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Tailoring the mass distribution and functional group density of dimethylsiloxane-based films by thermal evaporation

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The tailoring of molecular weight distribution and the functional group density of vinyl-terminated polydimethylsiloxane (PDMS) by molecular beam deposition is demonstrated herein. Thermally evaporated PDMS and its residue are characterized using gel permeation chromatography and nuclear magnetic resonance. Thermal fragmentation of vinyl groups occurs for evaporation temperatures above 487 K (214 °C). At a background pressure of 10^{-6} mbar, the maximum molecular weight distribution is adjusted from (700 ± 100) g/mol to (6100 ± 100) g/mol with a polydispersity index of 1.06 ± 0.02 . The content of vinyl-termination per repeating unit of PDMS is tailored from $(2.8 \pm 0.2)\%$ to $(5.6 \pm 0.1)\%$. Molecular weights of vinyl-terminated PDMS evaporated at temperatures above 388 K (115 °C) correspond to those attributed to trimethyl-terminated PDMS. Side groups of linear PDMS dominate intermolecular interactions and vapor pressure. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4949362>]

Poly(dimethylsiloxane) (PDMS) is the most widely used silicone polymer.¹ Its backbone exhibits relatively high flexibility associated with a glass transition temperature as low as -125 °C and a melting temperature of -50 °C.² Because of its thermal and chemical stability, PDMS serves a broad range of applications, such as lubricants, adhesives, or passivation layers in the electronic and automotive industries.¹ The excellent elasticity of cross-linked PDMS networks in combination with their biocompatibility renders PDMS the polymer of choice for a large range of medical applications, including dielectric elastomer actuators (DEAs) for artificial muscles.^{3,4} Nanometer-thin films, with a homogeneity superior to that reached by current spin-coating or electro-spraying, have to be prepared.^{5,6} Physical vapor phase deposition is a versatile technique employed to produce nanometer-thin films. The molecular beam deposition (MBD)^{7,8} of polymer materials, however, faces the challenge of evaporating oligomers at a reasonable rate at temperatures well below thermal degradation. The sublimation of intact organic molecules under ultra-high vacuum conditions (10^{-9} mbar) has been realized through growth rates ranging from 5 to 6 nm/min.^{9,10} A recently published study describes the successful MBD of PDMS under high-vacuum conditions (10^{-6} mbar) at evaporation temperatures of up to 453 K (180 °C) and showing growth rates above 2 nm/min.³ Thermal stability, characterized by bond dissociation energies, has been investigated in detail. The cleavage of the Si–O backbone bonds results in the formation of cyclic oligomers with a corresponding activation energy of 180 kJ/mol.¹¹ It is known that dissociation energies of functional side groups are below those of the backbone bonds. The thermally activated decomposition of trimethyl-terminated PDMS under vacuum conditions occurs at a temperature of about 573 K (300 °C) with an activation energy of 175 kJ/mol.¹² An activation energy level of 98 kJ/mol¹² and a decomposition temperature of 503 K (230 °C) are found for vinyl termination.³

The evaporated oligomer mass depends exponentially on the inverse temperature according to the Clausius-Clapeyron relation. Thus, we hypothesize that MBD influences molecular weight distribution, polydispersity, and the density of the functional termination of the deposited polymer film.

Since the chain length of the oligomers determines the elastic modulus of cross-linked PDMS,¹³ the choice of deposition parameters determines the performance of DEAs.¹⁴ So far, thermal evaporation has been restricted to linear or cyclic PDMS, focusing on oligomers, i.e., macromolecules with less than eleven repeating units, with molecular weights below 1000 g/mol,^{15–17} or on the vaporization of decomposed PDMS fractions, using an evaporation temperature of 573 K (300 °C) at atmospheric pressures.¹⁸ In the present communication, vinyl-terminated PDMS is evaporated with molecular weights of up to 6100 g/mol, maintaining vinyl termination.

