Synthesis and characterization of organosiloxane modified segmented polyether polyurethanes

L.F. Wang[a], Q. Ji[b], T.E. Glass[b], T.C. Ward[b], J.E. McGrath[b,*], M. Muggli[c], G. Burns[d], U. Sorathia[e]

[a]*Johns Manville Corporation, 10100 W. Ute Avenue, Littleton, CO 80162, USA*
[b]*Virginia Polytechnic Institute and State University, Department of Chemistry and NSF Science and Technology Center: High Performance Polymeric Adhesives and Composites, Blacksburg, VA 24061-0344, USA*
[c]*3M Center, Building 102-1W-28, St. Paul, MN 55144, USA*
[d]*Dow Corning, P.O. Box 994, 2200 West Salzburg, Midland, MI 48686, USA*
[e]*Naval Surface Warfare Center, Carderock Division, 1661, Bay Head Drive, Annapolis, MD 21401, USA*

Abstract

Segmented polyurethanes derived from a 1000 $\bar{M}_n$ hydroxyl terminated polytetramethylene oxide soft segment, 4,4$'$-methylene diphenyl diisocyanate, MDI, and 1,4-butanediol were modified with a 1200 $\bar{M}_n$ secondary aminoalkyl functional polydimethylsiloxane (PDMS) oligomer via solution polymerization in tetrahydrofuran (THF)/dimethylacetamide (DMAC). Various compositions were studied using FTIR and NMR spectroscopy, thermal analysis, quantitative size exclusion chromatography (SEC), cone calorimetry, transmission electron microscopy, XPS and mechanical testing. The results suggest that, with as little as 15% of the polydimethylsiloxane one may reduce the cone calorimetry heat release rate by a factor of about 2/3 and hence improve fire resistance, while maintaining mechanical behavior. It is suggested that the low surface energy characteristics of PDMS promote migration to the air–polymer interface to form a predominately PDMS enriched surface. The latter is oxidized at elevated temperatures in air to a silicate-like material and this serves as a protective layer, which further reduces burning of the underlying polyurethane. Dynamic mechanical behavior and electron microscopy suggest that a complex mutiphase structure is produced, particularly at low PDMS weight fractions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Improved fire resistance; Segmented polyurethanes; Organofunctional polydimethylsiloxane modification

1. Introduction

Thermoplastic polyurethanes are a versatile group of multi-phase segmented polymers that have excellent mechanical properties, good hardness, high abrasion and chemical resistance [1–3]. However, poor fire resistance restricts some of their applications. The increasing requirements of fire resistant systems have stimulated the development of new and modified material systems. Halogen containing fire retardant polyurethanes are known but they have severe drawbacks, such as the release of HX and other corrosive gases when burned [4,5]. Recently, interest in halogen free fire retardant polyurethanes has begun to focus on siloxane modifiers, which can significantly reduce heat release characteristics.

Polydimethylsiloxane polymers (PDMS) such as **1**, have found many applications due to their unique properties

which arise mainly from the nature of the siloxane bond [6–8].
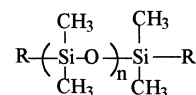
1

R = H, CH=CH₂, Aminoalkyl, Hydroxyalkyl, etc.

These properties include the low glass transition temperature, low surface energy, high permeability to gases, good insulating properties, and very good thermal stability. However, the mechanical properties of PDMS oligomers and polymers are usually low at room temperature, unless they are reinforced with silica and vulcanized. In order to develop useful properties, very high molecular weights are required and even for chemically crosslinked reinforced PDMS the tensile strength is still relatively low, compared to other elastomers.

* Corresponding author. Tel.: +1-540-231-4457; fax: +1-540-231-8517.
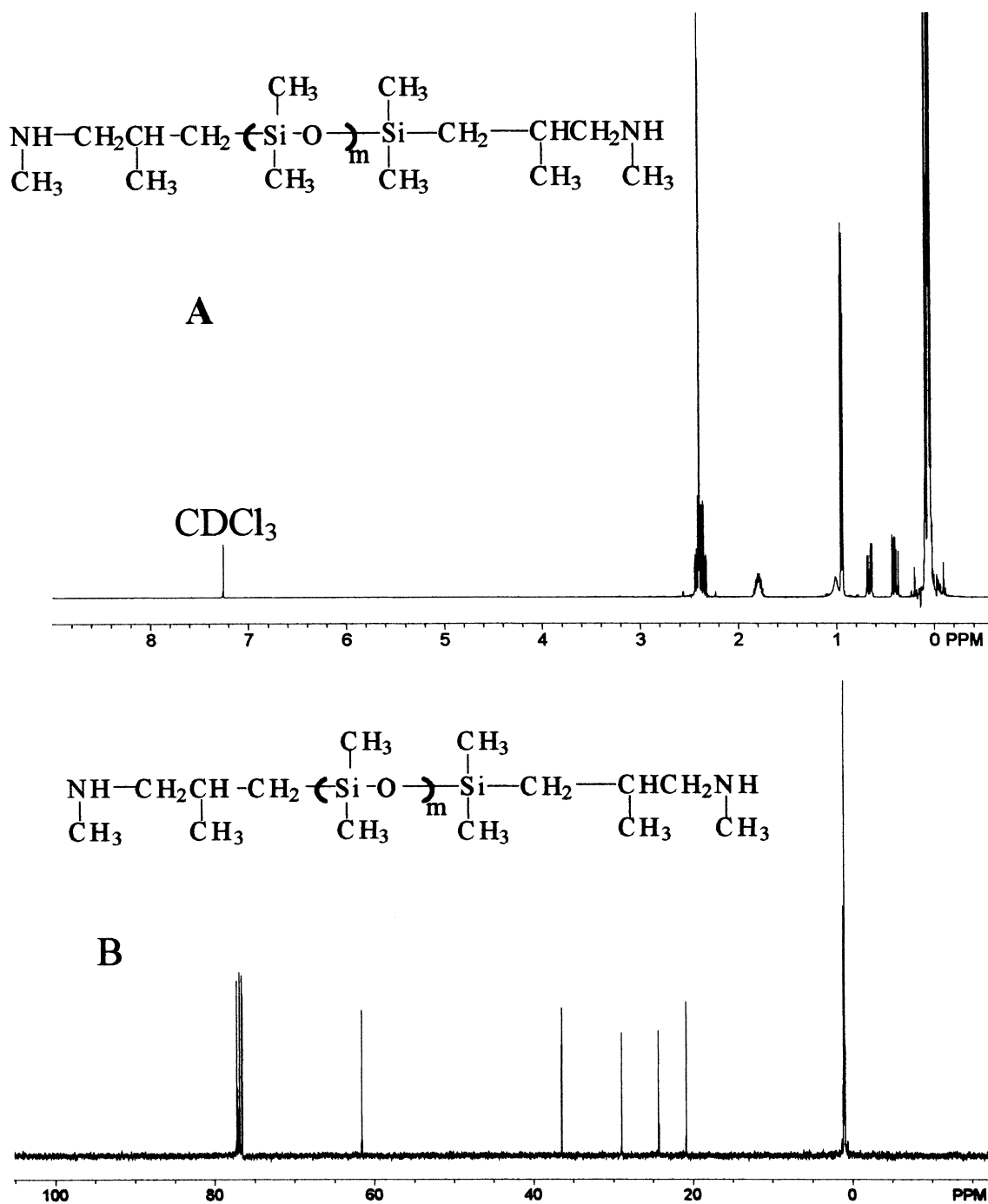*E-mail address:* jmcgrath@vt.edu (J.E. McGrath).

