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Silicone containing copolymers: Synthesis, properties and applications

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Abstract

A comprehensive survey of the recent developments on the synthesis, properties and applications of silicone containing copolymers is provided. Influence of $(-R_2Si-O-)$ backbone composition on the physicochemical properties of silicone copolymers, such as thermal transitions, solubility parameter and surface tension is discussed. Preparation and properties of well-defined α,ω -reactive organofunctionally terminated (telechelic) silicone oligomers and their utilization in the preparation of a wide range of block and segmented copolymers through step-growth, anionic, ring-opening and living free-radical polymerization techniques are provided. Use of silicone oligomers in the modification of polymeric network structures is also discussed. Special emphasis is given to the discussion of the effect of silicone oligomer and organic segment structure and molecular weight on the morphology and surface and bulk properties of the resultant silicone containing copolymers and networks.

Keywords

Silicone, siloxane, polydimethylsiloxane, oligomer, copolymer

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Nomenclature

AFM	Atomic force microscopy
ATR-FTIR	Attenuated total reflectance Fourier transform infrared spectroscopy
ATRP	Atom transfer radical polymerization
BD	1,4-Butanediol
D ₃	Hexamethylcyclotrisiloxane
D ₄	Octamethylcyclotetrasiloxane
DLS	Dynamic light scattering
DMA	Dynamic mechanical analysis or dynamic mechanical analyzer
DMAC	Dimethylacetamide
DMF	Dimethylformamide
DMT	Dimethylterephthalate
FTIR	Fourier transform infrared spectroscopy
HDPE	High density polyethylene
HMDI	Bis(4-isocyanatocyclohexyl)methane
HS	Hard segment
LC	Liquid crystalline
MDI	Bis(4-isocyanatophenyl)methane
<M _n >	Number average molecular weight
MWD	Molecular weight distribution
NMP	N-methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance spectroscopy
PA6	Polyamide 6 or nylon-6
PB	Polybutadiene
PBLG	Poly(γ -benzyl-L-glutamate)
PBT	Poly(butylene terephthalate)
PC	Polycarbonate
PCL	Polycaprolactone
PDI	Polydispersity index
PDMO	Poly(decamethylene oxide)
PDMS	Polydimethylsiloxane
PDPS	Polydiphenylsiloxane
PE	Polyethylene

PEO	Poly(ethylene oxide)
PHMO	Poly(hexamethylene oxide)
PI	Polyisoprene
PLA	Poly(D,L-lactide)
PLLA	Poly(L-lactide)
PMMA	Poly(methyl methacrylate)
PMPS	Polymethylphenylsiloxane
PMVS	Polymethylvinylsiloxane
PNBA	Poly(n-butyl acrylate)
POX	Poly(2-ethyloxazoline)
PP	Polypropylene
PPO	Poly(propylene oxide)
PS	Polystyrene
PSF	Polysulfone
PTFPMS	Poly(3,3,3-trifluoropropylmethylsiloxane)
PTMO	Poly(tetramethylene oxide)
ROP	Ring opening polymerization
SAXS	Small angle x-ray scattering
SEC	Size exclusion chromatography
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
T_g	Glass transition temperature
T_m	Melting temperature
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TPU	Thermoplastic urethane
TPUU	Thermoplastic urethaneurea
UV	Ultraviolet radiation
WAXD	Wide angle x-ray diffraction
WAXS	Wide angle x-ray scattering
XPS	X-Ray photoelectron spectroscopy
XRD	X-Ray diffraction

1. Introduction

Polymeric materials composed of a $(-\text{Si}-\text{O}-)$ backbone with two monovalent organic radicals attached to each silicon atom $(-\text{R}_2\text{Si}-\text{O}-)$, as shown in Figure 1, are generally called “silicone” polymers. The $(-\text{Si}-\text{O}-)$ repeat unit is also called as the “siloxane” bond or linkage and therefore other terms used to describe these types of polymers also include siloxane polymers and polysiloxanes. Since the polymer backbone is “inorganic” in nature, while the substituents attached to the silicon atom are generally “organic” radicals, silicones form an important bridge between inorganic and organic polymers. Because of the dual nature of their backbones another widely used name to describe silicone polymers is polyorganosiloxanes (1-4). In this manuscript we will use the term siloxane to describe the backbone unit and silicone to describe the polymers.

Figure 1

A main interest in silicone containing copolymers and silicone-modified networks is directly related to the interesting combination of properties offered by these materials, which include extremely high backbone flexibility and very low glass transition temperatures (T_g), around $120\text{ }^\circ\text{C}$, good thermal and oxidative stability, high gas permeability, excellent dielectric properties and physiological inertness or biocompatibility (1-4). In addition, polydimethylsiloxanes also display very low surface tension values around $21\text{--}22\text{ mN/m}$ (4-6), which is even lower at 13.6 mN/m for trifluoropropyl substituted silicones (4-6), comparable to highly fluorinated polymers. Another advantage offered by the silicones is their very flexible chemistry, which allows the preparation of α,ω -reactive functionally terminated (telechelic) silicone oligomers with; (i) controlled molecular weights ranging from 500 to 50,000 g/mol, (ii) a wide variety of reactive organofunctional end-groups, and (iii) tailor-designed backbone compositions displaying a wide range of physicochemical properties, as will be discussed in detail later on.

In this review a comprehensive survey of the recent developments, mainly during the last decade to fifteen years, on the synthesis, properties and applications of silicone containing copolymers will be provided. Composition-dependent structure-morphology-property behavior of silicone copolymers will be discussed in detail. Due to their fairly low surface energies, special emphasis will be given to the surface properties of silicone copolymers and

their blends. Chemistry, properties and applications of crosslinked silicone elastomers or silicone rubber, which is commercially the most important silicone polymer system, will not be discussed.

2. Physicochemical properties of the siloxane (–Si–O–) bond

Silicone polymers display an unusual combination of physical and chemical properties when compared with homologous carbon-based polymers. This is mainly due to the somewhat unusual physicochemical properties of the siloxane (–Si–O–) bond (2). In order to better understand the substantial differences between the behavior of silicone polymers and organic polymers, it is critical to compare the properties of (–C–O–) and (–Si–O–) bonds. Carbon and silicon belong to Group 4A elements, whereas oxygen belongs to Group 6A in the periodic table. Atomic radius of the carbon atom (0.77 Å) is much shorter than that of the silicon atom (1.17 Å), whereas oxygen has a radius of 0.66 Å. Electronegativity values of carbon and silicon are 2.5 and 1.7 respectively according to the Pauling electronegativity scale, compared with that of oxygen which has a much higher value of 3.5. These differences between the atomic radii and the electronegativities of carbon, silicon and oxygen atoms are the main parameters that lead to the remarkable differences in the physicochemical properties of (–C–O–) and (–Si–O–) bonds.

Using the additivity rule, the theoretically expected bond lengths for (C–O) and (Si–O) bonds are 1.43 and 1.83 Å respectively. From x-ray and neutron diffraction studies, experimentally determined average (C–O) and (Si–O) bond lengths are 1.426 Å and 1.622 Å (2). Although the experimental and theoretical values of (C–O) bond lengths are very similar to each other, the experimentally determined (Si–O) bond length is significantly shorter than its theoretical value. This shortening in the (Si–O) bond length is usually explained by the substantial ionic character (~40%) of the siloxane bond due to the large electronegativity difference between silicon and oxygen atoms together with its partially double bond character, due to p_{π} - d_{π} interaction between the silicon and oxygen atoms (2). The double bond character of the (Si–O) linkage results in a fairly large (Si–O–Si) bond angle, which also depends on the type and nature of the substituents on the silicon atom. For better visualization, the most stable conformations of hexahydrogensiloxane and hexamethyldisiloxane obtained by quantum mechanical calculations using the 6,31(d,p) basis set (7) are provided in Figure 2. The partial double bond character of the (Si–O–Si) linkage (shown by the dotted lines) results in a (Si–O–Si) bond angle of 152.7 degrees for hexahydrogensiloxane (Fig 2-a) and 165.4

degrees for hexamethyldisiloxane (Fig 2-c). These are much higher than the sp^3 hybridized (C–O–C) bond angle of dimethyl ether, which is 112.3 degrees (Fig 2-b). Such a large (Si–O–Si) bond angle results in a reduced energy barrier for the rotation of the organic groups attached to the silicon atom and thus provides substantial flexibility to the silicone polymer backbone.

Figure 2

Another very interesting property of the (Si–O) bond is its very high bond dissociation energy of 460 kcal/mol, when compared with the (C–O) (357 kcal/mol), (C–C) (345 kcal/mol) or even with (Si–C) (318 kcal/mol) bonds (2). The double bond character of (Si–O–Si) linkages also plays a critical role in such a high bond dissociation energy. Unusual thermal stability of silicone polymers is a direct result of such a high (Si–O) bond dissociation energy.

As will be discussed in detail later on, the partial ionic nature of the (Si–O) bond also provides great flexibility to synthetic chemists for the preparation of a wide range of siloxane backbone compositions through so-called “equilibration” or “redistribution” reactions, using strong acid or base catalysts. In addition, it also allows the preparation of telechelic or α,ω -organofunctionally terminated silicone oligomers with controlled molecular weights and well-defined reactive end groups (1, 3).

3. Composition-dependent properties of silicone polymers

One of the major advantages offered by the flexible chemistry of silicone polymers is the possibility of introducing a wide selection of substituents onto the silicon atom in the backbone. These substituents can be inert, such as methyl, phenyl and 3,3,3-trifluoropropyl (Figure 3) or reactive such as vinyl, hydrogen, epoxy or amino groups (Figure 4). For the preparation of silicone containing block or segmented copolymers inert backbones are preferred. On the other hand for crosslinked systems silicone backbones with reactive substituents may be more suitable.

Figure 3

Figure 4

As shown in Figures 3 and 4, the most common silicone polymer is polydimethylsiloxane (PDMS), although in principle there are a wide selection of substituents that can be attached to the siloxane backbone. In addition to its ease of commercial production, PDMS also displays an interesting combination of physical properties such as very low T_g ($-120\text{ }^\circ\text{C}$), high gas permeability, low dielectric constant, very low solubility parameter of $15.5\text{ (J/cm}^3)^{1/2}$, a fairly low surface tension of 21-22 mN/m (1-6) and excellent biocompatibility (8). High molecular weight PDMS (usually with $M_n > 5000\text{ g/mol}$) also displays crystallinity with a melting point around $-50\text{ }^\circ\text{C}$ (3, 4), which may limit its flexibility at very low temperatures. To disrupt the crystallinity of the PDMS backbone without affecting its T_g appreciably, it is generally modified by the incorporation of a small amount of a comonomer, such as diphenylsiloxane. When larger amounts of diphenylsiloxane are introduced into the PDMS backbone to form a random copolymer, it is also possible to obtain silicone copolymers with composition dependent glass transition temperatures as shown on Table 1. Due to its crystallinity and fairly high melting point, polydiphenylsiloxane (PDPS) has excellent thermal stability and therefore is also an important silicone polymer. In addition to PDMS and PDPS, poly(3,3,3-trifluoropropylmethylsiloxane) (PTFPMS) is also widely utilized.

Table 1

The backbone composition of silicone polymers has critical effects on their physicochemical properties, such as the T_g , solubility parameter, thermal stability and surface free energy. For example, the solubility parameters of dimethyl, methylphenyl and diphenyl substituted polysiloxanes are 15.5, 18.4, and $19.4\text{ (J/cm}^3)^{1/2}$, respectively (9). The flexibility in the preparation of silicone polymers with tailor-designed backbone structures and reactive functional end groups provide almost unlimited possibilities for their use as specialty polymers or as modifiers for common organic polymers that display a very interesting combination of bulk and surface properties (3).

4. Reactive functionally terminated silicone oligomers

Functionally terminated silicone oligomers with one or two reactive end groups can easily be synthesized. Monofunctional PDMS oligomers, which are also termed “macromonomers”, are usually synthesized by the living anionic polymerization of hexamethylcyclotrisiloxane (D_3), as shown in Figure 5(3). Since the use of monofunctional PDMS in copolymerization reactions is fairly limited, in this manuscript we will mainly focus on the preparation and

characterization of α,ω -reactive difunctionally terminated (telechelic) silicone oligomers(3, 10), which are critical starting materials for the preparation of a wide range of silicone copolymers through step-growth, free-radical (e. g. Atom Transfer Radical Polymerization (ATRP))or ring-opening polymerization reactions.

Figure 5

Figure 6 provides general structures of two different types of reactive difunctionally terminated (telechelic) silicone oligomers most widely utilized in copolymerization reactions. First type of oligomers have reactive functional group (X) directly linked to the terminal silicon atoms (Si–X termination). Second type oligomers, which are usually termed as“organofunctionally” terminated silicone oligomers have a short hydrocarbon bridge (R) between the terminal silicon atoms and the reactive functional groups (Si–R–X termination). (Si–X) terminated siloxane oligomers have higher reactivities towards nucleophilic reagents than their (Si–R–X) counterparts. However copolymerization of (Si–X) terminated oligomers with conventional organic monomers leads to the formation of (Si–O–C) linkages, which are thermally stable, but also quite susceptible to hydrolysis under acidic or basic conditions.

Figure 6

As can easily be seen in Figure 6, there are four important variables in (Si–R–X) terminated siloxane oligomers. These are the:

- (i) chemical structure of the reactive end group (X),
- (ii) structure and chemical composition of the hydrocarbon bridge (R),
- (iii) type and nature of the silicon substituents (R_1 and R_2) in the backbone, and
- (iv) average degree of polymerization (n) of the oligomer.

In this review we will mainly focus on the organofunctionally terminated telechelic silicone oligomers with (Si–R–X) type end groups. Oligomers with (Si–R–X) end groups are generally prepared by the reaction of (Si–H) terminated silicones with vinyl or allyl terminated functional monomers as shown in Figure 7 for a disiloxane(11, 12). Hydrosilylation is the name given to the addition reaction of hydridosilyl group to a C=C bond. It is catalyzed by various metal (platinum, palladium or rhodium) compounds, such as chloroplatinic acid, by

peroxides, such as di-*tert*-butyl peroxide, by amine complexes or aluminum chloride(11, 12).Chemical structures of important reactive end groups (X) and hydrocarbon bridges (R) that link these reactive groups to silicone backbone are summarized in Table 2.

Figure 7

Table 2

Controlled synthesis of telechelic, organofunctionally terminated silicone oligomers with number average molecular weights from about 500 to 50,000 g/mol can be achieved by several different methods. As shown in Figure 8, a very popular and simple approach is the acid or base catalyzed ring-chain equilibration or redistribution reactions of low molecular weight α,ω -organofunctionally terminated silicones, preferably a disiloxane as shown in the reaction scheme, which is usually termed as the “end-blocker” and cyclic silicone monomers such as octamethylcyclotetrasiloxane (D₄) or others(3, 10, 13, 14).Partially ionic character of the (Si–O) bond is the main rationale behind the equilibration reactions. During these ring-chain equilibration reactions the average molecular weight of the oligomer to be synthesized is controlled by ratio of the end-blocker to the cyclic monomer in the reaction mixture (3, 10, 13, 14). Strong acids such as sulfuric acid, trichloroacetic acid and sulfonic acids and strong bases such as sodium and potassium hydroxide or quaternary ammonium hydroxides can be used as catalysts in the equilibration reactions. Reaction temperatures between 50 to 100 °C usually provide reasonable rates for these equilibration reactions. Backbone structures of the silicone oligomers obtained by equilibration reactions can easily be modified through the use of various other cyclic siloxane monomers, such as cyclic diphenylsiloxane, methylphenylsiloxane or methyltrifluoropropylsiloxane together with D₄(3).

Figure 8

Selection of a specific acid or base catalyst in equilibration reactions is mainly determined by the nature and the reactivity of the organofunctional end group. In general strong acids are used for the preparation of oligomers with acidic end groups, such as carboxylic acids and strong bases are used for basic end groups, such as amines. Special care must be taken in catalyst selection for end groups such as epoxy, amine and vinyl groups, which may react

with strong acids and bases at high temperatures. In equilibration reactions catalysts can only cleave the (Si–O) bonds in the cyclic and linear species including that of the end-blocker and growing chains. However, under these conditions (Si–R) and (R–X) bonds are stable. Therefore, at the end of the reactions linear oligomers are functionally terminated and cyclic side products, which are around 10-15% by weight depending on the number average molecular weight of the oligomer prepared (3, 13, 14), are non-functional. At the end of ring-chain equilibration reactions, the catalyst is deactivated and the cyclic side products are removed from the reaction mixture by vacuum distillation.

Several other methods which can also be utilized for the preparation of organofunctionally terminated telechelic silicone oligomers include hydrosilylation of the hydride (Si–H) terminated silicone oligomers with organofunctional vinyl compounds ($\text{CH}_2=\text{CH}-\text{R}-\text{X}$) under the catalytic action of platinum compounds(11, 15, 16), derivatization of vinyl terminated PDMS oligomers through thiol-ene coupling reactions (17), reaction of tetrahydrofuran with chlorosilane terminated PDMS in the presence of magnesium metal (3) and others(4, 18).

5. Silicone containing copolymers

Due to their interesting combination of properties, silicone containing block or segmented copolymers have attracted the widespread attention of researchers both from academia and industry. This has led to the preparation and characterization of a wide variety of silicone-organic copolymers and silicone modified network systems, which are described in recently published books(4, 18-20), symposium series (21-23) and a large number of original research articles as will be discussed in this manuscript. An excellent review paper specifically on the synthesis of silicone copolymers by free radical polymerization is also available(24).

Silicone homopolymers, especially PDMS, display cold flow and extremely poor mechanical properties even at very high molecular weights of 500,000 g/mol (1). Therefore, in all major structural applications PDMS is used in crosslinked form and is also highly filled with reinforcing fillers, such as fumed silica. This usually limits the use of various flexible manufacturing techniques widely utilized in polymer processing. As a result, a major motivation for the preparation of silicone copolymers is to combine the mechanical integrity and strength of organic polymers together with the interesting bulk and surface properties of silicones, to produce polymeric materials which do not need crosslinking or fillers to be used in various applications(3). Such silicone-organic copolymers can be

processed easily by thermal or other methods applicable to thermoplastic polymers. As will be discussed in detail in Section 6, another motivation for the preparation of silicone copolymers is their use as surface modifying additives in polymer blends to provide low surface energy, water repellency, low coefficient of friction and other interesting properties to the system (25-27). In such applications the organic component of the silicone copolymer provides compatibility with the base polymer, through intermolecular interactions and/or entanglements, whereas the silicone moves to the material surface.

Silicone containing copolymers are generally prepared by using one of the four different polymerization methods. These methods are; (i) living anionic polymerization, (ii) ring-opening polymerization (ROP), (iii) atom transfer radical polymerization (ATRP) and (iv) step-growth polymerization. The first three methods are preferable for the preparation of well-defined diblock or triblock silicone copolymers, whereas step-growth polymerization is used for the preparation of segmented or multiblock copolymers.

5.1. Silicone containing diblock or triblock copolymers

Silicone containing diblock or triblock copolymers with well-defined structures can be prepared by living anionic polymerization through the sequential addition of monomers, using ROP or ATRP. Another widely utilized method is the chemical coupling of functionally terminated blocks usually prepared by anionic polymerization. Each of these synthetic techniques and the properties of copolymers obtained will be discussed separately in the forthcoming sections. Several other methods which can also be used for the preparation of silicone containing block copolymers include free radical copolymerization using macroinitiators (21, 28-30), iodine transfer polymerization (24, 31) and reversible addition-fragmentation chain transfer (RAFT) polymerization (32-34). Unfortunately, some of these techniques do not provide very good control of the block lengths, may require the use of specific monomers and also may lead to extensive homopolymer contamination (29, 30).

5.1.1. Silicone containing block copolymers by living anionic polymerization through sequential addition of monomers

5.1.1.1. All-silicone block copolymers

All-silicone diblock or triblock copolymers are interesting materials since they combine the low temperature flexibility and high gas permeability of PDMS together with very low

surface energy of PTFPMS or crystalline, rigid and high strength PDPS or vinyl side group reactivity of polymethylvinylsiloxane (PMVS) on the same macromolecule. Their synthesis is usually achieved by the sequential anionic polymerization of respective cyclic trimers in one pot, leading to the formation of well defined-copolymers with narrow molecular weights.

Three different types of PDPS containing, all-silicone diblock copolymers with well-defined structures and narrow molecular weight distributions were synthesized by n-butyllithium initiated anionic polymerization through the sequential addition of corresponding monomers(35). All-silicone diblock copolymers prepared included PDPS-PDMS, PDPS-b-polymethylphenylsiloxane (PDPS-PMPS) and PDPS-b-PTFPMS. The thermal transition behavior of these semicrystalline copolymers were investigated by DSC and polarized optical microscopy studies. The copolymers displayed composition dependent microphase separation. Mesophase formation and the effect of soft segment structure on phase transitions were investigated(36, 37).

