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Lipase-Catalyzed Synthesis and Properties of Silicone Aromatic Polyesters and Silicone Aromatic Polyamides

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ABSTRACT: *Candida antarctica* lipase B (CALB) immobilized on a macroporous acrylic resin (Novozym 435) was used to enzymatically synthesize silicone aromatic polyesters (SAPEs) and silicone aromatic polyamides (SAPAs) in toluene under mild reaction conditions. The SAPEs were synthesized using α,ω-(dihydroxyalkyl)-terminated poly(dimethylsiloxane) (HAT-PDMS, molar mass $M_n = 2500$ g mol^{-1}), and the SAPAs were synthesized using α,ω-(diaminopropyl)-terminated poly(dimethylsiloxane) (APT-PDMS, having two different molar masses, M_n, 1000 and 4700 g mol^{-1}, respectively). Each of the polymers was made by a transesterification reaction with dimethyl terephthalate (DMT) in toluene (1:2 w/v ratio of monomers to solvent) at a temperature in the range of 80−90 °C under vacuum. Toluene was employed as the solvent in order to solubilize the DMT in the reaction mixture. The methanol byproduct was recovered from the reaction mixture along with the toluene by applying vacuum, and thus the transesterification reaction was driven forward. The enzymatically synthesized polymers were characterized by GPC, FTIR, ^{1}H NMR, XRD, DSC, and TGA. Higher molar masses were obtained for the SAPEs compared to those of the SAPAs, even though similar reaction conditions were used. The thermal properties of the resulting polymers were seen to depend on the molar masses of the SAPEs and the SAPAs. Both types of polymer were found to be amorphous liquids at room temperature. However, below room temperature the SAPA samples were found to be a sticky wax-like material which contained a crystal-like phase that showed a melting endotherm by DSC analysis. The absence of a melting endotherm in the SAPEs and the relatively low melting point of the SAPAs may be attributed to the presence of long chain highly flexible PDMS segments in the polymers.

Introduction

Research on enzymatic polymerizations is receiving increased attention in the early 21st century due to the fact that "green" pathways to new materials are growing in importance. Enzymatic polymerization is an environmentally friendly approach to polymer synthesis, and it may be contrasted to traditional chemical methods, which often need harsh reaction conditions and metallic catalysts. It is sometimes required that residual catalysts and solvents be completely removed especially for biomedical and pharmaceutical applications.[1]

Poly(dimethylsiloxane) (PDMS) and poly(ethylene terephthalate) (PET) are two of the most commercially important polymers. PDMS can be prepared either as a fluid, gel, elastomer, or resin depending on its structure and functionality.[2,3] PET is a thermoplastic with excellent film forming and fiber properties.[4] Needless to say, linear PDMS and PET are incompatible with respect to forming binary polymer blends. The coating or grafting of silicones onto PET fibers is an important technology for improving fiber processing and for surface modification.[5] The conventional copolymerization pathways to PDMS and PET copolymers are paved with difficulties due to both physical incompatibility issues and chemical issues regarding the catalysts and temperatures used for esterification and transesterification reactions.[6] In particular, the strong acids typically used in esterification or transesterification reactions can cleave siloxane bonds Si−O−Si unless great care is taken. Likewise, the aliphatic polyamides and aromatic polyamides show remarkable properties—particularly as high-performance fibers. Similarly, incorporating siloxane components into the polyamides by conventional routes is problematic due to chemical and physicochemical compatibility issues between the polyamides and polysiloxanes. Here we document an enzymatic approach to building silicone aromatic polyesters (SAPEs) and silicone aromatic polyamides (SAPAs) containing PDMS units into the respective polymeric chains under mild reaction conditions.

Linear silicone-modified aliphatic polyesters have been synthesized from polyols, diacids, diols, and hydroxyl-terminated PDMS with a titanium isopropoxide catalyst at 140−180 °C for 12−16 h. Amphiphilic PEG-silicone polyester surfactants have been prepared by the polymerization of poly(ethylene glycol) (PEG), maleic anhydride (MA), poly(dimethylsiloxane), and fumaric acid using titanium isopropoxide as the catalyst at 180 °C under a nitrogen atmosphere and then maintained at this temperature for 8 h. Subsequently, 2 mol of PEG and 1 mol of PDMS were reacted in the presence of the same catalyst at 180 °C for 16 h.[7]

Polyamides are generally prepared by mixing equimolar amounts of dibasic acids and diamines at polymerization temperatures typically ranging between 260 and 280 °C or by the ring-opening polymerization of caprolactam. While high reaction rates and conversions may be achieved through acid or base catalysis, these catalysts may induce the decomposition of potentially useful functional groups. A polycondensation reaction between *O*-acetylgalactaric acid chloride and PDMS diamine was recently reported to give high molar mass polyamides (M_w = 103 600 g mol^{-1}).[8] 2,3,4,5-Tetra-*O*-acetylgalactaroyl dichloride was reacted with a PDMS diamine in chloroform solution for 5 days with triethylamine at 0 °C. The major disadvantage of this methodology is the liberation of hydrogen chloride, which is detrimental to polysiloxane chains and thus necessitates the

