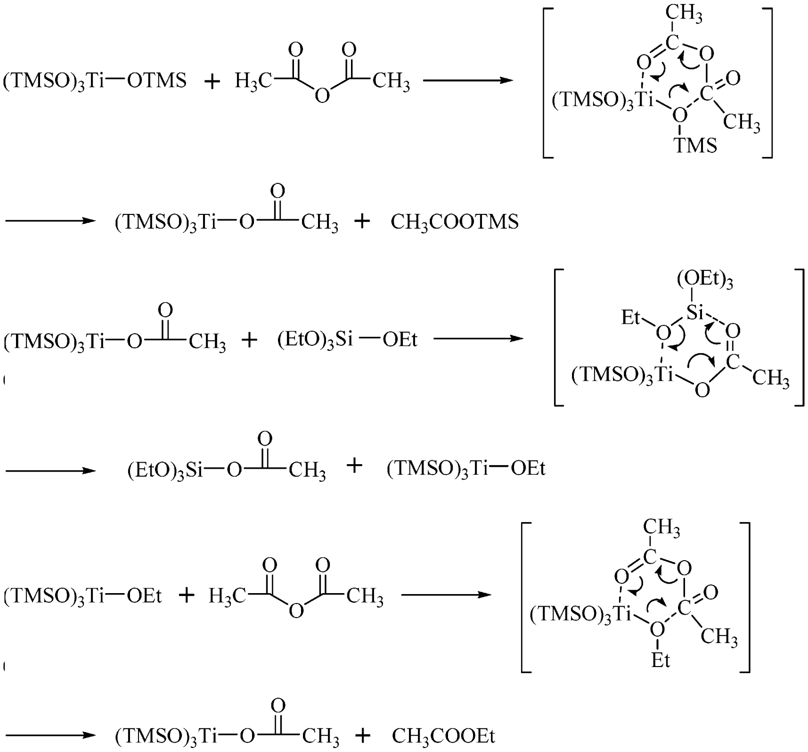
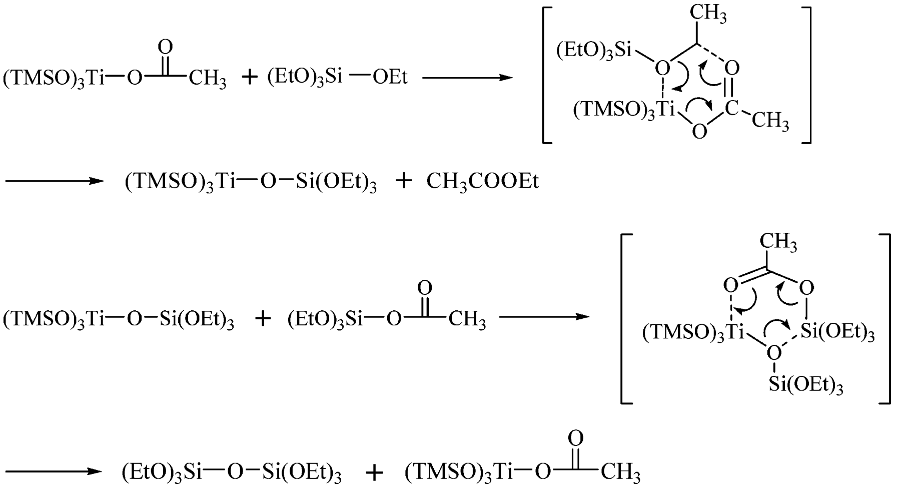
Scheme 2. Proposed Mechanism of the Monoacylation of TEOS with Acetic Anhydride Catalyzed by Organotitanium[a]



[a] TMSO = trimethylsiloxy group.

Scheme 3. Proposed Mechanism of Reaction between Acetoxysilane and Ethoxysilane Catalyzed by Organotitanium[a]



[a] TMSO = trimethylsiloxy group.

Experimental Section

Materials. Tetraethoxysilane (for synthesis, Merck), acetic anhydride (for synthesis, Merck), and titanium trimethylsiloxide (ABCR) were used without further purification. Argon (Technical Grade, Air Products) was dried over a 5 × 50 cm^2 column filled with silica gel and molecular sieves 0.4 nm.

Synthesis. Tetraethoxysilane was mixed with acetic anhydride and titanium trimethylsiloxide under an argon atmosphere in a 2 L three-neck round-bottom flask equipped with a mechanical stirrer and a 30 cm dephlagmator connected with a distillation bridge. The mixture was heated to 135 °C in a silicon oil bath under intensive stirring. The resulting ethyl acetate was continuously distilled off. The supply of heat was continued until the distillation of ethyl acetate stopped. Afterward, the product was cooled to room temperature and dried in a vacuum for 5 h. A yellowish oily liquid was obtained.

The volatile compounds were completely removed with a vacuum thin-film evaporator (type S 51/31; Normag; Germany) equipped with a rotary vane vacuum pump (model RZ-5; Vacubrand; Germany), magnetic coupling (Buddelberg; Germany) for the stirrer (model RZR 2020, Heidolph, Germany) operating at the highest level 10, and a heating device. The operating temperature was 150 °C, and the pressure was (1−2) × 10^{-2} mbar.

Characterization. Thermogravimetric analysis (TGA) measurements were performed using a NETZSCH TG 209c unit operating under a nitrogen atmosphere. 10−15 mg of the sample was placed in standard NETZSCH alumina 85 μL crucibles and heated at 10 K min^{-1}.