Our experimental setup has been described previously.³ Briefly, deposition experiments were carried out under high-vacuum conditions with a background pressure of 10^{-7} mbar. A low temperature effusion cell (Dr. Eberl MBE Komponenten GmbH, Weil der Stadt, Germany) with a 2 cm³ crucible was utilized. The temperature ramp of the evaporator was adjusted to 8.3×10^{-3} K/s to avoid boiling retardation. The final crucible temperature was held stable for one extra hour. With an opened shutter background pressure increased to 10^{-6} mbar, the substrate was mounted 300 mm in front of the evaporation source. The MBD study was based on two commercially available vinyl-terminated PDMS compounds both acquired from Gelest, Inc., Morrisville, PA, USA of which DMS-V21 has an average molecular weight of 6000 g/mol and DMS-V05 one of 800 g/mol. The PDMS starting materials were filled in the crucible as received from the supplier. Gel permeation chromatography (GPC) traces are recorded in WinGPC (v8.20 build 4815) and connected to an Agilent 1200 system equipped with a refractive index detector and a series of analytical SDV columns (pre-column (5 cm), 1×10^3 Å (30 cm), and 1×10^5 Å (30 cm), all 5 μm particles and 0.8 cm in diameter, PSS, Germany). The columns and the system were kept at a temperature of 35 °C and run at a flow rate of 0.017 ml s⁻¹. Average molecular weight M_n , mass average molecular weight M_w , peak molecular weight M_p , and the polydispersity index (PDI) were determined by calibrating the GPC system with narrow polystyrene standards from Sigma Aldrich.

The molecular weight distributions of the evaporated film fractions and the residues in the crucible after deposition are displayed as colored lines for DMS-V05 in Figs. 1(a) and 1(c) and for DMS-V21 in Figs. 1(b) and 1(d), respectively. The molecular weight distributions of the supplied materials are displayed as black lines. As expected, the peak molecular weight within the evaporated film fractions increases in line with temperature. The maximal evaporated molecular weight,

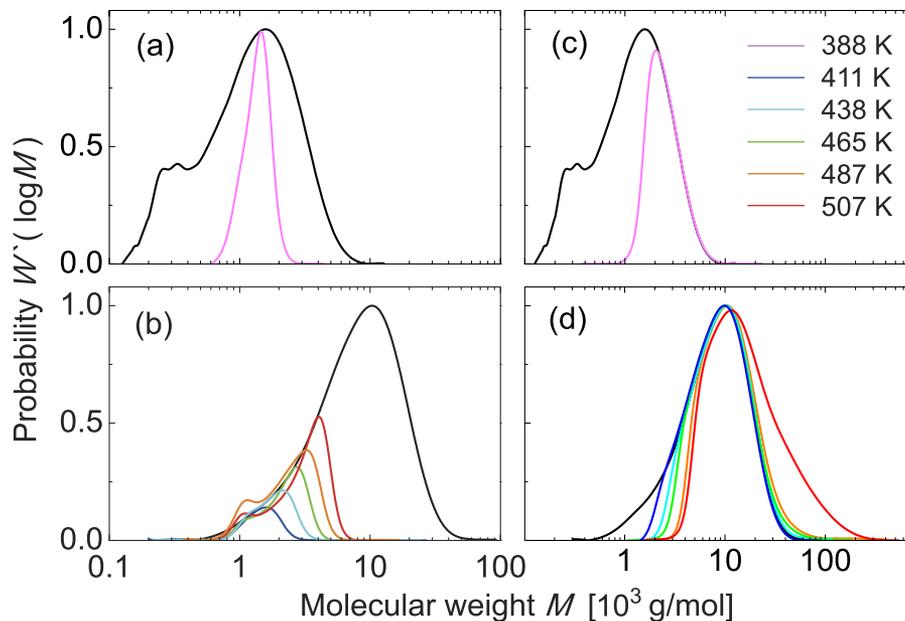


FIG. 1. Molecular weight distribution obtained from gel permeation chromatography traces of DMS-V05 [(a) and (c)] and DMS-V21 [(b) and (d)] is shown in black. The colored traces represent the film fractions evaporated from DMS-V05 (a) and DMS-V21 (b) as well as the corresponding residues [(c) and (d)] within the crucible at temperatures between 388 and 507 K.