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addition of equimolar amounts of base and therefore leads to the formation of organic salts. Additional disadvantages of this method include (i) the use of a protected sugar due to the nonselectivity of the reaction, (ii) the need to activate the diacid by the formation of an acid chloride, and (iii) the liberation of stoichiometric quantities of an organic salt byproduct.[6]

The enzyme-catalyzed synthesis of poly(1,6-hexanediyl terephthalate) and poly(1,6-hexanediyl isophthalate) in toluene at 60 °C using lipase from Novozyme as a catalyst was first reported by Gilles and co-workers.[9] Later, enzymatic synthesis of aromatic polyesters by direct polyesterification between a diacid and a diol was described by Wu and co-workers.[10] The polymerization of dimethyl terephthalate and diethylene glycol by enzymatic catalysis in toluene was carried out by Lalot and co-workers.[11] The condensation copolymerization of a range of linking molecules with poly(ethylene glycol)s (PEGs) of varying molecular weights catalyzed by lipases under solvent-less conditions was reported by Kumar and co-workers.[12]

We next consider the literature on silicone-modified systems by enzymatic routes. Bishwabhusan and co-workers[13] have performed the lipase-catalyzed esterification of organosiloxane carboxylic diacids and the C1-O-alkylated α,β-ethyl glucoside. The organosiloxane–sugar conjugates were prepared in a one-step reaction without protection–deprotection steps and without the activation of the acid groups. A finding of major significance in this work was the fact that the integrity of the siloxane bonds was maintained. Sharma and co-workers[6] have reported the lipase-catalyzed synthesis of aliphatic polyesteramides with poly(dimethylsiloxane) blocks in the bulk at 70 °C under reduced pressure (10–20 mmHg). In this system immobilized *Candida antarctica* lipase B on macroporous acrylic resin beads (Novozym 435) was used as the enzyme under mild reaction conditions to perform the polycondensation reaction using various feed mole ratios of diethyl adipate, 1,8-octanediol, and α,ω-(diaminopropyl)poly(dimethylsiloxane).

Recently, we have reported the synthesis of silicone aliphatic polyesters by the condensation polymerization of 1,3-bis(3-carboxypropyl)tetramethyldisiloxane with alkanediols (1,4-butanediol, 1,6-hexanediol, and 1,8-octanediol) in the bulk (without use of solvent) in the temperature range 50–90 °C under reduced pressure (50–300 mmHg vacuum gauge) using Novozym 435 as a catalyst.[14] An increase in the molar mass of the polyesters was found to be depend on the reaction temperature, enzyme activity, enzyme concentration, and to a lesser extent the applied vacuum.

In another study, we have reported the enzymatic synthesis of silicone polylactones—in particular, linear poly(ε-caprolactone)–poly(dimethylsiloxane)–poly(ε-caprolactone) triblock copolymers.[15] The copolymerization was performed by ring-opening polymerization of ε-caprolactone with α,ω-(dihydroxyalkyl)-terminated poly(dimethylsiloxane) using Novozym 435 as the catalyst in toluene at 70 °C. The copolymers were investigated by DSC and XRD and found to be semicrystalline. The degree of crystallinity increased with an increase of the precursor feed [ε-caprolactone]/[PDMS] ratio. The crystal structure of the copolymers was determined by WAXD and found to be similar to that of the poly(ε-caprolactone) (PCL) homopolymer. The thermal stability of these copolymers improved over the parent PCL homopolymer with increased fraction of PDMS as revealed by TGA analysis.

Furthermore, we have also enzymatically synthesized silicone polyethers—specifically poly(dimethylsiloxane)–poly(ethylene glycol) amphiphilic copolymers in the bulk at 80 °C and under reduced pressure (500 mmHg vacuum gauge).[16] Novozym 435 was used to catalyze the condensation polymerization of 1,3-bis(3-carboxypropyl)tetramethyldisiloxane with poly(ethylene glycol) (PEG having a number-average molar mass, M_n = 400, 1000, and 3400 g mol^{-1}, respectively). Novozym 435 was also used to copolymerize α,ω-(dihydroxyalkyl)-terminated poly(dimethylsiloxane) (HAT-PDMS, M_n = 2500 g mol^{-1}) with α,ω-(diacid)-terminated poly(ethylene glycol) (PEG, M_n = 600 g mol^{-1}). The thermal stability of the synthesized copolymers was found to increase with increased dimethylsiloxane content in the silicone polyethers.