Fig. 1. (A) ^{1}H NMR; (B) ^{13}C NMR; (C) ^{29}Si NMR of secondary amino alkyl terminated PDMS.

It was hypothesized that one way to improve the fire resistance of polyurethanes without significantly sacrificing the mechanical properties was to utilize PDMS as a reactive co-soft segment. These types of copolymers have been investigated previously but for other reasons [8–13,18]. For example, polymers from the reaction of hydroxyalkyl or primary aminoalkyl terminated siloxane oligomers with diisocyanates and diols have been reported. They generally behave as thermoplastic elastomers or elastoplastics and their ultimate properties depend on the nature of the hard segments and composition. The successful synthesis of such PDMS based polyurethane copolymers can be quite dependent on proper solvent selection. This is mainly due to the large difference in the solubility parameter of the non-polar PDMS and the highly polar urethane segments. This can easily result in undesirable macroscopic phase separation during the polymerization [14–16].

This paper describes the synthesis of PDMS containing polyurethane copolymers via solution polymerization in mixed dimethyl acetamide (DMAc) and tetrahydrofuran
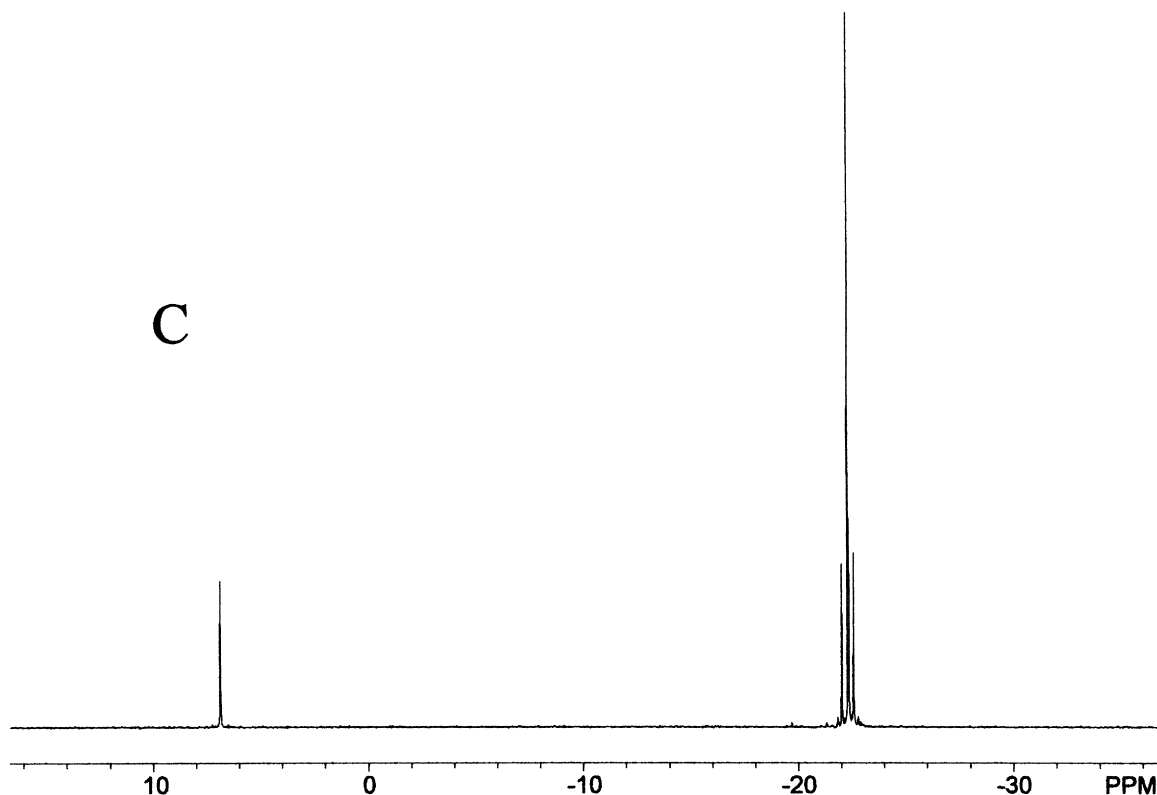
C

Fig. 1. (*continued*)

(THF). The polymerization employed secondary amino alkyl terminated polydimethylsiloxane and/or poly(tetramethylene oxide) (PTMO) as soft segment, 4,4′-methylene diphenyl diisocyanate (MDI) and 1,4-butanediol as chain extender. Molecular structure, thermal, morphological, surface, and mechanical characterization of the products were studied. Cone calorimetry investigations of fire resistance will also be reported.

2. Experimental

2.1. Materials

Primary hydroxyl terminated poly(tetramethylene oxide) (PTMO) ($M_n = 1000$) was supplied by BASF and used as received; 4,4-methylene diphenyl diisocyanate (MDI) (Bayer) and 1,4-butanediol (BDO) (Arco) were vacuum distilled before use. Dimethyl acetamide (DMAc) and toluene were dried over calcium hydride and then fractionally distilled under vacuum. Tetrahydrofuran was dried over sodium and benzophenone and distilled before use.

Secondary aminoalkyl terminated polydimethyl siloxane oligomer ($M_n = 1235$) was synthesized as described earlier [16,17].