All-silicone diblock copolymers consisting of PDMS and PMVS were synthesized by a one-pot, n-butyllithium initiated sequential anionic polymerization of D_3 and (methylvinyl)cyclotetrasiloxane. Copolymers with relatively short block lengths varying between 1000 and 6000 g/mol and polydispersity index (PDI) or molecular weight distribution (MWD) values between 1.13 and 1.61 were obtained and characterized. Vinyl groups in PMVS blocks could easily be modified with a variety of reactants containing Si—H groups through hydrosilylation reactions(38).

PDPS-PDMS-PDPS triblock copolymers were prepared in two steps, which consisted of; (i) the anionic polymerization of D_3 initiated by dilithiodiphenylsilanolate yielding α,ω -bis(lithio dimethylsilanolate) terminated PDMS, and (ii) subsequent addition to hexaphenylcyclotrisiloxane to yield the triblock copolymer. PDMS and PDPS block lengths were varied between 4,000 and 36,000 g/mol. Formation of distinct blocks with regular microstructures was confirmed by 1H , ^{13}C and ^{29}Si -NMR spectroscopy, differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA)(35, 39).

5.1.1.2. Silicone-organic block copolymers

Well-defined, narrow molecular weight polystyrene-PDMS diblock copolymers (PS-PDMS) with PDMS contents ranging from 3 to 63 percent by weight were synthesized by living

anionic polymerization through sequential addition of monomers(40). The copolymers obtained showed number average molecular weights $\langle M_n \rangle$ between 15,000 and 35,000 g/mol and narrow molecular weight distributions in the 1.04 -1.34 range. All copolymers displayed microphase separated morphologies. The sample with the highest PDMS content exhibited a lamellar morphology, whereas other samples showed hexagonally packed cylinders of PDMS in a PS matrix. Dimensions of the domains were between 80 and 160 nm. Small angle x-ray scattering (SAXS) studies on the sample containing only 3% by weight of PDMS indicated a disordered morphology(40).

PS-b-PDMS diblock and triblock copolymers were also prepared by both anionic and cationic polymerization of styrene using a macromolecular initiator(41). DSC analysis indicated microphase-separated morphologies. Depending on the polymer composition transmission electron microscopy (TEM) studies showed spherical, cylindrical or lamellar morphologies. Narrow molecular weight PS-PDMS-PS and PS-polyisoprene-PDMS (PS-PI-PDMS) triblock copolymers were also prepared by anionic polymerization (42).

PS-b-PDMS diblock copolymers with PS and PDMS block molecular weights of 114,000 and 124,000 g/mol and a PDI of 1.16 were prepared and characterized (43). As expected, the copolymers obtained displayed microphase separated morphologies. Electrospun webs with average fiber diameter of 300 nm were obtained from 3:1 by weight tetrahydrofuran (THF) and dimethylformamide (DMF) solutions. X-Ray photoelectron spectroscopy (XPS) studies showed that the fiber surfaces were rich in silicone, due to the migration of low surface energy PDMS to the surface. Electrospun webs displayed superhydrophobic surfaces with advancing and receding water contact angles of 164 and 149°, respectively.

A series of PS-PTFPMS diblock copolymers were synthesized by the sequential anionic polymerization of styrene and (3,3,3-trifluoropropylmethyl)cyclotrisiloxane in THF using n-butyllithium as the initiator. The PTFPMS content of the copolymers was varied between 15.4 and 78.8% by weight. The diblock copolymers obtained had number-average molecular weights $\langle M_n \rangle$ from 8,000 to 37,000 g/mol and fairly narrow molecular weight distributions between 1.06 and 1.20. (44). DSC studies indicated the formation of microphase separated morphologies where T_g values for PTFPMS and PS phases were observed at -69 and 100 °C, respectively.

Hammond and co-workers systematically investigated the synthesis and characterization of diblock copolymers of PS and side chain liquid crystalline (LC) silicones (45). Preparation of LC silicone monomers and details of the anionic copolymerization reactions to produce diblock copolymers with high molecular weights and LC silicone fractions in 0.40 to 0.91 were provided. Copolymers with large LC fractions and low T_g values (below $-25\text{ }^\circ\text{C}$), displayed elastomeric properties. TEM and SAXS studies indicated the formation of four different microphase morphologies depending on the composition and the block length of the copolymers(45). PS-PMVS diblock copolymers with varying block lengths were also prepared by anionic polymerization. The vinyl side groups on PMVS were later functionalized with six different liquid crystalline monomers via hydrosilylation(46). Copolymers displayed microphase morphologies, which were strongly dependent on the LC structure and content. Smectic-to-isotropic transition temperature could be tuned from ambient up to $150\text{ }^\circ\text{C}$, depending on the composition and LC type. It was reported that the ability to precisely control the degree of LC functionalization enabled tailoring of material properties for specific applications such as electro-mechanical, damping, and mechano-optical devices. PS-PMVS-PS triblock copolymers were also prepared by the sequential anionic polymerization. TEM and SAXS analyses indicated formation of a microphase separated system with a lamellar morphology. Vinyl side chains were used to attach mesogenic side groups onto the siloxane backbone. The resulting liquid crystalline triblock copolymers were shown to be both elastomeric and rapidly photoresponsive at room temperature(47).

Well-defined diblock copolymers of poly(1,4-butadiene) (PB) and PDMS (PB-PDMS) were synthesized by the sequential anionic polymerization of butadiene and D_3 in the presence of sec-butyllithium(42, 48, 49). By homogeneous hydrogenation of PB-PDMS, the corresponding polyethylene-PDMS (PE-PDMS) block copolymers, were also obtained (36, 42, 50). Size exclusion chromatography (SEC) analysis indicated that the PDI of the samples was very low (1.03 – 1.06). The PE blocks displayed melting peaks in DSC scans. TEM analysis revealed well-ordered microphase morphologies, which varied from spherical to cylindrical to lamellar domains depending on the polymer composition.

5.1.2. Silicone containing triblock copolymers by ring-opening polymerization

α,ω -Reactive functionally terminated PDMS oligomers can be utilized as macroinitiators for the preparation of triblock silicone copolymers by the ring opening polymerization of cyclic ester, amide or oxazoline monomers. To facilitate the reactions organometallic (tin octoate,

dibutyltin dilaurate)(51) or various organic compounds (amines, acids, imidazoles, phosphines)(52) are employed as catalysts. The molecular weight of the end blocks are usually controlled by the ratio of the cyclic monomer in the reaction mixture to the PDMS macroinitiator (which also becomes the middle block). The earliest examples of such triblock copolymers were polycaprolactone-*b*-PDMS (PCL-PDMS-PCL) and poly(2-ethylloxazoline)-*b*-PDMS (POX-PDMS-POX) triblock copolymers. Chemical structures of these copolymers are provided in Figure 9. PCL-PDMS-PCL copolymers, which have hydroxyl end groups are often used as reactive oligomers for the preparation of silicone-urethane segmented copolymers as will be discussed in section 5.2.1.

Figure 9

Poly(γ -benzyl-L-glutamate)-PDMS-poly(γ -benzyl-L-glutamate) (PBLG-PDMS-PBLG) triblock copolymers were prepared using α,ω -aminopropyl terminated PDMS oligomers as macroinitiators for the ring-opening polymerization of γ -benzyl-L-glutamate-*N*-carboxyanhydride in THF as shown in Figure 10(53). Fairly narrow molecular weight triblock copolymers with PDI values in 1.22 and 1.38 and PBLG and PDMS block lengths varying between 3,000 and 46,000 g/mol were obtained. ^{13}C -NMR, SAXS, wide angle x-ray scattering (WAXS), TEM and dielectric spectroscopy studies confirmed the microphase separated morphologies in copolymers with long peptide blocks, where PBLG α -helical segments were embedded within the block copolymer nanodomains. Lateral coherence length of the PBLG hexagonal lattice, which was composed of α -helices, also contained some amorphous defects. Separately it was shown that PBLG-PDMS-PBLG triblock copolymers exhibited reversible, thermally-induced transitions and the hexagonal structure within the polypeptide fibers remained intact, even at high temperatures(54). A series of PBLG-PDMS-PBLG triblock copolymers were also synthesized from high molecular weight aminopropyl terminated PDMS (24,000 g/mol). PBGL block lengths were varied between 2,300 and 37,000 g/mol as determined ^1H -NMR(55). Fourier transform infrared spectroscopy (FTIR) studies indicated a systematic increase in α -helical content and decrease in β -sheets and random coil contents with increasing volume fraction of the PBLG blocks. Triblock copolymers formed thermoreversible gels in toluene with critical gel concentration as low as 1.5 weight percent with a gel-solution transition around 50 °C, reverting back to original state when cooled down to room temperature. TEM studies showed that the

morphology of the organogels consisted of mainly nanofibrils, with an average thickness of 6–12 nm(55).

Figure 10

Poly(L-lactide)-PDMS-poly(L-lactide) (PLLA-PDMS-PLLA) triblock copolymers were synthesized by the ring-opening polymerization of L-lactide using telechelic hydroxyalkylether terminated PDMS oligomer with $\langle M_n \rangle$ value of 5,000 g/mol in toluene under the catalytic action of tin octoate (56). These copolymers also have hydroxyl end groups and can be used as reactive oligomers, similar to PCL-PDMS-PCL copolymers. SAXS and TEM studies indicated composition and block length dependent microphase morphologies for the copolymers, which changed from lamellar to spherical structures as a function of the volume fraction of PLLA and the molecular weight of the triblock copolymer.

Poly(lactide)-PDMS-poly(lactide) (PLA-PDMS-PLA) triblock copolymers were also obtained by the ring-opening polymerization of D,L-lactide using 3-(2-hydroxyethoxy)propyl-terminated PDMS macroinitiators with $\langle M_n \rangle$ values of 1,000, 5,000 and 8,000 g/mol in bulk or in toluene solution under tin octoate catalysis (57). SAXS, AFM and TEM studies indicated the formation of microphase separated morphologies with spherical, cylindrical or lamellar structures depending on the block lengths and polymer compositions. Selective etching of the PDMS domains using SF₆ or selective removal of the PLA and oxidation of the PDMS using O₂ and yielded ordered nanoporous films, which were evaluated as multifunctional nanolithographic templates(57). PLA-PDMS-PLA copolymers were also used as dispersants for magnetite nanoparticles (58).

A series of PLA-PDMS-PLA triblock copolymers was prepared by the ring-opening polymerization of mixed D,L-lactides using hydroxypropyl terminated PDMS-4000. Lactide blocks lengths consisted of 25, 50, and 100 lactic acid units. The polymers were characterized by a variety of techniques. The influence of block lengths on the thermal properties (T_g and T_m) of soft and hard segments and stereocomplex formation between PLA segments were studied (59). A similar study was also conducted by using PDMS-1000 and D-lactic acid (60). PLA-PDMS-PLA copolymers were also prepared through transesterification reactions in chloroform solution between aminopropyl terminated PDMS oligomers (2000 g/mol) and PLA (61). Block copolymers with molecular weights around 60,000 g/mol were

obtained in high yields. DSC analysis indicated the formation of microphase separated morphologies with well-defined PDMS glass transition and PLA melting peaks (61).

Hydroxyalkyl carbamate and dihydroxyalkyl carbamate terminated PDMS oligomers with $\langle M_n \rangle$ values of 900 g/mol were used as initiators for the ring-opening polymerization of ϵ -caprolactone to produce PCL-PDMS-PCL and $(PCL)_2$ -PDMS- $(PCL)_2$ type triblock and H-type block copolymers, respectively (62). Thermal characterization of the products indicated the formation of microphase separated morphologies even though the block lengths were fairly short. In a separate study PCL-PDMS-PCL copolymer surfaces were characterized by dynamic contact angle analysis, XPS and AFM. Surface morphology of the solvent cast films displayed semicrystalline structure with spherulites in the micron scale and alternating semicrystalline PCL-rich and amorphous PDMS-rich lamellae on the nanometer scale (63). XPS clearly showed surface enrichment by PDMS. Surface morphology strongly affected the protein adsorption and thus the biocompatibility of the copolymers.

Silicone containing triblock copolymers were synthesized by the cationic ring-opening polymerization of 2-methyl-2-oxazoline using bistosylate-terminated siloxane oligomers as macroinitiators (64). Triblock copolymers were shown to undergo vesicle formation with vesicle diameters ranging from 2 to 10 μm . The size of the vesicle was shown to depend on the composition and the overall polarity of the copolymer.

5.1.3. Silicone containing block copolymers by atom transfer radical polymerization

ATRP has been successfully utilized for the preparation of silicone (mainly PDMS) containing diblock and triblock copolymers. Bromoalkyl or chloroalkyl terminated PDMS oligomers which were used as macroinitiators in ATRP polymerizations, were generally prepared by the controlled anionic polymerization or through equilibration reactions. In most cases PDMS oligomers with $\langle M_n \rangle$ values in 1,000-10,000 g/mol range, were utilized as macroinitiators in the copolymerization reactions (24).

Matyjaszewski and co-workers were first to report the preparation of PS-PDMS-PS triblock copolymers by using benzyl chloride terminated telechelic PDMS macroinitiators with $\langle M_n \rangle$ values of 3,000 and 9,900 g/mol (65). Overall molecular weights of the copolymers obtained were around 20,000 g/mol, which was fairly low. The same group (66, 67) and others (68-70) also reported the preparation of PDMS-poly(methyl methacrylate) (PMMA)

and PDMS-poly(*n*-butyl acrylate) (PNBA) diblock and triblock copolymers using 2-bromoisobutyrate or benzyl chloride terminated PDMS oligomers with $\langle M_n \rangle$ values in 4,500 to 34,000 g/mol range. Figure 11 provides the reaction scheme and the chemical structure of the PS-PDMS-PS triblock copolymers obtained by ATRP polymerization(68). Diblock or triblock copolymers with molecular weights in 10,000 to 90,000 g/mol range and with a fairly narrow molecular weight distribution (PDI values of 1.05 - 1.20) were obtained. In the same report, the preparation and characterization of triblock copolymers of PS-PDMS-PMMA and PS-PDMS-PNBA were also discussed(70, 71). The Matyjaszewski group mainly investigated the basic polymerization parameters, such as conversion as a function of reaction time, the change in the copolymer molecular weight and PDI as a function of conversion and performed compositional analysis of the final copolymers by NMR(65-67, 72). No data on the morphologies or thermal or mechanical properties of the copolymers were provided.

Figure 11

2-Bromoisobutyrate terminated PDMS macroinitiators were prepared from aminopropyl and hydroxylalkyl terminated PDMS oligomers, which were subsequently used for the preparation of PMMA-PDMS-PMMA and PDMS-PMMA type block copolymers through ATRP polymerization (71). The efficiency of the macroinitiator prepared from amine terminated PDMS was reported to be low, which resulted in poor control of the block molecular weights. On the other hand DSC analysis of the copolymers indicated microphase separated morphologies in the copolymers obtained. Preparation of PS-PDMS-PS and PMMA-PDMS-PMMA triblock copolymers by ATRP polymerization with PDMS block lengths of 1,000 and 5,000 g/mol were discussed (68). DSC studies on PDMS-5000 based block copolymers showed respective glass transition temperatures for both blocks and melting for the PDMS blocks, clearly indicating the formation of microphase separated morphologies.

5.1.4. Silicone containing block copolymers by the chemical combination of preformed blocks

Chemical combination of oligomers with reactive functional end groups and telechelic PDMS oligomers have also been utilized for the preparation of silicone containing block copolymers. One of the preferred routes for the formation of PDMS copolymers through coupling reactions

is the addition of Si-H on PDMS to C=C end groups of the other block(73-75), as shown in Figure 12. Low molecular weight divinyloligodiphenylsiloxanes and α,ω -dihydridopentasiloxanes were copolymerized by Pt-catalyzed hydrosilylation. Oligomer and polymer structures and compositions were determined by NMR and FTIR spectroscopy. Due to the short segment lengths used, DSC analysis showed a single T_g for the copolymers obtained, which increased linearly with diphenylsiloxane content in the copolymer (76). All silicone copolymers were also obtained through the Pt-catalyzed reaction of α -vinyl dimethylsiloxypolydiphenylsiloxane and α,ω -bis(hydrido)polydimethylsiloxane(35). Formation of well-defined block copolymers was confirmed by ^1H , ^{13}C and ^{29}Si NMR spectroscopy. DSC clearly showed formation of microphase separated morphologies with well-defined PDMS T_g and melting and PDPS melting transitions (35). In another approach dihydroxy terminated PDPS oligomers were reacted with dichlorine (Si-Cl) terminated PDMS oligomers to obtain triblock copolymers. DSC and wide-angle X-ray diffraction (WAXD) studies indicated the formation of microphase separated morphologies, which was strongly dependent on polymer composition (77).

Figure 12

Epoxy terminated telechelic PDMS oligomers were reacted with polybutadienyllithium to prepare PBD-PDMS-PBD triblock copolymers (78). The copolymers were purified by fractional precipitation and characterized using NMR, vapor pressure osmometry, SEC and elemental analysis. PDMS-Oxetane-PDMS triblock elastomers were prepared by the reaction of isocyanate terminated fluorinated oxetane oligomers with an excess of aminopropyl terminated PDMS oligomers (79). Copolymers were all optically transparent due to similar refractive indices of PDMS and oxetane oligomers. AFM images obtained on the fracture surfaces of copolymers revealed microphase separation. Despite fairly low hard segment contents, the triblock copolymers displayed good tensile strengths(79). Elastomeric PDMS-poly(olefin sulfone) networks were prepared by click chemistry through the coupling reactions of azide functional PDMS oligomers and alkyne functional poly(olefin sulfone) oligomers(80). Mechanical properties and hardness of the materials obtained were strongly dependent on their chemical compositions. Under mild basic conditions composite networks

could easily be degraded into their individual components so they were recyclable (80). Low temperature metal free, azide-to alkyne cycloaddition reactions were also used to prepare a wide range of silicone-PEO graft copolymers with amphiphilic properties (81, 82). Polybutadiene-PDMS graft copolymers were obtained by the hydrosilylation of Si-H terminated PDMS macromonomers and polybutadiene, which were subsequently hydrogenated into polyolefin-PDMS graft copolymers (83).

5.2. Silicone containing segmented or multiblock copolymers by step-growth polymerization

Due to the ease of preparation of reactive, telechelic silicone oligomers and availability of a very large number of reactive difunctional organic monomers and oligomers, step-growth polymerization has been the most important method for the preparation of a wide variety of segmented or multiblock silicone containing copolymers, such as silicone-urea and urethanes, silicone-amides, silicone-imides and many others. Synthesis, characterization, structure-morphology-property behavior and potential uses of each of these copolymers will be discussed in detail.

5.2.1. Silicone-urea and silicone-urethane segmented copolymers

Silicone-urea and silicone-urethane copolymers are the most widely investigated silicone copolymers. This is mainly due to; (i) availability of a large number of starting materials enabling the preparation of copolymers with a wide range of compositions, (ii) flexible synthetic chemistry of segmented thermoplastic polyurethanes, and (iii) interesting combination of structure-morphology and surface and bulk properties of the resulting materials. Potential applications of silicone-urethane and silicone-urea copolymers as fouling-release coatings (84-86), biomaterials (87, 88) and surface modifiers for various polymers and fibers (25-27) have also attracted interest for the investigation of these systems.

A critical problem for the preparation of chain extended, high molecular weight silicone-urea copolymers has been the choice of the proper reaction solvent during the chain extension reaction that would successfully dissolve very non-polar PDMS (solubility parameter $\delta = 15.5(\text{J}/\text{cm}^3)^{1/2}$) and extremely polar urea hard segments (solubility parameters $\delta \sim 40$ to $45 (\text{J}/\text{cm}^3)^{1/2}$) (5). This has been overcome by the use of isopropyl alcohol (IPA) as the reaction solvent for the preparation of high molecular weight silicone-urea copolymers with fairly high urea hard segment contents of up to 42% by weight (89). IPA is an unusual solvent for

polyurea or polyurethaneurea synthesis, since it can potentially react with the diisocyanates to form urethane linkages. However, it was demonstrated that reactivity of IPA with aliphatic diisocyanates is fairly negligible at room temperature, for up to several hours(89), which is sufficient for chain extension with diamines to form urea hard segments.

Another potential problem regarding silicone-urethane polymer synthesis, which is quite often disregarded, is the stability of the hydroxyalkyl end groups on the PDMS oligomers. It has been demonstrated that hydroxypropyl-, or hydroxybutyl end groups can backbite the terminal silicon atoms in the PDMS oligomers, leading to the formation of 5 and 6-membered stable cyclic silicone compounds and the loss of end-group functionality, as shown in Figure 13(90). Hydroxalkyl terminated PDMS oligomers with long alkyl bridges between silicon atom and the hydroxyl end groups, such as C₆ or longer alkyls are shown to be stable (10, 90).