In the present investigation, Novozym 435 was used to successfully synthesize silicone aromatic polyesters (SAPEs) and silicone aromatic polyamides (SAPAs). The SAPEs were synthesized using α,ω-(dihydroxyalkyl)-terminated poly(dimethylsiloxane) (HAT-PDMS, M_n = 2500 g mol^{-1}) as reported elsewhere,[17] and the SAPAs were synthesized using α,ω-(diaminopropyl)-terminated poly(dimethylsiloxane) (APT-PDMS having two different molar masses, M_n, 1000 and 4700 g mol^{-1}, respectively). The respective polymers were made by transesterification reactions with dimethyl terephthalate (DMT) in toluene (1:2 w/v ratio of monomers to solvent) at 80–90 °C under vacuum. Toluene was employed as a solvent in order to solubilize DMT in the reaction mixture. The byproduct methanol was recovered from the reaction mixture along within toluene by applying vacuum, and thus the transesterification reaction was driven forward. The synthesized polymers were characterized by gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^{1}H NMR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

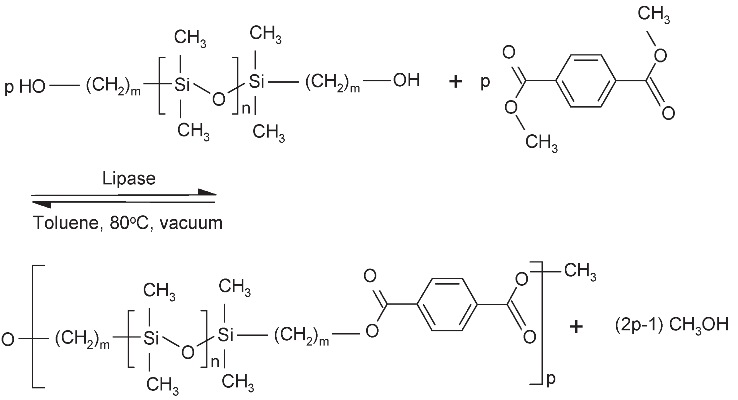
Experimental Section

Materials. All of the chemicals were analytical grade and were used as received. *Candida antarctica* Lipase B (CALB) immobilized on macroporous acrylic resin (Novozym 435, Lot No. 047 K1672 (with an activity in propyl laurate units of 11 200 PLU/g)) and dimethyl terephthalate were purchased from Aldrich Co. HPLC/Spectro grade toluene and tetrahydrofuran (THF) were purchased from Tedia Co. Inc. α,ω-(Diaminopropyl)-terminated poly(dimethylsiloxane) (APT-PDMS) (M_n = 1000, M_w/M_n = 1.7 and M_n = 4700, M_w/M_n = 2.13) was purchased from Gelest, Inc. (Tullytown, PA). The α,ω-(dihydroxyalkyl)-terminated poly(dimethylsiloxane) (HAT-PDMS) (TEGOMER H-Si 2311, M_n = 2500 g mol^{-1}, PDI (M_w/M_n) = 2) was a kind gift from Degussa.

Synthetic Methods. About 50 mg of Novozym 435 (5 wt % relative to the total weight of the monomers) was transferred into a round-bottom flask (25 mL) containing 1 g of 1:1 mole ratio of the monomers. The reactions were performed in toluene (1:2 w/v ratio of monomers to solvent) at a temperature of 80 °C and under reduced pressure 400 mmHg (vacuum gauge). The flask was capped with an adaptor connected to a vacuum pump and placed in an oil bath, maintained at the desired temperature (±0.1 °C). The reaction contents were mixed with a magnetic stirrer. The solvent vapors were condensed and collected in a condenser trap. Before the reaction, the enzyme was dried at ambient temperature under vacuum for 24 h. Aliquots of about 20 μL were removed at selected time intervals and dissolved in about 2 mL of THF or toluene. The enzyme was removed by filtration using a glass-fritted filter (medium porosity). Then the crude polymer samples were characterized by various techniques as described below.

Instrumental Methods. The molar masses of the silicone aromatic polyesters and silicone aromatic polyamides were determined by GPC using a Shimadzu LC-20AT pump, an RID-10A refractive index detector, and a Phenogel GPC 300 × 7.8 mm × 5 μm column. THF was used as the eluent at a flow rate of 1.0 mL/min. Sample concentrations of 5–10 mg/mL and injection volumes of 50–100 μL were used. Narrow distribution polystyrene standards with molar masses ranging from 550 to 480 000 g mol^{-1} (Millipore, Waters Chromatography Division, Milford, MA) were used to calibrate the system. System calibration data and relative molar

Scheme 1. Lipase-Catalyzed Polyesterification of α,ω-(Dihydroxyalkyl)-Terminated Poly(dimethylsiloxane) (HAT-PDMS) ($m \approx 7$, $n \approx 30$, and $M_n \approx 2500$ g mol^{-1}) with Dimethyl Terephthalate (DMT) Carried out in Toluene at 80 °C under Reduced Pressure



Scheme 2. Lipase-Catalyzed Polyamidation of α,ω-(Diaminopropyl)-Terminated Poly(dimethylsiloxane) (APT-PDMS) with Dimethyl Terephthalate (DMT) Carried Out in Toluene at 80 °C under Reduced Pressure