2.2. Polymerization

PTMO/MDI/ BDO segmented polyether polyurethanes and PDMS containing polyurethane copolymers were prepared via solution polymerization of PTMO, secondary amino alkyl functional PDMS, and 1,4-butanediol with MDI.

All reactions were conducted in a 4-neck round bottom flask equipped with a mechanical stirrer, nitrogen inlet and a Dean-Stark trap. The soft segments: PDMS and/or PTMO were dissolved in DMAc/Toluene (1:1) with the chain extender 1,4-butanediol to afford a 30 wt% solution. The solution was heated to 130°C by refluxing toluene for 4 h, which effectively dehydrates the solution. The solution was then cooled to 60°C, and dry THF (DMAc/THF = 1/1) and MDI were added. The reaction was catalyzed by 0.5 mol% of stannous octoate. The polyurethane control did not require a catalyst to achieve high molecular weight copolymers. The solution was maintained at 60°C for 3 h and became viscous during this period. After cooling to room temperature the copolymer was precipitated into methanol/ water (1:1) solution, washed with methanol and water several times, filtered and dried in a vacuum oven at 90°C for 24 h.

2.3. Characterization

Gel permeation chromatography (GPC): The molecular weight of the polymers were measured by GPC using a Waters Model 150C instrument operated at 60°C with Styragel columns (10^3 and 10^4) in NMP containing 0.2% P_2O_5.
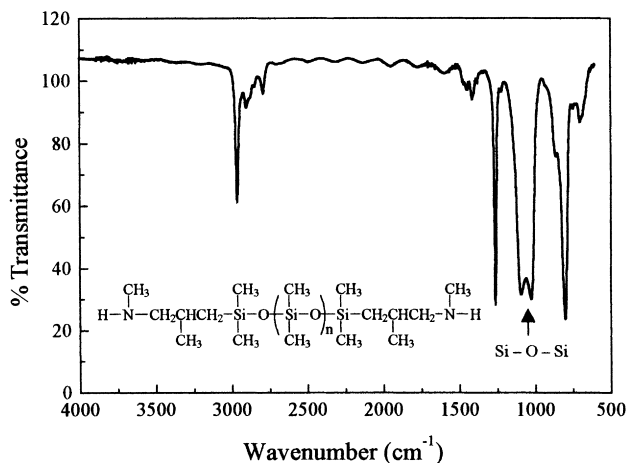
Fig. 2. FTIR spectrum of secondary amine terminated PDMS.

The flow rate was maintained at 1 ml/min. A GPC universal calibration curve was established using a viscosity detector and polystyrene standards.

NMR spectroscopy: NMR spectra (^{1}H, ^{13}C, ^{29}Si) were recorded on a Varian Unity 400 spectrometer operating at 400MHz for ^{1}H, 100 MHz for ^{13}C, and 79.4 MHz for ^{29}Si acquisition, respectively. Spectra of the PMDS oligomer and PDMS containing polyurethanes were measured in CDCl$_3$ and D7 dimethyl formamide (DMF), respectively.

FTIR spectroscopy: FTIR spectra were obtained using a Nicolet Impact 400 FTIR Spectrometer using solution cast films on KBr discs.

Thermal analysis: Differential scanning calorimetry was performed on a Du Pont DSC 913 instrument at a heating rate of 10°C/min. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer TGA 7 Thermogravimetric Analyzer at a 10°C/min heating rate in air.

Transmission electron microscopy: the samples for the transmission electron microscopy (TEM) study were cryo-ultramicrotomed at −120°C and the resulting sections were analyzed with TEM at 100 kV using a Phillips 420T TEM.

Mechanical testing: dynamic mechanical analysis was performed on a Perkin–Elmer DMA 7 dynamic mechanical analyzer using a 2°C/min scanning rate at 1 Hz. Stress–strain tests were performed with an Instron model 4204 at room temperature. Dog-bone specimens were cut from the DMF solution cast films with a D638 Die. The films had been dried at room temperature for 5 h, at 60°C in an oven for 12 h, and at 100°C in a vacuum oven for 24 h. All films were stored at room temperature in a desiccator for a week before testing. The stress–strain measurements were carried out at a crosshead speed of 100%/min based on the initial sample length.

X-ray photoelectonic spectroscopy: angular dependent X-ray photoelectronic spectroscopy (XPS) was performed on a Perkin–Elmer physical Electronic Model 5400 with a hemisphere analyzer and a position sensitive detector. The spectrometer was equipped with a Mg/Kα (1253.6 eV) achromatic X-ray source operated at a power of 400 W and three take off angles: 15, 45, 90°, were used with the X-ray source. The spot size used was 1 mm × 3 mm. Survey scans were taken in the range of 0–1100 eV. Any significant peaks in the survey scan were then subjected to narrow scans in the appropriate ranges for atomic concentration analysis. Photopeaks were curve fitted using Apollo Version 4.0 ESCA software to obtain information on the bonding state of the elements. The binding energy of each photopeak was referenced to the C 1s level at 285.0 eV. A pass energy of 44.75 eV was chosen for all angle-dependent acquisitions. The spectrometer was typically run at the 10^{-8} Torr vacuum range.

Cone calorimetry: cone calorimetry [5,21] was performed at 25 kW/m^2 at the Naval Surface Warfare Center using 10 × 10 × 0.3 cm^3 films, which had been melt pressed at 210°C.