Figure 13

Several research groups, especially those led by Yilgor and Wilkes (91-98), Runt (88, 99-102) and Gunatillake (87, 103-107) have been very active regarding the preparation, characterization and investigation of the structure-morphology-property behavior of silicone-urea and silicone-urethane copolymers. Webster and co-workers (84-86, 108-116) have mainly investigated the synthesis and characterization of silicone containing crosslinked polyurethane networks and their performance as antifouling or foul release coatings.

A comprehensive investigation on the effect of a large number of variables, including PDMS molecular weight, type and structure of the diisocyanate and the chain extender and hard/soft segment content, on the structure-morphology-property behavior of homologous silicone-urethane and silicone-urea copolymers was performed(89, 91-98, 117). Silicone-urethane and silicone-urea copolymers were prepared in two steps, using hydroxyhexyl and aminopropyl terminated PDMS oligomers with number average molecular weights of 900, 2,500 and 7,000 g/mole, a cycloaliphatic diisocyanate and various diol and diamine chain extenders. Due to very high reactivity of amine and isocyanate groups, silicone-urea copolymers can easily be prepared at room temperature in IPA solution (89). On the other hand silicone-urethane copolymers are prepared at 60-80 °C and under the catalytic action of tin catalysts (117). Figure 14 provides the reaction scheme for the preparation of silicone-urethane copolymers. Hard segment contents of the copolymers covered a wide range from

16 to 50% by weight(89). Silicone-urea and silicone-urethane copolymers based on PDMS-2500 and PDMS-7000 displayed well microphase separated morphologies based on DMA and SAXS studies(117).As shown in Figure 15, the silicone-urea copolymer based on PDMS-7000 with a hard segment content of 18% by weight exhibited a well-defined PDMS T_g at -120 °C, followed by crystallization starting at -100 °C and a sharp melting at -60 °C. It also displayed a remarkable service temperature range of 230 °C (from -55 to +175 °C). As expected, due to stronger bidentate hydrogen bonding between the urea hard segments, silicone-urea copolymers displayed better tensile properties when compared with homologous polyurethanes (89, 117). Interestingly, ultimate tensile strengths of silicone-urea copolymers showed a linear dependence on the urea hard segment content, as reproduced in Figure 16(89). Molecular dynamics and mesoscale dynamics simulation studies were also used to study the morphology and properties of silicone-urea copolymers with PDMS segment lengths varying between 700 and 15,000 g/mol and urea hard segment content between 1.7 and 34% by weight (98). Results clearly indicated the presence of well microphase separated morphologies and very strong bidentate hydrogen bonding between urea hard segments, leading to the formation of strong elastomers. Other reports describing the preparation, characterization and various properties of silicone-urea and silicone-urethane copolymers based on different silicone oligomers, diisocyanates and chain extenders are available (118-127).

Figure 14

Figure 15

Figure 16

In another study, the influence of PDMS molecular weight (10,800 and 31,500 g/mol) on microphase morphology and tensile properties of silicone-urea copolymers with hard segment contents of 2 to 15% by weight was investigated (96). In spite of their very low hard segment contents, all copolymers displayed excellent microphase separation as indicated by DMA studies. Interestingly, ultimate tensile strengths of silicone-urea copolymers with similar hard segment contents increased with PDMS molecular weight. When copolymers based on the same PDMS soft segment were compared, hysteresis increased linearly and instantaneous set decreased slightly with increasing hard segment content (96, 97). On the other hand when the

PDMS soft segment molecular weight increased from 10,800 to 31,500 g/mol, significant decrease in the hysteresis and constant load creep was observed. Since the critical entanglement molecular weight of the PDMS is stated to be 24,500 g/mol (128), these results suggest contribution of chain entanglements on the tensile properties of silicone-urea copolymers. Silicone-urea/fumed silica nanocomposites were also prepared using these copolymers (129). Incorporation of silica improved tensile and thermomechanical properties of silicone-urea segmented copolymers significantly. Very interestingly, silicone-urea copolymer nanocomposites prepared using long alkyl chain quaternary ammonium modified montmorillonite displayed excellent long-term antibacterial properties against *E Coli* (130).

In addition to polyurea and polyurethane copolymers containing only PDMS soft segments, there have been intensive efforts on the preparation and characterization of silicone copolymers with mixed PDMS, polyether, polyester and polycarbonate soft segments. Structure-property behavior of poly(propylene oxide) (PPO) modified PDMS-urea copolymers, synthesized using aminopropyl terminated PDMS oligomers with number average molecular weights of 3,200 and 7,000 g/mol and amine terminated PPO with number average molecular weights of 450 or 2,000 g/mol, containing 10-35% by weight hard segments were investigated (95). SAXS and DMA analysis indicated the formation of microphase separated morphologies with a limited amount of inter-segmental mixing between PPO and the urea hard segments, leading to the formation of a gradient interphase between hard and soft microphases. Incorporation of PPO resulted in distinct improvements in the Young's modulus, tensile strength and elongation at break values of the copolymers, however it also resulted in an increase in the mechanical hysteresis displayed by the materials. Kinning (131) also investigated the synthesis, bulk, surface properties and interfacial structures of a series of PDMS-PPO-urea polymers prepared using aminopropyl terminated PDMS (5,000 g/mol) amine terminated PPO (900 g/mol) isophorone diisocyanate and 1,3-diamino pentane chain extender. PDMS content of the polymers was fixed at 25% by weight. PPO and urea hard segment (HS) contents in the copolymers were varied between 10-55 and 20-65% by weight respectively (131). As reproduced in Figure 17 TEM studies clearly showed well phase separated spherical PDMS domains with approximate diameters of 10-20 nm, in a continuous PPO/HS mixed matrix. DSC studies showed a single T_g for the matrix, which increased systematically as the HS/PPO ratio increased. XPS and static water contact angle studies clearly indicated the formation of silicone rich surfaces for all polymers.

Figure 17

The synthesis and characterization of PDMS modified poly(tetramethylene oxide) (PTMO) based polyurethanes was reported(132). All polymers displayed complex multiphase morphologies and surfaces rich in silicone, which could be oxidized to a silica type protective layer, leading to improved fire resistance (132). Other studies on the preparation and characterization of PDMS modified PTMO (133-135) and poly(ethylene oxide) based polyurethanes (136, 137) also reports the formation of multiphase polymers with improved tensile properties.

Gunatillake and co-workers investigated the synthesis, composition dependent morphological behavior, mechanical properties and biostability of a large number of segmented silicone containing polyurethanes(87, 103-107). Silicone-urethane copolymers based on MDI, 1,4-butanediol (BD) and PDMS-1,000, 2,000 and 3,000 g/mol, with a fixed hard segment content of 40% by weight, showed two phase morphologies regardless of the PDMS molecular weight(106). These copolymers also displayed fairly good ultimate tensile strengths around 22 MPa. Young's modulus values of the copolymers with constant hard segment content increased with increasing PDMS molecular weight, which is attributed to longer hard segment molecular weights. They also carried out a systematic investigation on polyurethanes with 40% by weight hard segment content based on MDI and BD and mixed PDMS and polyether or polycarbonate soft segments(104). The soft segments were based on 80/20 mixtures of PDMS-1000 and a polyether glycol or a polycarbonate glycol with an average molecular weight of 700 g/mol. Polyethers included poly(ethylene oxide) (PEO), PPO, PTMO, poly(hexamethylene oxide) (PHMO) and poly(decamethylene oxide) (PDMO). Polycarbonate glycols included poly(hexamethylene carbonate) and two other oligomers. Results of DSC and DMA studies indicated that all polyurethanes had microphase separated morphologies, the extent of which strongly depended on the chemical structure of the polyether or polycarbonate oligomer(104). While PTMO and PHMO containing systems displayed very good microphase separation, PEO based copolymers showed significant mixing with the urethane hard segments leading to a broad interphase region between soft matrix and urethane hard segment domains(7, 104, 138). As expected, microphase morphology strongly affected the tensile properties, where PTMO and PHMO containing copolymers displayed much higher tensile strengths when compared with their PEO homologs(104, 105). In a separate study, they also

investigated the influence of the chain extender and diisocyanate (HMDI) structures on the morphology and properties of polyurethanes based on mixed PDMS-1000/PHMO-700 (80/20) soft segments (107). It was shown that HMDI based copolymers displayed similar morphology and properties as those of homologous MDI based systems. On the other hand structure of the chain extender used (BD versus bis(4-hydroxybutyl)tetramethyldisiloxane showed very significant effect on the morphology and properties, where BD chain extended copolymers displayed better microphase separation and formation of stronger elastomers (103, 105, 107). Due to their elasticity, biostability, hemocompatibility and toughness, these types of silicone containing copolymers are of interest as biomaterials for applications such as cardiac and orthopedic devices, plastic surgery and drug release. *In vitro* and *in vivo* stability tests on these materials are discussed in the next section.

Runt and co-workers also studied the influence of soft segment compositions on the microphase morphology and properties of segmented polyurethanes(88, 99-102, 139). They reported that the silicone-urethane copolymers prepared from ethoxypropyl terminated PDMS-1000, MDI and BD, with hard segment contents of 26 to 52% by weight, displayed a three-phase morphology consisting of a soft PDMS matrix, hard urethane domains and a mixed ethoxypropyl/urethane mixed phase(102). They indicated that the extent of microphase separation increased with an increase in hard segment content, which is expected. Interestingly, when they used PDMS and PHMO mixed soft segments they also observed a three-phase morphology consisting of PDMS matrix, urethane hard segment domains and a mixed PHMO/urethane phase(99). No data on the mechanical properties of the copolymers were provided. They also reported the preparation and characterization of segmented polyurethanes using a silicone-carbonate macrodiol as the soft segment, with fairly high hard segment contents of 40 to 60% by weight(88). These materials showed extensive phase mixing when compared with polyurethanes consisting of only PDMS soft segments, which resulted in softer materials with low Young's modulus, but with fairly high ultimate tensile strengths of up to 40 MPa and elongation at break values of 400-700% depending on the composition. The effect of temperature on the microphase behavior of silicone-urethane copolymers also containing polycarbonate and polyether soft segments was investigated(140). FTIR and SAXS results indicated that, depending on their chemical composition and urethane hard segment contents, at temperatures above 150 °C all copolymers displayed single phase, clear melts. Upon cooling all materials displayed microphase separated morphologies, typical of silicone-urethane copolymers (140). The effect of the soft segment structure on the

microphase morphologies of polyurethanes based on PTMO, aliphatic polycarbonate and a mixed PDMS/PHMO soft segments and MDI and BD hard segments was also investigated (141). Polyurethanes containing mixed PDMS/PHMO were reported to display three-phase core-shell morphology, while the others exhibited typical two-phase structures (141).

Hydroxy terminated triblock silicone copolymers, such as PCL-PDMS-PCL and PLLA-PDMS-PLLA were also utilized as reactive oligomers for the preparation of silicone-ester-urethane type segmented polymers(51, 62, 142, 143). The presence of PCL groups provide excellent solubility to the PDMS containing oligomer in polar solvents such as DMF and DMAC, which are widely utilized in polyurethane synthesis. Silicone-ester-urethane polymers based on PCL-PDMS-PCL triblock oligomers, various diisocyanates and chain extenders displayed multiple transitions in DSC analysis, where distinct T_g values were observed for PDMS around $-120\text{ }^\circ\text{C}$ and for PCL around $-55\text{ }^\circ\text{C}$ and a sharp crystalline melting peak for PCL around $50\text{ }^\circ\text{C}$, clearly indicating formation of microphase separated morphologies. Polymers also showed formation of silicone-rich surfaces as determined by XPS and contact angle measurements (51, 142, 144). Crosslinked PDMS-ester-urethane polymers displayed composition dependent tensile properties, which also showed strong dependence on degree of crosslinking (145).

Webster and co-workers used combinatorial methods for the synthesis and characterization of a wide range of crosslinked silicone-urethane copolymer compositions as antifouling and fouling-release coatings(84-86, 108-116). Due to its low surface energy and low modulus, PDMS has received widespread attention in marine coatings (146). One drawback regarding pure PDMS elastomers was their poor adhesion to most substrates and rather poor mechanical strength. To develop a tougher PDMS containing coating system, which also maintained its properties after long-term under water immersion, the Webster group investigated crosslinked silicone-polyurethane systems, which were also modified by reactive polyester (mainly polycaprolactone) oligomers. Since the coating systems included many variables, such as PDMS and polycaprolactone (PCL) oligomers with different molecular weights, crosslinkers, catalysts, fillers, solvents, etc., they used combinatorial high-throughput experimentation in order to optimize the coating formulations. In some studies they also utilized reactive hydroxyl terminated PCL-PDMS-PCL oligomers (62). DSC and DMA studies clearly demonstrated the formation of microphase separated bulk and surface morphologies in these crosslinked PDMS-PCL-urethanes (62, 108, 110). XPS and water contact angle studies indicated the

formation of PDMS rich surfaces. SEM image and its silicon map are provided in Figure 18-A and 18-B, together with the topographical AFM image (Figure 18-C) of a coating containing 37% by weight of PCL-PDMS-PCL (10% by weight of PDMS)(108). These results clearly showed the presence of well-defined and homogeneously distributed spherical PDMS domains on the coating surface with an average size of about 1.5 μm (62, 108). It was reported that there was a dramatic effect of the PDMS oligomer molecular weight on the surface energies of the coatings obtained with constant PDMS content of 20% by weight. As the molecular weight of the PDMS oligomers increased from 1,000 to about 35,000 g/mol, surface energy of the coating decreased dramatically (110). Performance of fouling-release coatings are determined by the pseudobarnacle adhesion tests performed according to ASTM D 5618, where wooden studs of known diameters are glued to the surface of the coatings and the shear force required to remove each stud is measured by a force gauge. When coating formulations containing 10, 20, 30 and 40% by weight PDMS were compared for their foul-releasing efficiency, interestingly the lowest pseudobarnacle adhesion was obtained with 10% PDMS containing systems. The average force of release increased linearly as the PDMS content increased from 10 to 40% by weight (110). Crosslinked PDMS-acrylic-urethane coatings were also prepared and characterized (113). Linear PDMS-urea copolymers that display microphase separated morphologies and good mechanical properties were also shown to exhibit advanced fouling-release properties depending on their chemical compositions and PDMS molecular weight (118).

Figure 18

5.2.1.1. *In vitro* and *in vivo* hydrolytic and oxidative stability (biostability) of silicone-urethane copolymers

One of the important applications of polyurethane elastomers is in implantable biomedical devices, such as artificial blood vessels, catheters and components of pacemaker leads(8). A major problem regarding the long-term use of polyether or polyester based polyurethanes in contact with tissue, blood and other bodily fluids is their hydrolytic and oxidative stability(8). It has been well documented that both *in vivo* and *in vitro* applications conventional polyester based polyurethanes undergo hydrolysis(87, 147), whereas polyether and to a lesser extent polycarbonate based polyurethanes show oxidation over time. These types of degradation

reactions ultimately result in environmental stress cracking and lead to the failure of the devices(8). Modification of polyurethanes through the chemical incorporation of low surface energy PDMS soft segments have shown to improve the hemo and/or biocompatibility of these materials (87, 88, 148, 149). Similar effects have also been observed through the blending of polyurethanes with silicone containing copolymers (3, 51, 150). As discussed in section 5.2.1 in detail, extensive studies have been carried out on the preparation and characterization of PDMS containing polyurethanes with the expectation that incorporation of low surface energy, hydrophobic PDMS soft segments would also provide better thermal, oxidative and hydrolytic stability to the polyurethanes for *in vivo* applications.

Biostability of different ratios of PDMS/PHMO containing polyurethanes based on MDI and BD hard segments (40% by weight) were investigated by Gunatillake (151). Biostability was assessed by strained subcutaneous implantation in sheep for three months followed by SEM investigation and mechanical testing (151-153). For comparison, commercial polyurethanes were also investigated as control materials. It was reported that PDMS modified polyurethanes displayed much better biostability when compared with polyether based polyurethanes, where the best performance was displayed by the copolymer containing 80% by weight PDMS [129-131]. Hydrolytic and oxidative stabilities of polyether and polycarbonate based polyurethanes and a PDMS modified polyether-urethane copolymer containing 20% by weight PDMS were studied by Runt(154). *In vitro* stability tests were carried out on unstrained film samples, at $37\pm 1^\circ\text{C}$ in an oxidative solution containing 20% hydrogen peroxide in 0.1 M cobalt chloride solution, for 72 hours. SEM, ATR-FTIR, AFM, SAXS and DMA were used for the characterization of the samples. Results showed that silicone modified polyurethane was more stable toward hydrolysis or oxidation, when compared with polycarbonate or polyether based polyurethanes (154).

Anderson and Ward also carried out stability studies both *in vitro* and *in vivo* for a polyether (PTMO), MDI and BD based polyurethane as control and PDMS containing homologs, where PDMS content was 10, 20, 35 and 61% by weight (155-157). Characterization techniques included optical microscopy, FTIR and molecular weight determination by SEC. *In vitro* tests were performed in 3% hydrogen peroxide in saline solution at 37°C for up to 252 days. For *in vivo* studies sterile films were implanted in the dorsal subcutis of rabbits and were explanted after 6, 12, 18 and 24 months. *In vitro* studies showed that 20 and 35% PDMS containing polyurethanes were the most stable against degradation. *In vivo* studies also indicated similar

results, with no deterioration in the appearance or properties of 20 and 35% PDMS containing polyurethanes even after 2 years, while polyether based polyurethane showed significant degradation (156). These materials were also tested *in vivo* under stress (400% elongation) for up to 18 months. Results obtained were similar, where PDMS containing polyurethanes showed dramatically reduced autooxidation and stress cracking when compared with polyether based control (155, 156, 158). It was demonstrated that in addition to polyether containing polyurethanes, PDMS incorporation also increased the biostability of polycarbonate based polyurethanes dramatically (158).

Comprehensive investigation of the stability of PDMS containing commercially available polyurethanes Elast-Eon E2A and Pursil 3 and a control polyether based aromatic polyurethane were carried out (159). Samples were aged in a phosphate based buffered saline solution at $\text{pH}=7.4\pm 0.5$ at 37, 55, 70 and 85 °C, for up to one year. Samples were characterized by molar mass determination, SAXS, DMA and tensile testing. All of the samples showed a decrease in molar mass with increased time and temperature. The degradation was slower in PDMS modified Pursil 35, when compared with other samples. It was also reported that the reduction in the molar mass resulted in substantial degradation in the tensile strengths and the toughness of the materials (159).

5.2.2. Silicone-ester copolymers

The synthesis, characterization and structure-property behavior of silicone-polyester block and segmented copolymers have been investigated. Detailed discussions on the preparation and structure-property behavior of triblock silicone-ester (PCL-PDMS-PCL) copolymers have already been provided in Section 5.1.2 (51, 62). Here, the synthesis and properties of silicone-ester multiblock or segmented copolymers will be discussed.

5.2.2.1. Silicone-ester segmented copolymers through enzyme catalyzed condensation

Segmented silicone-ester copolymers were synthesized in high yields by the direct polycondensation of diacids and hydroxypropyl terminated PDMS oligomers using Novozym 435 (Lipase B from *Candida antarctica*) as the catalyst (160). During the polymerization reactions butane, hexane and octanedioic acids were used together with hydroxypropyl terminated PDMS oligomers with molecular weights of about 500 and 800 g/mol. Reactions were second order with a fairly low activation energy of 50.6 kJ/mol (161, 162). Copolymers

obtained displayed overall molecular weights in 6,000 to 9,000 g/mol range and PDMS T_g values at between -103 and -123 °C.

Novozym 435 was also used as a catalyst for the synthesis of PDMS-aromatic polyester segmented copolymers by transesterification reactions between hydroxyalkyl terminated PDMS-2500 and dimethylterephthalate (DMT) in toluene at 80-90 °C. Copolymer molecular weight increased substantially with reaction time reaching to 38,000 g/mol after 96 hours (163). Copolymers obtained were reported to be amorphous liquids at room temperature, due to very long PDMS and very short ester segments that are not capable of forming hydrogen bonding observed between urethane, urea or amide groups. DSC studies clearly showed PDMS T_g at -120 °C, however no melting transition was observed for the aromatic ester segments. It may be possible to obtain high strength PDMS-ester copolymers through the use of short chain diols, such as ethylene glycol or BD as “chain extenders” for the ester segments during the synthesis reactions. Same group also investigated the synthesis and characterization of PDMS-aliphatic ester segmented copolymers by the transesterification of carboxypropyl terminated PDMS with BD, 1,6-hexanediol and 1,8-octanediol using Novozym 435 as the catalyst(164). The molecular weights of the copolymers obtained strongly depended on the reaction temperature, enzyme activity and enzyme concentration.