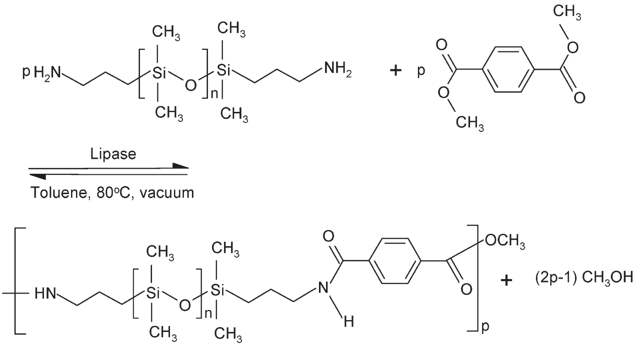


Table 1. Molar Mass Buildup of the Silicone Aromatic Polyesters (SAPEs) by the Novozym 435-Catalyzed Transesterification of Dimethyl Terephthalate (DMT) with α,ω-(Dihydroxyalkyl)-Terminated Poly(dimethylsiloxane) (HAT-PDMS) Carried Out in Toluene, at 80 °C and under 400 mmHg Vacuum

polymer (reaction time)	M_w (g mol^{-1})	M_n (g mol^{-1})	PDI (M_w/M_n)
HAT-PDMS[a]	5 000	2 500	2.00
SAPE (24 h)	17 300	10 300	1.68
SAPE (48 h)	47 000	31 000	1.52
SAPE (72 h)	50 000	35 000	1.48
SAPE (96 h)	52 000	38 000	1.37

[a] The starting material, namely α,ω-(dihydroxyalkyl)-terminated PDMS.

mass calculations were acquired and processed using Shimadzu Class-VP software. The molar mass buildup of the polyesters and the polyamides, namely, weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity index (PDI = M_w/M_n), were calculated from the respective chromatograms.

FTIR spectral analysis was carried out using a Bio-Rad Digilab Division FTS 40 IR spectrometer. The IR spectra were recorded by averaging 20 scans at 1 cm^{-1} resolution. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker NMR spectrometer (DPX300) at 300 MHz using deuterated chloroform as the solvent. ^{1}H NMR chemical shifts (δ) in parts per million (ppm) were referenced relative to chloroform (δ = 7.26 ppm) as an internal standard.

Wide-angle X-ray diffraction (WAXD) was performed using an X′ Pert PRO and Cu Kα radiation, with a wavelength of λ = 0.154 nm. The experimental setup included a linear detector for acquiring 1D WAXS measurement distance 32 cm. WAXD of the polymer samples were obtained by setting a step size of 0.025 and time per step of 1 s with a scattering angle 2θ ranging between 5° and 45°.

Thermogravimetric analysis (TGA) was performed by means of a TA Instruments TGA2050 thermogravimetric analyzer. The measurements were carried out with a heating rate of 20 °C/min in a N_2 atmosphere and temperature ranging from room temperature to 800 °C. Differential scanning calorimetry (DSC) analysis was performed using a TA Instruments 2010 DSC. DSC scans were run in the temperature range from −150 to 150 at 10 °C/min. A controlled cooling rate of −10 °C/min was applied between heating runs.

Results and Discussion

Immobilized *Candida antarctica* Lipase B (Novozym 435) was used to synthesize silicone aromatic polyesters (SAPEs) and silicone aromatic polyamides (SAPAs) with poly(dimethylsiloxane) segments as shown in Schemes 1 and 2, respectively. The SAPEs were synthesized using α,ω-(dihydroxyalkyl)-terminated poly(dimethylsiloxane) (HAT-PDMS, M_n = 2500 g mol^{-1}) with dimethyl terephthalate (DMT). The SAPAs were synthesized using α,ω-(diaminopropyl)-terminated poly(dimethylsiloxane) (APT-PDMS, M_n = 1000 and 4700 g mol^{-1}) with DMT in toluene (1:2 w/v ratio of monomers to solvent) at 80 °C under vacuum by polyamidation reaction.

As the reactions progressed, visual observation showed that the magnetic stirring slowed significantly and the reaction viscosity continually increased. Control reactions performed exactly as described above at 80 °C but without the addition of Novozym 435 gave a mixture of monomers with no detectable increase in the molar mass. Therefore, the control reactions demonstrate that the reactions were catalyzed by Novozym 435 alone. The molar mass buildup of the synthesized polymers was studied using GPC analysis.

Gel Permeation Chromatography Analysis. Results from the GPC analysis of the polymer samples that were collected at various time intervals from the reaction mixtures of the SAPEs are presented in Table 1. The molar masses of the SAPAs are presented in Table 2. Values of M_n, M_w, and PDI corresponding to the chromatograms of the SAPEs are plotted, and these are shown in Figure 1. By 24 h, most of the toluene and methanol (byproduct) had been removed from the reaction mixture by the applied vacuum. The GPC peak corresponding to the HAT-PDMS starting material at 10.25 mL elution time was no longer observed after 24 h, suggesting that the conversion of HAT-PDMS and DMT to trimers and tetramers of SAPE polymers. After 96 h, the peak at 10.25 mL corresponding to the HAT-PDMS had completely disappeared, indicating its complete conversion to the SAPEs (M_n = 38 000 g mol^{-1}, M_w/M_n = 1.37). Moreover the PDI narrowed with increasing reaction time, most likely due to more rapid consumption of the low molecular weight oligomer population due to its relatively higher diffusivity in the reaction medium.[6]