End group titration: the molecular weights of PDMS terminated with aminoalkyl end groups were obtained by titration. The potentiometric titrations were performed on a MCI Automatic Titrator Model GT-05 which employed microprocessor control and a built-in cathode ray tube screen. The titrator automatically allows for control of the titration, detection of the inflection points and appropriate calculation of the molecular weight. The apparatus includes a standard glass electrode that functions as a detection electrode and a reference that is comprised of a Ag/AgCl double junction type electrode. A movable piston delivers titrant from the reservoir and discharges it through a microburet of 20 ml capacity. The titrant used was HCl aqueous solution and its normality was standardized with sodium carbonate. The aminoalkyl PDMS sample (0.1 meq (molecular weight
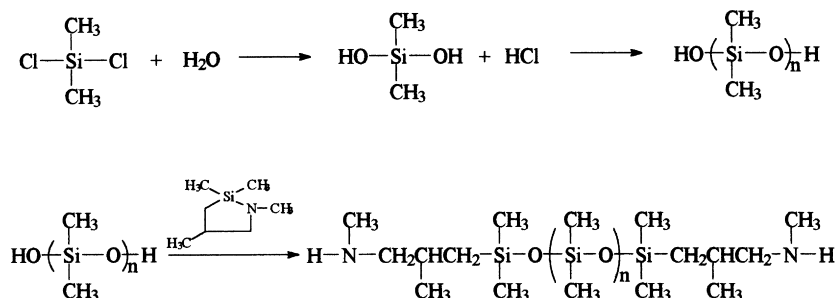
Scheme 1.
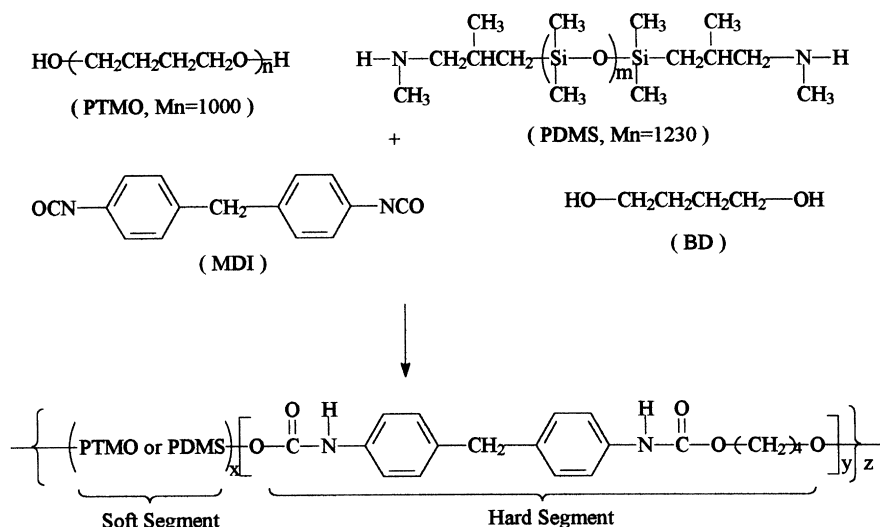
Scheme 2.

divided by functionality)) was dissolved in 75 ml isopropanol and stirring was maintained through the titration. The process was repeated and the molecular weight was calculated as the average of three titrations.

3. Results and discussions

3.1. Monomer synthesis

Secondary aminoalkyl terminated polydimethylsiloxane oligomers ($M_n = 1200$) were synthesized, as illustrated in Scheme 1 [19,20].

The NMR (^{1}H, ^{13}C, ^{29}Si) spectra of the secondary amino isobutyl terminated polydimethylsiloxane are provided in Fig. 1. The NMR spectra confirmed the structure of the secondary amino isobutyl silyl terminated polydimethylsiloxane. In the ^{1}H NMR spectrum, Fig. 1A, the protons from the isobutyl end groups were observed at 2.4, 1.8, 0.9, 0.6, 0.4 ppm and the amine protons were observed at 1.1 ppm. The protons associated with the methyl group attached to silicon show a large peak at 0.1 ppm. The ^{13}C spectrum, Fig. 1B, showed six peaks corresponding to five end group carbons and the carbon of the methyl group attached to silicon. The ^{29}Si NMR spectrum, Fig. 1C, showed one peak at 7 ppm, which corresponds to the silicon attached
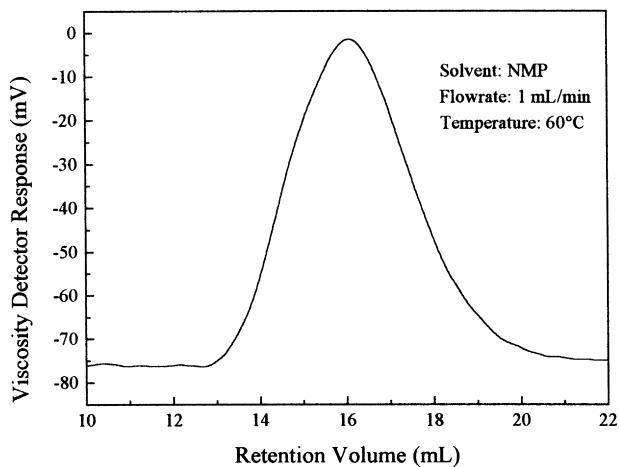

Fig. 3. GPC chromatogram of PDMS containing (15%) segmented thermoplastic polyurethane.

to three carbons on the end group. The multiple peaks at -22 ppm represent the principal silicon atoms in the PDMS backbone, which are only attached to two carbon atoms.

The FTIR spectrum of PDMS, Fig. 2, shows a strong Si–O–Si stretching absorption at 1023 and 1091 cm^{-1}, that is characteristic of a siloxane backbone. In addition, the CH$_3$ bending and rocking peaks were observed at 1260 and 801 cm^{-1}.

Table 1
Molecular weights for various compositions of PDMS and PTMO soft segment based polyurethane block copolymers

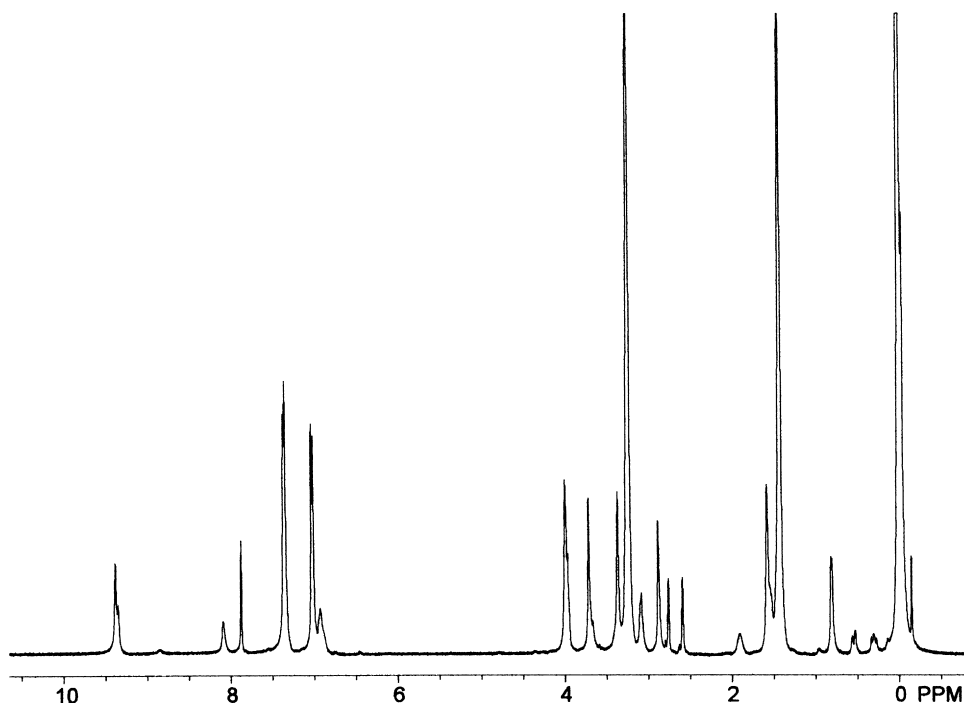| Sample ID	Soft segment (%)	PTMO (wt%)	PDMS (wt%)	M_n (g/mol)	M_w (g/mol)
1	63	63	0	32,600	67,100
2	63	48	15	26,000	54,000
3	65	37	28	14,100	26,700
4	65	23	42	14,400	33,200
5	66	11	55	14,500	26,100
6	67	0	67	14,200	27,600