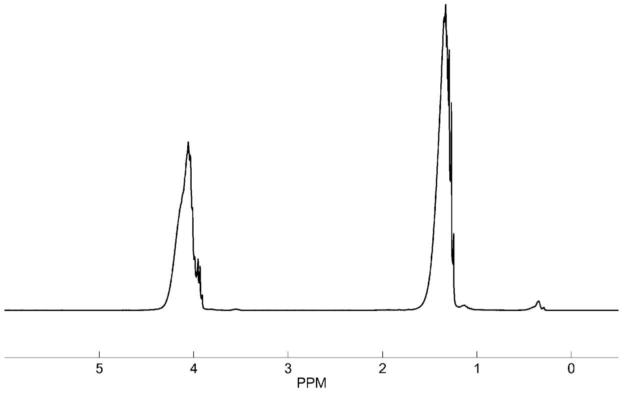
^{1}H NMR (300 MHz) spectra were recorded on a Bruker DPX-300 NMR spectrometer using tetramethylsilane as an internal standard. Solid-state ^{1}H NMR (500 MHz) spectra were recorded on a Bruker DSX-500 NMR spectrometer under 5 kHz magic-angle sample spinning using tetramethylsilane as an internal standard.

Solid-state ^{29}Si NMR spectra were obtained with a Bruker DSX-500 NMR spectrometer operating at 99.362 MHz in static conditions (for liquid samples) or under magic-angle sample spinning (for solid

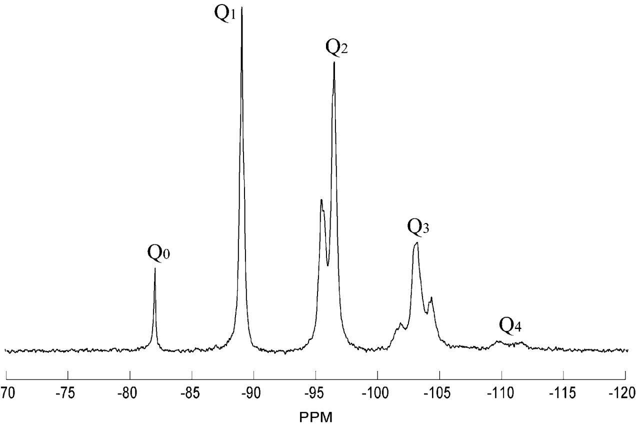
Table 1. Relative Contents of Different Building Units of PEOS Obtained at Different Molar Ratio of Acetic Anhydride to TEOS (*f*)

	units					
f	TEOS, Q_0 [%]	terminal, Q_1 [%]	linear, Q_2 [%]	semidendritic, Q_3, [%]	dendritic, Q_4, [%]	DB
1.00	3.5	23.6	42.1	26.9	3.9	0.48
1.05	2.8	21.9	43.1	28.4	3.8	0.49
1.10	2.0	18.9	42.6	31.7	4.8	0.51
1.15	n.d.[a]	14.2	42.4	37.3	6.1	0.55
1.20	n.d.	14.4	39.5	38.5	7.6	0.58
1.30	n.d.	10.1	42.5	41.0	6.4	0.56
theoretical[b]		29.6	44.4	22.2	3.7	0.44

[a] n.d. = not detected. [b] Following ref 15 assuming the same reactivity of the different units for coupling a new monomer, no cyclization reaction.



(a)



(b)

Figure 1. ^{1}H NMR (in C_6D_6) (a) and solid-state ^{29}Si NMR (b) spectra of PEOS obtained from a stoichiometrical one to one mixture of TEOS and acetic anhydride with 0.3 mol % of catalyst.

samples). The spectra were recorded during ^{1}H decoupling pulse of 50 ms following excitation with a 6 μs long radio-frequency pulse. For the measurements 0.015 mol/L chromium(III) acetylacetonate (purum, Fluka) was dissolved in the liquid PEOS samples as a paramagnetic relaxing agent to shorten the recycle delays to 10 s. The ^{29}Si NMR spectra were recoded at room temperature with 6000 scans and a dwell time of 20 μs. The spectra were corrected for the background signal from the probe by numerical subtraction.

Size-exclusion chromatography (SEC) analyses were conducted with a high-pressure liquid chromatography pump (LC 1120, Polymer laboratories) and an evaporative light scattering detector (PL-ELS-1000, Polymer laboratories). The eluting solvent was chloroform (für HPLC, Fisher Scientific). The flow rate was 0.8 mL/min. The sample concentration was around 5 mg/mL. The setup consisted of four MZ-DVB gel columns with the nominal pore sizes of 50, 100, 1000, and 10 000 Å. Calibration with polystyrene standards was used to estimate the molecular weight.

Zero-shear viscosity η_0 values for the liquid samples were obtained from a controlled stress rheometer (Rheometric Scientific DSR). The sample was placed on a 25 mm plate, electrically heated to the desired temperature, and the corresponding cone was lowered into position. The measurement was performed at 25 ± 0.1 °C. Following a creep analysis of the polymer melt, the zero-shear viscosity η_0 was calculated within the Burger model.

MALDI-ToF mass spectrometry measurements were conducted with a Bruker Biflex III mass spectrometer operating in the reflectron mode. The samples were mixed with a THF solution of 1,8,9-anthracenetriol and potassium trifluoroacetate under an inert gas atmosphere.