extracted at $1/10^2$ - halfwidth of the GPC trace, ranges from (2000 ± 100) to (6100 ± 100) g/mol for evaporation temperatures between 388 K (115 °C) and 507 K (234 °C). The 100 g/mol error arises from estimating baseline variation. The molecular weight distributions of the supplied polymers cover a range between 150 to about 8000 g/mol for DMS-V05 and 600 to about 50 000 g/mol for DMS-V21, see black traces in Figure 1. These broad distributions offer the evaporation of same polymer fractions with both supplied polymers at a given temperature. Though, the increased availability of short-chain polymer within the DMS-V05 weight distribution results in increased growth rates pronounced for evaporation temperatures below 465 K. For an evaporation temperature of 388 K, a twenty times higher evaporation rate of (0.685 ± 0.005) nm/s for DMS-V05 compared to one of (0.035 ± 0.001) nm/s for DMS-V21 is detected within the present experimental configuration. Within the residual fraction, only polymers with a higher molecular weight than those deposited are detected. Their weight distribution exhibits a lower limit that corresponds to the highest molecular weights found in the evaporated fraction. At a crucible temperature of 507 K, molecular weights higher than those originally found in the supplied materials are detected. We attribute this finding to the thermal stability limit of the vinyl-double bond, which exhibits the lowest bond dissociation energy along the PDMS chain.¹⁹ The radicalization of vinyl groups leads to bond formation between PDMS chains, thus accounting for the increase in molecular weight.

Nuclear magnetic resonance (¹H-NMR) PDMS spectra were recorded on a Bruker DPX-400 spectrometer in deuterated chloroform without tetramethylsilane. They were then analyzed and processed (phase correction and Wittaker Smoother to adjust the baseline) in MestReNova 10.0.1-14 719 (Mestrelab Research S.L., Spain). The supplied PDMS is characterized by a distinct multiplet of around 0.1 ppm, attributed to the methyl side groups on the silicon atoms, three doublets of doublets between 5.6 and 6.2 ppm associated with vinyl termination (Fig. 2(a)). Signals between 0.5 and 4.1 ppm result from contaminants representing most likely residuals from the polymer synthesis. The characteristic peaks of vinyl and methyl groups are present at all evaporation temperatures ranging from 388 to 507 K in the evaporated as well as in the residual fractions. Thus, the combination of NMR with GPC analysis indicates the suitability of vinyl-terminated PDMS for thermal evaporation at temperatures of up to 487 K. At an evaporation temperature of 507 K, chain prolongation is observed within the residual fraction. Nevertheless, within the NMR data, no pronounced decrease in the vinyl chemical shift is found at that temperature (Fig. 2(c)).

The measured intensities of methyl and vinyl peaks are not calibrated values. They depend on the polymer concentration within the NMR tube. The density of vinyl groups is obtained by creating the ratio of the integral over the vinyl doublets of doublets and the integral over the chemical shifts of the methyl peak, cf. Fig. 2. Vinyl content, which specifies the number of vinyl terminations per repeating unit, is plotted in Fig. 3(a) as a function of deposition temperature. The vinyl content of the supplied material is determined to be $(1.35 \pm 0.07)\%$ for DMS-V21 and $(9.2 \pm 0.2)\%$ for DMS-V05 displayed at a temperature of 293 K in Fig. 3(a). Within the standard derivation, this agrees with the vinyl content of peak molecular weight derived from GPC measurements with $(1.28 \pm 0.03)\%$ and $(9.5 \pm 0.3)\%$ for supplied DMS-V21 and DMS-V05, respectively. For DMS-V05 deposited at a temperature of 388 K, a decrease in vinyl content to $(5.6 \pm 0.2)\%$ is observed. Conversely, an increase in vinyl content to $(4.0 \pm 0.2)\%$ is detected for DMS-V21 evaporated at a temperature of 407 K. Thus, either a reduction in vinyl group density for the evaporated DMS-V05 or an increase in the evaporated DMS-V21 fractions is realized. Independent of the molecular weight distribution of the supplied materials, the vinyl content of evaporated PDMS decreases with increasing evaporation temperature (Fig. 3(a) filled symbols) in line with an increased PDI (Fig. 3(b)). Within the range of thermal stability, i.e., at temperatures below 487 K, the vinyl content of deposited PDMS fractions decreases from $(5.6 \pm 0.2)\%$ to $(2.8 \pm 0.1)\%$ in line with increasing temperature.