Fig. 4. ^{1}H NMR of PDMS containing segmented polyetherurethane (42% PDMS).

The number average molecular weight of the polydimethyl siloxane oligomer was determined by end group analysis by titrating the amine end groups, using standardized HCl as titrant and also by NMR end group analysis. The end group analysis results suggested an M_n of 1230 g/mol.

3.2. Polymer synthesis

The control segmented polyether polyurethane and PDMS modified polyurethanes were synthesized by the reaction of amino functional PDMS and/or hydroxyl functional PTMO and 1,4-butanediol with MDI in DMAc/THF as shown in Scheme 2 (see Ref. [23] and Fig. 3).

The solvent system, DMAc/THF (1:1), was found to maintain homogeneous reaction conditions for the PDMS copolymers. A series of polyurethanes were obtained where both systematic soft segment concentrations and different siloxane contents could be produced by varying the ratio of PDMS and/or PTMO, and 1,4-butanediol. The molecular weights obtained from GPC for the various polymers are summarized in Table 1, and a representative monomodal chromatogram is shown in Fig. 3. The molecular weights are absolute
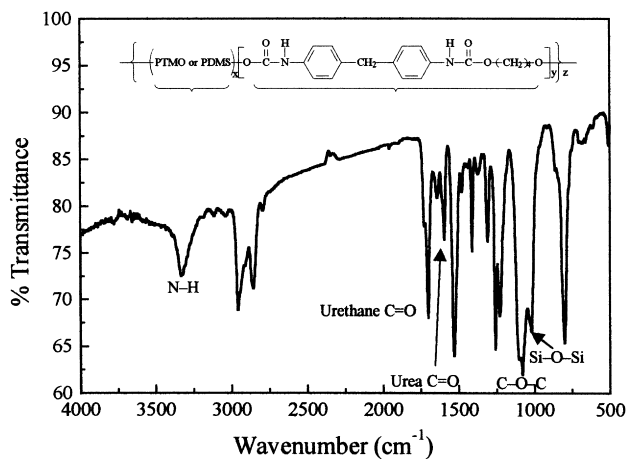

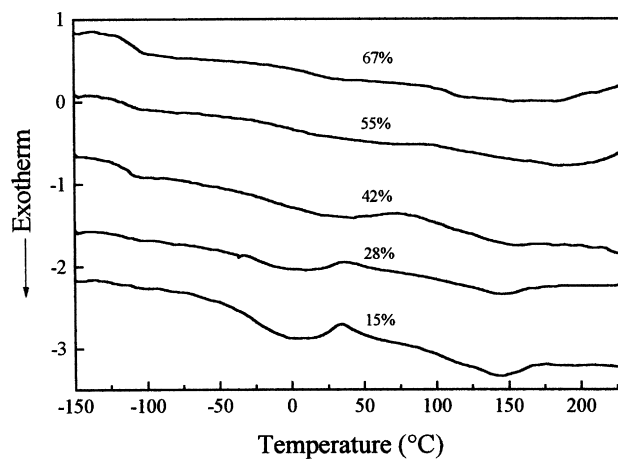Fig. 5. FTIR spectrum of PDMS containing polyetherurethane with 42% PDMS.

Fig. 6. Influence of PDMS Concentration on the Soft Segment glass Transition (DSC) Temperature.
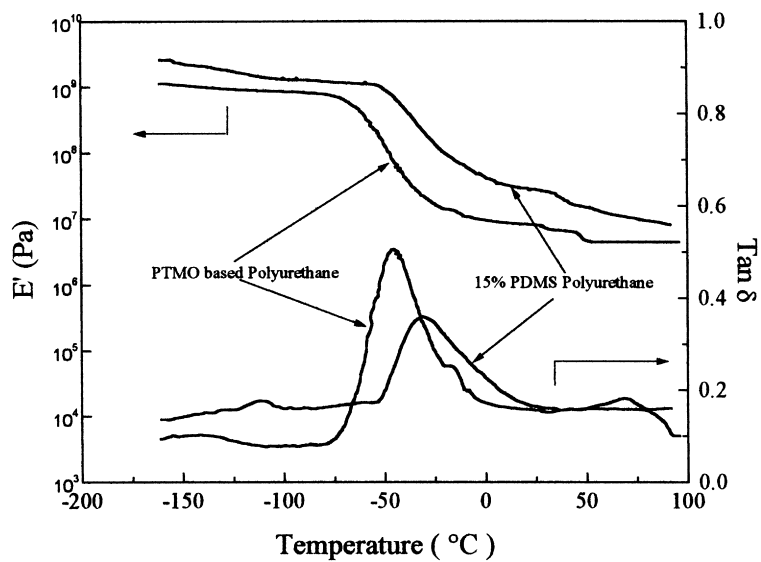
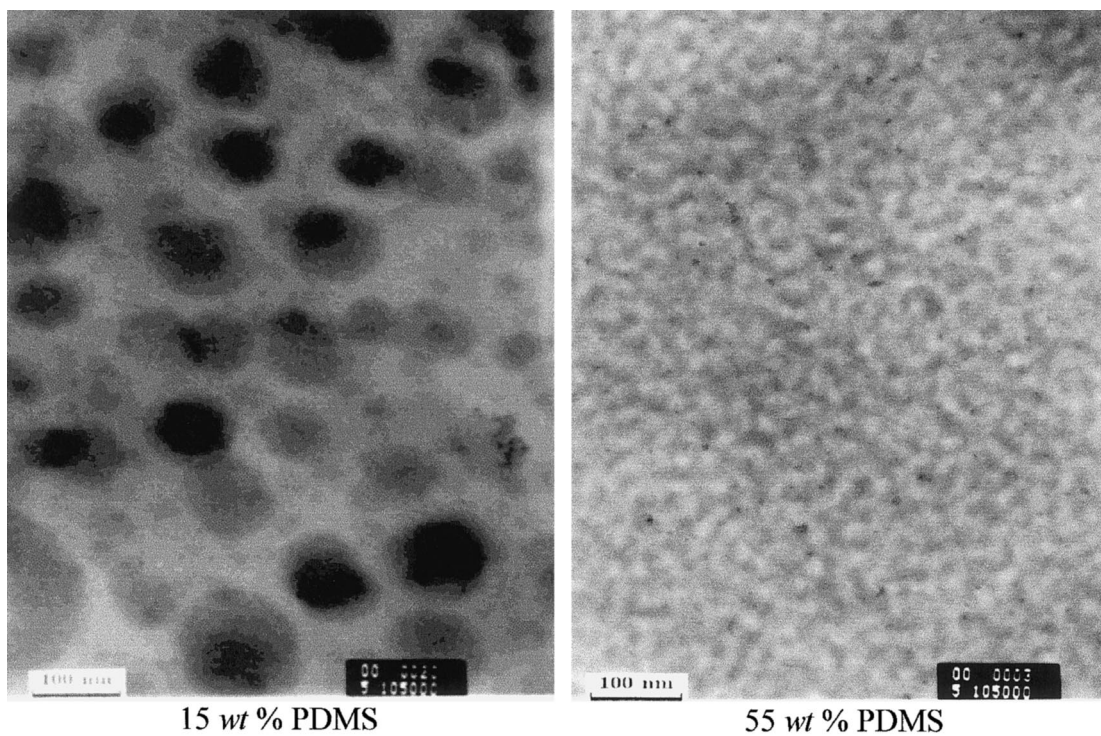Fig. 7. Dynamic Mechanical Behavior of a segmented polyurethane control and PDMS copolymer (15% PDMS).