Results and Discussion

Hyperbranched polyethoxysiloxanes (PEOS) were prepared via a one-pot catalytic condensation reaction of tetraethoxysilane (TEOS) with acetic anhydride as depicted in Scheme 1. Because of the significantly higher reactivity of the first of four ethoxy groups in TEOS, only acetoxytriethoxysilane was formed. As demonstrated earlier,[12] condensation of acetoyxtrietoxysilane with itself or with TEOS was slower compared to the reaction of TEOS with acetic anhydride. In any case such a reaction will not interfere with the formation of a hyperbranched polymer without cross-linking, and the one-pot reaction can be considered a condensation of AB_3 monomer in the presence of core molecules B_4. To enhance the rate of conversion, we employed titanium trimethylsiloxide as a catalyst. Organotitanium compounds are usually used for transesterification reaction of alkoxysilanes[13] and vulcanization of room temperature vulcanizable (RTV) silicone rubber.[14]

In the case of a stoichiometrical one to one reaction mixture of TEOS and acetic anhydride with 0.3 mol % of catalyst (relative to TEOS), the reaction finished within 8 h at 135 °C. This reaction could be further accelerated by the increase of the catalyst amount. For example, it was completed within half an hour when 0.9 mol % of catalyst was added. It must, however, be noted that the catalyst remains in the product after the reaction, where it can catalyze rearrangement reactions and enhance the sensitivity of the product toward humidity. To synthesize PEOS, we therefore used only a small amount of catalyst (0.3 mol % relative to TEOS).

Comparing the reactions with and without a catalyst, we can conclude that titanium trimethylsiloxide catalyzes not only the condensation reaction but also the acylation of ethoxysilane. Scheme 2 demonstrates a reaction mechanism for the reaction of TEOS with acetic anhydride in the presence of the organotitanium catalyst. Titanates are Lewis acids, so the mechanism can be postulated whereby the nonbonding electrons of the carbonyl oxygen form a coordinative bond with the empty d-orbitals on the titanium atom. Through a six-membered cyclic transition state an active intermediate acetoxytitanium is generated. In a second step, the nonbonding electrons of the ethoxy oxygen of TEOS also form a coordinative bond with the empty d-orbitals on the metal to generate an activated complex, in

Scheme 4. Reaction of TEOS with Acetic Anhydride at Different Molar Ratio (*f*)

$$\mathrm{Si(OC_2H_5)_4} + f\,\mathrm{(CH_3CO)_2O} \rightarrow \mathrm{SiO}_f\mathrm{(OC_2H_5)}_{4\text{-}2f} + 2f\,\mathrm{CH_3COOC_2H_5}$$

which an acetoxy group exchange reaction takes place between the titanium and the silicon atoms. As depicted in Scheme 3, the active intermediate—acetoxytitanium—also catalyzes the reaction between acetoxysilane and ethoxysilane through six-membered cyclic transition states.

Figure 1a shows the ^{1}H NMR spectrum of PEOS obtained from a stoichiometrical one to one mixture of TEOS and acetic anhydride with 0.3 mol % of catalyst. The two signals correspond to CH_3 and CH_2 in the ethoxy group; there is, however, no signal of acetoxy groups detected, indicating the completeness of the condensation reaction.

The ^{29}Si NMR spectrum of the same sample showed five groups of peaks (Figure 1b). These peaks can be assigned (from left to right) to silicon atoms bearing: four ethoxy groups Q_0 (−81.74 ppm, TEOS), three ethoxy groups Q_1 (−88.70 ppm, terminal units), two ethoxy groups Q_2 (−96.1 ppm, linear units), one ethoxy group Q_3 (−102.7 ppm, semidendritic units), and no ethoxy group Q_4 (−110.0 ppm, dendritic units).[12]

The areas of the individual peaks allow the determination of the relative amounts of all different silicon atoms in the polymer. The degree of branching (DB) was calculated according to eq 1, where it is expressed as a ratio of the actual growth direction R in a macromolecule to the maximum possible growth directions $R_{\max}$.[15] The calculated DB value for the above-mentioned PEOS was 0.48 (see Table 1). This value as well as the distribution of different building units is close to the theoretical value expected for equal reactivity of all ethoxy groups.[15]

$$\mathrm{DB} = \frac{R}{R_{\max}} = \frac{2Q_4 + Q_3}{\frac{2}{3}(3Q_4 + 2Q_3 + Q_2)} \qquad (1)$$

It can be expected that an excess of acetic anhydride will improve the degree of condensation and yield eventually a cross-linked product. A maximum degree of condensation without gelation, i.e., maximum branching and even intramolecular loop formation, will be most favorable for most applications while the product remains still liquid. We found that under the same reaction conditions liquid and soluble PEOS products were obtained at molar ratio (f) of acetic anhydride to TEOS up to 1.2 (Scheme 4). At $f = 1.3$, a solid gel was formed (Scheme 4). ^{29}Si NMR spectroscopy was used to follow the structure change in PEOS products with different f.

Figure 2 shows the representative ^{29}Si NMR spectra of PEOS obtained at $f = 1.15$ and 1.30. Table 1 summarizes the ^{29}Si NMR data of PEOS obtained at different f. These data show that the distribution of different building units changed with increasing f. First of all, it should be noted that the amount of TEOS in product decreased, and at $f = 1.15$ it was barely detectable. The relative amount of linear units Q_2 remained almost constant, and the amount of the semidendritic and dendritic groups increased at the expense of terminal groups; the degree of branching, hence, also increased. For $f = 1.30$ the signals corresponding to acetoxysilane groups can still be found in the ^{29}Si NMR spectrum. For instance, a silicon atom, carrying two ethoxy and one acetoxy groups, appeared at −93.3 ppm. The signal of acetoxy group can be more clearly observed in the ^{1}H NMR spectrum of this sample in the area near 2 ppm (Figure 2c). The gel was quite soft, and all the building units including Q_1, Q_2, Q_3, and Q_4 can be clearly distinguished in the ^{29}Si NMR spectrum obtained under magic-angle sample spinning.