PDMS-polyesteramide copolymers were synthesized using aminopropyl terminated PDMS-1000, 1,8-octanediol or fluorinated diols and diethyl adipate in bulk, under the catalysis of Novozym 435. Copolymers with $\langle M_n \rangle$ values around 10,000 g/mol were obtained (165, 166). Due to fairly low molecular weight and poor microphase separation, the copolymers did not form strong films.

5.2.2.1. Silicone-ester segmented copolymers by melt esterification

Segmented PDMS-polyester copolymers were synthesized using PDMS-2000, BD and adipic acid or 1,4-cyclohexanedicarboxylic acid, in melt under the catalysis of titanium tetraisopropoxide(167). The PDMS content of the copolymers varied between 5 and 50% by weight. DSC and AFM studies clearly demonstrated the formation of microphase separated morphologies with highly crystalline polyester segments as indicated by WAXD and DSC results. Copolymers displayed three distinct morphologies as a function of increasing PDMS content, which were: (i) spherical microdomains of PDMS in a polyester matrix, (ii)

bicontinuous double-diamond type morphology, and (iii) spherical microdomains of polyester in a continuous PDMS matrix.

The effect of structural variables on the properties of silicone-polyester segmented copolymers has been investigated(168-173). Melt transesterification reactions were used for the preparation of PDMS-polyester segmented copolymers. In one method hydroxyalkyl or carboxypropyl terminated PDMS oligomers were reacted with DMT and BD under the catalysis of titanium isopropoxide to prepare PDMS-poly(butylene terephthalate) (PBT) copolymers (168-170). The copolymers obtained, which contained 10 to 40% by weight of PDMS soft segments with molecular weights of 600 to 2,500 g/mol, displayed microphase separated morphologies as evidenced by the DSC studies, where a PDMS T_g around -115 °C and PBT melting endotherms in $205-235$ °C were observed(168-170, 174). Melting temperatures displayed by the PBT microphase gradually increased with an increase in the molecular of PBT segments in the copolymers. In a recent work (174) same group reported some inefficiencies related to the complete incorporation of hydroxyalkyl terminated PDMS into the copolymers. Although not clearly mentioned in the article, this was most probably due to the instability of hydroxyalkyl end groups under the reaction conditions(90). As a result, in their recent publications they used a different transesterification approach for the PDMS-polyester copolymer synthesis, which has also been reported earlier by Yilgor(175). In this method telechelic, hydroxyl terminated PCL-PDMS-PCL copolymers were used instead of hydroxyalkyl terminated PDMS oligomers, together with DMT and BD(171). By using this technique PDMS-PCL-PBT segmented copolymers with PDMS contents varying from 6 to 33% by weight were prepared. SEC measurement indicated formation of high molecular weight copolymers with $\langle M_n \rangle$ values of 22,000 to 66,000 g/mol. The structure and composition of the copolymers were determined by $^1\text{H-NMR}$. DSC analyses clearly showed the formation of microphase separated systems with a clear T_g around -120 °C for PDMS segments and crystallization and melting peaks for PCL and PBT segments(171). PDMS-polyester segmented copolymers were also prepared by the transesterification reactions of α,ω -hydroxyalkylether terminated PDMS oligomers(1000 g/mol), dimethylterephthalate and 1,4-butanediol (173). Copolymers with PDMS content between 10 and 60% by weight were prepared. The effect of the polymer composition on crystallinity and thermal stability of the copolymers were investigated.

Liquid crystalline PDMS-polyester segmented copolymers were synthesized in solution using hydroxypropyl terminated PDMS oligomers with molecular weights of 250 and 1,200 g/mol, 2,6-bis(4-hydroxybenzylidene)cyclohexanone and sebacoyl and terephthaloyl chlorides (176, 177). All copolymers exhibited nematic textures. LC behavior and transition temperatures showed a strong dependence on the chemical structure (aliphatic or aromatic) of the ester linkages, PDMS molecular weight and PDMS content of the copolymers.

Side-chain liquid crystalline, crosslinked PDMS-polyester elastomers were synthesized by hydrosilylation reactions (178). DSC analyses clearly indicated the presence of microphase separation with a well-defined PDMS glass transition and the presence of an isotropic transition temperature, which decreased with an increase in the mesomorphic crosslinking agent. Lightly crosslinked copolymers showed good elasticity and reversible phase transitions on heating and cooling cycles, as indicated by optical microscopy and WAXD studies. Thermal stability of the copolymers increased with crosslinking.

5.2.3. Silicone-amide copolymers

Similar to silicone-ureas and urethanes, silicone-amide segmented copolymers also display interesting morphologies and thermal and mechanical properties. This is due to strong hydrogen bonding between amide hard segments and substantial differences between the solubility parameters of PDMS and amide groups (179). Another advantage offered by the polyamides is their melt processibility (especially the aliphatic polyamides) due to their high thermal stability, when compared with polyurethane or polyurea hard segments, which start to degrade above 200 °C (180). However, very interestingly, in spite of the availability of a large number of starting materials, when compared with PDMS-urea or urethane copolymers, studies on the preparation and characterization of PDMS-amide segmented copolymers have been fairly limited.

Akashi and co-workers investigated the synthesis and various properties of PDMS-aromatic polyamide segmented copolymers extensively (181-190). Special emphasis was given to their evaluation and performance as biomaterials (184, 186, 187). Copolymers were synthesized by low-temperature solution polycondensation using a two-step process shown in Figure 19 (181, 184). First step involved the preparation of α,ω -dichloroformyl-terminated aramid oligomers by the reaction of isophthaloyl chloride and diaminodiphenyl. In the second step aramid oligomers were reacted with aminopropyl terminated PDMS oligomers (1,700 g/mol) to form

PDMS-amide segmented copolymers. Reactions were conducted in chloroform, at $-15\text{ }^{\circ}\text{C}$ in the presence of triethylamine as a hydrogenchloride acceptor. The PDMS content of the copolymers varied between 8 to 71% by weight. TEM studies clearly showed the formation of multiphase morphologies which strongly depended on the copolymer composition. Copolymers containing 8 to 24% by weight PDMS displayed discrete spherical domains of silicone ($100\text{-}150\text{ \AA}$ in size) in an aramid matrix. Copolymer containing 41% by weight PDMS displayed a cylindrical morphology. Very interestingly, when the PDMS content increased to 71% by weight, morphology reverted back to spherical PDMS domains. This is attributed to the polarity of the casting solvent, which was dimethylacetamide (DMAC). Surface characterization by XPS clearly showed the formation of silicone rich, hydrophobic surfaces (181-183). In a separate study, PDMS-aromatic polyamide multiblock copolymers containing 26 to 75% by weight PDMS-1700 were prepared (183). Films cast from DMAC solution were transparent, displayed composition dependent microphase separated morphologies and elastomeric properties. Copolymers containing 53% by weight of PDMS showed oxygen permeabilities similar to crosslinked silicone rubber.

Figure 19

The preparation and characterization of PDMS-amide segmented copolymers containing ferrocene groups was reported (191). Very high molecular weight copolymers with $\langle M_n \rangle$ values in 4.3×10^6 to 7.8×10^6 g/mol were prepared in solution using terephthaloyl or isophthaloyl chlorides, aromatic diamine chain extenders and aminopropyl terminated PDMS oligomer with $\langle M_n \rangle$ value of 27,000 g/mol. DSC studies clearly showed formation of microphase separated structures with well-defined T_g and T_m values for PDMS around -120 and $-50\text{ }^{\circ}\text{C}$ respectively and polyamide hard segment T_g values in $243\text{-}278\text{ }^{\circ}\text{C}$ range depending on their chemical structures. All copolymers displayed very high melting points above $300\text{ }^{\circ}\text{C}$. TEM and AFM studies confirmed the formation of multiphase morphologies (191). The same group also reported the synthesis of high molecular weight PDMS-polyamide segmented copolymers which also contained trichlorogermyl pendant groups by using one-pot solution polycondensation reactions (192). The copolymers obtained were characterized by spectroscopic (FTIR and NMR) techniques, SEM and DSC analyses. All copolymers were reported to display microphase separated morphologies as indicated by DSC results and TEM analysis.

PDMS-amide copolymers were prepared through the stoichiometric reactions of aminopropyl terminated PDMS oligomers (1,000, 3,800 and 7,500 g/mol) and terephthaloyl chloride (193). Copolymers were characterized by various NMR analyses and were reported to display microphase morphologies with PDMS domain sizes in 10-50 nm range depending on the PDMS molecular weight and content in the copolymers.

Several groups also investigated the synthesis of PDMS-polyamide and PDMS-polyesteramide copolymers using *candida antarctica* lipase B, immobilized on a macroporous acrylic resin (Novozym 435) as the catalyst (163, 164, 166). In one study aminopropyl terminated PDMS oligomers with $\langle M_n \rangle$ values of 1,000 and 4,700 g/mol were reacted with DMT to produce PDMS-amide copolymers (163). In another study aminopropyl terminated PDMS-900 was reacted with diethyl adipate to form PDMS-amide copolymers (166). Unfortunately, in both cases the copolymers obtained had fairly low molecular weights and did not form strong films. This was most probably due to the absence of diamine chain extenders in the reaction mixture which is needed to form long amide segments in order to form strong self-supporting films. Enzymatic synthesis of PDMS-esteramide copolymers were also reported through the solution reactions of aminopropyl terminated PDMS-1700, diethyl adipate and various fluorinated alkanediols, which were used as chain extenders (165). These materials were also of low molecular weight, most probably due to solubility problems encountered during polymerization reactions in toluene.

PDMS-amide networks were prepared by the UV initiated free radical polymerization of telechelic acrylamido and methacrylamido terminated PDMS oligomers with $\langle M_n \rangle$ values of 5000 to 55,000 g/mol (194, 195). Due to the extremely flexible PDMS matrix and substantial differences in the solubility parameters of PDMS and amide groups, which are 15.5, and 43.2 $(\text{J}/\text{cm}^3)^{1/2}$ respectively (179), these crosslinked polyamides showed microphase separation and formed fairly strong films due to the strong hydrogen bonding between the amide hard segments. FTIR was employed to investigate the temperature dependent hydrogen bonding in these systems. Effect of PDMS molecular weight on the dynamic-mechanical behavior and stress-strain properties was investigated. Modulus of rubbery plateau obtained from DMA and Young's modulus were dependent on the PDMS molecular weight. The synthesis and characterization of aliphatic and aromatic siloxane-amide copolymers with different compositions were also discussed (196, 197).

5.2.4. Silicone-imide copolymers

Silicone-imide copolymers have been extensively investigated since they combine the excellent thermal and thermooxidativestability, solvent resistance, mechanical and electrical properties of high performance polyimides together with extremely high flexibility, good solubility, high gas permeability, reduced water absorption and interesting surface properties of silicones.

Voit and co-workers reported the preparation of linear and graft PDMS-imide copolymers containing 10-30% by weight PDMS(198-204). Chemical structures of a linear and a graft PDMS-imide copolymer prepared by Voit (204) are provided on Figure 20. Strong copolymer films with ultimate tensile strengths in the 26-60 MPa range were obtained by casting from dichloromethane solutions. DSC studies clearly indicated microphase separated copolymers with PDMS melting endotherms around $-45\text{ }^{\circ}\text{C}$ and well defined polyimide T_g values in the $200\text{-}220\text{ }^{\circ}\text{C}$ range. Copolymers were thermally stable up to $400\text{ }^{\circ}\text{C}$, as determined by thermogravimetric analysis under nitrogen. Static water contact angle measurements showed the formation of silicone rich copolymer surfaces with contact angles in $100\text{-}108^{\circ}$ range compared to 83° for the polyimide homopolymer. The same group also prepared segmented PDMS-imide copolymers containing fluorinated anthracene groups using one-pot solution imidization or thermal imidization methods. PDMS content was constant at 40% by weight(200). The copolymers showed good solubility in polar organic solvents. Their water uptake after 72 hours of water immersion was almost negligible due to the presence of PDMS and fluorinated anthracene in the copolymer backbone. Copolymers displayed good thermal stability under nitrogen. Transparent thin films exhibited ultimate tensile strengths between 25 and 31 MPa and elongation at break values up to 110%.

Figure 20

PDMS-imide block and segmented copolymers were prepared using aminopropyl terminated PDMS-900, 3,3',4,4'-diphenylthioether dianhydride and 4,4'-oxydianiline, using a two step reaction in N-methyl-2-pyrrolidone (NMP) solution (205). The copolymers were characterized by spectroscopic (FTIR, NMR), thermal (DSC, TGA), dynamic mechanical (DMA) methods, polarized optical microscopy and tensile tests. All copolymers displayed two T_g values, one around $-100\text{ }^{\circ}\text{C}$ and the other in $129\text{-}184\text{ }^{\circ}\text{C}$ range depending on the chemical structure and composition of the copolymers. All samples displayed excellent tensile properties with

ultimate tensile strengths in 26 to 33 MPa range and elongation at break values of 120-130%(205, 206).

PDMS-imide segmented and graft copolymers containing fluorinated imide hard segments were also investigated (198-204, 207-210). Copolymers were prepared from aminopropyl terminated PDMS oligomers with $\langle M_n \rangle$ values 900, 1,680 and 4,600 g/mol (203, 211, 212). High molecular weight copolymers obtained displayed microphase separated morphologies based on the DSC studies and good thermal stability. Morphological behavior, thermal, mechanical, dielectric and permeabilities of solution cast copolymer films were investigated. as organophilic pervaporation membranes. Copolymers synthesized using high molecular weight PDMS showed reasonably good mechanical strength and showed improved flux and selectivity as membranes (212).

A series of pyridine-containing PDMS-imide segmented copolymers containing 5, 10 and 15% by weight of PDMS (900, 1,680 and 4,600 g/mol) were prepared. Poly(amic acid) formation reactions were carried out in solution, followed by thermal imidization of the poly(amic acid) at 350 °C (213). Effects of the amount and the block length of PDMS on the thermal behavior, dielectric properties and surface electrical resistivity of the copolymers were investigated. When compared with conventional aromatic polyimides, the PDMS-imide copolymers showed stronger adhesion to copper foils, lower moisture absorption and low dielectric constant, making them preferable for various microelectronic applications.

Linear and crosslinked silicone-containing liquid crystalline (LC) polyimides with different substituents on the mesogenic units were prepared (214-218). Wide angle x-ray diffraction WAXD experiments confirmed the formation of layered morphologies in these LC polyimides with siloxane spacer units and their d-spacings. It was shown that chloro and fluoro substituents were effective for the formation of LC phases. The isotropization temperature was not affected but the crystal-LC transition temperatures were significantly decreased by PDMS. Fluoro-substituted silicone-imide copolymer exhibited the lowest crystalline-LC transition temperature of 134 °C. It also showed a wide liquid crystal temperature up to 238 °C. The transition temperatures decreased with an increase in siloxane spacer unit lengths. X-ray diffraction (XRD) measurements indicated formation of smectic A and smectic C as high and low-temperature mesophases, respectively. Crosslinked versions of silicone-imides were also shown to display liquid crystalline properties (218). Reports on

various aspects of synthesis, characterization and structure-property behavior of other types of silicone-imide copolymers are available (219-225).

5.2.5. Other types of silicone containing copolymers

Due to the interesting combination of properties of PDMS, which include very low T_g and excellent chain flexibility, low surface energy and hydrophobicity, good thermal and oxidative stability, high gas permeability, biocompatibility and good dielectric properties and the availability of a wide range of reactive functionally terminated silicone oligomers, researchers have tried to incorporate PDMS into the backbone of a large variety of organic polymers (3), some of which has already been discussed in the preceding sections. In this section a general overview of the synthesis and properties of silicone containing copolymers based on other organic backbones will be provided.

Copolymers based on PDMS and hydrophilic PEO segments are important surfactants that find critical applications in polyurethane foam production, the cosmetics industry and as wetting agents in agriculture. The synthesis and properties of silicone-polyether surfactants are discussed in detail in literature (226-229). PDMS-PEO block and graft copolymers were prepared by hydrosilylation reactions of allyl terminated PEO and Si-H terminated PDMS oligomers(230, 231). TEM studies showed microphase separated morphologies in polymer films. Surface tension of aqueous solutions increased with an increase in PEO content. PDMS-PEO copolymers were also prepared using metal-free click reactions(82). Products displayed composition-dependent amphiphilic properties. PDMS-PEO copolymers doped with various metal ions or organic acids were characterized as polymeric electrolytes(232-234). Metallosupramolecular A-B type diblock copolymers where PEO and PDMS linked together by Ru(II) bis-terpyridine complex was reported (235). Well-defined micelles of the amphiphilic supramolecular structures with a moderate polydispersity were observed in aqueous medium by dynamic light scattering (DLS) and cryogenic TEM studies. Thermotropic phase behaviors and microstructures of PDMS-PEO copolymers were studied in melt by DSC, SAXS and optical microscopy. Three different microphase morphologies were observed as a function of the block lengths and copolymer composition (236). PDMS-PEO copolymers containing quaternary ammonium groups were shown to possess biocidal activity (237). Hydrophobic drug carrying polymeric nanovesicles were also prepared from PDMS-PEO copolymers by using THF/water mixtures. Vesicle size was controlled by copolymer concentrations and THF/water ratio (238). PEO-PDMS-PEO triblock copolymers with

different block lengths and compositions were prepared and used in the modification of chitosan(239-241). PDMS-PEO graft copolymers were blended with PEO-amide segmented copolymers at different concentrations and the resulting materials were evaluated as gas separation membranes (242). A blend containing 50% by weight of PDMS-PEO copolymer showed 5 fold increase in CO₂ permeability when compared with the unmodified PEO-amide membrane.

Copolymers of PDMS and engineering thermoplastics such as aromatic polyethersulfone (PSF), aromatic polyethers, aromatic polycarbonate (PC) and others have also been studied. Chemical structures of PDMS-PSF and PDMS-PC copolymers are provided in Figure 21. Chemical incorporation of PDMS into these polymers provide improved low temperature flexibility, enhanced gas permeability and silicone rich hydrophobic surfaces, which play critical roles in various applications. PDMS-polysulfone segmented (243-248)and graft (249)copolymers with a wide range of compositions were prepared by the reaction of α,ω -phenol terminated PSF oligomers with α,ω -chlorosilane (Si-Cl) or α,ω -hydrogensilane (Si-H) terminated PDMS oligomers (244).High molecular weight copolymers displayed microphase separated morphologies, hydrophobic surfaces and improved thermal stabilities.

Figure 21

Segmented(250, 251) and graft or branched (252, 253) silicone-carbonate copolymers were synthesized by various techniques, such as transesterification of polycarbonate (PC) and PCL-PDMS-PCL copolymers (175), interfacial phosgenation of aminopropyl terminated PDMS and bisphenol-A (251) or by the hydrosilylation of allyl functional PC and Si-H terminated PDMS oligomers (252-254). PDMS-PC copolymers formed clear and highly transparent films, similar to polycarbonate. All copolymers displayed multiphase morphologies and silicone-rich hydrophobic surfaces. They also had higher impact strengths, especially at low temperatures, when compared with PC homopolymer and improved thermo-oxidative stability and oxygen-to-nitrogen permselectivity(252-254). Segmented PDMS-PC copolymers were prepared through the reaction of preformed blocks (255). TEM and SAXS studies on solution cast films showed phase separated morphologies, which was strongly dependent on the solvent used (255).

Preparation and characterization of silicone-aromatic polyether copolymers with good thermal and hydrolytic stability(256), silicone-benzimidazoles with proton conductivity (257), silicone-ferrocene copolymers with interesting rod-coil structures (258-260) and photochemical activity (261, 262) were reported. Silicone-azomethine copolymers with interesting physical, chemical and spectroscopic properties and their complexation behavior with various metal ions were investigated (263-266).

Silicone-acrylic block, segmented and graft copolymers and interpenetrating networks have also been extensively investigated(267-289). In addition to basic studies on the composition dependent structure-morphology-surface behavior(270, 274, 276, 281, 282, 284, 285, 290), these materials were also investigated as protective coatings(271, 279, 287), adhesives (273, 277, 283), membranes (286, 288, 289) and biomaterials (268, 272).

5.3. Silicone modified epoxy networks

Organofunctionally terminated silicone oligomers and silicone containing copolymers such as PCL-PDMS-PCL or polyether-PDMS-polyether are used as impact modifiers for epoxy, novolac and bismaleimide resins(291-294). Due to its simple curing chemistry and wide range of applications, most of the work has been carried out on epoxy resin toughening(292, 293, 295), which will mainly be discussed here. Reports on the modification of novolac resins (294, 296), bismaleimides (297, 298), various interpenetrating networks (299-301) and others (291) are also available.