15 *wt* % PDMS   55 *wt* % PDMS

Fig. 8. Transmission electron microscopy of PDMS containing polyurethane.

Table 2
Influence of composition on the glass transition temperature (T_g) of the control and PDMS copolymers

Sample ID	PDMS (wt%)	T_g of PDMS segment (°C)[a]	T_g of PTMO segment (°C)[a]
1	0	–	−45
2	15	−104	−22
3	28	−99	0
4	45	−98	11
5	55	−92	26

[a] Measured as tan δ peak from DMA.

values that were obtained by using online differential refractive index and viscosity detectors.

3.3. Structure analysis

The structure of the copolymers was verified by ^{1}H NMR as shown in Fig. 4. The peaks at 9.5, and 8.2 ppm are due to urethane and urea protons, and those at 7.2, 7.5, 3.8 ppm are assigned to aromatic protons and benzyl protons on MDI. Methylene protons from 1,4-butanediol and PTMO are also observed at 4.1, 1.7, 3.4, and 1.5 ppm along with protons from the isobutyl end group of PDMS at 3.2, 3.0, 2.1, 1.0, 0.5, and 0.7 ppm. The protons associated with the methyl group attached to a silicon show a large peak at 0.1 ppm. Elemental analysis also confirmed that all of the PDMS added in the system was incorporated into the copolymer

A typical FTIR spectrum of the PDMS containing copolymer is shown in Fig. 5. The absorption bands around 3320 cm^{-1} (urea N–H stretch) and 1645 cm^{-1} (H-bonded urea C=O) are assigned to the urea linkage. The peak at 3331 cm^{-1} (urethane N–H stretch), 1700 cm^{-1} (H-bonded urethane C=O), and 1080 cm^{-1} (C–O–C) stretch showed the formation of the urethane linkage. The peaks at 1260 cm^{-1} (sym. CH$_3$ bending), 1020 and 1100 cm^{-1} (Si–O–Si stretching), 803 cm^{-1} (CH$_3$ rocking) are assigned to the PDMS in the copolymer.

3.4. Thermal analysis

Thermal transitions of the control and PDMS copolymers were investigated using DSC and DMA. The glass transition temperature of the soft segment in the control was observed at −40°C by DSC. The PDMS containing copolymers showed clearly the T_g of PDMS from −111 to −120°C, depending on the composition, indicating that the PDMS microphase separated from both the PTMO soft segment and hard segment phase. The broad transitions at −40°C and 100°C might be due to the glass transition of PTMO and hard segment, respectively, as shown in Fig. 6.

The dynamic mechanical behavior also illustrates the two-phase nature of these materials, as shown in Fig. 7, where two low temperature glass transitions can be easily detected. In the PDMS copolymers, the main glass transition of the PTMO soft phase is higher than that of polyurethane control, suggesting complex microphase separation behavior. The PDMS tan δ is observed around −100°C,
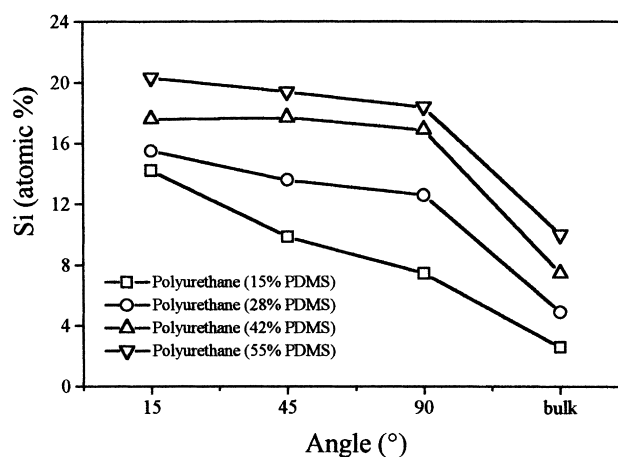

Fig. 9. Quantitative XPS study of the angular dependant profile of PDMS containing segmented thermoplastic polyurethanes.

but the principal soft tan δ is moved somewhat higher, Table 3.

3.5. Morphological and surface analysis

The multi-phase nature of these copolymers has been strongly implied from the above results of DSC and DMA. Transmission electron microscopy was conducted to further verify these conclusions. Fig. 8 shows the PDMS soft segments appear to form dark domains, about 0.1 μm in diameter, at 15 wt%. In contrast they become co-continuous phase at higher concentrations (55 wt%). The large particle size of PDMS at 15% implies that a complex morphology is developing that involves both the PDMS soft segment and hard segment. The DMA results seem to support this argument as well, since incorporation of PDMS caused the T_g of PDMS shift to a higher temperature (see Table 2, Fig. 6).

