Synthesis and Characterization of Novel Hydroxyalkyl Carbamate and Dihydroxyalkyl Carbamate Terminated Poly(dimethylsiloxane) Oligomers and Their Block Copolymers with Poly(ϵ-caprolactone)

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ABSTRACT: Novel hydroxyalkyl carbamate, dihydroxyalkyl carbamate terminated poly(dimethylsiloxane) (PDMS) oligomers, and carbamate-linked block copolymers with poly(ϵ-caprolactone) (PCL) were designed, synthesized, and characterized using combinatorial and high-throughput experimentation (CHTE). Novel hydroxyalkyl carbamate terminated PDMS oligomers were synthesized by reacting 3-aminopropyl terminated PDMS oligomers with ethylene carbonate (EC); further reaction of these oligomers with ϵ-caprolactone (ϵ-CL) resulted in novel carbamate-linked PCL−PDMS−PCL triblock copolymers. Novel dihydroxyalkyl carbamate terminated PDMS oligomers were synthesized by reacting 3-aminopropyl terminated PDMS with glycerine carbonate (GC); further reaction of these oligomers with ϵ-CL resulted in novel H-type block copolymers of PDMS and PCL. Structural characterization of the synthesized oligomers and block copolymers was carried out with high-throughput FTIR, DSC, and NMR. Molecular weights of the oligomers and block copolymers were characterized using Rapid GPC.

1. Introduction

Silicones are the most important of the semi-inorganic polymers. Each year over 10^9 kg of silicones are produced industrially. Among all of the silicone polymers, poly(dimethylsiloxane) (PDMS) is the most important in terms of commercial applications. PDMS finds use in many fields such as elastomers, coatings, biomaterials, electronics, microlithography, and aerospace applications. The high interest in PDMS is due to its intriguing properties such as high thermal and electrical stability, very low surface energy, high lubricity, high gas permeability, low glass transition temperature, and low toxicity.[1−3] PDMS polymers are prepared by the ring-opening polymerization of the cyclic trimer or a tetramer with either acid or base catalysis due to the polar nature of Si−O bond.[4−7] Despite their interesting properties, extremely high molecular weight is needed in order to obtain useful mechanical properties. Therefore, to improve the mechanical properties of PDMS, it is either cross-linked or modified via functionalization, block copolymerization, or grafting.[8−10]

Block copolymers are useful in creating materials having hybrid properties by combining different polymers having different properties. Over the past few decades, a significant amount of research has been carried out mainly focusing on AB diblock or ABA triblock copolymers.[11] With the development of new synthetic methods, novel block copolymer structures such as H-type block copolymers have been introduced.[12−14] Block copolymers of poly(ϵ-caprolactone) (PCL) and PDMS can be obtained by reacting organofunctional PDMS with ϵ-caprolactone (ϵ-CL).[15] PCL is known to be miscible with a variety of polymers and PDMS is immiscible with many polymers because of its low solubility parameter. Block copolymers of PDMS and PCL combine the excellent properties (surface modifying, toughening, etc.) of PDMS with the compatibilizing effect of PCL. The combination of properties of PCL and PDMS makes these block copolymers excellent candidates for surface modifying additives, drug encapsulation, and biomaterials applications.[15−19]

Cyclic carbonates undergo reactions with various nucleophiles without releasing a volatile byproduct. The reaction of five- and six-membered cyclic carbonates with amines (aminolysis) yields carbamate or urethane groups without using isocyanates and has received a lot of attention. The reaction of cyclic carbonates with amines finds use in the formation of linear polymers and also in thermosetting systems with promising features such as lower viscosity, higher pot-life, high flexibility, good impact resistance, and good adhesion.[20−25]

Combinatorial experimentation using high throughput methods increases the efficiency of research since a number of chemically distinct compositions can be prepared in a single experiment. The use of combinatorial and high throughput experimentation (CHTE) in polymer science is fairly new when compared with its use in pharmaceutical science and catalysis. The successful use of CHTE in polymer and coatings science depends on the design and development of new tools and new software for experiment execution, design of experiments, and analysis of results.[26,27] Webster has reported the use of CHTE for the development of coating systems. The workflow includes systems for polymer synthesis, polymer characterization, coating formulation, and screening of the final coating.[28,29] In addition, reports have been presented focusing on method development for polymer synthesis and characterization of a number of polymer systems using CHTE.[30−36]

This study demonstrates the design, synthesis, and characterization of novel hydroxyalkyl carbamate and dihydroxyalkyl carbamate terminated PDMS oligomers and carbamate-linked triblock and H-type block copolymers of PDMS and PCL. The entire study was carried out in a single combinatorial library where a range of compositions of PDMS and PCL were explored. In addition, both high-throughput and conventional methods were used in order to characterize these compounds.

2. Experimental Section

2.1. Starting Materials. Bis(3-aminopropyl)tetramethyldisiloxane (BAPTMDS), and 3-aminopropyl terminated poly(dimeth-

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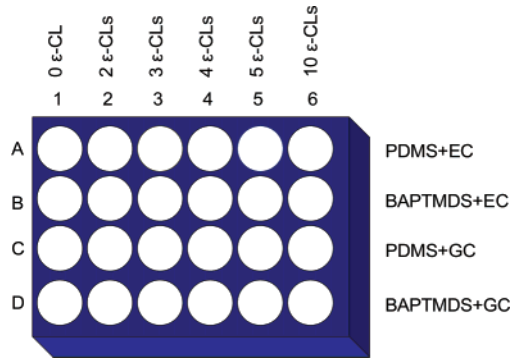


Figure 1. Combinatorial experimental design for the synthesis experiment.

ylsiloxane) (PDMS; number-average molecular weight $M_n = 875$ g/mol) were purchased from Gelest Inc. Ethylene carbonate (EC), tin(II) 2-ethylhexanoate, and $CDCl_3$ were received from Aldrich. Glycerine carbonate (GC) and ϵ-caprolactone (ϵ-CL) were provided by Huntsman and Solvay Caprolactones, respectively. Toluene and THF were received from VWR International. All materials were used as received without further purification.

2.2. Instrumentation. 2.2.1. Symyx Library Studio. Library Studio was used as a primary design tool for designing polymer libraries and coating formulations. The software allows for both full factorial and statistical experimental designs and these designs are stored in a common database. Here, 6 × 4 arrays of experiments were designed in this study.

2.2.2. Symyx Batch Reactor System. The batch reactor is composed of a dual-arm liquid dispensing robot housed in a triple glovebox purged with nitrogen. The robot dispenses liquid reagents according to Library Studio formulations. The three center wells in the synthesis platform can hold arrays of reaction vials and up to 288 simultaneous 1 mL reactions can be run with magnetic stirring and heating to 120 °C. Here, 6 × 4 arrays of 8 mL vials were used in this experiment.