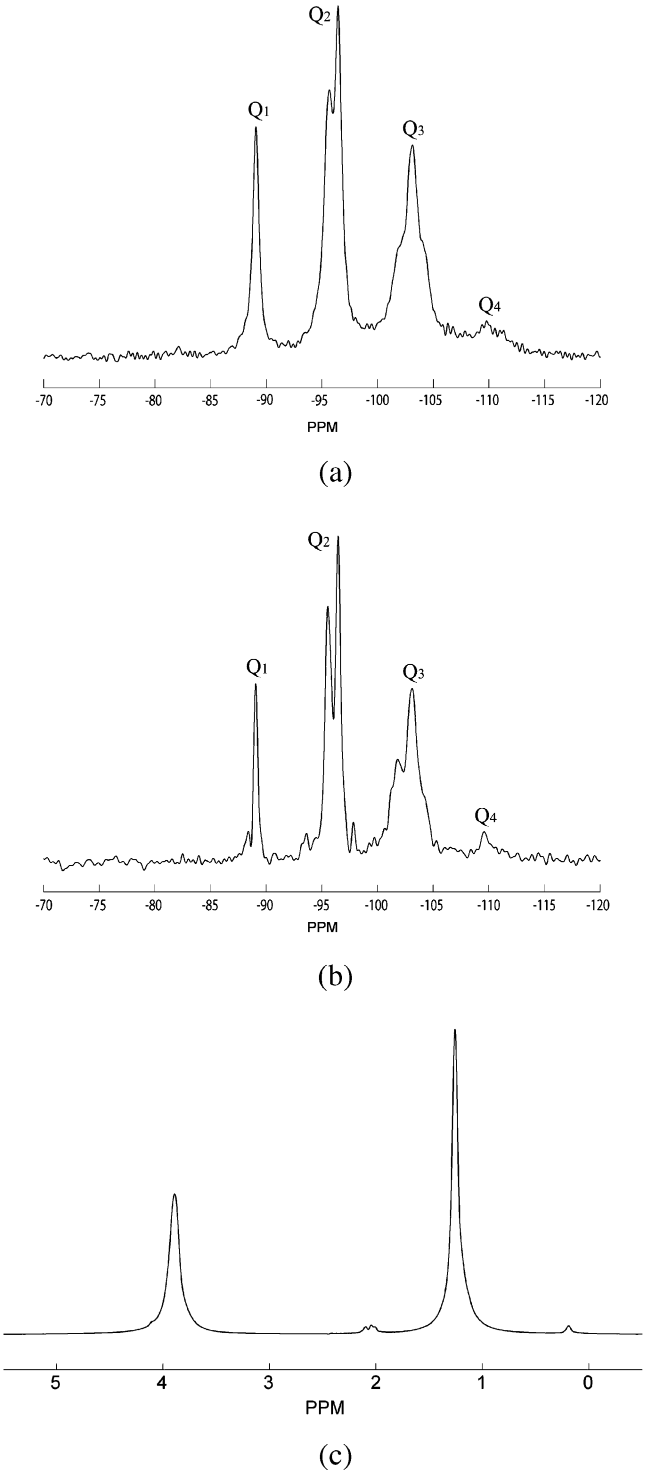
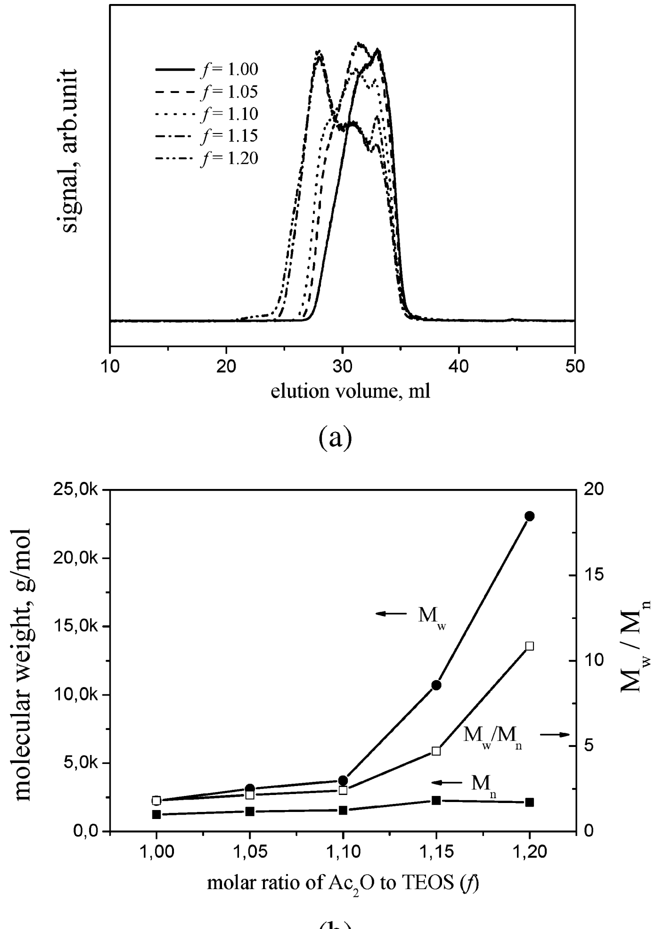


Figure 2. ^{29}Si NMR spectra of PEOS obtained (a) at molar ratio of acetic anhydride to TEOS $f = 1.15$ and (b) 1.30. (c) depicts the solid-state ^{1}H NMR spectrum of PEOS obtained at molar ratio of acetic anhydride to TEOS $f = 1.30$. Spectra b and c were recorded with 5 kHz magic-angle sample spinning.