It is well documented that in order to obtain optimum toughening in epoxy resins, the additive should preferably be miscible with the resin before curing and microphase separate into discrete domains during curing(302, 303). Although low molecular weight silicones (< 500 g/mol) are miscible (304), high molecular weight PDMS is quite immiscible with the epoxy resins. In order to improve the compatibility, functionally terminated PDMS oligomers are first reacted with the epoxy resin before adding the curing agent (295, 303, 305). When block copolymers such as PCL-PDMS-PCL(292), polyether-PDMS(306, 307) or others (308-312) are used as modifiers, organic segments act as compatibilizers with the epoxy resin and perform well as impact modifiers. Most of the reports available mainly discuss the curing kinetics and mechanism of epoxy network formation reactions in the presence of silicone modifiers(295, 304, 310). The effect of the structure and molecular weight of the silicone

modifier and the amount of additive on the morphology, thermal and mechanical properties, impact strength and surface properties were also investigated.

Hydroxy terminated PDMS oligomers with molecular weights in 650-24,000 g/mol range were used as modifiers for epoxy resins (305). As expected modified networks displayed microphase separated morphologies and silicone rich surfaces. Slight improvement in the fracture energy was observed (305). Amine terminated PDMS with a molecular weight of 1,600 g/mol was used as a curing agent and modifier for epoxy resins. Initially immiscible mixtures resulted in microphase separated structures upon curing (295). Low molecular weight amine terminated silicones were also used as a curing agent and modifier for epoxy resins (304). Initial mixture and the cured networks were transparent and homogenous. Impact strengths of the networks increased linearly with the amount of silicone additive (304).

Silicone containing block and segmented copolymers, which provide good miscibility with the epoxy resin in the uncured state are more effective tougheners than PDMS oligomers, where one of the favorites is the PCL-PDMS-PCL copolymers (292, 313, 314). Initially homogeneous modifier/epoxy mixtures lead to microphase separated morphologies upon curing. Mechanical and thermal properties of the modified networks are strongly dependent on the amount of silicone modifier incorporated. Surfaces of the modified networks are fairly hydrophobic (313). PDMS-epoxy copolymers prepared by the reaction of epoxy resin and hydroxy terminated PDMS oligomers with molecular weights of 600 and 1,700 g/mol were also used as impact modifiers for epoxy resins at concentrations of 5-20% by weight (293). SEM studies showed microphase separated morphologies with fairly homogeneous distribution of PDMS domains, which resulted in substantial improvement in the impact strength. Polyhydroxyether-PDMS segmented copolymers were also used as tougheners for epoxy resins at concentrations of 5-25% by weight (308). SEM, AFM and SAXS studies clearly showed formation of microphase separated morphologies with PDMS domains around 50 nm (308). The fracture toughness (K_{Ic}) of the network increased from 1.70 to about 3.0 MN/m^{3/2} as a function of PDMS content (308). Epoxy resins were also modified with PEO-PDMS diblock copolymers. Initially miscible system containing 10-50% by weight PEO-PDMS copolymer displayed composition dependent microphase separation upon curing (307). Electron microscopy showed PDMS domains sizes in 10-20 nm, with the average distance between the neighboring microdomains being in 20-50 nm.

6. Surface properties of silicone copolymers and their blends with other polymers

When compared with other polymeric materials, with the exception of highly fluorinated systems, one of the most interesting phenomena displayed by polydimethylsiloxane containing copolymers is their very low surface energies around 20-22 mN/m. Silicone rich surfaces provide interesting properties to the copolymers, which include hydrophobicity, water repellency, lubricity, reduced coefficient of friction, improved biocompatibility and antifouling or foul release properties(3, 8, 86, 315). Surface chemical compositions of silicone containing block and segmented copolymers, based on polystyrene, polycarbonate, polyamide, polyimide, polyurethane and others have been investigated using XPS, AFM, SIMS and water contact angle measurements (270, 316-321). The extent of the surface silicone coverage was shown to be strongly dependent on the copolymer composition, PDMS segment length in the copolymers and method of sample preparation.

It was shown that when silicone copolymers are blended with other polymers in fairly small amounts (0.1-5% by weight), blend surfaces are enriched in PDMS(112, 316, 322-326), while the bulk properties of the base resin are unaffected. Surface enrichment was shown to be dependent on the structure and composition of the base polymer and the silicone copolymer, PDMS segment length, amount of silicone copolymer additive in blend, method of sample preparation and annealing (3, 26, 27, 320). In order to obtain permanent surface modification through blending, the organic segments in the silicone copolymer must provide strong “anchoring sites” with the base polymer through entanglements or intermolecular interactions, such as van der Waals forces or hydrogen-bonding (3, 26, 27, 326).

Polypropylene (PP) and high density polyethylene (HDPE) were surface modified by blending with small amounts (0.1 to 5.0% by weight) of PCL-PDMS-PCL or silicone-urea segmented copolymers(25, 26). Blends were prepared in melt using a twin-screw extruder. The influence of the type and amount of silicone copolymer on the processing behavior, surface and bulk properties of the blends were investigated. Silicone copolymers acted as efficient processing aids and increased the extruder output by up to 200% depending on additive structure and concentration as shown in Figure 22. Surface characterization by XPS and water contact angle measurements clearly showed formation of silicone rich surfaces even with very small amounts of additives, such as 0.1% by weight(26). Tribological properties of silicone modified HDPE and PP surfaces were investigated by pin-on-ring type measurements according to ASTM G 77 method. Silicone modified HDPE and PP surfaces

displayed lower friction coefficients and higher abrasion resistance when compared with virgin polyolefins. Extent of improvements depended on the structure, composition and amount of the silicone additive in the system. Friction coefficients of virgin HDPE and HDPE modified with 5% by weight of silicone copolymer were 0.32 and 0.24 respectively. Abrasion resistance of HDPE, determined by the volume of the worn material, was dramatically reduced from 0.34 mm³ to 0.05 mm³ by incorporation of 5% by weight silicone copolymer(25). Bulk properties, such as T_g, crystallinity and melting behavior or tensile properties were not affected(25).

Figure 22

Surface modification of polyamide-6 (PA6) was investigated by melt blending with silicone-urea copolymers and aminopropyl or glycidoxypropyl terminated PDMS oligomers (27). Effect of the structure, composition, average molecular weight and amount of the silicone additive and the influence of the thermal history on the surface properties were investigated. The surfaces were characterized by static water contact angle measurements and XPS. Higher molecular weight PDMS oligomers resulted in more effective surface modification. The type of the oligomer end groups (amine or epoxy) did not have an effect on the surface properties. Silicone-urea copolymer was reported to be more effective as a surface modifier when compared with silicone oligomers(27). Since PA6 is a semi-crystalline polymer, annealing at 110 °C for 2 hours had a critical effect on the development of silicone rich surfaces as observed by the dramatic increase in the contact angles as shown in Figure 23. No change was observed in the water contact angle values obtained on silicone modified PA6 samples before and after methylene chloride extraction (a good solvent for the silicone copolymer additive). This clearly indicated that the surface modification was permanent due to either the chemical bond formation between PDMS oligomers and PA6 or very strong hydrogen bonding between urea and amide groups.

Figure 23

Surface modification of polycarbonate with a polycarbonate-polydimethylsiloxane copolymer was investigated (327). Effect of the chemical composition, block size and casting solvent on the surface and wear properties of the blend was determined by angle-dependent

XPS, tapping mode AFM and mechanical testing. XPS results showed silicone enrichment on the surface at bulk concentrations of less than 1 weight percent of silicone copolymer, which was a function of silicone block size and casting solvent. The friction coefficient was dependent on surface silicone concentration and the molecular weight of silicone segment in the copolymer (327).

Surface modification of PVC with PCL-PDMS-PCL copolymers has also been investigated (150, 328-330). Blends with different concentrations of silicone copolymers were generally prepared by solution casting. The surface properties of the blends were investigated by FTIR, XPS, SEM and contact angle measurements, which clearly indicated formation of PDMS rich surfaces. *In vitro* experiments indicated improved biocompatibility of blends compared to pure PVC (150).

7. Applications of silicone containing copolymers

Silicone-containing copolymers which combine unique properties of polydimethylsiloxane, such as excellent low temperature flexibility, high gas permeability, low surface energy and biocompatibility with the mechanical strength of organic blocks offer broad range of possible applications. As already discussed, the most important commercial application of silicone-polyether copolymers is as surfactants in polyurethane foam formulations, personal care products and wetting and spreading agents in agriculture (226, 229). Silicone-urea copolymers are also offered commercially as general purpose elastomers for various applications (331). One of the most promising applications of silicone-urethane copolymers as biomaterials is their long-term use as artificial blood vessels, catheters or other implants (8, 87). Another very promising application of crosslinked silicone-urethane polymers is as non-fouling or foul-release marine coatings (86, 146, 332-335). Silicone copolymers are also utilized as surface modifying additives in polymer blends to provide improved processibility, water repellency and reduced friction (25-27). Due to their very high gas permeabilities, combined with the selectivity provided by the organic segments, silicone copolymers are also evaluated as gas separation membranes (202, 212).

8. Conclusions

Silicone polymer chemistry provides almost endless opportunities for the preparation of a wide range of block or segmented silicone-organic copolymers with interesting combinations of bulk and surface properties such as; glass transition temperatures as low as $-120\text{ }^{\circ}\text{C}$ and very

flexible backbone, good thermal and oxidative stability, high gas permeability, excellent dielectric properties, hydrophobic low energy surfaces with excellent water repellency, physiological inertness and biocompatibility. Although polydimethylsiloxane is the most widely used backbone, possibility of attaching a variety of inert or reactive substituents (R) on the tetravalent silicon atom in the siloxane ($-R_2Si-O-$) backbone, together with the ease of reactive oligomer preparation through acid or base catalyzed equilibration reactions also play critical roles that make silicones attractive intermediates in polymer synthesis. Very low solubility parameter of polydimethylsiloxane, around $15.5 \text{ (J/cm}^3\text{)}^{1/2}$ allows the synthesis of block and segmented copolymers with interesting structure-morphology-property behavior.

Another advantage offered by silicone polymer chemistry is the possibility of using different polymerization techniques for copolymer synthesis, which includes step-growth (condensation or addition), chain growth (free radical, ATRP and anionic) and ring-opening polymerization methods. Cyclic silicone monomers, reactive intermediates and functionally terminated oligomers are commercially available from various sources, which is critical for the synthetic polymer chemists. Flexible silicone polymer chemistry offers unique advantages for the preparation of a wide range of tailor-designed copolymers with interesting combinations of properties, which make them useful for applications, such as biomaterials, foul release coatings and gas separation membranes.

9. References

- [1] Noll W. Chemistry and Technology of Silicones. New York: Academic Press, 1978. p. 1-23.
- [2] Voronkov MG, Mileshkevich VP, Yuzhelevskii YA. The Siloxane Bond. New York: Consultants Bureau, 1978. p. 1-54.
- [3] Yilgor I, McGrath JE. Polysiloxane Containing Copolymers: A Survey of Recent Developments. *Adv Polym Sci* 1988;86:1-86.
- [4] Clarson JS, Semlyen JA, editors. Siloxane Polymers. Englewood Cliffs NJ: PTR, Prentice Hall, 1993. 673 pp.

- [5] Wu S. Surface and Interfacial Tensions of Polymers, Oligomers, Plasticizers and Organic Pigments. In: Brandrup J, Immergut EH, editors. Polymer Handbook. New York: John Wiley and Sons, 1989. p. 411-34.
- [6] Krevelen DWV. Properties of Polymers. Amsterdam: Elsevier Science Publishers, 1990. p. 231-235.
- [7] Yilgor E, Yilgor I, Yurtsever E. Hydrogen bonding and polyurethane morphology. I. Quantum mechanical calculations of hydrogen bond energies and vibrational spectroscopy of model compounds. *Polymer* 2002;43:6551-9.
- [8] Lambla NMK, Woodhouse KA, Cooper SL. Polyurethanes in Biomedical Applications. Boca Raton FL: CRC Press, 1998. p. 158-164.
- [9] Morariu S, Brunchi CE, Cazacu M, Bercea M. The Behavior of Poly(dimethylsiloxane-co-diphenylsiloxane)s in Good and Theta Solvents. *J Chem Eng Data* 2011;56:1468-75.
- [10] Yilgor I, Riffle JS, McGrath JE. Reactive Difunctional Siloxane Oligomers: Synthesis and Characterization. In: Harris FW, Spinelli HJ, editors. Reactive Oligomers, ACS Symposium Series, Vol 282. Washington DC: ACS, 1985. p. 161-74.
- [11] Marcienec B, editor. Hydrosilylation: A Comprehensive Review on Recent Advances. Dordrecht: Springer, 2009. p. 1-158.
- [12] Marcienec B. Comprehensive Handbook on Hydrosilylation. New York: Pergamon Press, 1992. p. 1-98.
- [13] McGrath JE, Riffle JS, Banthia AK, Yilgor I, Wilkes GL. An Overview of the Polymerization of Cyclosiloxanes. Vandenberg EJ, Blumstein A, Bowden MJ, Arthur JC, Lal J, Ottenbrite RM, In: Bailey Jr FE, Vandenberg EJ, Blumstein A, Bowden MJ, Arthur JC, Lal J, Ottenbrite RM, editors. Initiation of Polymerization. ACS Symposium Series. Vol 212. Washington DC: ACS, 1983. p. 145-72.
- [14] Jacobsen H, Stockmayer WH. Intramolecular Reaction in Polycondensations. I. The Theory of Linear Systems. *J Chem Phys* 1950;18:1600-6.
- [15] Chakraborty R, Soucek MD. Synthesis of amine and epoxide telechelic siloxanes. *Macromol Chem Phys* 2008;209:604-14.
- [16] Boileau S, Bouteiller L, Kowalewska A. Telechelic polydimethylsiloxanes with terminal acetylenic groups prepared by phase-transfer catalysis. *Polymer* 2003;44:6449-55.

- [17] Cohen C, Damiron D, Ben Dkhil S, Drockenmuller E, Restagno F, Leger L. Synthesis of well-defined poly(dimethylsiloxane) telechelics having nitrobenzoxadiazole fluorescent chain-ends via thiol-ene coupling. *J Polym Sci Part A Polym Chem* 2012;50:1827-33.
- [18] Kricheldorf HR, editor. *Silicon in Polymer Synthesis*. Berlin: Springer-Verlag, 1996. p. 113-222.
- [19] Jones RG, Ando W, Chojnowski J, editors. *Silicone Containing Polymers: The Science and Technology of Their Synthesis and Applications*. Dordrecht: Kluwer Academic Publishers, 2000. 792 pp.
- [20] Ganachaud F, Boileau S, Boury B, editors. *Silicon Based Polymers: Advances in Synthesis and Supramolecular Organization*. Berlin: Springer, 2008. 285 pp.
- [21] Clarson SJ, Fitzgerald JJ, Owen MJ, Smith SD, editors. *Silicones and Silicone-Modified Materials*. ACS Symposium Series, Vol 729. Washington DC: ACS, 2000. 602 pp.
- [22] Clarson SJ, Fitzgerald JJ, Owen MJ, Smith SD, Dyke MEV, editors. *Synthesis and Properties of Silicones and Silicone-Modified Materials*. ACS Symposium Series, Vol 838. Washington DC: ACS, 2003. 401 pp.
- [23] Clarson SJ, Fitzgerald JJ, Owen MJ, Smith SD, Dyke MEV, editors. *Science and Technology of Silicones and Silicone-Modified Materials*. ACS Symposium Series, Vol 964. Washington DC: ACS, 2007. 384 pp.
- [24] Pouget E, Tonnar J, Lucas P, Lacroix-Desmazes P, Ganachaud F, Boutevin B. Well-Architected Poly(dimethylsiloxane)-Containing Copolymers Obtained by Radical Chemistry. *Chem Rev* 2010;110:1233-77.
- [25] Yilgor E, Sinmazcelik T, Yilgor I. Modification of polyolefins with silicone copolymers. II. Thermal, mechanical, and tribological behavior of PP and HDPE blended with silicone copolymers. *J Appl Polym Sci* 2002;84:535-40.
- [26] Yilgor I, Yilgor E, Suzer S. Modification of polyolefins with silicone copolymers. 1. Processing behavior and surface characterization of PP and HDPE blended with silicone copolymers. *J Appl Polym Sci* 2002;83:1625-34.
- [27] Yilgor E, Yilgor I, Suzer S. Surface properties of polyamides modified with reactive polydimethylsiloxane oligomers and copolymers. *Polymer* 2003;44:7271-9.
- [28] Kim Y, Graiver D, Decker GT, Hamilton FJ, Harwood HJ. Block and graft copolymers containing poly(dimethylsiloxane) and poly(4-vinyl-pyridine) segments by free radical polymerization. In: Clarson SJ, Fitzgerald JJ, Owen MJ, Smith D,

- VanDyke ME, editors. Synthesis and Properties of Silicones and Silicone-Modified Materials. ACS Symposium Series, Vol 838. Washington, DC: ACS, 2003. p. 296-305.
- [29] Baysal BM, Uyanik N, Hamurcu EE, Cvetkovska M. Styrene polymerization with a macroinitiator having siloxane units. *J Appl Polym Sci* 1996;60:1369-78.
- [30] Hamurcu EE, Hazer B, Misirli Z, Baysal BM. Preparation and characterization of block and graft copolymers using macroazoinitiators having siloxane units. *J Appl Polym Sci* 1996;62:1415-26.
- [31] Pouget E, Tonnar J, Eloy C, Lacroix-Desmazes P, Boutevin B. Synthesis of poly(styrene)-b-poly(dimethylsiloxane)-b-poly(styrene) triblock copolymers by iodine transfer polymerization in miniemulsion. *Macromolecules* 2006;39:6009-16.
- [32] Guan CM, Luo ZH, Qiu JJ, Tang PP. Novel fluorosilicone triblock copolymers prepared by two-step RAFT polymerization: Synthesis, characterization, and surface properties. *Eur Polym J* 2010;46:1582-93.
- [33] Guan CM, Luo ZH, Tang PP. Poly(dimethylsiloxane-b-styrene) Diblock Copolymers Prepared by Reversible Addition-Fragmentation Chain-Transfer Polymerization: Synthesis and Characterization. *J Appl Polym Sci* 2010;116:3283-90.
- [34] Zhou YN, Guan CM, Luo ZH. Kinetic modeling of two-step RAFT process for the production of novel fluorosilicone triblock copolymers. *Eur Polym J* 2010;46:2164-73.
- [35] Gadda TM, Weber WP. Polydiphenylsiloxane-polydimethylsiloxane-polydiphenylsiloxane triblock copolymers. *J Polym Sci Part A Polym Chem* 2006;44:3629-39.
- [36] Qu LL, Huang GS, Wang Q, Xie ZJ. Effect of diphenylsiloxane unit content on aggregation structure of poly(dimethylsiloxane-co-diphenylsiloxane). *J Polym Sci Part B Polym Phys* 2008;46:72-9.
- [37] Qu LL, Xie ZJ, Huang GS, Tang ZH. Effect of diphenylsiloxane unit content on relaxation behavior of poly(dimethylsiloxane-co-diphenylsiloxane). *J Polym Sci Part B Polym Phys* 2008;46:1652-9.
- [38] Boehm P, Mondeshki M, Frey H. Polysiloxane-Backbone Block Copolymers in a One-Pot Synthesis: A Silicone Platform for Facile Functionalization. *Macromol Rapid Commun* 2012;33:1861-7.
- [39] Gadda TM, Weber WP. Copolymers Based on Dimethylsiloxane and Diphenylsiloxane Units. In: Clarson SJ, Fitzgerald JJ, Owen MJ, Smith D, VanDyke

- ME, editors. *Synthesis and Properties of Silicones and Silicone-Modified Materials*. ACS Symposium Series, Vol 964. Washington DC: ACS, 2007. p. 964:82-99.
- [40] Ninago MD, Satti AJ, Ciolino AE, Valles EM, Villar MA, Vega DA, Sanz A, Nogales A, Rueda DR. Synthesis and Morphology of Model PS-*b*-PDMS Copolymers. *J Polym Sci Part A Polym Chem* 2010;48:3119-27.
- [41] Rosati D, Perrin M, Navard P, Harabagiu V, Pinteala M, Simionescu BC. Synthesis of poly(styrene-dimethylsiloxane) block copolymers: Influence of the phase-separated morphologies on the thermal behaviors. *Macromolecules* 1998;31:4301-8.
- [42] Bellas V, Iatrou H, Hadjichristidis N. Controlled anionic polymerization of hexamethylcyclotrisiloxane. *Macromolecules* 2000;33:6993-7.
- [43] Ma ML, Hill RM, Lowery JL, Fridrikh SV, Rutledge GC. Electrospun poly(styrene-*b*-dimethylsiloxane) block copolymer fibers exhibiting superhydrophobicity. *Langmuir* 2005;21:5549-54.
- [44] Yi LM, Zhan XL, Chen FQ, Du F, Huang LB. Synthesis and characterization of poly(styrene-*b*-methyl(3,3,3-trifluoropropyl)siloxane) diblock copolymers via anionic polymerization. *J Polym Sci Part A Polym Chem* 2005;43:4431-8.
- [45] Moment A, Hammond PT. Block copolymers of polystyrene and side-chain liquid crystalline siloxanes: morphology and thermal properties. *Polymer* 2001;42:6945-59.
- [46] Verploegen E, Zhang T, Murlo N, Hammond PT. Influence of variations in liquid-crystalline content upon the self-assembly behavior of siloxane-based block copolymers. *Soft Matter* 2008;4:1279-87.
- [47] Petr M, Katzman BA, DiNatale W, Hammond PT. Synthesis of a New, Low-T-g Siloxane Thermoplastic Elastomer with a Functionalizable Backbone and Its Use as a Rapid, Room Temperature Photoactuator. *Macromolecules* 2013;46:2823-32.
- [48] Ciolino AE, Gomez LR, Vega DA, Villar MA, Valles EM. Synthesis and physicochemical characterization of a well-defined poly(butadiene 1,3)-*b*-poly(dimethylsiloxane) copolymer. *Polymer* 2008;49:5191-4.
- [49] Ciolino AE, Villar MA, Valles EM, Hadjichristidis N. Synthesis and characterization of model polybutadiene-1,4-*b*-polydimethylsiloxane-*b*-polybutadiene-1,4 copolymers. *J Polym Sci Part A Polym Chem* 2007;45:2726-33.
- [50] Ciolino A, Sakellariou G, Pantazis D, Villar MA, Valles E, Hadjichristidis N. Synthesis and characterization of model diblock copolymers of poly(dimethylsiloxane) with poly(1,4-butadiene) or poly(ethylene). *J Polym Sci Part A Polym Chem* 2006;44:1579-90.