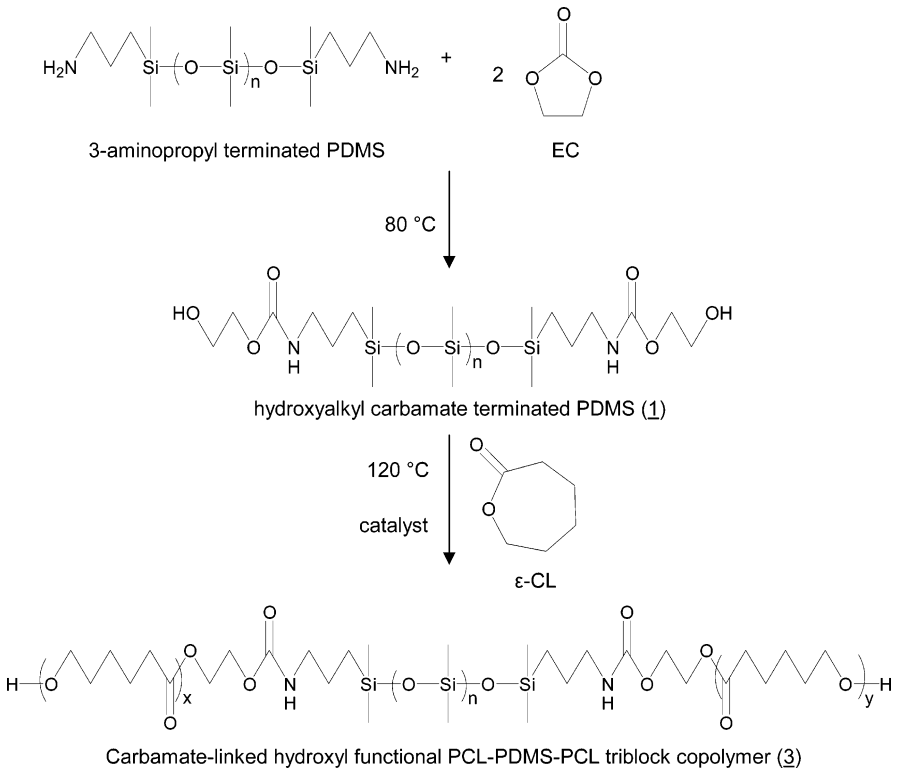
Table 1. Library Design for the Synthesis of Hydroxyalkyl Carbamate and Dihydroxyalkyl Carbamate Terminated PDMS Oligomers and Their Block Copolymers with PCL

array position	type of siloxane	type of carbonate	siloxane (mmol)	carbonate (mmol)	ϵ-CL (mmol)	no. of ϵ-CL per hydroxyl
A1	PDMS	EC	3.43	6.86	0.00	0.00
A2	PDMS	EC	2.29	4.57	9.14	2.00
A3	PDMS	EC	2.00	4.00	12.00	3.00
A4	PDMS	EC	1.71	3.43	13.71	4.00
A5	PDMS	EC	1.43	2.86	14.29	5.00
A6	PDMS	EC	0.91	1.83	18.29	10.00
B1	BAPTMDS	EC	8.05	16.10	0.00	0.00
B2	BAPTMDS	EC	4.02	8.05	16.10	2.00
B3	BAPTMDS	EC	3.22	6.44	19.31	3.00
B4	BAPTMDS	EC	2.41	4.83	19.31	4.00
B5	BAPTMDS	EC	2.01	4.02	20.12	5.00
B6	BAPTMDS	EC	1.21	2.41	24.14	10.00
C1	PDMS	GC	3.43	6.86	0.00	0.00
C2	PDMS	GC	1.71	3.43	13.71	2.00
C3	PDMS	GC	1.43	2.86	17.14	3.00
C4	PDMS	GC	1.14	2.29	18.29	4.00
C5	PDMS	GC	0.91	1.83	18.29	5.00
C6	PDMS	GC	0.57	1.14	22.86	10.00
D1	BAPTMDS	GC	8.05	16.10	0.00	0.00
D2	BAPTMDS	GC	2.41	4.83	19.32	2.00
D3	BAPTMDS	GC	2.01	4.02	24.15	3.00
D4	BAPTMDS	GC	1.61	3.22	25.76	4.00
D5	BAPTMDS	GC	1.21	2.41	24.15	5.00
D6	BAPTMDS	GC	0.70	1.41	28.17	10.00

2.2.3. Autodose Powdernium. Automated powder dispensing is done using an Autodose Powdernium housed in the same triple glovebox as the batch reactor. It can dispense powders over a weight range of 0.2 mg to a few hundred grams. Dispensed weights are recorded using a balance to an accuracy of 0.1 mg.

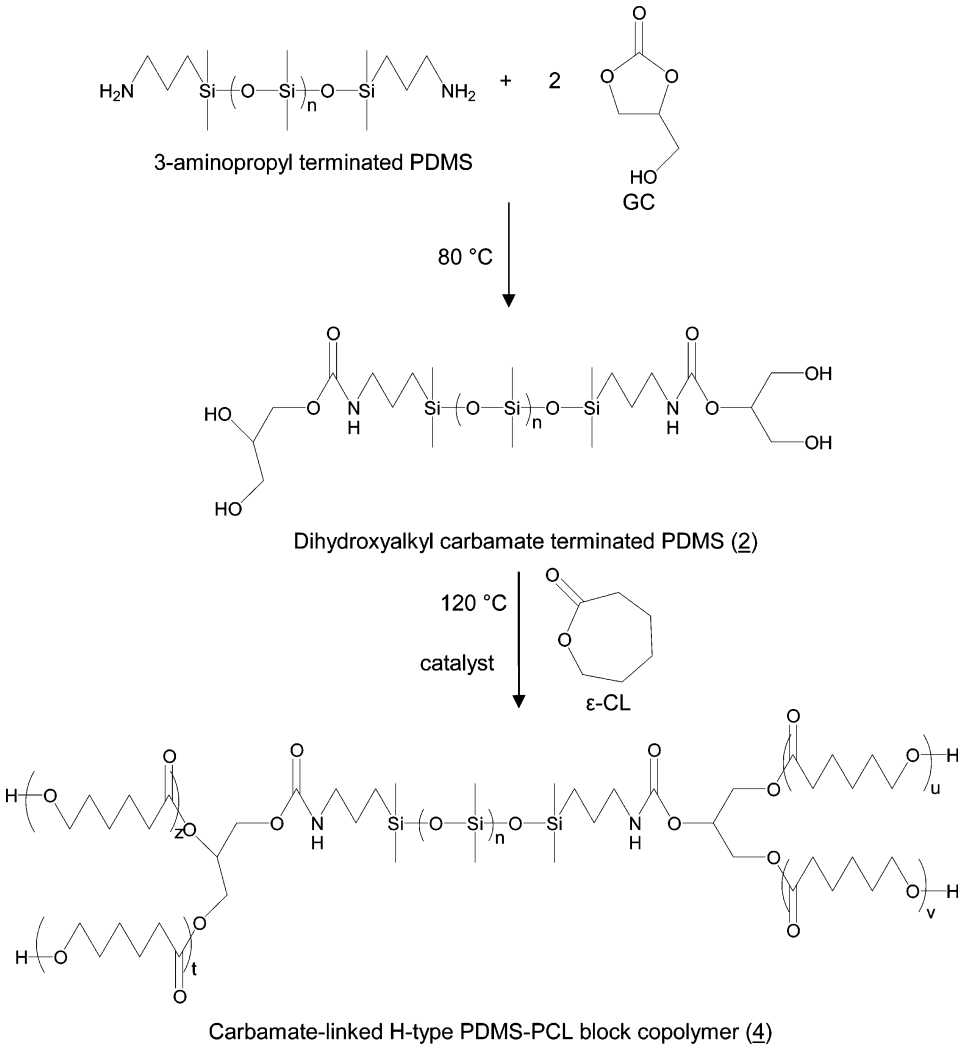
2.2.4. Symyx Rapid GPC. High-throughput GPC was performed on a Symyx Rapid GPC with an evaporative light scattering detector (PL-ELS 1000), equipped with 2xPLgel Mixed-B columns (10 μm particle size) at 45 °C. Solutions of 1 mg/mL sample in THF were prepared before run; calibration was carried out using polystyrene