The molar mass buildup of the SAPAs was much slower compared to that of SAPEs. Furthermore, the reaction mixture became highly viscous (by visual observation) and the magnetic stirrer stopped after 48 h, and no further increase in the molar mass of the polymers was found even after 96 h. As can be seen from Table 2, the number-average molar masses of the SAPA−PDMS(4700) polymers, M_n = 10 200 g mol^{-1}, and the SAPA−PDMS(1000) polymers, M_n = 3000 g mol^{-1}, were obtained after 48 h. This indicates that only diblock and triblock aromatic polyamides resulted unlike the multiblock aromatic polyesters obtained under similar reaction conditions. However, when the reactions of SAPAs were continued beyond 48 h at higher temperature, 90 °C, with an additional 1 mL of toluene under 400 mmHg vacuum, higher molar mass polymers were obtained. The number-average molar masses of the SAPA−PDMS(4700) polymers, M_n = 40 000 g mol^{-1}, and the SAPA−PDMS(1000) polymers, M_n = 5700 g mol^{-1}, were obtained after 96 h. Because of the highly viscous nature of the SAPAs, the reaction medium appeared to be diffusion controlled. The additional solvent at elevated temperature significantly reduced the viscosity (by visual observation of mechanical stirring) and thus allowed the reaction to be driven forward. Furthermore, the samples collected from the reaction mixtures were analyzed by FTIR, and the results are discussed below.

Table 2. Molar Mass Buildup of the Silicone Aromatic Polyamides (SAPAs) Synthesized by the Novozym 435-Catalyzed Polyamidation of α,ω-(Diaminopropyl)-Terminated Poly(dimethylsiloxane) (APT-PDMS) with Dimethyl Terephthalate (DMT) Carried Out in Toluene, at 80 °C and under 400 mmHg Vacuum

polymer (reaction time)	M_w (g mol^{-1})	M_n (g mol^{-1})	PDI (M_w/M_n)
APT-PDMS (1000)[a]	1 700	1 000	1.70
SAPA−PDMS(1000) (48 h)	4 800	3 000	1.60
SAPA−PDMS(1000) (96 h)[b]	9 600	5 700	1.68
APT-PDMS (4700)[a]	10 000	4 700	2.13
SAPA−PDMS(4700) (48 h)	20 250	10 200	1.98
SAPA−PDMS(4700) (96 h)[b]	60 000	40 000	1.50

[a] The starting material, namely α,ω-(diaminopropyl)-terminated PDMS. [b] The reactions were continued at 90 °C with an additional 1 mL of toluene.

FTIR Analysis. The Novozym 435-catalyzed SAPEs gave high molar mass polymers when compared to the SAPAs. These results are in contrast to the reported high molar mass aliphatic polyamides with poly(dimethylsiloxane) blocks.[6] This can be explained by the fact that in aromatic polyamides the steric hindrance of the amide segment in (−NH−(C═O)−Ph−) is much higher compared to that of the aliphatic polyamides (−NH−(C═O)−$(CH_2)_n$−) due the proximity of the aromatic ring.

However, in aromatic polyesters the above steric hindrance does not arise because the ester segments (−O−(C═O)−Ph−) in the monomer DMT were retained. Albeit, the methyl group is now being replaced by the aliphatic subchain (−$(CH_2)_m$−) attached to the PDMS in α,ω-(dihydroxyalkyl)-terminated poly(dimethylsiloxane) (HAT-PDMS). Furthermore, the spacer group (−$(CH_2)_m$−) in SAPE is longer than the spacer group (−$(CH_2)_3$−) in SAPAs. Therefore, as expected, the transesterification gave high molar mass aromatic polyesters compared to the aromatic polyamides prepared under similar reaction conditions.

The FTIR spectra of the polyamide SAPAs are shown in Figure 2. The peak at 1735 cm^{-1} corresponds to the ester carbonyl (R−O−(**C═O**)−R′) group, the peak at 1700 cm^{-1} is represented by the acid carbonyl (H−O−(**C═O**)−R′) group, and the peak at 1650 cm^{-1} corresponds to the amide carbonyl (R−NH−(**C═O**)−R′) group. From Figure 2, the partial hydrolysis of DMT into terephthalic acid can be clearly seen, probably due to water present in the reaction mixture or on the surface of the enzyme. The hydrolysis of DMT was apparently more favored than polyamidation for the same steric effects as explained above. Furthermore, the hydrolysis of DMT was also detected during the initial stage of the aromatic polyesterification reaction (spectra are not shown here), but the acid peak corresponding to the terephthalic acid was found to disappear as the reaction was continued. However, no attempts were made to synthesize aromatic polyesters or polyamides using terephthalic acid instead of DMT in the present investigation; nevertheless, we speculate that similar kinds of steric effects may hinder the polyamidation.