The PDIs of the supplied materials are determined at 1.98 ± 0.02 (DMS-V05) and 1.87 ± 0.02 (DMS-V21) displayed at a temperature of 293 K in Fig. 3(b). For DMS-V05 evaporated at a temperature of 388 K, an explicit reduction of PDI to 1.06 ± 0.02 has been realized. DMS-V21 evaporated at a temperature of 411 K exhibited a PDI of 1.08 ± 0.02 . Using an evaporation temperature of 507 K for DMS-V21, the PDI became significantly larger and corresponded to 1.26 ± 0.20 . Thus, one can generally state that the PDI increases with the evaporation temperature, as the probability

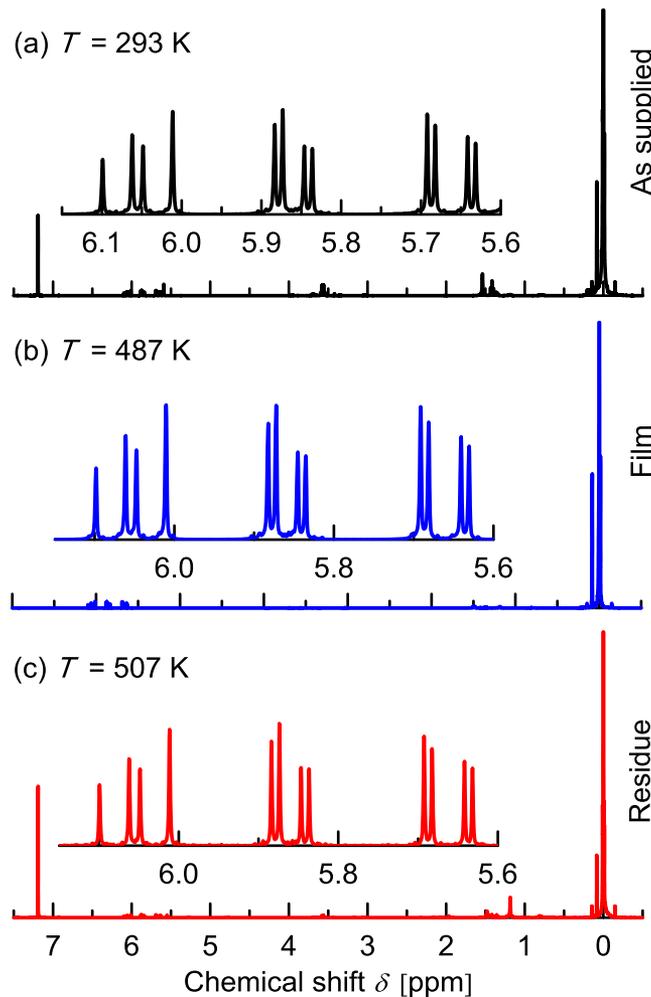


FIG. 2. Exemplary nuclear magnetic resonance spectra of supplied DMS-V21 at room temperature: (a) the film evaporated at a temperature of 487 K (b) and its residue in the crucible evaporated at a temperature of 507 K (c). The peaks attributed to the vinyl groups (multiplet from 5.6 to 6.1 ppm) are present before and after evaporation. ^1H NMR (400 MHz, CHCl_3 , δ): 0.1, m, $-\text{Si}-\text{O}-\text{Si}((\text{CH}_3)_2)-$, 6.06 (dd, $J = 20.3, 14.8$ Hz, 1H), 5.86 (dd, $J = 14.8, 4.0$ Hz, 1H), 5.66 (dd, $J = 20.2, 4.0$ Hz, 1H), m, $-\text{CHCH}_2$.

of long-chain molecule evaporation rises and the molecular weight distribution broadens to higher molecular weights. It is anticipated that by controlling the substrate temperature, low-molecular weight chains will desorb during film deposition, and narrow molecular weight distributions will also be approachable at evaporation temperatures already above 388 K. The half-width of the molecular weight distribution is then determined solely by the broadening of the Boltzmann energy distribution, which enables the tailoring of a well-defined molecular weight and vinyl content of evaporated PDMS. Within the residue, the PDI decreases in line with increasing temperature caused by the extraction of low-molecular weight polymer. At an evaporation temperature of 507 K, a distinct increase in the PDI to 2.02 ± 0.03 occurs in the residue. This broadening behavior is correlated to PDMS chain extensions, cf. Fig. 1(d).