Figure 3 shows the size exclusion chromatography (SEC) analysis results of PEOS products synthesized at various f. As shown previously, the refractive index (RI) increment of PEOS depends on the molecular weight.[12] Thus, instead of a RI detector an evaporative light scattering (ELS) detector was used. The apparent average molecular weight (compared to polysty-



(b)

Figure 3. Size exclusion chromatogram (a) of PEOS obtained at different molar ratio (*f*) of acetic anhydride to TEOS (a) and the dependence of the number- and weight-average molecular weights on *f* (b).

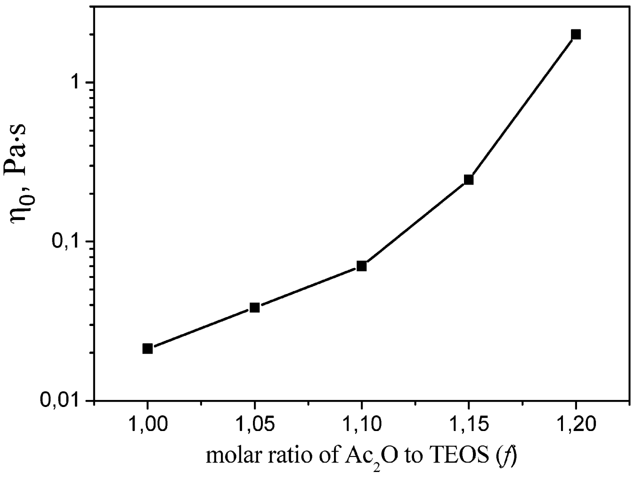
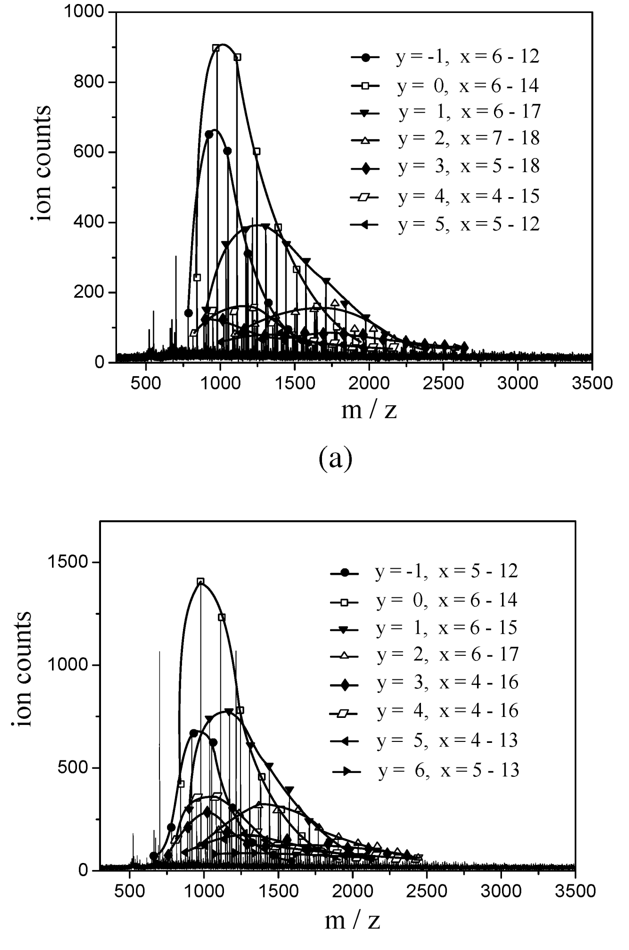


Figure 4. Dependence of zero-shear viscosity η_0 of PEOS on the molar ratio (*f*) of acetic anhydride to TEOS.

rene standard samples) as well as the molecular weight distribution increased exponentially by increasing *f*. The condensation reaction became less controlled at higher values of *f* due to the extended coupling reaction between macromolecules, leading to multimodal distribution of molecular weight. Zero-shear viscosity of PEOS increased exponentially with *f* as well (Figure 4). Thus, it is demonstrated that the molecular weight of PEOS in the one-pot synthesis can be tuned simply varying the reagent ratio *f*.



(b)

Figure 5. MALDI-ToF mass spectra of PEOS synthesized at molar ratio of acetic anhydride to TEOS $f = 1.05$ (a) and 1.15 (b).