Scheme 1. Reaction Scheme for the Synthesis of Hydroxyalkyl Carbamate Terminated PDMS Oligomers and Their Block Copolymers with PCL[a]



[a] When $n = 0$, siloxane = BAPTMDS, and products were named **1′** and **3′**.

Scheme 2. Reaction Scheme for the Synthesis of Dihydroxyalkyl Carbamate Terminated PDMS Oligomers and Their Block Copolymers with PCL[a]



[a] When $n = 0$, siloxane = BAPTMDS, and products were named **2′** and **4′**.

standards and THF was used as eluent at a flow rate of 2.0 mL/min. Molecular weight and polydispersity index were determined using Epoch software.

2.2.5. High Throughput FTIR. A Bruker Vertex 70 with HTS accessory was used. First, 3% (w/w) sample solutions were prepared in THF, and then 5 μL sample solutions were deposited on a 96 position silicon wafer with a liquid handling robot and placed in an oven at 60 °C overnight to evaporate THF. The samples were run in absorbance mode, with a resolution of 4 cm^{-1} and 6 scans per sample.

2.2.6. Differential Scanning Calorimetry (DSC). DSC Q1000 from TA Instruments with an autosampler was used for glass transition temperature (T_g) and melting point (T_m) determinations. Samples synthesized from PDMS were subjected to a heat−cool−heat cycle from −160 to +200 °C and samples synthesized from BAPTMDS were subjected to a heat−cool−heat cycle from −100 to +200 °C by ramping 10 °C/min for both cooling and heating. The second heating cycle was used to characterize the samples.

2.2.7. Nuclear Magnetic Resonance Spectroscopy (NMR). ^{1}H NMR measurements were done using a JEOL-ECA 400 (400 MHz) NMR spectrometer coupled with an autosampler accessory. Data acquisition was done using 16 scans with a 0.3 s delay time. Sample concentration was 25 mg/mL and $CDCl_3$ was used as the solvent.

2.3. Synthesis Experiments. A combinatorial experiment was designed with Library Studio as seen in Figure 1. The amount and type of siloxane used, array positions, amounts of EC, GC, and ϵ-CL used and theoretical number of ϵ-CL per hydroxyl are summarized in Table 1.

2.3.1. Library Synthesis of Hydroxyalkyl Carbamate and Dihydroxyalkyl Carbamate Terminated Siloxane Oligomers. BAPTMDS, PDMS, and GC were placed into the reagent holders of the synthesis robot and EC was placed into the holders of the Autodose Powdernium. PDMS, BAPTMDS, and GC were dispensed into the vials with the liquid handling robot and EC was dispensed with Autodose Powdernium according to the library design. After the reagents were dispensed, the gasketed array lid was screwed tightly to the 6 × 4 array. The reaction was run at 80 °C for 10 h with magnetic stirring. After 10 h, the array was cooled to room temperature, and the array lid was removed from the system.

2.3.2. Library Synthesis of Carbamate-Linked Triblock and H-Type Block Copolymers of PDMS and PCL. The products from the previous step were used as reagents in this step. The 6 × 4 array and ϵ-CL were placed into the holders of the synthesis robot to synthesize block copolymers of PDMS and PCL with carbamate linking groups. The vials containing carbamate-linked functional PDMS oligomers that were not to be reacted with ϵ-CL (column 1) were replaced with empty vials. ϵ-CL was dispensed to the vials with the liquid handling robot and 1 drop of tin(II) 2-ethylhexanoate in 10% toluene solution (approximately 0.05% v/v tin(II) 2-ethylhexanoate to total solids) was also added to the vials as a catalyst. Following dispensing of the ϵ-CL, the gasketed array lid was screwed tightly to the 6 × 4 array. The reaction was run at 80 °C