Observations of surface segregation of the low surface energy segment (e.g. PDMS) has been widely reported in the siloxane containing block polyurethane systems [8,13,15] and this was also confirmed by XPS angular dependent studies of these copolymers. Three take off angles, 15, 45, and 90°, were used, which corresponds approximately to a sampling depth from 1 to 6 nm. Quantitative results are shown in Fig. 9. The silicon atom concentration increased dramatically from the calculated bulk value as one approach the surface. The polyurethane with

Table 3
Influence of PDMS wt% content on 5% weight loss in air and char yield at 700°C

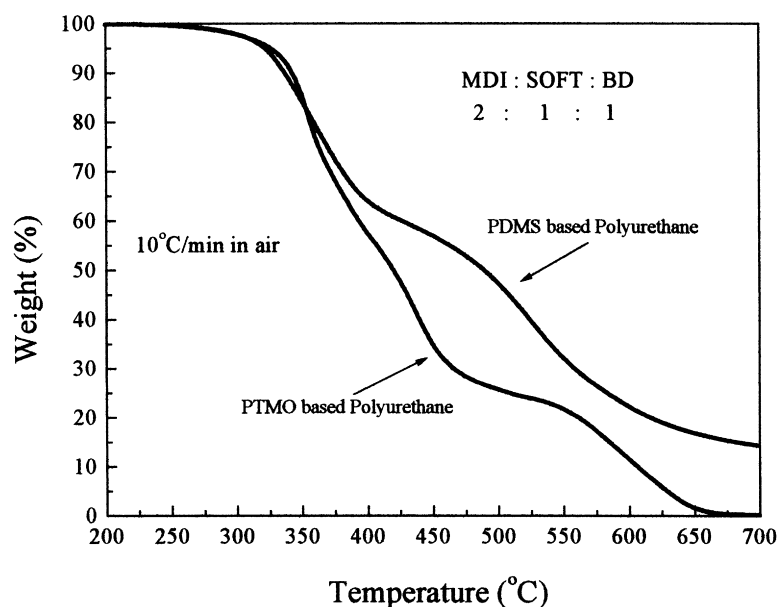| PDMS (%)	5% weight loss temperature (°C)	Char yield at 700°C (wt%)
0	325	0
15	319	3.4
28	340	5.9
42	327	8.7
55	305	10.9
67	321	14.3

Fig. 10. TGA weight loss behavior in air for control and all PDMS soft segment copolymers.

the lowest PDMS content (15 wt%) shows PDMS concentrations that are much more angular dependent than the higher PDMS concentrations.

3.6. Thermal stability and fire resistance

The weight loss behavior of the PDMS copolymers was investigated using dynamic thermogravimetric analysis from 30 to 700°C in air. The initial 5% weight loss occurs around 310°C, suggesting that the incorporation of PDMS does not influence this value. This is not surprising because the weakest link thermally is the urethane bond, which starts to dissociate at around 200°C. However, Fig. 10 shows that for the same soft segment concentration, the PDMS containing polyurethane has lower weight loss over a wide

temperature range and also higher char yield in air at 700°C than the polyether polyurethane control. Moreover, grayish char formation at 700°C was observed which increased with PDMS content in the copolymers as shown in Table 3. This suggests that complex silicates were indeed formed upon pyrolysis in air. This is further illustrated by the XPS surface analysis of the PDMS containing polyurethane before and after exposure to 700°C. Fig. 11 qualitatively compares the nature of the surface of the 45 wt% PDMS composition before and after its exposure to 700°C via their Si_{2p} peak. The Si_{2p} peak of PDMS was observed at 102.1 eV, due to O–Si–O, for the surface before exposure to 700°C. However, after the sample had been heated to 700°C in the TGA pan in air, the Si_{2p} peak shifted from 102.1 to 103.5 eV, which is consistent with SiO_2-like bonding. This indicates that the PDMS on the surface has been oxidized to complex silicates during the heating process in air. This conversion may help improve the fire resistance, since it can act as an insulation layer, which retards the further burning of the solid polymer.

Quantitative measurement of fire resistance is often based on cone calorimetry [5,22] and results on the current system are shown in Table 4.
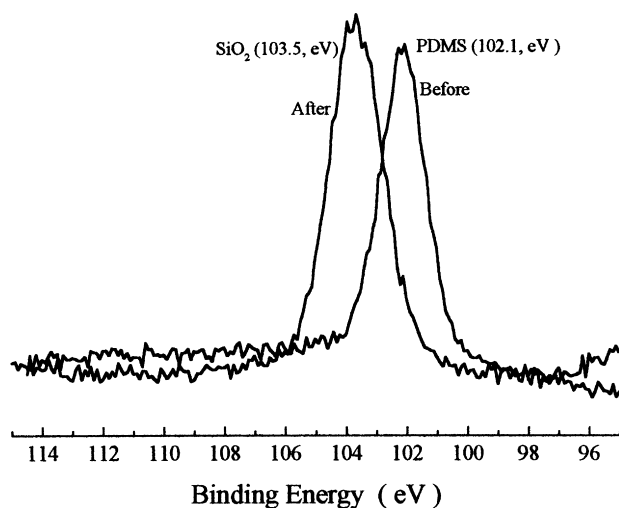

Fig. 11. XPS analysis of PDMS copolymers (a) before and (b) after exposure to 700°C in air.