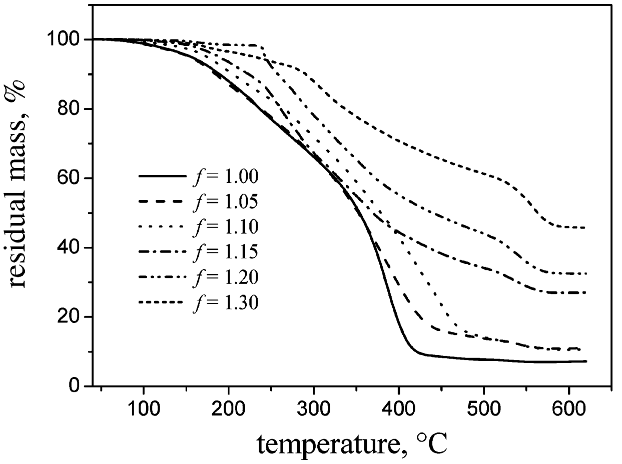
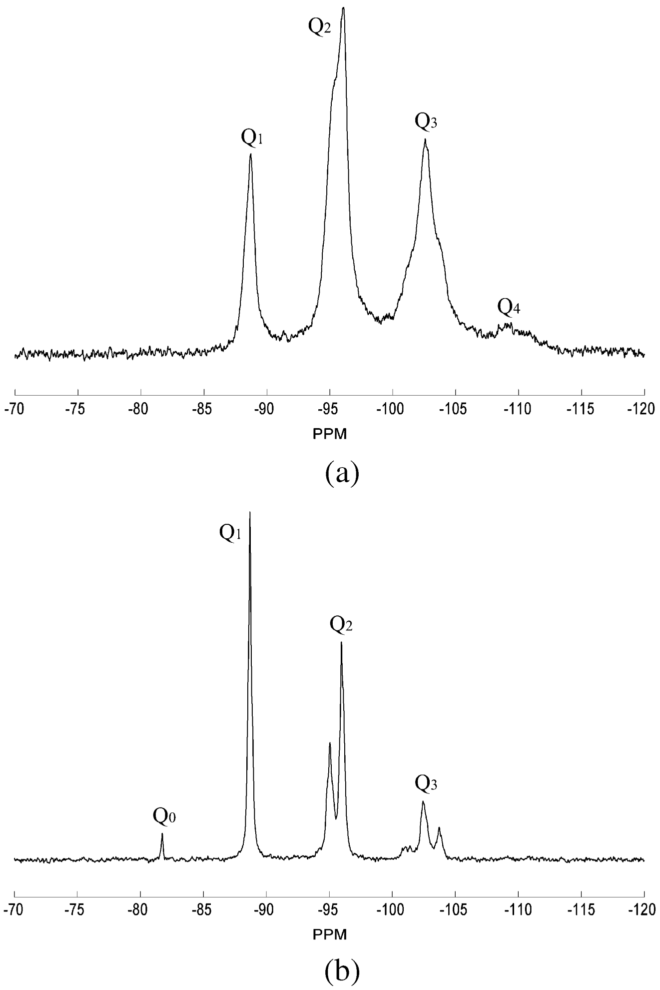


Figure 6. Thermogravimetric analysis curves of PEOS obtained at different molar ratio (*f*) of acetic anhydride to TEOS.

We have performed matrix-assisted laser desorption ionization−time-of-flight (MALDI-ToF) mass spectrometry for PEOS products to follow the change in the molecular structure with *f*. In Figure 5 two representative spectra of PEOS corresponding to $f = 1.05$ and 1.15 are depicted. For comparison, see also Figure 9a for PEOS corresponding to $f = 1.00$. Although MALDI-ToF mass spectrometry normally yields accurate average molecular weight distributions only for low-polydispersity samples,[16] useful information concerning the loop formation could be obtained.[12] On the basis of the mass and isotope pattern,



(a)

(b)

Figure 7. ^{29}Si NMR spectra of PEOS obtained from a stoichiometrical one to one mixture of TEOS and acetic anhydride with 0.3 mol % of catalyst: (a) and (b) depict the spectra of the high and the low molecular weight fractions of PEOS after thin-film evaporator at 150 °C and (1$-$2) $\times$ 10^{-2} mbar.

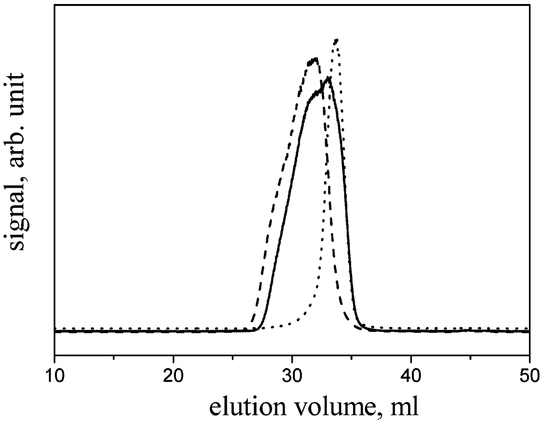
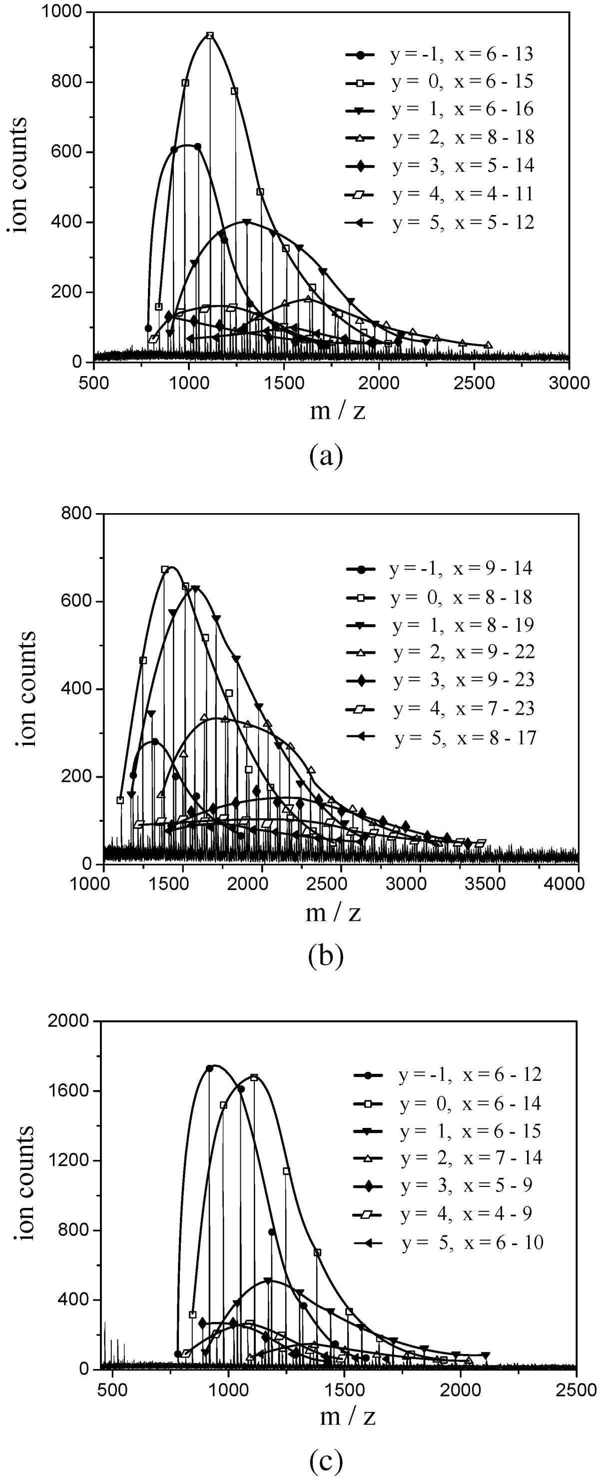