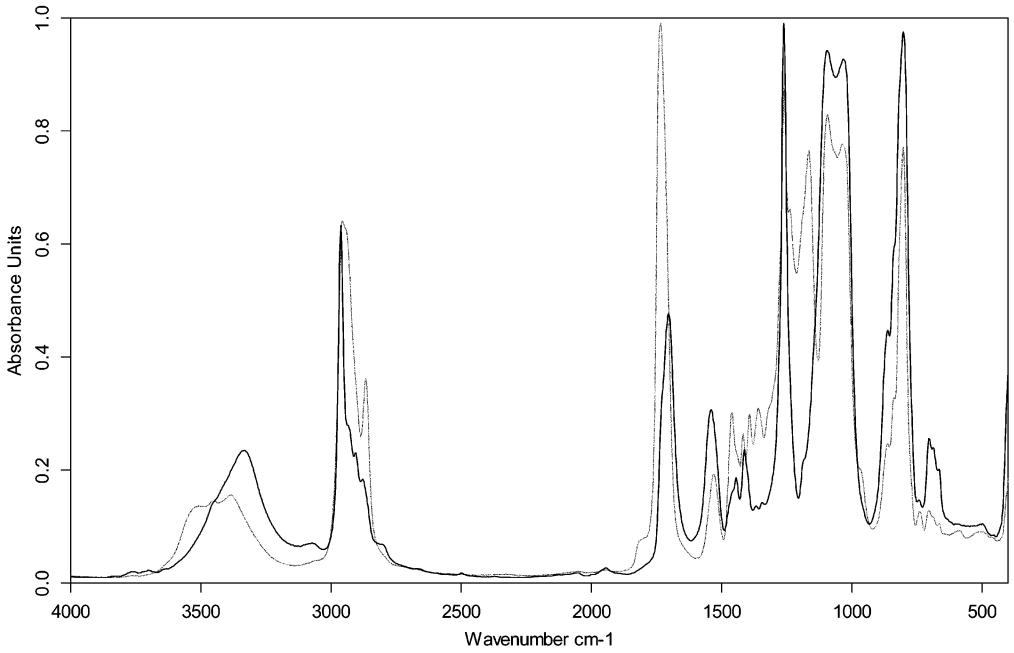


Figure 2. FTIR spectra of dihydroxyalkyl carbamate terminated PDMS (**2**) (sample C1 (black)) and carbamate-linked H-type PDMS−PCL block copolymer (**4**) (sample C4) (gray)).

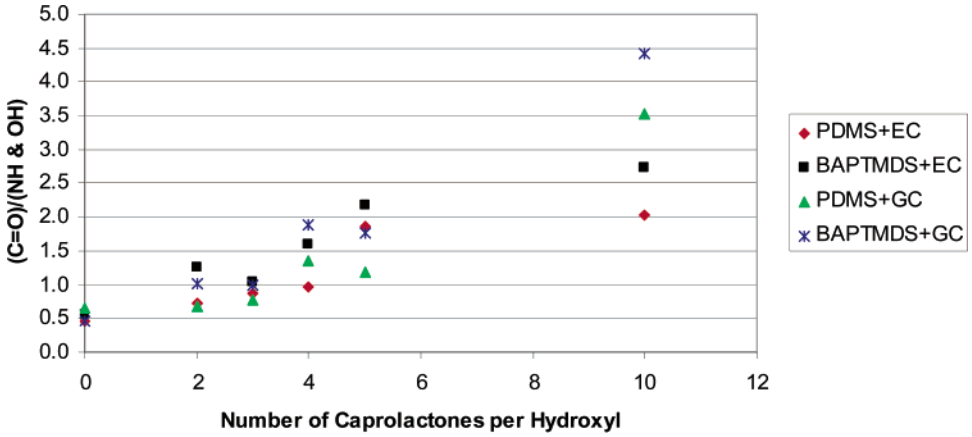


Figure 3. Plots of $A_{(C=O)}/A_{(NH\&OH)}$ (peak area) vs number of ϵ-CLs per hydroxyl.

for 10 h with magnetic stirring, and then the reaction temperature was increased to 120 °C and held for 10 more hours. After cooling to room temperature, the polymers were characterized without further purification.

3. Results and Discussion

We are interested in the design, formulation, and characterization of cross-linked siloxane−polyurethane systems for advanced marine coating applications. These cross-linked siloxane−polyurethane systems provide coatings having low surface energy, toughness, good adhesion, and stability during water immersion.[37] PDMS oligomers with hydroxyalkyl carbamate end groups are of interest in order to increase the compatibility between the PDMS chain ends and the polyurethane component in the coating system. In addition, PCL is known to form compatible blends with several polymers such as polyurethane and a PCL polyol is used as one of the components in the siloxane-urethane coating system. Therefore, PCL blocks were added to the functional PDMS oligomers to further increase their compatibility between the polyurethane and PDMS. The use of dihydroxyalkyl carbamate terminated PDMS oligomers and the resulting H-type block copolymers with PCL might also result in a coating having a different morphology than difunctional polymers when used in the polyurethane coating formulation. Automated combinatorial and high-throughput synthesis and characterization methods were used in order to be able to rapidly achieve the goals of this study. One of the advantages of using automated high-throughput experimentation is that the same experimental conditions are applied to all of the samples.

The reaction of 3-aminopropyl terminated PDMS with EC results in novel hydroxyalkyl carbamate terminated PDMS (**1**) oligomers, as shown in Scheme 1. Further reaction with ϵ-CL results in novel carbamate-linked PCL−PDMS−PCL triblock copolymers (**3**), also shown in Scheme 1. Both a low molecular weight 3-aminopropyl terminated PDMS and BAPTMDS were used as siloxanes. BAPTMDS is disiloxane with 3-aminopropyl end groups. When BAPTMDS was used, reaction products are denoted as **1′** and **3′**. Reaction of BAPTMDS with cyclic siloxane (octamethylcyclotetrasiloxane) results in 3-aminopropyl terminated PDMS. Here, BAPTMDS was used as a model compound to help characterize the compositions.

The reaction of 3-aminopropyl terminated PDMS with GC results in novel dihydroxyalkyl carbamate terminated PDMS (**2**) oligomers. Scheme 2 summarizes the reaction products for

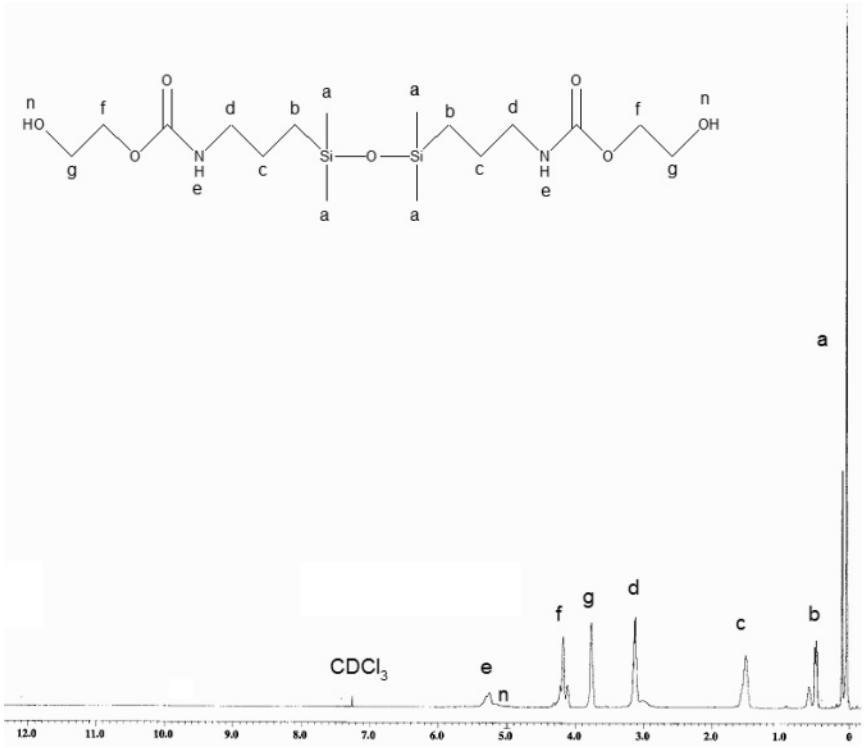


Figure 4. [1]H NMR spectrum of hydroxyalkyl carbamate terminated siloxane (**1′**) (sample B1).