- [51] Yilgor I, Steckle WP, Yilgor E, Freelin RG, Riffle JS. Novel trisiloxane copolymers: Synthesis, characterization and their use as surface modifying additives. *J Polym Sci Part A Polym Chem* 1989;27:3673-90.
- [52] Kiesewetter MK, Shin EJ, Hedrick JL, Waymouth RM. Organocatalysis: Opportunities and Challenges for Polymer Synthesis. *Macromolecules* 2010;43:2093-107.
- [53] Papadopoulos P, Floudas G, Schnell I, Lieberwirth I, Nguyen TQ, Klok HA. Thermodynamic confinement and alpha-helix persistence length in poly(γ -benzyl-L-glutamate)-b-poly(dimethyl siloxane)-b-poly(γ -benzyl-L-glutamate) triblock copolymers. *Biomacromolecules* 2006;7:618-26.
- [54] Ibarboure E, Rodriguez-Hernandez J, Papon E. Thermotropic liquid crystal behavior on PBLG-PDMS-PBLG triblock copolymers. *J Polym Sci Part A Polym Chem* 2006;44:4668-79.
- [55] Kotharangannagari VK, Sanchez-Ferrer A, Ruokolainen J, Mezzenga R. Thermoreversible Gel-Sol Behavior of Rod-Coil-Rod Peptide-Based Triblock Copolymers. *Macromolecules* 2012;45:1982-90.
- [56] Ho CH, Jang GW, Lee YD. Crystallization of poly(L-lactide-dimethyl siloxane-L-lactide) triblock copolymers and its effect on morphology of microphase separation. *Polymer* 2010;51:1639-47.
- [57] Rodwogin MD, Spanjers CS, Leighton C, Hillmyer MA. Polylactide - Poly(dimethylsiloxane) - Polylactide Triblock Copolymers as Multifunctional Materials for Nanolithographic Applications. *ACS Nano* 2010;4:725-32.
- [58] Ragheb RT, Riffle JS. Synthesis and characterization of poly(lactide-b-siloxane-b-lactide) copolymers as magnetite nanoparticle dispersants. *Polymer* 2008;49:5397-404.
- [59] Kricheldorf HR, Rost S, Wutz C, Domb A. Stereocomplexes of A-B-A triblock copolymers based on poly(L-lactide) and poly(D-lactide) A blocks. *Macromolecules* 2005;38:7018-25.
- [60] Kricheldorf HR, Langanke D. ABA triblock copolymers derived from epsilon-caprolactone or L-lactide and a central polysiloxane block. *Macromol Biosci* 2001;1:364-9.
- [61] Hazer B, Baysal BM, Koseoglu AG, Besirli N, Taskin E. Synthesis of Polylactide-b-Poly (Dimethyl Siloxane) Block Copolymers and Their Blends with Pure Polylactide. *J Polym Environ* 2012;20:477-84.

- [62] Ekin A, Webster DC. Synthesis and characterization of novel hydroxyalkyl carbamate and dihydroxyalkyl carbamate terminated poly(dimethylsiloxane) oligomers and their block copolymers with poly(epsilon-caprolactone). *Macromolecules* 2006;39:8659-68.
- [63] Childs MA, Matlock DD, Dorgan JR, Ohno TR. Surface morphology of poly(caprolactone)-b-poly(dimethylsiloxane)-b-poly(caprolactone) copolymers: Effects on protein adsorption. *Biomacromolecules* 2001;2:526-37.
- [64] Theogarajan L, Desai S, Baldo M, Scholz C. Versatile synthesis of self-assembling ABA triblock copolymers with polymethyloxazoline A-blocks and a polysiloxane B-block decorated with supramolecular receptors. *Polym Int* 2008;57:660-7.
- [65] Nakagawa Y, Miller PJ, Matyjaszewski K. Development of novel attachable initiators for atom transfer radical polymerization. *Polymer* 1998;39:5163-70.
- [66] Miller PJ, Matyjaszewski K. Atom transfer radical polymerization of (meth)acrylates from poly(dimethylsiloxane) macroinitiators. *Macromolecules* 1999;32:8760-7.
- [67] Strissel C, Matyjaszewski K, Nuyken O. Block copolymers from organomodified siloxane-containing macroinitiators by atom transfer radical polymerization. *Macromol Chem Phys* 2003;204:1169-77.
- [68] Brown DA, Price GJ. Preparation and thermal properties of block copolymers of PDMS with styrene or methyl methacrylate using ATRP. *Polymer* 2001;42:4767-71.
- [69] Duquesne E, Habimana J, Degee P, Dubois P. Synthesis of silicone-methacrylate copolymers by ATRP using a nickel-based supported catalyst. *Macromol Chem Phys* 2006;207:1116-25.
- [70] Muppalla R, Jewrajka SK. Synthesis, morphology and properties of poly(dimethylsiloxane)/poly(n-butyl acrylate) mixed soft block-based copolymers: A new class of thermoplastic elastomer. *Polymer* 2012;53:1453-64.
- [71] Huan K, Bes L, Haddleton DM, Khoshdel E. Synthesis and properties of polydimethylsiloxane-containing block copolymers via living radical polymerization. *J Polym Sci Part A Polym Chem* 2001;39:1833-42.
- [72] Shinoda H, Matyjaszewski K. Improving the structural control of graft copolymers. *Macromol Rapid Commun* 2001;22:1176-81.
- [73] Sherman MA, Kennedy JP. Novel polyisobutylene/poly(dimethylsiloxane) bicomponent networks. I. Synthesis and characterization. *J Polym Sci Part A Polym Chem* 1998;36:1891-9.

- [74] Mabry JM, Runyon MK, Paulasaari JK, Weber WP. Ru-catalyzed hydrosilylation polymerization - An overview of RuH₂(CO)(PPh₃)₃-catalyzed hydrosilylation copolymerizations of alpha,omega-diketones with alpha,omega-dihydrido-oligo-dimethylsiloxanes and polymerizations of omega-dimethylsilyloxy ketones. In: Clarson SJ, Fitzgerald JJ, Owen MJ, Smith D, VanDyke ME, editors. *Synthesis and Properties of Silicones and Silicone-Modified Materials*. ACS Symposium Series, Vol. 838. Washington DC: ACS, 2003.. p. 50-60.
- [75] Cai GP, Weber WP. Synthesis and chemical modification of poly(divinylsiloxane). *Polymer* 2002;43:1753-9.
- [76] Gadda TM, Weber WP. Synthesis and characterization of alt-copoly(carbosiloxane)s containing oligodiphenylsiloxane segments. *J Polym Sci Part A Polym Chem* 2005;43:2155-63.
- [77] Mukbaniani O, Matsaberidze M, Achelashvili V, Mukbaniani N, Samsonia A. Poly(1,3-disila-1,3-diphenyl-2-oxaindane)-diphenylsiloxane-poly(dimethyl siloxane) block copolymers. *J Appl Polym Sci* 2006;101:3462-7.
- [78] Hetflejs J, Sabata S, Podesva J, Netopilik M, Latalova P, Spevacek J. Syntheses of triblock polybutadiene-polydimethylsiloxane copolymers by coupling reactions. *J Appl Polym Sci* 2006;101:3233-40.
- [79] Chakrabarty S, Nisenholt M, Wynne KJ. PDMS-Fluorous Polyoxetane-PDMS Triblock Hybrid Elastomers: Tough and Transparent with Novel Bulk Morphologies. *Macromolecules* 2012;45:7900-13.
- [80] Lobez JM, Swager TM. Disassembly of Elastomers Poly(olefin sulfone)-Silicones with Switchable Mechanical Properties. *Macromolecules* 2010;43:10422-6.
- [81] Rambarran T, Gonzaga F, Brook MA. Generic, Metal-Free Cross-Linking and Modification of Silicone Elastomers Using Click Ligation. *Macromolecules* 2012;45:2276-85.
- [82] Rambarran T, Gonzaga F, Brook MA. Multifunctional Amphiphilic Siloxane Architectures Using Sequential, Metal-Free Click Ligations. *J Polym Sci Part A Polym Chem* 2013;51:855-64.
- [83] Ciolino AE, Pieroni OI, Vuano BM, Villar MA, Valles EM. Synthesis of polybutadiene-graft-poly(dimethylsiloxane) and polyethylene-graft-poly(dimethylsiloxane) copolymers with hydrosilylation reactions. *J Polym Sci Part A Polym Chem* 2004;42:2920-30.

- [84] Bodkhe RB, Thompson SEM, Yehle C, Cilz N, Daniels J, Stafslie SJ, Callow ME, Callow JA, Webster DC. The effect of formulation variables on fouling-release performance of stratified siloxane-polyurethane coatings. *J Coat Technol Res* 2012;9:235-49.
- [85] Ekin A, Webster DC, Daniels JW, Stafslie SJ, Casse F, Callow JA, Callow ME. Synthesis, formulation, and characterization of siloxane-polyurethane coatings for underwater marine applications using combinatorial high-throughput experimentation. *J Coat Technol Res* 2007;4:435-51.
- [86] Majumdar P, Ekin A, Webster DC. Thermoset Siloxane-Urethane Fouling Release Coatings. In: Provder T, Baghdachi J, editors. *Smart Coatings*. ACS Symposium Series, Vol 957. Washington DC: ACS, 2007. p. 61-75.
- [87] Gunatillake PA, Martin DJ, Meijs GF, McCarthy SJ, Adhikari R. Designing biostable polyurethane elastomers for biomedical implants. *Aust J Chem* 2003;56:545-57.
- [88] Choi T, Masser KA, Moore E, Weksler J, Padsalgikar A, Runt J. Segmented Polyurethanes Derived from Novel Siloxane-Carbonate Soft Segments for Biomedical Applications. *J Polym Sci Part B Polym Phys* 2011;49:865-72.
- [89] Yilgor E, Atilla GE, Ekin A, Kurt P, Yilgor I. Isopropyl alcohol: an unusual, powerful, 'green' solvent for the preparation of silicone-urea copolymers with high urea contents. *Polymer* 2003;44:7787-93.
- [90] Yilgor I, Yilgor E. Thermal stabilities of end groups in hydroxyalkyl terminated polydimethylsiloxane oligomers. *Polym Bull* 1998;40:525-32.
- [91] Yilgor I, Riffle JS, Wilkes GL, McGrath JE. Siloxane-urea segmented copolymers 1. *Polym Bull* 1982;8:535-42.
- [92] Tyagi D, Wilkes GL, Yilgor I, McGrath JE. Siloxane-urea segmented copolymers 2. *Polym Bull* 1982;8:543-50.
- [93] Yilgor I, Shaaban AK, Steckle WP, Tyagi D, Wilkes GL, McGrath JE. Segmented organosiloxane copolymers 1. *Polymer* 1984;25:1800-6.
- [94] Tyagi D, Yilgor I, McGrath JE, Wilkes GL. Segmented siloxane-urea copolymers 2. *Polymer* 1984;25:1807-16.
- [95] Sheth JP, Yilgor E, Erenturk B, Ozhalici H, Yilgor I, Wilkes GL. Structure-property behavior of poly(dimethylsiloxane) based segmented polyurea copolymers modified with poly(propylene oxide). *Polymer* 2005;46:8185-93.

- [96] Yilgor I, Eynur T, Yilgor E, Wilkes GL. Contribution of soft segment entanglement on the tensile properties of silicone-urea copolymers with low hard segment contents. *Polymer* 2009;50:4432-7.
- [97] Yilgor I, Eynur T, Bilgin S, Yilgor E, Wilkes GL. Influence of soft segment molecular weight on the mechanical hysteresis and set behavior of silicone-urea copolymers with low hard segment contents. *Polymer* 2011;52:266-74.
- [98] Yildirim E, Yurtsever M, Yurtsever E, Yilgor I, Yilgor E. Multiscale Modeling of the Morphology and Properties of Segmented Silicone-Urea Copolymers. *J Inorg Organomet Polym Mater* 2012;22:604-16.
- [99] Hernandez R, Weksler J, Padsalgikar A, Runt J. Microstructural organization of three-phase polydimethylsiloxane-based segmented polyurethanes. *Macromolecules* 2007;40:5441-9.
- [100] Choi T, Weksler J, Padsalgikar A, Hernandez R, Runt J. Polydimethylsiloxane-Based Polyurethanes: Phase-Separated Morphology and In Vitro Oxidative Biostability. *Aust J Chem* 2009;62:794-8.
- [101] Choi T, Weksler J, Padsalgikar A, Runt J. Influence of soft segment composition on phase-separated microstructure of polydimethylsiloxane-based segmented polyurethane copolymers. *Polymer* 2009;50:2320-7.
- [102] Choi T, Weksler J, Padsalgikar A, Runt J. Microstructural organization of polydimethylsiloxane soft segment polyurethanes derived from a single macrodiol. *Polymer* 2010;51:4375-82.
- [103] Adhikari R, Gunatillake PA, McCarthy SJ, Meijs GF. Effect of chain extender structure on the properties and morphology of polyurethanes based on H12MDI and mixed macrodiols (PDMS-PHMO). *J Appl Polym Sci* 1999;74:2979-89.
- [104] Adhikari R, Gunatillake PA, McCarthy SJ, Meijs CF. Mixed macrodiol-based siloxane polyurethanes: Effect of the comacrodiol structure on properties and morphology. *J Appl Polym Sci* 2000;78:1071-82.
- [105] Adhikari R, Gunatillake PA, McCarthy SJ, Meijs GF. Low-modulus siloxane-based polyurethanes. I. Effect of the chain extender 1,3-bis(4-hydroxybutyl)1,1,3,3-tetramethyldisiloxane (BHTD) on properties and morphology. *J Appl Polym Sci* 2002;83:736-46.
- [106] Adhikari R, Gunatillake PA, Bown M. Effect of polydimethylsiloxane macrodiol molecular weight on properties and morphology of polyurethane and polyurethaneurea. *J Appl Polym Sci* 2003;90:1565-73.

- [107] Adhikari R, Gunatillake PA, McCarthy SJ, Bown M, Meijs GF. Low-modulus siloxane-polyurethanes. Part II. Effect of chain extender structure on properties and morphology. *J Appl Polym Sci* 2003;87:1092-100.
- [108] Majumdar P, Webster DC. Preparation of siloxane - Urethane coatings having spontaneously formed stable biphasic microtopographical surfaces. *Macromolecules* 2005;38:5857-9.
- [109] Majumdar P, Webster DC. Influence of solvent composition and degree of reaction on the formation of surface microtopography in a thermoset siloxane-urethane system. *Polymer* 2006;47:4172-81.
- [110] Ekin A, Webster DC. Combinatorial and high-throughput screening of the effect of siloxane composition on the surface properties of crosslinked siloxane-polyurethane coatings. *J Comb Chem* 2007;9:178-88.
- [111] Majumdar P, Stafslie S, Daniels J, Webster DC. High throughput combinatorial characterization of thermosetting siloxane-urethane coatings having spontaneously formed microtopographical surfaces. *J Coat Technol Res* 2007;4:131-8.
- [112] Majumdar P, Webster DC. Surface microtopography in siloxane-polyurethane thermosets: The influence of siloxane and extent of reaction. *Polymer* 2007;48:7499-509.
- [113] Pieper RJ, Ekin A, Webster DC, Casse F, Callow JA, Callow ME. Combinatorial approach to study the effect of acrylic polyol composition on the properties of crosslinked siloxane-polyurethane fouling-release coatings. *J Coat Technol Res* 2007;4:453-61.
- [114] Sommer S, Ekin A, Webster DC, Stafslie SJ, Daniels J, VanderWal LJ, Thompson SEM, Callow ME, Callow JA. A preliminary study on the properties and fouling-release performance of siloxane-polyurethane coatings prepared from poly(dimethylsiloxane) (PDMS) macromers. *Biofouling* 2010;26:961-72.
- [115] Sommer SA, Byrom JR, Fischer HD, Bodkhe RB, Stafslie SJ, Daniels J, Yehle C, Webster DC. Effects of pigmentation on siloxane-polyurethane coatings and their performance as fouling-release marine coatings. *J Coat Technol Res* 2011;8:661-70.
- [116] Bodkhe RB, Stafslie SJ, Cilz N, Daniels J, Thompson SEM, Callow ME, Callow JA, Webster DC. Polyurethanes with amphiphilic surfaces made using telechelic functional PDMS having orthogonal acid functional groups. *Prog Org Coat* 2012;75:38-48.

- [117] Sheth JP, Aneja A, Wilkes GL, Yilgor E, Atilla GE, Yilgor I, Beyer FL. Influence of system variables on the morphological and dynamic mechanical behavior of polydimethylsiloxane based segmented polyurethane and polyurea copolymers: a comparative perspective. *Polymer* 2004;45:6919-32.
- [118] Fang J, Kelarakis A, Wang DY, Giannelis EP, Finlay JA, Callow ME, Callow JA. Fouling release nanostructured coatings based on PDMS-polyurea segmented copolymers. *Polymer* 2010;51:2636-42.
- [119] Riess G, Schmidt HW. Novel urea-siloxane polymers as gelling agents for silicone fluids: Influence of the hard segment. *Monatsh Chem* 2006;137:935-41.
- [120] Kwiatkowski R, Wlochowicz A, Kozakiewicz J, Przybylski J. WAXS and SAXS study of (m)TMXDI-PDMS siloxane-urethaneureas. *Fibres Text East Eur* 2003;11:107-14.
- [121] Wang TM, Zhao G, Wang QH. Influence of the hard segment content on the mechanical and tribological properties of the polyurethane modified by hydroxyl-terminated polydimethylsiloxane under different lubricated conditions. *Polym Compos* 2012;33:812-8.
- [122] Pandey S, Rath SK, Samui AB. Structure-Thermomechanical Property Correlations of Highly Branched Siloxane-Urethane Networks. *Ind Eng Chem Res* 2012;51:3531-40.
- [123] Ma CCM, Kuan HC, Hsieh JC, Chiang CL. Effects of chain extender and hard/soft segment content on the surface and electrical properties of PDMS based polyurea-urethane. *J Mater Sci* 2003;38:3933-44.
- [124] Cho G, Natansohn A, Ho T, Wynne KJ. Phase structure of poly(dimethylsiloxane-urea-urethane)segmented copolymers as observed by solid-state nuclear magnetic resonance spectra. *Macromolecules* 1996;29:2563-9.
- [125] Ho T, Wynne KJ. A method to assess the average molecular weight for surface soft segments in poly (dimethylsiloxane)-ureas. *Macromolecules* 1996;29:3991-5.
- [126] Pike JK, Ho T, Wynne KJ. Water-induced surface rearrangements of poly(dimethylsiloxane-urea-urethane) segmented block copolymers. *Chem Mater* 1996;8:856-60.
- [127] Su T, Wang GY, Hu CP. Preparation and properties of well-defined waterborne polyurethaneurea with fluorinated siloxane units in hard or soft segments. *J Polym Sci Part A Polym Chem* 2007;45:5005-16.