Peak molecular weights M_p of thin film fractions evaporated at selected temperatures between 388 K and 507 K are displayed in Fig. 4. The range of accessible molecular weights is framed by thermal degradation (above 487 K)—upper limit—and by background pressure—the lower limit. At a pressure of 10^{-6} mbar, oligomers with molecular weights below (700 ± 100) g/mol are not detected within the deposited film, cf. Fig. 1(a), because, presumably, they evaporated at rather low temperatures before the deposition experiment started. This correlates with vapor pressure data

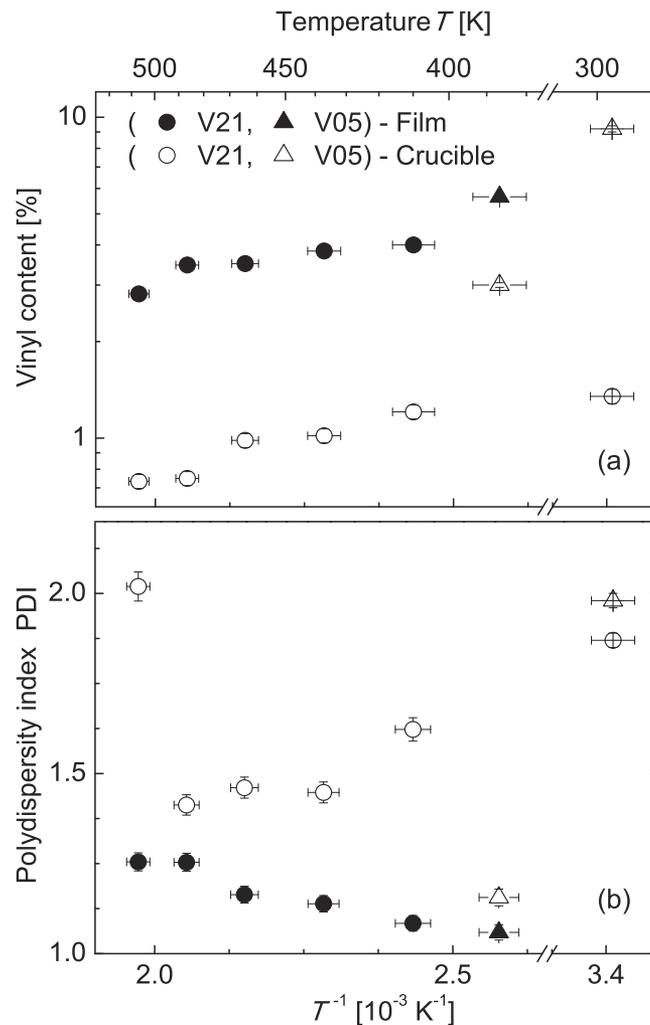


FIG. 3. The density of vinyl groups (a) and the polydispersity index (b) are presented with respect to the crucible temperature for the deposited films (filled circles, triangles) and its residue in the crucible (open circles, triangles). The supplied materials are shown as crossed symbols at a temperature of 293 K.

reported for trimethyl-terminated polysiloxanes.^{16,17} Thus, the peak molecular weights of deposited vinyl-terminated PDMS can be tailored within the range (700 ± 100) to (4050 ± 100) g/mol. The present data for vinyl-terminated PDMS, shown by the filled squares in Fig. 4, are compared with the experimental results from Ref. 16 represented by the open triangles in Fig. 4, where enthalpies of linear dimethylsiloxane oligomer vaporization with up to ten repeating units were determined at a background pressure of 10^{-2} mbar. To calculate the molecular weights of trimethyl-terminated PDMS evaporated at a background pressure of 10^{-6} mbar, the Clausius-Clapeyron relation with the coefficients of Ref. 17 is applied. Therefore, the molecular weights of the evaporated molecules depend linearly on the logarithm of the vapor pressure. For example, the reduction of the background pressure from 10^{-2} to 10^{-6} mbar results in a shift of the evaporated peak molecular weight at room temperature from 400 to 700 g/mol. In general, a reduced background pressure enables the evaporation of polymer with higher molecular weights. A comparison between the molecular weights of vinyl-terminated and trimethyl-terminated PDMS exhibits reasonable agreement between molecular weights of 700 to 1600 g/mol—a range which corresponds to eight to 19 repeating units of dimethylsiloxane. It is known that for PDMS oligomers with more than two repeating units of dimethylsiloxane, the side groups dominate intermolecular chain interactions and vaporization heat.¹⁷ Within the present study, evaporated polymers have molecular weights higher than