Figure 5. [1]H NMR spectrum of dihydroxyalkyl carbamate terminated siloxane (**2′**) (sample D1).

reaction of PDMS with GC and further reaction with ϵ-CL, which results in novel carbamate-linked H-type block copolymers of PDMS and PCL (**4**). As above, both 3-aminopropyl terminated PDMS and BAPTMDS were used as siloxanes. When BAPTMDS was used, the reaction products were noted as **2′** and **4′**. As seen in both Schemes 1 and 2, the reaction of 3-aminopropyl terminated PDMS with EC results in only one isomer, whereas the reaction with GC results in two isomers depending on which ester bond is broken during the reaction. The first isomer, which contains a 1° and 2° alcohol, is the major product and the second isomer, which contains only 1° alcohol, is the minor product.[20,21] When reacted with ϵ-CL the result will be H-type block copolymers, which are also known as A_2-BA_2 block copolymers. In this case A will be PCL and B will be PDMS; therefore, the product can be denoted as $(PCL)_2$PDMS-$(PCL)_2$.

All of the synthesis experiments were carried out in parallel in a single two-step experiment and the experiment design is seen in Figure 1. The rows are labeled A through D and the columns are labeled 1 through 6. The compositions vary both

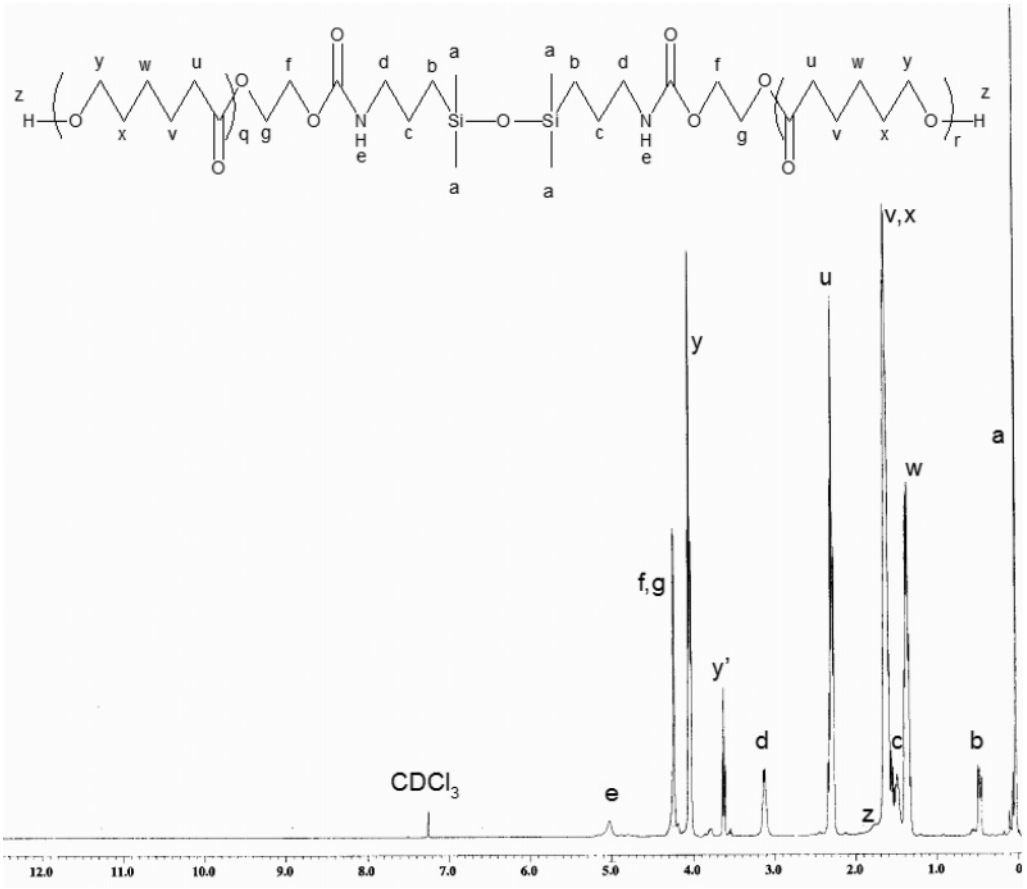


Figure 6. ^{1}H NMR spectrum of carbamate-linked PCL−PDMS−PCL triblock copolymer (**3′**) (sample B5). Peak y′ is from the methylene protons at the chain end.

row-wise and column-wise in the experimental design resulting in 24 unique compositions. Row A consists of reacting PDMS with EC, row B consists of reacting BAPTMDS with EC, row C consists of reacting PDMS with GC, and finally row D consists of reacting BAPTMDS with GC. Furthermore, column-wise, the length of PCL blocks increases from 2 ϵ-CLs per hydroxyl (column 2) up to 10 ϵ-CLs per hydroxyl (column 6). No ϵ-CL was added to column 1; thus, column 1 consists of only the hydroxyalkyl terminated compounds.

Structural characterization of hydroxyalkyl carbamate terminated PDMS oligomer (**1**) (sample A1) with FTIR shows characteristic peaks of −OH, −NH, −CH, −C═O, and −Si−O at 3450, 3340, 2960, 1700, and 1100 cm^{-1}, respectively. No evidence of cyclic carbonate carbonyl peak was seen at 1790 cm^{-1}, which indicates that all of the EC has been consumed and the reaction has reached completion. The primary amine peak from the aminopropyl-functional starting materials cannot be followed here to determine whether all of the amine has been reacted. Since the absorbance of both primary amine (from 3-aminopropyl terminated PDMS) and secondary amine (from hydroxyalkyl carbamate terminated PDMS) is around 3400 cm^{-1}, the primary and secondary amine peaks overlap. In addition, the primary amine from the PDMS does not have a strong absorbance peak in the FTIR. When ϵ-CL is added to hydroxyalkyl carbamate terminated PDMS (**1**), characteristic peaks at 3550, 3380, 2960, 1740, and 1100 cm^{-1} are seen for −OH, −NH, −CH, −C═O, and −Si−O, respectively, indicating that the carbamate-linked PCL−PDMS−PCL triblock copolymer (**3**) has been synthesized.