Figure 8. Size exclusion chromatograms of PEOS obtained from a stoichiometrical mixture of TEOS and acetic anhydride. Solid line, raw PEOS; dashed line, PEOS after thin-film evaporator (TFE); dotted line, distillate after TFE.



(a)

(b)

(c)

Figure 9. MALDI-ToF mass spectra of PEOS before (a) and after (b) thin-film evaporator as well as the distillate (c). Each point marked with a symbol corresponds to a molecule with the sum formula K[SiO(OEt)$_2$]$_x$(SiO$_2$)$_y$.

the peaks can be assigned to potassium adducts with the sum formula K[SiO(OEt)$_2$]$_x$(SiO$_2$)$_y$. At least seven to eight different peak groups can be distinguished. Peaks marked with the same symbol correspond to the molecules of the same y but different molecular mass. Here $y + 1$ is the amount of loops in the molecules. The main species in raw PEOS products were hyperbranched macromolecules without any loops and with the formation of one and two loops. Comparing them with the spectrum of PEOS obtained at $f = 1.00$ (Figure 9a), it is quite clear that with increasing f more cyclic structures were formed.

Corresponding to the ^{29}Si NMR results, thermogravimetric analysis (TGA) under an inert gas atmosphere demonstrated a clear decrease in the content of volatile compounds and an increase of the solid SiO$_2$ fraction that remained after thermal decomposition as the excess of acetic anhydride, f, was raised. The solid SiO$_2$ fraction is listed in Table 2. The TGA experimental values were systematically lower than the theoreti-

Table 2. SiO_2 Content of PEOS Products Obtained at Different Molar Ratio (*f*) of Acetic Anhydride to TEOS Determined by Different Methods

f	SiO_2 content after full hydrolysis, %	SiO_2 content according to ^{29}Si NMR, %	theoretical SiO_2 content, %	SiO_2 residue at 600 °C in TGA, %
1.00	45.4	45.3	44.8	7.1
1.05	45.9	45.8	46.0	10.9
1.10	47.6	47.2	47.4	10.6
1.15	48.9	49.6	48.8	27.0
1.20	49.5	50.2	50.3	32.6
1.30	52.1	50.9	53.7	45.9

Table 3. Relative Contents of Different Building Units of PEOS Obtained from a Stoichiometrical One to One Mixture of TEOS and Acetic Anhydride before and after Using a Thin-Film Evaporator (TFE)

	units					
PEOS	TEOS, Q_0 [%]	terminal, Q_1 [%]	linear, Q_2 [%]	semidendritic, Q_3, [%]	dendritic, Q_4, [%]	DB
raw PEOS	3.5	23.6	42.1	26.9	3.9	0.48
product after TFE	n.d.[a]	15.2	43.2	35.2	6.4	0.54
distillate after TFE	1.2	34.9	45.8	18.1	n.d.	0.33

[a] n.d. = not detected.

Table 4. Comparison of the Average Molecular Weights of PEOS before and after Thin-Film Evaporator (TFE) Determined by Size Exclusion Chromatography (SEC) Using Polystyrene Standards and MALDI-ToF Mass Spectrometry

	M_n, g/mol		M_w, g/mol		M_w/M_n	
PEOS	SEC	MALDI-ToF	SEC	MALDI-ToF	SEC	MALDI-ToF
raw PEOS	1120	1300	2010	1390	1.8	1.07
product after TFE	1740	1840	3330	1960	1.9	1.07
distillate after TFE	700	1150	830	1200	1.2	1.04

cal ones as well as those calculated from the ^{29}Si NMR spectra. With increasing *f* the residual SiO_2 mass approached steadily the real SiO_2 content of the products. This can be explained by the cooperativity of the formation of polycyclic structure.