Table 4
Effect of PDMS content on the peak heat release rate by cone calorimetry (heat flux of 25 kW/m^2)

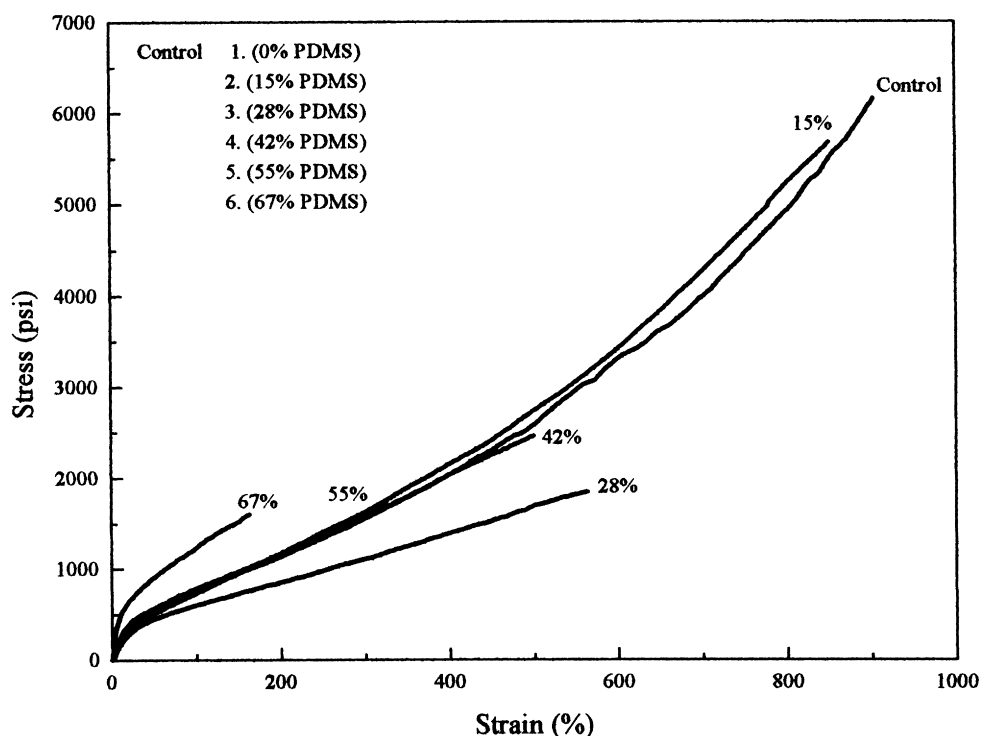| Soft segment (wt%)	PDMS (wt%)	Peak heat release rate (kW/m^2)
63	0	2671
63	15	825
65	28	1118
65	42	818
67	67	776

Fig. 12. Influence of PDMS concentration in the copolymer on stress–strain behavior at room temperature.

It is significant to note that the heat release rate of the 15% siloxane modified samples decreased 67%, relative to the polyurethane control. However, as the siloxane content further increased from 15 to 67 wt%, there was no further change. This suggests that surface phenomena are involved and that bulk physical properties could be maintained (e.g. 80% PTMO in soft segment) while improving fire resistance. Further verification of this behavior is needed.

3.7. Mechanical properties

Stress–strain behavior was performed on dog-bone specimens which were prepared following the procedure described in the Experimental section. The engineering stress–strain curves of PDMS containing polyurethanes and the control are shown in Fig. 12, where all curves are shown up to the fracture stress of the sample. The elastomers had the same soft segment concentration of about 65%. A tensile strength value of 5700 psi (38 MPa) and an ultimate elongation of 850% was obtained for the 15 wt% PDMS copolymers. These values are comparable to the polyurethane control, which had a tensile strength of 6450 psi (43 MPa) and 930% elongation.

4. Conclusions

Segmented siloxane–urethane urea copolymers have been successfully synthesized from secondary amino alkyl terminated poly(dimethyl siloxane), PTMO, 1,4-butanediol,

and MDI. The composition of the copolymers was characterized by FT-IR, NMR and chromatography. A complex microphase separation of PDMS soft segment from PTMO and the hard segment was demonstrated by DSC, DMA, and TEM results. Thermal stability of the PDMS based polyurethanes are similar to the polyurethane control, but the char yields at 700°C are higher than the control and increase with silicon content. Cone calorimetry results showed that with 15% of PDMS content, the heat release rate can be reduced to one third of the polyurethane control and the mechanical properties of polyurethane urea copolymer were comparable to the high molecular weight polyurethane control. This results is believed to be due to the low surface energy of the PDMS soft segment, which tends to migrate to the air–polymer interface and form a PDMS enriched surface. PDMS layer may be oxidized at high temperatures in air to produce a silicate-like material layer, which protects the underlying polymer. XPS results were generated that support this hypothesis.

References

[1] Woods G. The ICI polyurethane book, 2. New York: Wiley, 1990.

[2] Noshay A, McGrath JE. Block copolymers: overview and critical survey, New York: Academic Press, 1977.

[3] Oertel G, editor. Polyurethane handbook 2. New York: Hanser, 1993.

[4] Hilado CJ, Casey CJ, Christenson DF, Lipowitz J. J Combust Toxicol 1978;5:130.

[5] Nelson GL, editor. Fire and polymer II ACS Symposium Series No. 599, 1995.

[6] Voronkvov MG, Mileshkevich VP, Yuzhelevskii YA. The siloxane bond, New York: Consultants Bureau, 1978.

[7] Eaborn C. Organosilicon compounds, London: Butterworths, 1960.

[8] Noll W. Chemistry and technology of silicones, New York: Academic Press, 1968.

[9] Yilgor I, Wilkes GL, McGrath JE. Polym Prep 1983;24(2):80.

[10] Yilgor I, Shaaban AK, Steckle Jr. WP, Tyagi D, Wilkes GL, McGrath JE. Polymer 1984;25:1800.

[11] Tyagi D, Yilgor I, McGrath, JE, Wilkes GL. Polymer 1984;25:1807.

[12] Shibayama M, Inoru M, Yamamoto T, Nomura S. Polymer 1990;31:749.

[13] Ho T, Wynne KJ, Nissan RA. Macromolecules 1993;26:7029.

[14] Chen X, Gardella JA, Ho T, Wynne KJ. Macromolecules 1995;28:1635.

[15] Yu XH, Nagarajan MR, Grasel TG, Gibson PE, Cooper SL. J Polym Sci, Polym Phys Ed 1985;23:2319.

[16] Benrashid K, Nelson GL. J Polym Sci A: Polym Chem 1994;32:1847.

[17] Kazama H, Ono T, Tezuka Y, Imai K. Polymer 1989;30:553.

[18] Yilgor I, McGrath JE. Adv Polym Sci 1988;86:1.

[19] Speier JL, Roth CA, Ryan JW. J Org Chem 1971;36:3120.

[20] Burns GT, Decker GT, Roy AK. US Patent 5,290,901, 1994.

[21] Sorathia U, Dapp T, Kerr J. SAMPE 1991;36:1868–78.

[22] Babrauskas V, Peacock RD. Fire Safety J 1992;18:255.

[23] Wang L. PhD thesis, Virginia Polytechnic Institute and State University, 1998.