From Figure 2, it can be seen that similar behavior was observed for dihydroxyalkyl carbamate terminated PDMS (**2**) and PDMS−PCL H-type block copolymer (**4**). Again, no evidence of the cyclic carbonate carbonyl peak was observed. One of the most striking observations from FTIR analysis is the shift in the carbonyl peak (Figure 2). Carbamate carbonyl is seen at 1700 cm^{-1} and when ϵ-CL is added the carbonyl peak shifts to 1740 cm^{-1} due to the addition of ester groups to the siloxane backbone. The carbamate carbonyl does not actually disappear but becomes dominated by the ester carbonyl; therefore, ester carbonyl is more apparent than the carbamate carbonyl due to presence of the large amount of ester groups relative to the carbamate groups.

Figure 3 shows a plot of peak area of the (−C═O) peak to the peak area of the (−NH) and (−OH) peaks vs the number of theoretical ϵ-CLs per hydroxyl. It can be clearly seen that the peak area ratio of (−C═O) relative to (−NH) and (−OH) increases as the number of ϵ-CLs per hydroxyl is increased which is an indication of increase in the PCL block length.

The ^{1}H NMR spectrum in Figure 4 shows all of the characteristic peaks of hydroxyalkyl carbamate terminated disiloxane (**1′**) (sample B1). No evidence of primary amine protons at 1.15 ppm or ethylene carbonate protons at 4.50 ppm were seen which indicates that all amine and ethylene carbonate reacted to completion. Therefore, the NMR spectrum in Figure 4 shows that the hydroxyalkyl carbamate terminated siloxane oligomers (**1′**) were successfully synthesized. Similarly, the NMR spectrum in Figure 5 shows all of the characteristic peaks of dihydroxyalkyl carbamate terminated disiloxane (**2′**) (sample D1). No evidence of primary amine protons at 1.15 ppm or glycerine carbonate protons at 4.50 ppm (the most intense peak) were seen which indicates that all of the amine has reacted with glycerine carbonate. Therefore, the NMR spectrum in Figure 5

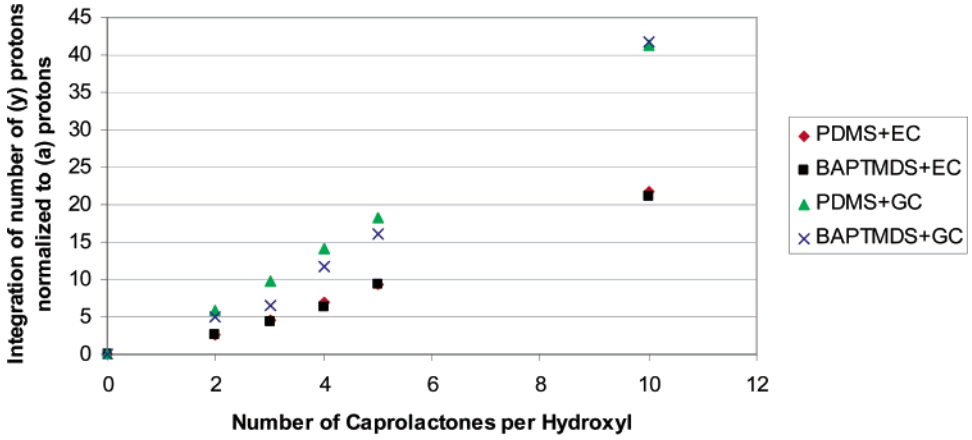


Figure 7. Number of "y" protons normalized to "a" protons vs number of ϵ-CLs per hydroxyl (see Figures 4−6).

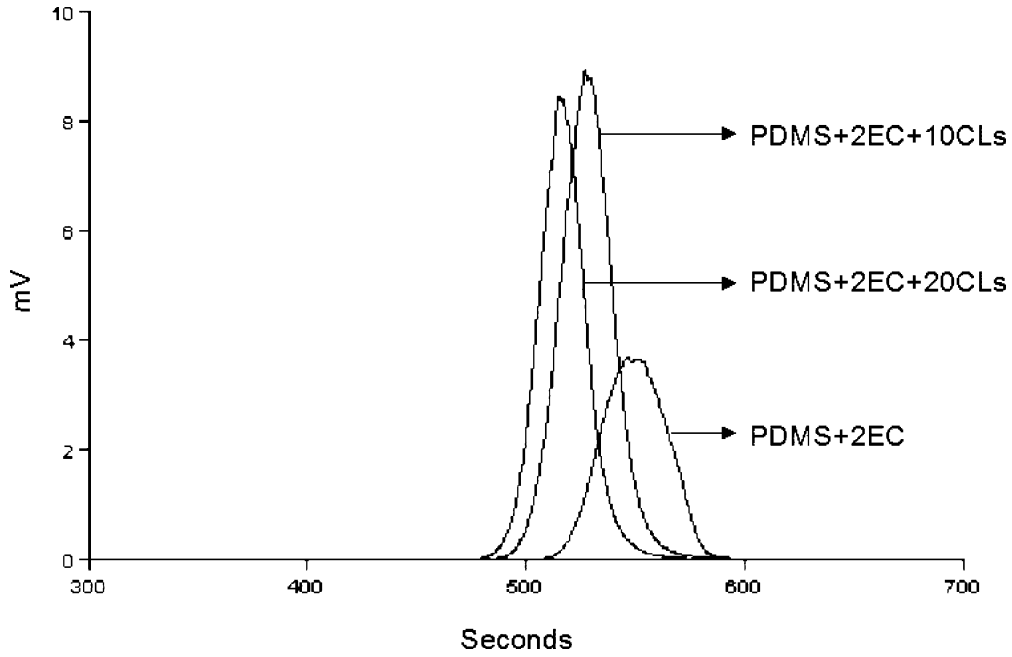


Figure 8. Rapid-GPC curves of hydroxyalkyl carbamate terminated PDMS oligomer and its block copolymers with 5 and 10 CLs per hydroxyl (samples A1, A5, and A6 respectively).

shows the successful synthesis of dihydroxyalkyl carbamate terminated siloxane with both isomeric end groups. Figure 6 shows the NMR spectrum of (**3′**) (sample B5) and it can be clearly seen that a PCL−PDMS−PCL triblock copolymer with carbamate linking groups has been synthesized. All of the characteristic peaks can be clearly seen which indicates synthesis of the intended product. Figure 7 shows a plot of the integration of the proton (y) in the PCL block (see Figure 6) normalized to the proton (a) in the siloxane block (see Figures 4−6) vs the theoretical number of ϵ-CLs per hydroxyl. As the number of ϵ-CLs per hydroxyl increases the peak ratio increases systematically, which is an indication of an increase in the block length of PCL which is expected.