TGA cannot yield correct SiO_2 content of PEOS due to the SiO_2 loss in the form of TEOS and other volatile oligosiloxanes, which are evaporated during TGA. To get the right result the samples were first fully hydrolyzed using a mixture of ethanol and aqueous solution of ammonia (volume ratio 1:1). The solvent was then slowly removed at 80 °C, and after calcination in a Muffel oven at 900 °C until a constant mass the residue was weight. SiO_2 contents obtained in this gravimetrical way are listed in Table 2 (first row). We can see that the SiO_2 contents determined by gravimetry and ^{29}Si NMR were identical, and for all liquid PEOS products they were also very close to the theoretical values calculated according to Scheme 4. The solid gel obtained at $f = 1.30$ had a slightly lower SiO_2 content than the theoretically expected one. This is explained by the incompleteness of the condensation reaction because of the fast solidification process.

From the ^{29}Si NMR data as well as from TGA it is apparent that a small amount of TEOS and other volatile components remained in the condensation products. This is most pronounced when acetic anhydride was not employed in excess ($f = 1.00$). For this sample, the low molecular weight fraction was removed by means of thin-film short-path distillation at 150 °C and $(1-2) \times 10^{-2}$ mbar vacuum. A volatile-fraction-free PEOS product was obtained with yield of 65%.

Comparing the ^{29}Si NMR spectra of PEOS before (Figure 1b) and after (Figure 7a) thin film distillation, we see the ^{29}Si signal of TEOS has vanished, and at the same time the relative distribution of the PEOS building units has also changed. The molar fraction of different building units according to ^{29}Si NMR is listed in Table 3.

The relative amount of linear units Q_2 remained practically unchanged, while the semidendritic and dendritic groups increased their portions at the expense of terminal groups. Hence, the degree of branching increased. Even though the product was heated to 150 °C only for a short period, further Si−O−Si linkages were formed. The ^{29}Si NMR spectrum of the distillate (Figure 7b) depicts four groups of signals including TEOS, terminal, linear, and semidendritic units. Upon distillation the SiO_2 content of the remaining PEOS slightly increased from 45.3% to 49.2% due to the removal of low molecular weight fractions and TEOS that were depleted in SiO_2 content because of their relative large content of organic end groups. ^{29}Si NMR analysis showed that the distillate contained only 42.5% of SiO_2 (Figure 7b).

Size exclusion chromatography clearly confirmed the increase in average molecular weight after TFE treatment at 150 °C. Figure 8 shows the SEC curves of PEOS before and after TFE. The average molecular weight and molecular weight distribution calculated using polystyrene standards are shown in Table 4.

Figure 9 shows the MALDI-ToF mass spectra of PEOS before and after TFE including the distillate. After TFE, more loop formation was detected. The molecules without loop formation were either partly distilled off (see MALDI-ToF mass spectrum of the distillate, Figure 9c) or converted into loop containing molecules via inter- and/or intramolecular cross-linking reactions.

The number- and weight-average molecular weights of the PEOS products before and after TFE treatment calculated from the MALDI-ToF mass spectra are summarized in Table 4. The number-average molecular weights derived from MALDI-ToF mass spectrometry were in a quite good agreement with the SEC data. The weight-average molecular weights, however, were found to be much lower than those obtained by SEC. The discrepancy between the SEC and MALDI-ToF data might be caused by the different desorption and ionization ability of molecules with different molecular weight and cyclic structures.

TGA measurement clearly showed that the volatile fractions in PEOS were completely removed by TFE treatment (Figure 10).

Conclusions

In this work a simple one-pot synthetic route has been developed to synthesize industrial relevant hyperbranched polyethoxysiloxanes. The procedure was based on a catalytic

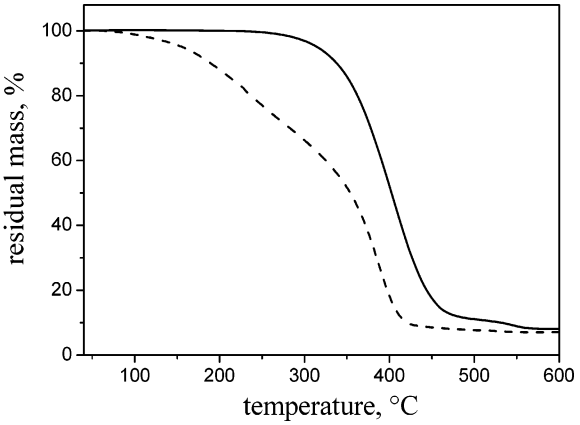


Figure 10. Thermogravimetric analysis curves of PEOS obtained from a stoichiometrical one to one mixture of TEOS and acetic anhydride before (dashed line) and after thin-film evaporator (solid line).

condensation reaction of tetraethoxysilane with acetic anhydride, and the reaction mechanism has been proposed. A relative narrowly distributed hyperbranched polyethoxysiloxane was synthesized when a stoichiometrical amount of tetraethoxysilane and acetic anhydride was reacted. A unique hyperbranched polyethoxysiloxane product without any volatile fractions was obtained with a high yield using a thin-film evaporator, which did not cause a significant structural change in the product. The molecular weight as well as the SiO_2 content control of the products has been achieved varying the molar ratio of acetic anhydride to tetraethoxysilane in combination with thin film evaporation. The products are stable (the change in the chemical structure as well as the melt viscosity was negligible after storing in a closed vessel under air at room temperature for 2 years), as they do not contain any reactive groups, such as silanol and acetoxysilane. The SiO_2 content can easily reach 50 wt % and even higher values. The hyperbranched polyethoxysiloxanes will be used as unique precursor polymers of SiO_2 to prepare polymer/silica nanocomposites.

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