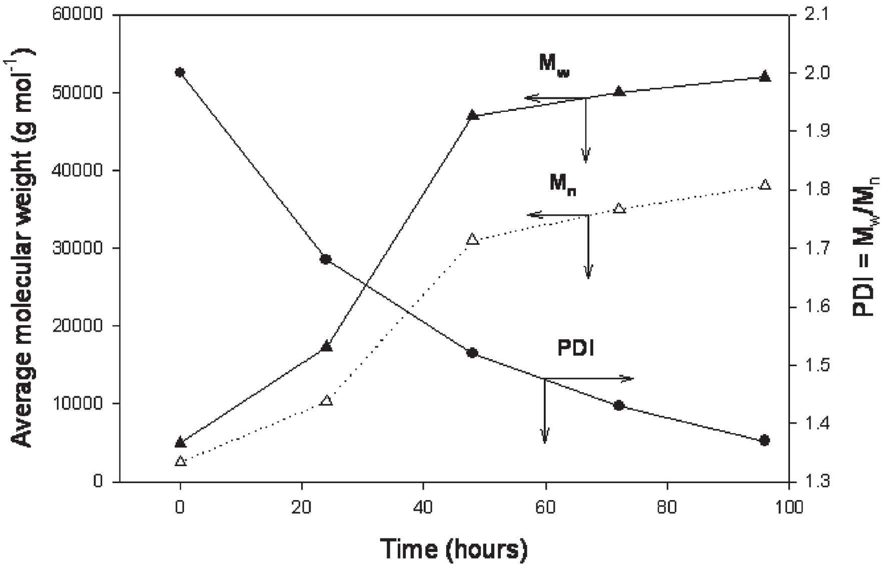


Figure 1. Average molar masses and the polydispersity index of the silicone aromatic polyesters (SAPEs) synthesized by the Novozym 435-catalyzed transesterification of dimethyl terephthalate (DMT) with α,ω-(dihydroxyalkyl)-terminated poly(dimethylsiloxane) (HAT-PDMS) carried out in toluene, at 80 °C and under 400 mmHg vacuum (as listed in Table 1).

^{1}H NMR Analysis. All of the methyl protons in the silicone segments ($-\text{Si}(\text{CH}_3)_2-\text{O}-$) in the ^{1}H NMR spectra appear together at 0.0 ppm as shown in Figure 3. Chemical shifts corresponding to the methylene protons 1, 2, and 3 were found at 1.55, 1.77, and 4.33 ppm, respectively, in the SAPE, which confirms the polyesterification reaction. Other signals in the SAPE spectrum at 8.1 ppm (4), 3.95 ppm (5), 3.6 ppm (6), 1.44 ppm (7), 1.37 ppm (8), and 0.54 ppm (9) were also identified. The protons of the amide groups ($-\text{NHCO}-$) (6) of SAPA were found at 7.5−8.0 ppm, which confirms the polyamidation reaction. Other signals in the SAPA spectrum at 0.54 ppm (1), 1.66 ppm (2), 3.43 ppm (3), 8.06 ppm (4), 3.93 ppm (5), 4.2 ppm (7), 1.3 ppm (8), 0.9 ppm (9), and 0.58 ppm (10) were also indicated.

Wide-Angle X-ray Diffraction Analysis. Thin films of the SAPE and SAPAs were cast onto glass plates using the respective solutions prepared by dissolving the polymer samples in THF. The solution-coated glass plates were dried in a vacuum chamber at room temperature for 48 h. Both the SAPE and SAPAs samples showed no crystal peaks at room temperature and simply showed a broad amorphous diffraction curve. However, at low scattering angle in the range of 10°−15° a much wider peak is seen for the SAPE and for the SAPAs samples, as shown in Figure 4. This indicates the presence of a "crystal-like phase" in the polymer samples apparently due to the hard segments of aromatic polyesters and aromatic polyamides in the SAPE and SAPAs, respectively.

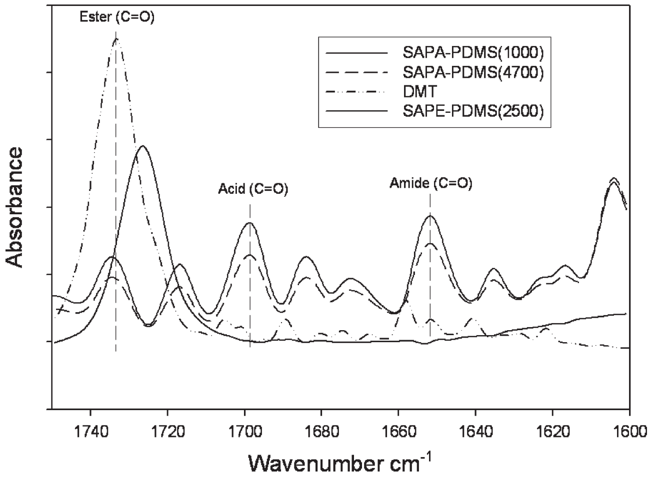


Figure 2. FTIR spectra of the silicone aromatic polyester (SAPE) and the silicone aromatic polyamides (SAPAs) samples collected after 48 h. The FTIR spectrum of a sample corresponding to dimethyl teraphthalate (DMT) is also shown.

Differential Scanning Calorimetry Analysis. The thermal transitions of the SAPE and SAPAs were determined by DSC, using a TA Instruments 2010 DSC. The scans were run under a nitrogen atmosphere, and the DSC curves are shown in Figure 5. Each sample was first cooled from ambient temperature to −150 at 10 °C/min and then heated from −150 to 150 at 10 °C. From the corresponding endotherm of the last step, the glass transition temperature (T_g) of the PDMS segments of the SAPE and SAPAs in the range −125 to −120 °C were recorded. In addition, the melting peaks and the corresponding areas are due to the presence of crystal-like structures in the SAPAs were determined to give both melting temperature (T_m) and melting enthalpy (ΔH_m), respectively.