Figure 8 shows GPC plots of a hydroxyalkyl carbamate terminated PDMS (sample A1), and carbamate-linked PCL−PDMS−PCL triblock copolymers (samples A5 and A6). For all compositions only one peak is seen which indicates the formation of block copolymers and no formation of single PCL blocks. In addition, sample A6 has a shorter retention time than sample A5 and sample A5 has a shorter retention time than sample A1 which indicates increase in M_n as more ϵ-CLs are added. From Figure 9 it can be seen that M_n increases systematically as the number of ϵ-CL per hydroxyl is increased which is expected. At each PCL block length, the M_n for compositions based on PDMS is higher than the M_n for compositions based on BAPTMDS due to the higher molecular weight of PDMS compared to BAPTMDS. In addition, the M_n values for the compositions based on the dihydroxyalkyl terminated PDMS or BAPTMDS (H-type copolymers) are higher than the M_n values for compositions based on the hydroxyl terminated oligomers. This is due to the fact that the copolymers were prepared having the same number of e-CL units per hydroxyl, thus the H-type copolymers have a higher molecular weight than the linear triblock copolymers.

For further characterization, the thermal properties of the compounds were determined and several interesting features were observed. Figure 10 shows the DSC plots of the hydroxyalkyl carbamate terminated PDMS oligomer (**1**) (sample A1) and a carbamate-linked PCL−PDMS−PCL triblock copolymer (**3**) (sample A2). From the plots, two T_g values are seen. The first T_g (T_{g1}) is around −121 °C which is characteristic of PDMS and is only seen for the oligomers that used PDMS as the siloxane starting material. The second T_g (T_{g2}) is seen for all 24 compositions and the value depends on the composition of the oligomer. T_{g2} values for all compositions are shown in Table 2. Recently, we reported the library synthesis and characteriza-

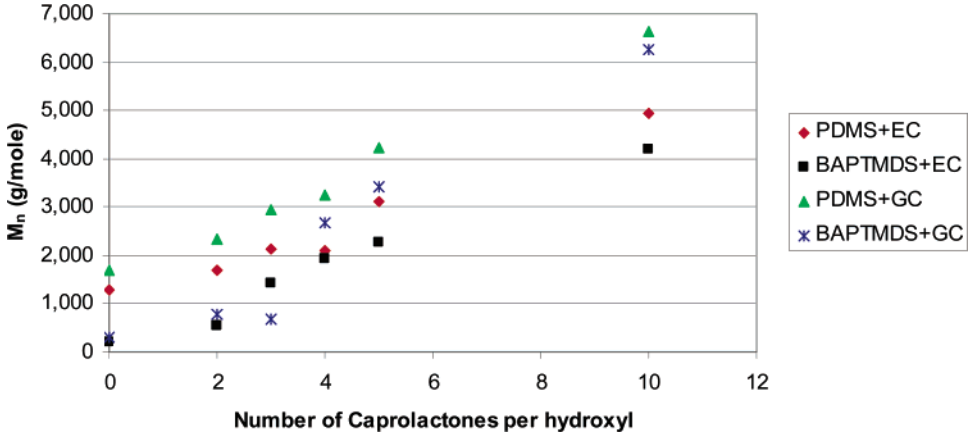


Figure 9. Rapid GPC results of the combinatorial library.

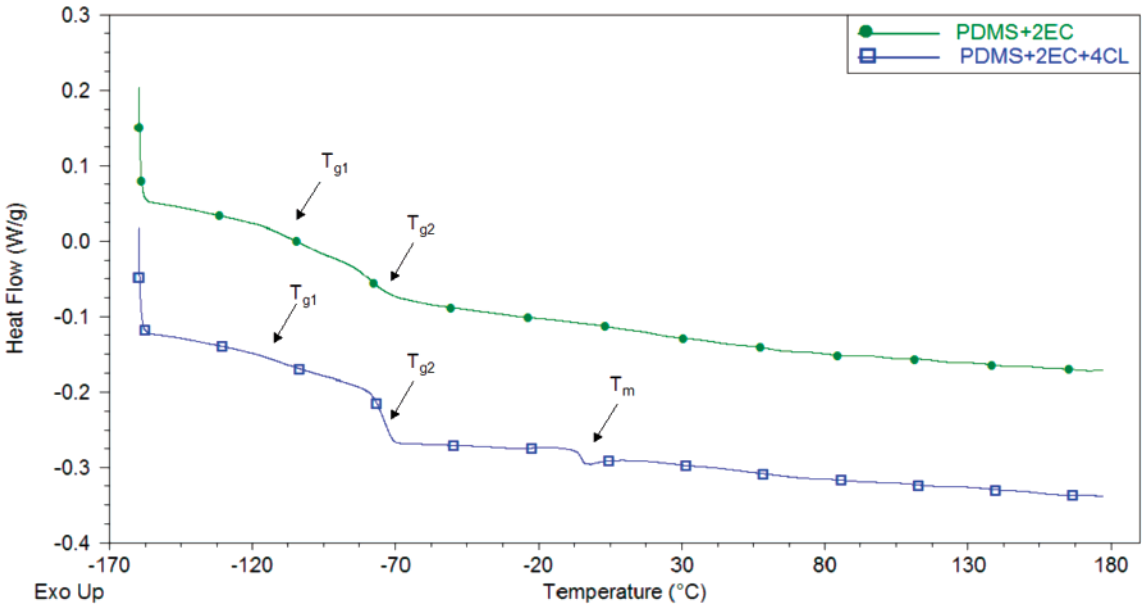


Figure 10. DSC curves of hydroxyalkyl carbamate terminated PDMS oligomer (**1**) (sample A1) and carbamate-linked PCL−PDMS−PCL triblock copolymer (**3**) (sample A2).