- [128] Aharoni SM. Correlation between chain parameters and the plateau modulus of polymers. *Macromolecules* 1986;19:426-34.
- [129] Yilgor E, Eynur T, Kosak C, Bilgin S, Yilgor I, Malay O, Menciloglu Y, Wilkes GL. Fumed silica filled poly(dimethylsiloxane-urea) segmented copolymers: Preparation and properties. *Polymer* 2011;52:4189-98.
- [130] Yilgor E, Nugay II, Bakan M, Yilgor I. Antibacterial Silicone-Urea/Organoclay Nanocomposites. *Silicon* 2009;1:183-90.
- [131] Kinning DJ. Bulk, surface, and interfacial characterization of silicone - Polyurea segmented copolymers. *J Adhes* 2001;75:1-26.
- [132] Wang LF, Ji Q, Glass TE, Ward TC, McGrath JE, Muggli M, Burns G, Sorathia U. Synthesis and characterization of organosiloxane modified segmented polyether polyurethanes. *Polymer* 2000;41:5083-93.
- [133] Fei GQ, Shen YD, Wang HH, Shen Y. Effects of polydimethylsiloxane concentration on properties of polyurethane/polydimethylsiloxane hybrid dispersions. *J Appl Polym Sci* 2006;102:5538-44.
- [134] Chen RS, Chang CJ, Chang YH. Study on siloxane-modified polyurethane dispersions from various polydimethylsiloxanes. *J Polym Sci Part A Polym Chem* 2005;43:3482-90.
- [135] Rochery M, Vroman I, Lam TM. Incorporation of poly(dimethylsiloxane) into poly(tetramethylene oxide) based polyurethanes: The effect of synthesis conditions on polymer properties. *J Macromol Sci Pure Appl Chem Part A* 2003;40:321-33.
- [136] Zhang YH, Shang JW, Lv FZ, Chu PK. Synthesis and characterization of novel organosilicon-modified polyurethane. *J Appl Polym Sci* 2012;125:1486-92.
- [137] Kuo PL, Liang WJ, Lin CL. Solid polymer electrolytes, 2 - Preparation and ionic conductivity of solid polymer electrolytes based on segmented polysiloxane-modified polyurethane. *Macromol Chem Phys* 2002;203:230-7.
- [138] Yilgor E, Burgaz E, Yurtsever E, Yilgor I. Comparison of hydrogen bonding in polydimethylsiloxane and polyether based urethane and urea copolymers. *Polymer* 2000;41:849-57.
- [139] Hernandez R, Weksler J, Padsalgikar A, Runt J. Microstructural organization of polydimethylsiloxane based segmented polyurethane copolymers. *Polym Prepr Am Chem Soc Div Polym Chem* 2007;48(1):835.

- [140] Pongkitwitoon S, Hernandez R, Weksler J, Padsalgikar A, Choi T, Runt J. Temperature dependent microphase mixing of model polyurethanes with different intersegment compatibilities. *Polymer* 2009;50:6305-11.
- [141] Hernandez R, Weksler J, Padsalgikar A, Choi T, Angelo E, Lin JS, Xu LC, Siedlecki CA, Runt J. A Comparison of Phase Organization of Model Segmented Polyurethanes with Different Intersegment Compatibilities. *Macromolecules* 2008;41:9767-76.
- [142] Pergal MV, Antic VV, Govedarica MN, Goevac D, Ostojic S, Djonlagic J. Synthesis and Characterization of Novel Urethane-Siloxane Copolymers with a High Content of PCL-PDMS-PCL Segments. *J Appl Polym Sci* 2011;122:2715-30.
- [143] Ho CH, Wang CH, Lin CI, Lee YD. Synthesis and characterization of (AB)(n)-type poly(L-lactide)-poly(dimethyl siloxane) multiblock copolymer and the effect of its macrodiol composition on urethane formation. *Eur Polym J* 2009;45:2455-66.
- [144] Pergal MV, Antic VV, Tovilovic G, Nestorov J, Vasiljevic-Radovic D, Djonlagic J. In Vitro Biocompatibility Evaluation of Novel Urethane-Siloxane Co-Polymers Based on Poly(epsilon-Caprolactone)-block-Poly(Dimethylsiloxane)-block-Poly(epsilon-Caprolactone). *J Biomater Sci Polym Ed* 2012;23:1629-57.
- [145] Ioan S, Grigorescu G, Stanciu A. Effect of segmented poly(ester-siloxane)urethanes compositional parameters on differential scanning calorimetry and dynamic-mechanical measurements. *Eur Polym J* 2002;38:2295-303.
- [146] Stein J, Truby K, Wood CD, Takemori M, Vallance M, Swain G, Kavanagh C, Kovach B, Schultz M, Wiebe D, Holm E, Montemarano J, Wendt D, Smith C, Meyer A. Structure-property relationships of silicone biofouling-release coatings: Effect of silicone network architecture on pseudobarnacle attachment strengths. *Biofouling* 2003;19:87-94.
- [147] Jewrajka SK, Yilgor E, Yilgor I, Kennedy JP. Polyisobutylene-Based Segmented Polyureas. I. Synthesis of Hydrolytically and Oxidatively Stable Polyureas. *J Polym Sci Part A Polym Chem* 2009;47:38-48.
- [148] Farrar DJ, Litwak P, Lawson JH, Ward RS, White KA, Robinson AJ, Rodvien R, Hill JD. In vivo evaluations of a new thromboresistant polyurethane for artificial heart-blood pumps. *J Thoracic Cardiovasc Surg* 1988;95:191-200.
- [149] White KA, Ward RS, Gill RS, Lim F, Coviello SK. Surface modification of segmented polyurethaneureas via oligomeric end groups incorporated during

- synthesis. In: Ratner BD, Castner DG, editors. *Surface Modification of Polymeric Biomaterials*. New York: Plenum Press, 1997. p. 27-33.
- [150] Tang LP, Sheu MS, Chu TM, Huang YH. Anti-inflammatory properties of triblock siloxane copolymer-blended materials. *Biomaterials* 1999;20:1365-70.
- [151] Simmons A, Hyvarinen J, Odell RA, Martin DJ, Gunatillake PA, Noble KR, Poole-Warren LA. Long-term in vivo biostability of poly(dimethylsiloxane)/poly(hexamethylene oxide) mixed macrodiol-based polyurethane elastomers. *Biomaterials* 2004;25:4887-900.
- [152] Martin DJ, Warren LAP, Gunatillake PA, McCarthy SJ, Meijs GF, Schindhelm K. New methods for the assessment of in vitro and in vivo stress cracking in biomedical polyurethanes. *Biomaterials* 2001;22:973-8.
- [153] Martin DJ, Warren LAP, Gunatillake PA, McCarthy SJ, Meijs GF, Schindhelm K. Polydimethylsiloxane/polyether-mixed macrodiol-based polyurethane elastomers: biostability. *Biomaterials* 2000;21:1021-9.
- [154] Hernandez R, Weksler J, Padsalgikar A, Runt J. In vitro oxidation of high polydimethylsiloxane content biomedical polyurethanes: Correlation with the microstructure. *J Biomed Mater Res Part A* 2008;87:546-56.
- [155] Ward R, Anderson J, McVenes R, Stokes K. In vivo biostability of shore 55D polyether polyurethanes with and without fluoropolymer surface modifying endgroups. *J Biomed Mater Res Part A* 2006;79:836-45.
- [156] Ward R, Anderson J, McVenes R, Stokes K. In vivo biostability of polysiloxane polyether polyurethanes: Resistance to biologic oxidation and stress cracking. *J Biomed Mater Res Part A* 2006;77:580-9.
- [157] Ward R, Anderson J, McVenes R, Stokes K. In vivo biostability of polyether polyurethanes with fluoropolymer and polyethylene oxide surface modifying endgroups; resistance to metal ion oxidation. *J Biomed Mater Res Part A* 2007;80:34-44.
- [158] Wiggins MJ, MacEwan M, Anderson JM, Hiltner A. Effect of soft-segment chemistry on polyurethane biostability during in vitro fatigue loading. *J Biomed Mater Res Part A* 2004;68:668-83.
- [159] Chaffin KA, Buckalew AJ, Schley JL, Chen XJ, Jolly M, Alkatout JA, Miller JP, Untereker DF, Milmyer MA, Bates FS. Influence of Water on the Structure and Properties of PDMS-Containing Multiblock Polyurethanes. *Macromolecules* 2012;45:9110-20.

- [160] Guo L, Zhang ZJ, Zhu YP, Li JP, Xie ZM. Synthesis of polysiloxane-polyester copolymer by lipase-catalyzed polycondensation. *J Appl Polym Sci* 2008;108:1901-7.
- [161] Frampton MB, Subczynska I, Zelisko PM. Biocatalytic Synthesis of Silicone Polyesters. *Biomacromolecules* 2010;11:1818-25.
- [162] Frampton MB, Seguin JP, Marquardt D, Harroun TA, Zelisko PM. Synthesis of polyesters containing disiloxane subunits: Structural characterization, kinetics, and an examination of the thermal tolerance of Novozym-435. *J Molec Catal B* 2013;85-86:149-55.
- [163] Poojari Y, Clarson SJ. Lipase-Catalyzed Synthesis and Properties of Silicone Aromatic Polyesters and Silicone Aromatic Polyamides. *Macromolecules* 2010;43:4616-22.
- [164] Poojari Y, Palsule AS, Cai M, Clarson SJ, Gross RA. Synthesis of organosiloxane copolymers using enzymatic polyesterification. *Eur Polym J* 2008;44:4139-45.
- [165] Palsule AS, Poojari Y. Enzymatic synthesis of silicone fluorinated aliphatic polyesteramides. *Polymer* 2010;51:6161-7.
- [166] Sharma B, Azim A, Azim H, Gross RA, Zini E, Focarete ML, Scandola M. Enzymatic synthesis and solid-state properties of aliphatic polyesteramides with polydimethylsiloxane blocks. *Macromolecules* 2007;40:7919-27.
- [167] Abdullah ABE, Mallon PE. Microscopic Surface and Bulk Morphology of Semicrystalline Poly(dimethylsiloxane)-Polyester Copolymers. *J Appl Polym Sci* 2010;115:1518-33.
- [168] Antic VV, Balaban MR, Djonlagic J. Synthesis and characterization of thermoplastic poly(ester-siloxane)s. *Polym Int* 2001;50:1201-8.
- [169] Antic VV, Govedarica MN, Djonlagic J. The effect of segment length on some properties of thermoplastic poly(ester-siloxane)s. *Polym Int* 2003;52:1188-97.
- [170] Antic VV, Govedarical MN, Djonlagic J. The effect of the mass ratio of hard and soft segments on some properties of thermoplastic poly(ester-siloxane)s. *Polym Int* 2004;53:1786-94.
- [171] Antic VV, Pergal MV, Govedarica MN, Antic MP, Djonlagic J. Copolymers based on poly(butylene terephthalate) and polycaprolactone-block-polydimethylsiloxane-block-polycaprolactone. *Polym Int* 2010;59:796-807.
- [172] Vuckovic MV, Antic VV, Dojcinovic BP, Govedarica MN, Djonlagic J. Synthesis and characterization of poly(ester ether siloane)s. *Polym Int* 2006;55:1304-14.

- [173] Vuckovic MV, Antic VV, Govedarica MN, Djonlagic J. Synthesis and Characterization of Copolymers Based on Poly(butylene terephthalate) and Ethylene Oxide-Poly(dimethylsiloxane)-Ethylene Oxide. *J Appl Polym Sci* 2010;115:3205-16.
- [174] Antic VV, Vuckovic MV, Dojcinovic BP, Antic MP, Barac MB, Govedarica MN. About the mode of incorporation of silanol-terminated polysiloxanes into butylene terephthalate-b-dimethylsiloxane copolymers. *React Funct Polym* 2008;68:851-60.
- [175] Ardal D, Yilgor E, Yilgor I. Catalyst effect on the transesterification reactions between polycarbonate and polycaprolactone-B-polydimethylsiloxane triblock copolymers. *Polym Bull* 1999;43:207-14.
- [176] Racles C, Cozan V, Cazacu M. New arylidene-siloxane polyesters. *High Perform Polym* 2003;15:231-42.
- [177] Racles C, Airinei A, Cozan V, Cazacu M, Sajo IE. New arylidene-siloxane polyethers: Liquid-crystalline and photosensitive properties. *J Appl Polym Sci* 2003;90:3093-9.
- [178] Jana RN, Cho JW. Silicone-Based Cholesteric Liquid Crystalline Polymers: Effect of Crosslinking Agent on Phase Transition Behavior. *J Appl Polym Sci* 2009;114:3566-73.
- [179] Yilgor E, Yilgor I. Hydrogen bonding: a critical parameter in designing silicone copolymers. *Polymer* 2001;42:7953-9.
- [180] Hentschel T, Munstedt H. Kinetics of the molar mass decrease in a polyurethane melt: a rheological study. *Polymer* 2001;42:3195-203.
- [181] Senshu K, Furuzono T, Koshizaki N, Yamashita S, Matsumoto T, Kishida A, Akashi M. Novel functional polymers: Poly(dimethylsiloxane)-polyamide multiblock copolymer. 8. surface studies of aramid-silicone resin by means of XPS, static SIMS, and TEM. *Macromolecules* 1997;30:4421-8.
- [182] Furuzono T, Seki K, Kishida A, Ohshige TA, Waki K, Maruyama I, Akashi M. Novel functional polymers: Poly(dimethylsiloxane)polyamide multiblock copolymer. 3. Synthesis and surface properties of disiloxane-aromatic polyamide multiblock copolymer. *J Appl Polym Sci* 1996;59:1059-65.
- [183] Matsumoto T, Koinuma Y, Waki K, Kishida A, Furuzono T, Maruyama I, Akashi M. Novel functional polymers: Poly(dimethylsiloxane)polyamide multiblock copolymer. 4. Gas permeability and thermomechanical properties of aramid-silicone resins. *J Appl Polym Sci* 1996;59:1067-71.

- [184] Furuzono T, Yashima E, Kishida A, Maruyama I, Matsumoto T, Akashi M. A novel biomaterials: Poly(dimethylsiloxane)-polyamide multiblock copolymer 1. *J Biomater Sci Polym Ed* 1993;5:89-98.
- [185] Kishida A, Furuzono T, Ohshige T, Maruyama I, Matsumoto T, Itoh H, Murakami M, Akashi M. Study of the surface properties of ultrathin films of poly(dimethylsiloxane)-polyamide multiblock copolymers. *Angew Makromol Chem* 1994;220:89-97.
- [186] Furuzono T, Kishida A, Matsumoto T, Maruyama I, Nakamura T, Akashi M. Adsorption of biomolecules onto multiblock copolymer consisting of aromatic polyamide and poly(dimethylsiloxane). In: Ogata N, Kim SW, Feijen J, Okano T, editors. *Advanced Biomaterials in Biomedical Engineering and Drug Delivery Systems*. Tokyo: Springer, 1996. p. 211-2.
- [187] Furuzono T, Kishida A, Yanagi M, Matsumoto T, Kanda T, Nakamura T, Aiko T, Murayama I, Akashi M. Novel functional polymers: Poly(dimethylsiloxane)polyamide multiblock copolymer. 5. The interaction between biomolecules and the surface of aramid-silicone resins. *J Biomater Sci Polym Ed* 1996;7:871-80.
- [188] Furuzono T, Senshu K, Kishida A, Matsumoto T, Akashi M. Novel functional polymers: Poly(dimethylsiloxane)-polyamide multiblock copolymer. 6. A transmission electron microscopic study on microphase-separated structure in aramid-silicone resin. *Polym J* 1997;29:201-3.
- [189] Matsumoto T, Uchida T, Kishida A, Furuzono T, Maruyama I, Akashi M. Novel functional polymers: Poly(dimethylsiloxane)-polyamide multiblock copolymer. 7. Oxygen permeability of aramid-silicone membranes in a gas-membrane-liquid system. *J Appl Polym Sci* 1997;64:1153-9.
- [190] Kishida A, Kanda T, Furuzono T, Maruyama I, Akashi M. Novel functional polymers: Poly(dimethylsiloxane)polyamide multiblock copolymer. IX. Surface properties blend film of aramid-silicone resins with aramid. *J Appl Polym Sci* 2000;78:2198-205.
- [191] Khan MSU, Akhter Z, Naz T, Bhatti AS, Siddiqi HM, Siddiq M, Khan A. Study on the preparation and properties of novel block copolymeric materials based on structurally modified organometallic as well as organic polyamides and polydimethylsiloxane. *Polym Int* 2013;62:319-34.

- [192] Gill R, Mazhar M, Siddiq M. Structural characterization and thermal behaviour of block copolymers of polydimethylsiloxane and polyamide having trichlorogermyl pendant groups. *Polym Int* 2010;59:1598-605.
- [193] Kretschmer A, Drake R, Neidhoefer M, Wilhelm M. Quantification of composition and domain sizes of industrial poly (phthalamide)/Poly(dimethylsiloxane) block copolymers using different H-1 solid state NMR methods. *Solid State Nucl Magn Reson* 2002;22:204-17.
- [194] Leir CM, Galkiewicz RK, Kantner SS, Mazurek M. Telechelic Siloxanes with Hydrogen-Bonded Polymerizable End Groups. I. Liquid Rubbers and Elastomers. *J Appl Polym Sci* 2010;117:756-66.
- [195] Mazurek M, Leir CM, Galkiewicz RK. Telechelic Siloxanes with Hydrogen-Bonded Polymerizable End-Groups. II. IR Studies of End-Groups Interactions-Model Amides and Ureas. *J Appl Polym Sci* 2010;117:982-95.
- [196] Henkensmeier D, Abele BC, Candussio A, Thiem J. Synthesis, characterisation and degradability of polyamides derived from aldaric acids and chain end functionalised polydimethylsiloxanes. *Polymer* 2004;45:7053-9.
- [197] Kang BM, Park YW. A Study on Phase Separation of PA-PDMS Composites Dependent on Molecular Weight. *Polym Plast Technol Eng* 2010;49:223-7.
- [198] Ghosh A, Banerjee S, Komber H, Schneider K, Haussler L, Voit B. Synthesis and characterization of fluorinated poly(imide siloxane) block copolymers. *Eur Polym J* 2009;45:1561-9.
- [199] Ghosh A, Banerjee S, Haussler L, Voit B. New Fluorinated Poly(imide siloxane) Random and Block Copolymers with Variation of Siloxane Loading. *J Macromol Sci Part A* 2010;47:671-80.
- [200] Ghosh A, Banerjee S, Voit B. Synthesis and Characterization of Fluorinated Poly (imide siloxane) Copolymers Containing Anthracene Moieties in the Main Chain. *High Perform Polym* 2010;22:28-41.
- [201] Ghosh A, Banerjee S, Voit B. New Silicone Grafted Copoly(ether imide) from 4,4'-(hexafluoro-isopropylidene)diphthalic Anhydride. *J Macromol Sci Part A* 2010;47:1069-74.
- [202] Ghosh A, Sen SK, Dasgupta B, Banerjee S, Voit B. Synthesis, characterization and gas transport properties of new poly(imide siloxane) copolymers from 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride). *J Membr Sci* 2010;364:211-8.

- [203] Ghosh A, Banerjee S, Komber H, Haussler L, Schneider K, Voit B. New Semifluorinated Siloxane-Grafted Copolyimides: Synthesis and Comparison with Their Linear Analogs. *Macromol Mater Eng* 2011;296:391-400.
- [204] Ghosh A, Banerjee S, Wang DY, Komber H, Voit B. Synthesis, characterization, and properties of new siloxane grafted copolyimides. *J Appl Polym Sci* 2012;123:2959-67.
- [205] Pei XL, Chen GF, Fang XZ. Preparation and characterization of poly(imide siloxane) block copolymers based on diphenylthioether dianhydride isomer mixtures. *High Perform Polym* 2011;23:625-32.
- [206] Pei X, Chen G, Fang X. Synthesis and Properties of Poly(imide siloxane) Block Copolymers with Different Block Lengths. *J Appl Polym Sci* 2013;129:3718-27.
- [207] Ghosh A, Banerjee S. Structure-property co-relationship of fluorinated poly(imide-siloxane)s. *Polym Adv Technol* 2008;19:1486-94.
- [208] Ghosh A, Banerjee S. Thermal, mechanical, and dielectric properties of novel fluorinated copoly(imide siloxane)s. *J Appl Polym Sci* 2008;109:2329-40.
- [209] Ghosh A, Banerjee S. Synthesis, characterization, and comparison of properties of novel fluorinated poly(imide siloxane) copolymers. *J Appl Polym Sci* 2008;107:1831-41.
- [210] Pareek K, Ghosh A, Sen SK, Banerjee S. Synthesis, Characterization and Properties of New Fluorinated Poly(imide siloxane) Co-polymers from 4,4'-(Hexafluoroisopropylidene)diphthalic Anhydride. *Des Monomers Polym* 2010;13:221-36.
- [211] Jiang X, Gu JA, Shen Y, Wang SG, Tian XZ. Formation of Honeycomb-Patterned Microporous Films Based on a Fluorinated Poly(siloxane imide) Segmented Copolymer. *J Appl Polym Sci* 2011;119:3329-37.
- [212] Jiang X, Gu JA, Shen Y, Wang SG, Tian XZ. New fluorinated siloxane-imide block copolymer membranes for application in organophilic pervaporation. *Desalination* 2011;265:74-80.
- [213] Ku CK, Ho CH, Chen TS, Lee YD. Synthesis and characterization of pyridine-containing poly(imide-siloxane)s and their adhesion to copper foil. *J Appl Polym Sci* 2007;104:2561-8.
- [214] Shoji Y, Higashihara T, Watanabe J, Ueda M. Synthesis of Thermotropic Liquid Crystalline Polyimides with Siloxane Linkages. *Chem Lett* 2009;38:716-7.