The DSC curves of SAPAs showed similar melting endotherms, whose temperature location and area increased with the amide content. The aromatic polyamide SAPA−PDMS(1000) polymers exhibited cold crystallization and melting phenomena with a 1:2 ratio (ΔH_c = 2.5 J/g and ΔH_m = 5 J/g).

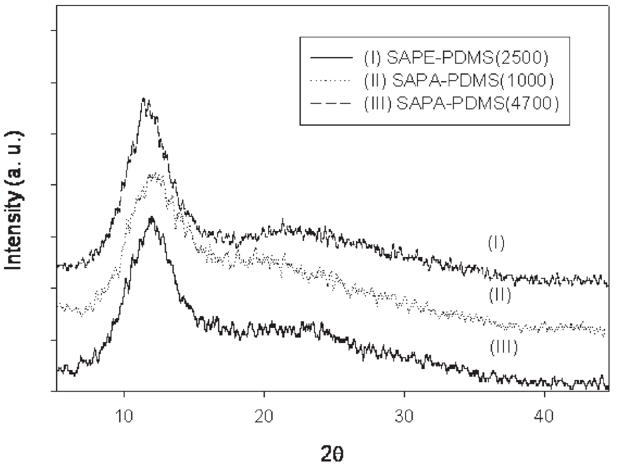


Figure 4. Wide-angle X-ray diffraction of the silicone aromatic polyester (SAPE) and the silicone aromatic polyamides (SAPAs).

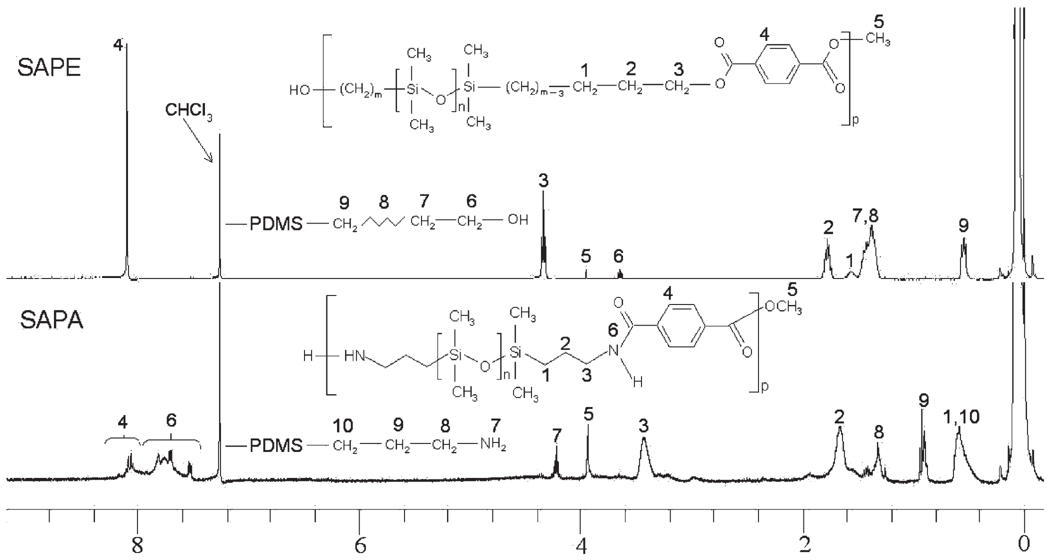


Figure 3. ^{1}H NMR spectra of the silicone aromatic polyester (SAPE) and the silicone aromatic polyamide (SAPA) samples in CDCl$_3$.

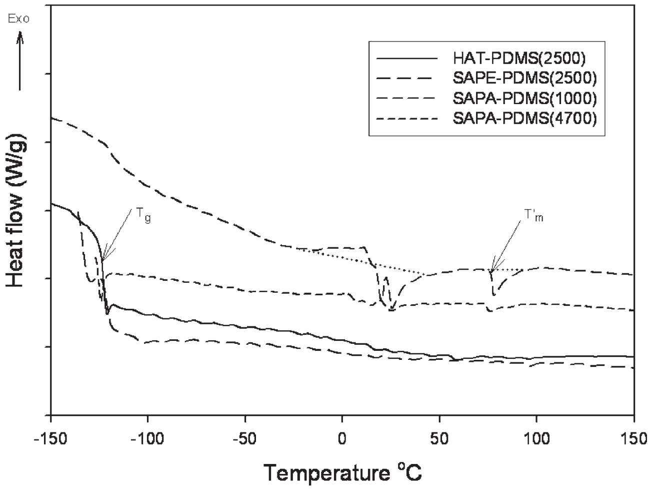


Figure 5. DSC curves (10 °C/min, after controlled cooling at 10 °C/min) of the silicone aromatic polyester (SAPE) and the silicone aromatic polyamides (SAPAs).