Table 2. Glass Transition Temperatures of Siloxane−Carbamate Mixing and Melting Temperatures of PCL Blocks

array position	T_{g2} (°C)	T_m (°C)	array position	T_{g2} (°C)	T_m (°C)
A1	−79.36		C1	−63.96	
A2	−73.56	−2.16	C2	−64.37	7.02
A3	−72.43	8.49	C3	−66.82	11.57
A4	−73.24	17.28	C4	−63.02	23.30
A5	−72.01	28.86	C5	−59.66	31.64
A6	−75.69	42.29	C6	−60.86	44.61
B1	−34.42		D1	−20.37	
B2	−53.85		D2	−52.94	
B3	−57.25	12.62	D3	−55.21	13.65
B4	−58.90	21.98	D4	−51.11	23.72
B5	−53.38	31.71	D5	−53.32	33.44
B6	−52.64	46.64	D6	−52.35	46.29

tion of 3-aminopropyl terminated PDMS oligomers and PCL−PDMS−PCL block copolymers having amide linking groups between PCL and PDMS blocks.[30] T_{g2} was not observed in any of the polymers that were reported. Therefore, T_{g2} is unique to these novel compositions. For the alkyl carbamate terminated PDMS oligomers, T_{g2} is likely due to the formation of a separate end group phase that is induced by the strong hydrogen bonding that can form between carbamate groups. T_{g2} values are on average 8 °C higher for compositions containing GC than EC due to presence of a higher number of hydroxyl groups, which can also participate in hydrogen bonding. When BAPTMDS is used, there is no T_{g1} and T_{g2} values are on average 20 °C higher than for compositions containing PDMS, indicating the formation of a single amorphous phase. The absence of T_{g1} is due to the fact that there are insufficient siloxane segments to phase separate from the hydrogen bonded alkyl carbamate phase. That the T_{g2} values are 20° higher for the compositions containing BAPTMDS as compared to those from PDMS indicates that the T_{g2} phase, when the PDMS oligomer is used, contains some additional siloxane segments which reduce the glass transition temperature.

In addition, it can be seen from Figure 11 that the T_m for PCL blocks shifts to higher values as the PCL block length increases. The trend in T_m of PCL blocks can better be seen from Table 2. T_m values of samples containing 2 and 3 ϵ-CLs per hydroxyl are below room temperature indicating that those polymers are amorphous at 25 °C. The samples containing 5 and 10 ϵ-CLs per hydroxyl are more crystalline than amorphous when compared to other samples containing less ϵ-CLs per hydroxyl. Obtaining a T_m value with as low as 2 ϵ-CL repeat units is very unusual for many conventional block copolymers and indicates that these block copolymers are highly phase separated, even at these very low block lengths.

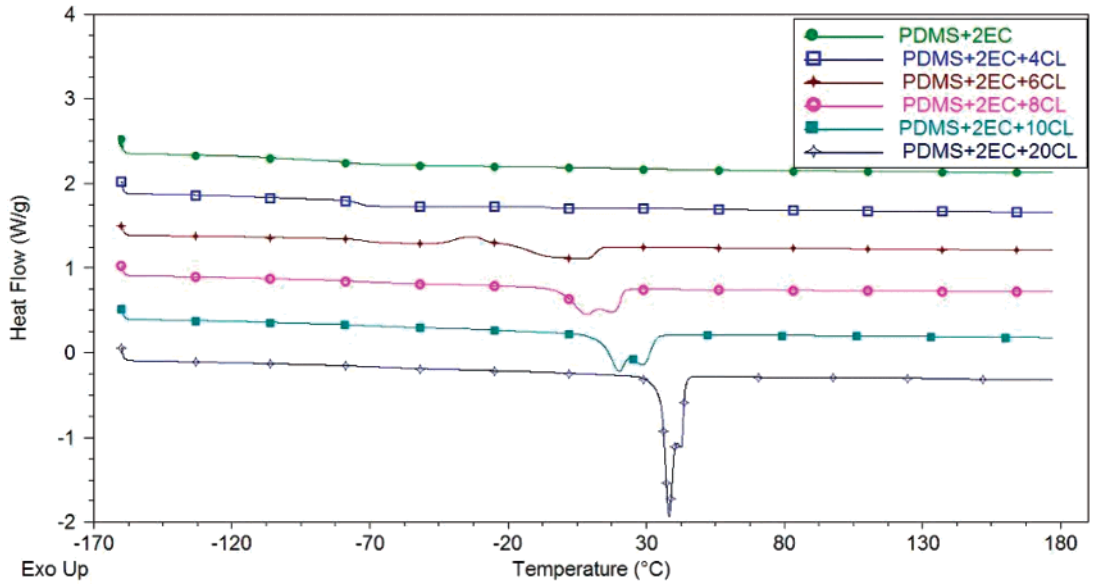


Figure 11. DSC plots of row A compositions (see Figure 1).

The T_m data of the PCL blocks provides additional structural information. The shift in T_m of the PCL blocks as more ϵ-CL is added to the compositions verifies an increase in the PCL block length. The T_m of PCL is expected to increase as the degree of polymerization increases and is known to stabilize around 60 °C.[15] The T_m of the PCL blocks in the same array column being in the same range is also indicative of the formation of di- (hydroxyalkyl carbamate terminated) and tetra-(dihydroxyalkyl carbamate terminated) functional compounds and the corresponding block copolymers. The experiment was designed on the basis of PCL repeat units per hydroxyl end group which means that in the same column twice as much ϵ-CL was added to the compositions having the dihydroxy end groups compared to the hydroxyl terminated oligomers. Thus, the degree of polymerization of the PCL blocks is the same for the linear block copolymers and the H-type block copolymers. The bimodal nature of the PCL melting peak indicates that there is more than one crystalline phase. The lower melting point for the PCL segments in the copolymers may be due to the presence of the low T_g PDMS creating a more mobile environment for the PCL crystalline areas.[38]

Finally, this report also demonstrates the power of combinatorial and high-throughput experimentation in novel polymer synthesis and characterization. All synthesis experiments were carried out in a single library. In part of the library, the block length of PCL was increased one ϵ-CL unit at a time. Even though one ϵ-CL repeat unit may not appear to be a very significant increase, with the use of high throughput experimentation this difference can be efficiently explored. The results of the integration of peaks from ^{1}H NMR (Figure 7) and the results of T_m values from DSC (Table 2 and Figure 11) demonstrate that single ϵ-CL unit increments can be detected. Thus, using high-throughput experimentation the effect of fine increments in composition on performance properties can be efficiently explored. An additional benefit comes from applying the same experimental conditions to all the samples, dispensing of all the reagents very accurately, and using disposable, clean vials for each experiment. Thus, the change in performance properties observed is known to be due to compositional changes and not due to experimental variations.

4. Conclusions

Novel hydroxyalkyl carbamate terminated PDMS, dihydroxyalkyl carbamate terminated PDMS, carbamate-linked PCL−PDMS−PCL block copolymers and H-type block copolymers of PDMS and PCL with carbamate linking groups were synthesized using an automated high throughput polymer synthesis unit. The design of the experiment was done combinatorially to explore a range of compositions. Characterization with high-throughput FTIR, NMR, DSC, and Rapid-GPC verified the formation of di- and tetrahydroxy functional PDMS oligomers and block copolymers with PCL blocks. PCL block length was set to a maximum of 10 ϵ-CLs per hydroxyl and successfully linked to the PDMS backbone.

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Supporting Information Available: Additional information reagarding the GPC characterization (Table S1) and FTIR analysis (Figure S1) used in this study. This material is available free of charge via the Internet at http://pubs.acs.org.

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