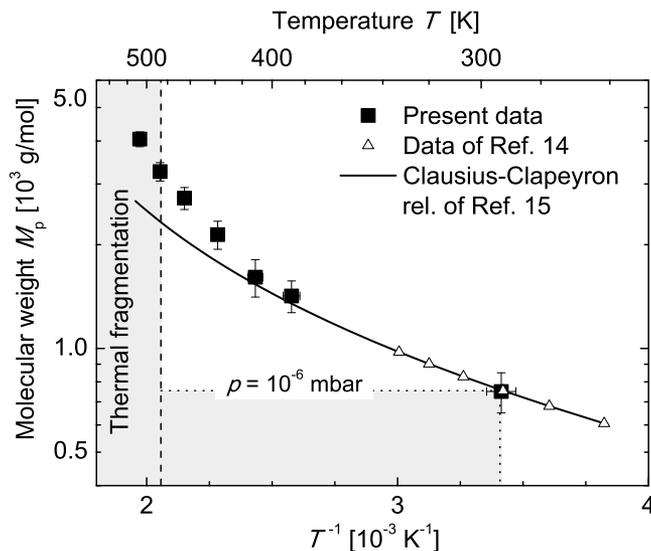


FIG. 4. The crucible temperature dependence of the peak molecular weight M_p of vinyl-terminated PDMS polymer (filled squares) is compared with derived vapor pressure data of trimethyl-terminated PDMS from Lei *et al.* (Ref. 16) (open triangles) and from Wilcock (Ref. 17) (line). Gray shading marks the boundaries of thermal fragmentation (dashed line) and the background gas pressure (dotted line).

(700 ± 100) g/mol with more than eight repeating units of dimethylsiloxane. Hence, we expect the contribution of vinyl groups to van der Waals interactions to be negligible for these chain lengths. Moreover, methyl side group interactions dominate the evaporation process.

For evaporation temperatures above 400 K, evaporated vinyl-terminated PDMS shows molecular weights higher than predicted by the Clausius-Clapeyron relation. The unique flexibility of the Si–O backbone presumably enables linear PDMS to form folded chains on the crucible surface. A conformational energy of 5 kJ/mol depicts the energy barrier of linear bending, which has to be overcome.²⁰ Energy barriers of 3.3 kJ/mol, corresponding to Si–O–Si rotation, and 0.4 kJ/mol, for methyl side group rotation, are even well below the energy barrier of linear bending.²⁰ This offers PDMS the chance to arrange its conformation at the melt-vacuum interface more easily than, for example, hydrocarbon or silane-based polymers. Thus, a stepwise breaking of intermolecular bonds and the subsequent bending of the PDMS chain explain the reduced vaporization heat, which emerge for PDMS with a molecular weight above 1600 g/mol, i.e., 19 repeating units. In general, the linear dimethylsiloxane exhibits exceptionally low intermolecular interactions obtained by shielding the Si–O backbone through the methyl groups. Thus, linear dimethylsiloxane with exclusively functional end termination offers the broadest range of molecular weights that can be tailored by MBD before thermal degradation. This behavior distinguishes PDMS from polyaniline-C₆₀,⁷ with a reduced oxidation state, or polythiophene (PTh),⁸ with a reduced conjugation length after thermal evaporation.

The maximal vinyl content of end-terminated PDMS can be adjusted to 11.1%, corresponding to nine repeating units of dimethylsiloxane evaporated just above a temperature of 293 K. Using copolymers with altered side terminations can extend the accessible range of functional group density. As a drawback, the substitution of methyl groups, for example, by vinyl or phenyl groups results in increased steric hindrance or polarity. The resulting increase in vaporization heat would narrow the spectrum of accessible molecular weights. The low PDI enables the well-defined functional group density content of evaporated PDMS. We anticipate that this technique will qualify for realizing the functionalized surfaces of biomedical devices, such as microfluidic applications,²¹ or tailoring cell-polymer interactions.¹⁸ We propose the incorporation of phenyl terminations, which helps to manipulate the refractive index to qualify for biosensor applications.²² Based on this functionalization, the dielectric constant can be adapted to influence actuation efficiency positively in dielectric elastomer actuators. Furthermore, the evaporation of high molecular weight polymer

is of great importance to realize low elastic modulus cross-linked thin elastomer films. This enables high actuation strains of dielectric elastomer actuators. Together with unique homogeneity, MBD of PDMS is expected to realize biocompatible dielectric actuators serving artificial muscle implants.^{23,24}

In summary, thermally evaporated linear dimethylsiloxane serves thin polymer films with a tailored molecular weight distribution. Limited by intermolecular interactions between the methyl side groups, molecular weights corresponding to up to 80 repeating units of dimethylsiloxane are evaporated before thermal degradation.

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