The crystal phase formation and its melting during the heating run just below room temperature (25 °C) were similar to the reported observation made for linear aliphatic amides with PDMS blocks.[6] A melting endotherm corresponding to the unreacted DMT was also recorded at T'_m = 75 °C for the SAPAs. However, no such endotherm was observed in the silicone aromatic polyester (SAPE), which further confirms the complete conversion of the monomer for that system and thus their successful synthesis.

Thermogravimetric Analysis. The thermal stability of linear poly(dimethylsiloxane) (PDMS) has been widely studied.[18] A recent paper reports a two-step TGA curve in linear PDMS containing a fraction of low molar mass chains. This behavior may be attributed to molecular mass heterogeneity, since it is known that the thermal stability of PDMS is molecular weight dependent.[3,19] Furthermore, Clarson and Semlyen reported the onset temperature of weight loss for linear PDMS was ≈360 °C and that essentially 100% weight loss was achieved by 580 °C.[3] A residue of about 0.3% of the PDMS remained after heating under nitrogen, and 62% of the residue was found thermally inert white powder after heating under oxidative conditions in oxygen. The onset of an exothermic process in oxygen was observed at 260 °C, which attained a maximum rate at 325 °C. This was proposed to be associated with the oxidative cross-linking via the methyl groups and is typically observed for high molar mass linear PDMS.

The TGA curves of the SAPE and SAPAs are presented in Figure 6. The SAPE showed better thermal stability than that of α,ω-(dihydroxyalkyl)-terminated poly(dimethylsiloxane) (HAT-PDMS) partly due to their higher molar mass and partly due to the absence of low molar mass oligomer/polymer chains that were present in the HAT-PDMS polymer samples. It should be noted that the GPC analysis of the HAT-PDMS polymer sample gave a broad molar mass distribution with a polydispersity index PDI = 2 (see Table 1). While the SAPE sample had a PDI = 1.37 (for the sample collected after 98 h of reaction period, also see Table 1).

The SAPAs displayed very high thermal stability, particularly SAPA−PDMS(4700) polymer. This is because of the high molar mass of the SAPA−PDMS(4700) polymer, which also had longer PDMS segments when compared to the SAPA−PDMS(1000) polymer. The SAPAs were highly viscous and sticky glue-like in appearance, probably due to the presence of the strong hydrogen bonding between the amide linkages, compared to that of SAPE polymers. However, there was no marked difference in the thermal degradation behavior of the polyesters except for the reasons explained above. All of the investigated polymer samples displayed minimal residual mass and a very similar solid residue at 700 °C, which ranged between 0.25 and 0.5 wt %. While siloxane bond interchange reactions[3,18,19] are common to both systems leading to the formation of cyclic oligomers, the SAPE seem to exhibit a "two-step" depolymerization/degradation (see Figure 6).

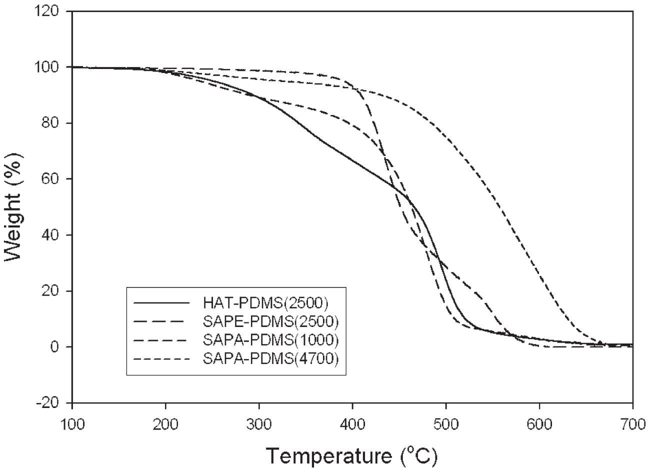


Figure 6. TGA curves (20 °C/min, in N_2) of the silicone aromatic polyester (SAPE) and the silicone aromatic polyamides (SAPAs).

Conclusions

In the present investigation, silicone aromatic polyesters and silicone aromatic polyamides were prepared in reactions that were enzymatically catalyzed by Novozym 435 in toluene at 80 °C and under reduced pressure (400 mmHg, vacuum gauge). High molar mass SAPE was obtained when compared to SAPAs under similar reaction conditions. However, when the reactions of SAPAs were continued beyond 48 h at higher temperature 90 °C with additional 1 mL of toluene under 400 mmHg vacuum, higher molar mass SAPAs were obtained. The SAPAs were highly viscous and sticky glue-like in appearance compared to SAPE. Because of the high viscous nature of the SAPAs, the reaction appeared to be diffusion controlled. Adding additional solvent to the reaction mixture of the SAPAs at elevated temperature was found to reduce the viscosity (by visual observation of mechanical stirring), and thus the reaction was allowed to be driven forward. Both the SAPE and SAPAs were found to be amorphous liquids at room temperature but were found to contain hard domains resulting from the segregation of the segments of aromatic polyesters and aromatic polyamides, respectively. The DSC analysis of the SAPA's indicated that the melting temperature (T_m) and melting enthalpy (ΔH_m) increased with increased amide content.

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