- [215] Shoji Y, Ishige R, Higashihara T, Kawauchi S, Watanabe J, Ueda M. Synthesis and Liquid Crystalline Behavior of Laterally Substituted Polyimides with Siloxane Linkages. *Macromolecules* 2010;43:8950-6.
- [216] Shoji Y, Ishige R, Higashihara T, Watanabe J, Ueda M. Thermotropic Liquid Crystalline Polyimides with Siloxane Linkages: Synthesis, Characterization, and Liquid Crystalline Behavior. *Macromolecules* 2010;43:805-10.
- [217] Shoji Y, Ishige R, Higashihara T, Watanabe J, Ueda M. Thermotropic Liquid Crystalline Polyimides with Siloxane Linkages: Synthesis, Characterization and Liquid Crystalline Behavior (errata: vol 43, pg 805, 2010). *Macromolecules* 2010;43:3123-3123.
- [218] Shoji Y, Ishige R, Higashihara T, Morikawa J, Hashimoto T, Takahara A, Watanabe J, Ueda M. Cross-Linked Liquid Crystalline Polyimides with Siloxane Units: Their Morphology and Thermal Diffusivity. *Macromolecules* 2013;46:747-55.
- [219] Hamciuc C, Hamciuc E, Cazacu M, Okrasa L. Poly(ether-imide) and poly(ether-imide)-polydimethylsiloxane containing isopropylidene groups. *Polym Bull* 2008;59:825-32.
- [220] Hamciuc C, Hamciuc E, Serbezeanu D, Vlad-Bubulac T, Cazacu M. Phosphorus-containing poly(ester-imide)-polydimethylsiloxane copolymers. *Polym Int* 2011;60:312-21.
- [221] Hamciuc E, Hamciuc C, Cazacu M, Ignat M, Zarnescu G. Polyimide-polydimethylsiloxane copolymers containing nitrile groups. *Eur Polym J* 2009;45:182-90.
- [222] Hamciuc E, Hamciuc C, Cazacu M, Lisa G, Okrasa L. Polyimide-polydimethylsiloxane copolymers. *J Macromol Sci Part A* 2007;44:1069-78.
- [223] Harneluc E, Hamciuc C, Cazacu M. Poly(1,3,4-oxadiazole-ether-imide)s and their polydimethylsiloxane-containing copolymers. *Eur Polym J* 2007;43:4739-49.
- [224] Cazacu M, Vlad A, Airinei A, Nicolescu A, Stoica I. New imides based on perylene and siloxane derivatives. *Dyes Pigm* 2011;90:106-13.
- [225] Simionescu M, Marcu M, Cazacu M. New poly(amide-imide) siloxane copolymers by polycondensation. *Eur Polym J* 2003;39:777-84.
- [226] Hill RM. Silicone (siloxane) surfactants. In: Meyers RA, editor. *Encyclopedia of Physical Science and Technology* Amsterdam: Elsevier, 2003. p. 793-804.
- [227] Hill RM. Silicone surfactants - new developments. *Curr Opin Colloid Interface Sci* 2002;7:255-61.

- [228] Stoebe T, Lin ZX, Hill RM, Ward MD, Davis HT. Surfactant-enhanced spreading. *Langmuir* 1996;12:337-44.
- [229] Hill RM, editor. *Silicone Surfactants*. New York: Marcel Dekker, 1999. 360 pp.
- [230] Hamciuc V, Pricop L, Pricop DS, Marcu M. Polydimethylsiloxane-polyalkyleneoxide block copolymers. *J Macromol Sci Pure Appl Chem Part A* 2001;38:79-89.
- [231] Pricop L, Hamciuc V, Marcu M, Ioanid A, Alazaroaie S. Graft copolymers polydimethylsiloxane-polyethyleneoxide. *High Perform Polym* 2005;17:303-12.
- [232] Bathista A, Deazevedo ER, Bloise AC, Dahmouche K, Judeinstein P, Bonagamba TJ. Effects of lithium doping on the polymer chain dynamics in siloxane/poly(ethylene oxide) ormolyte nanocomposites: A C-13 and Li-7 exchange solid-state NMR study. *Chem Mater* 2007;19:1780-9.
- [233] de Souza PH, Bianchi RF, Dahmouche K, Judeinstein P, Faria RM, Bonagamba TJ. Solid-state NMR, ionic conductivity, and thermal studies of lithium-doped siloxane-poly(propylene glycol) organic-inorganic nanocomposites. *Chem Mater* 2001;13:3685-92.
- [234] Liang WJ, Chen YP, Wu CP, Kuo PL. Study of microstructural characterization and ionic conductivity of a chemical-covalent polyether-siloxane hybrid doped with LiClO₄. *J Phys Chem B* 2005;109:24311-8.
- [235] Landsmann S, Winter A, Chiper M, Fustin CA, Hoepfener S, Wouters D, Gohy JF, Schubert US. Poly(dimethylsiloxane)-substituted 2,2':6,2''-Terpyridines: Synthesis and characterization of new amphiphilic supramolecular diblock copolymers. *Macromol Chem Phys* 2008;209:1666-72.
- [236] Uddin MH, Rodriguez C, Lopez-Quintela A, Leisner D, Solans C, Esquena J, Kunieda H. Phase behavior and microstructure of poly(oxyethylene)-poly(dimethylsiloxane) copolymer melt. *Macromolecules* 2003;36:1261-71.
- [237] Pant RR, Fulmer PA, Harney MB, Buckley JP, Wynne JH. Synthesis and Biocidal Efficacy of Self-Spreading Polydimethylsiloxane Oligomers Possessing Oxyethylene-Functionalized Quaternary Ammoniums. *J Appl Polym Sci* 2009;113:2397-403.
- [238] Li DX, Li CF, Wan GQ, Hou WG. Self-assembled vesicles of amphiphilic poly(dimethylsiloxane)-b-poly (ethylene glycol) copolymers as nanotanks for hydrophobic drugs. *Colloids Surf A* 2010;372:1-8.

- [239] Rutnakornpituk M, Ngamdee P. Surface and mechanical properties of microporous membranes of poly(ethylene glycol)-polydimethylsiloxane copolymer/chitosan. *Polymer* 2006;47:7909-17.
- [240] Rutnakornpituk M, Ngamdee P, Phinyocheep P. Synthesis, characterization and properties of chitosan modified with poly(ethylene glycol)-polydimethylsiloxane amphiphilic block copolymers. *Polymer* 2005;46:9742-52.
- [241] Rutnakornpituk M, Ngamdee P, Phinyocheep P. Preparation and properties of polydimethylsiloxane-modified chitosan. *Carbohydr Polym* 2006;63:229-37.
- [242] Reijerkerk SR, Knoef MH, Nijmeijer K, Wessling M. Poly(ethylene glycol) and poly(dimethyl siloxane): Combining their advantages into efficient CO₂ gas separation membranes. *J Membr Sci* 2010;352:126-35.
- [243] Bercea M, Airinei A, Hamciuc V, Ioanid A. Confirmation of polysulfone-block-polydimethylsiloxane chains in solutions and in the solid state. *Polym Int* 2004;53:1860-5.
- [244] Hamciuc V, Giurgiu D, Marcu M, Butuc E, Ionescu C, Pricop L. Polysulfone-polydimethylsiloxane block copolymers containing Si-O-C bonds. *J Macromol Sci Part A* 1998;35:563-75.
- [245] Hamciuc V, Giurgiu D, Butuc E, Marcu M, Ionescu C, Pricop L. Synthesis of polysulfone block copolymers containing polydimethylsiloxane. *Polym Bull* 1996;37:329-36.
- [246] Rusu GI, Airinei A, Hamciuc V, Rusu GG, Rambu P, Diciu M, Garoi P, Rusu M. Electronic and Optical Properties of Some Polysulfone-Polydimethylsiloxane Copolymers in Thin Films. *J Macromol Sci Part B* 2009;48:238-53.
- [247] Bronnikov S, Racles C, Cozan V, Nasonov A, Sokolov S. Micro-domain structure of the siloxane-sulfone segmented polyesters: Statistical investigations. *J Macromol Sci Part B* 2005;44:21-9.
- [248] Racles C, Cozan V, Marcu M, Cazacu M, Vlad A. New siloxane-arylidene sulfone segmented copolymers. *Eur Polym J* 2000;36:1951-7.
- [249] Chen Z, Yang JS, Guan SW, Li XJ, Rong CR, Jiang ZH. Synthesis and Characterization of Poly(ether sulfone)-graft-polydimethylsiloxane Copolymers. *J Appl Polym Sci* 2010;118:2434-41.
- [250] Ma CCM, Gu JT, Fang WC, Yang JC, Tsai LD. Bisphenol-A polycarbonate/polydimethylsiloxane multiblock copolymers. 2. Effects of siloxane oligomer structure on the properties of copolymers. *J Appl Polym Sci* 1997;66:67-75.

- [251] Ma CCM, Gu JT, Shaoh LH, Yang JC, Fang WC. Bisphenol-A polycarbonate/polydimethylsiloxane multiblock copolymers. 1. Synthesis and characterization. *J Appl Polym Sci* 1997;66:57-66.
- [252] Islam MM, Seo DW, Jang HH, Lim YD, Shin KM, Kim WG. Synthesis and characterization of branched bisphenol-A polycarbonates functionalized with siloxane. *Macromol Res* 2011;19:1278-86.
- [253] Mollah MSI, Seo DW, Islam MM, Lim YD, Cho SH, Shin KM, Kim JH, Kim WG. Synthesis and Characterization of Grafted Silicone Polycarbonates. *J Macromol Sci Part A* 2011;48:400-8.
- [254] Mollah MSI, Kwon YD, Islam MM, Seo DW, Jang HH, Lim YD, Lee DK, Kim WG. Synthesis and characterization of polycarbonates containing terminal and chain interior siloxane. *Polym Bull* 2012;68:1551-64.
- [255] van Aert HAM, Nelissen L, Lemstra PJ, Brunelle DJ. Poly(bisphenol A carbonate)-poly(dimethylsiloxane) multiblock copolymers. *Polymer* 2001;42:1781-8.
- [256] Cella J, Rubinsztajn S. Preparation of polyaryloxysilanes and polyaryloxysiloxanes by B(C₆F₅)₃ catalyzed polyetherification of dihydrosilanes and bis-phenols. *Macromolecules* 2008;41:6965-71.
- [257] Persson JC, Jannasch P. Intrinsically proton-conducting benzimidazole units tethered to polysiloxanes. *Macromolecules* 2005;38:3283-9.
- [258] Raez J, Manners I, Winnik MA. Fiberlike structures from the self-assembly of a highly asymmetric poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) in dilute solution. *Langmuir* 2002;18:7229-39.
- [259] Raez J, Manners I, Winnik MA. Nanotubes from the self-assembly of asymmetric crystalline-coil poly(ferrocenylsilane-siloxane) block copolymers. *J Am Chem Soc* 2002;124:10381-95.
- [260] Wang XS, Winnik MA, Manners I. Synthesis and solution self-assembly of coil-crystalline-coil polyferrocenylphosphine-*b*-polyferrocenylsilane-*b*-polysiloxane triblock copolymers. *Macromolecules* 2002;35:9146-50.
- [261] Cazacu M, Munteanu G, Racles C, Vlad A, Marcu M. New ferrocene-containing structures: Poly(silyl ester)s. *J Organomet Chem* 2006;691:3700-7.
- [262] Cazacu M, Vlad A, Marcu M, Racles C, Airinei A, Munteanu G. New organometallic polymers by polycondensation of ferrocene and siloxane derivatives. *Macromolecules* 2006;39:3786-93.

- [263] Vasiliu M, Cazacu M, Marcu M, Ioan S. New siloxane-azomethine alternating copolymers. *Polym Plast Technol Eng* 2005;44:993-1002.
- [264] Vlad A, Cazacu M, Munteanu G, Airinei A, Budrugaec P. Polyazomethines derived from polynuclear dihydroxyquinones and siloxane diamines. *Eur Polym J* 2008;44:2668-77.
- [265] Racles C, Sillion M, Arvinte A, Iacob M, Cazacu M. Synthesis and characterization of poly(siloxane-azomethine) iron(III) coordination compounds. *Des Monomers Polym* 2013;16:425-35.
- [266] Cazacu M, Vlad A, Munteanu G, Airinei A. Multifunctional materials based on polyazomethines derived from 2,5-dihydroxy-1,4-benzoquinone and siloxane diamines. *J Polym Sci Part A Polym Chem* 2008;46:1862-72.
- [267] Allers A, Baumeister M, Steinkamp GWK, Ohrloff C, Kohnen T. Intraindividual comparison of intraocular lenses made of highly refractive silicone (Allergan SI40NB) and hydrophobic acrylic (Alcon Acrysof MA60BM). *Ophthalmologe* 2000;97:669-75.
- [268] Erdodi G, Kennedy JP. Third-generation amphiphilic conetworks. I. Synthesis and swelling behavior of poly(N,N-dimethyl acrylamide)/polydimethylsiloxane conetworks. *J Polym Sci Part A Polym Chem* 2007;45:295-307.
- [269] Hamdani S, Longuet C, Perrin D, Lopez-Cuesta JM, Ganachaud F. Flame retardancy of silicone-based materials. *Polym Degrad Stab* 2009;94:465-95.
- [270] Hou YX, Tulevski GS, Valint PL, Gardella JA. Synthesis and surface analysis of siloxane-containing amphiphilic graft copolymers, poly(2-hydroxyethyl methacrylate-g-dimethylsiloxane) and poly(2,3-dihydroxypropyl methacrylate-g-dimethylsiloxane). *Macromolecules* 2002;35:5953-62.
- [271] Kanai T, Mahato TK, Kumar D. Synthesis and characterization of novel silicone acrylate-soya alkyd resin as binder for long life exterior coatings. *Prog Org Coat* 2007;58:259-64.
- [272] Karunakaran R, Kennedy JP. Synthesis, characterization, and crosslinking of methacrylate-telechelic PDMAAm-b-PDMS-b-PDMAAm copolymers. *J Polym Sci Part A Polym Chem* 2007;45:4284-90.
- [273] Lee Y, Akiba I, Akiyama S. Syntheses of poly(methyl methacrylate)/poly(dimethyl siloxane) graft copolymers and their surface enrichment of their blend with acrylate adhesive copolymers. *J Appl Polym Sci* 2002;86:1736-40.

- [274] Li JW, Yi LM, Lin HM, Hou RG. Synthesis of Poly(tert-butyl methacrylate)-graft-poly(dimethylsiloxane) Graft Copolymers via Reversible Addition-Fragmentation Chain Transfer Polymerization. *J Polym Sci Part A Polym Chem* 2011;49:1483-93.
- [275] Lim KT, Webber SE, Johnston KP. Synthesis and characterization of poly(dimethyl siloxane)-poly alkyl(meth)acrylic acid block copolymers. *Macromolecules* 1999;32:2811-5.
- [276] Luo ZH, He TY, Yu HJ, Dai LZ. A novel ABC triblock copolymer with very low surface energy: Poly(dimethylsiloxane)-block-poly(methyl methacrylate)-block-poly(2,2,3,3,4,4,4-heptafluorobutyl methacrylate). *Macromol React Eng* 2008;2:398-406.
- [277] Mazurek M, Kinning DJ, Kinoshita T. Novel materials based on silicone-acrylate copolymer networks. *J Appl Polym Sci* 2001;80:159-80.
- [278] Naghash HJ, Mohammadrahimpanah R. Synthesis and characterization of new polysiloxane bearing vinylic function and its application for the preparation of poly (silicone-co-acrylate)/montmorillonite nanocomposite emulsion. *Prog Org Coat* 2011;70:32-8.
- [279] Park HS, Yang IM, Wu JP, Kim MS, Hahm HS, Kim SK, Rhee HW. Synthesis of silicone-acrylic resins and their applications to superweatherable coatings. *J Appl Polym Sci* 2001;81:1614-23.
- [280] Pavlovic D, Linhardt JG, Kunzler JF, Shipp DA. Synthesis of Amphiphilic Multiblock and Triblock Copolymers of Polydimethylsiloxane and Poly(N,N-Dimethylacrylamide). *J Polym Sci Part A Polym Chem* 2008;46:7033-48.
- [281] Sugimoto H, Nishino G, Koyama H, Daimatsu K, Inomata K, Nakanishi E. Preparation and morphology of transparent poly(methyl methacrylate)-poly(dimethylsiloxane) hybrid materials using multifunctional silicone macromonomer. *J Appl Polym Sci* 2012;124:1316-22.
- [282] Sugimoto H, Nishino G, Tsuzuki N, Daimatsu K, Inomata K, Nakanishi E. Preparation of high oxygen permeable transparent hybrid copolymers with silicone macro-monomers. *Colloid Polym Sci* 2012;290:173-81.
- [283] Tsai MF, Lee YD, Long YC. Synthesis of a polydimethylsiloxane-block-hydroxyl grafted acrylate prepolymer copolymer to improve the adhesion between silicone rubber and polyurethane by induced surface reconstruction. *J Polym Res Taiwan* 2000;7:73-9.

- [284] Vargun E, Usanmaz A. Synthesis and surface properties of polydimethylsiloxane-based block copolymers: poly dimethylsiloxane-block- (ethyl methacrylate) and poly dimethylsiloxane-block-(hydroxyethyl methacrylate). *Polym Int* 2010;59:1586-97.
- [285] Wang HB, Tao QS, Wang JF, Khoshdel E. Atomic force microscopy study of self-assembly behaviors of hydrophobic poly(n-butyl methacrylate)-block-polydimethylsiloxane-block-poly(n-butyl methacrylate) ABA triblock copolymers. *Polym Int* 2011;60:798-806.
- [286] Wang JJ, Li XS. Preparation and Characterization of Interpenetrating Polymer Network Silicone Hydrogels with High Oxygen Permeability. *J Appl Polym Sci* 2010;116:2749-57.
- [287] Yang J, Zhou SX, You B, Wu LM. The preparation and surface properties of silicone-grafted acrylic copolymer coatings. *High Perform Polym* 2005;17:85-102.
- [288] Yokota M, Ajiro H, Akashi M. Effect of copolymerizing fluorine-bearing monomers on the relationship among internal structure, gas permeability, and transparency in copolymer networks composed of methacrylates and siloxane macromers. *J Appl Polym Sci* 2013;127:535-43.
- [289] Yokota M, Miwa Y, Ajiro H, Akashi M. The systematic study of the microstructure of crosslinked copolymers from siloxane macromonomers and methacrylates by changes in composition and components. *Polym J* 2012;44:301-5.
- [290] Bas S, Soucek MD. Synthesis, characterization and properties of amphiphilic block copolymers of 2-hydroxyethyl methacrylate and polydimethylsiloxane prepared by atom transfer radical polymerization. *Polym J* 2012;44:1087-97.
- [291] Deng LL, Shen MM, Yu J, Wu K, Ha CY. Preparation, Characterization, and Flame Retardancy of Novel Rosin-Based Siloxane Epoxy Resins. *Ind Eng Chem Res* 2012;51:8178-84.
- [292] Ozarslan O, Yildiz E, Inan TY, Kuyulu A, Gungor A. Novel Amine Terminated Elastomeric Oligomers and Their Effects on Properties of Epoxy Resins as a Toughener. *J Appl Polym Sci* 2010;115:37-45.
- [293] Zhao F, Sun QC, Fang DP, Yao KD. Preparation and properties of polydimethylsiloxane-modified epoxy resins. *J Appl Polym Sci* 2000;76:1683-90.
- [294] Li WW, Liu F, Wei LH, Zhao T. Curing behavior study of polydimethylsiloxane-modified allylated novolac/4,4'-bismaleimidodiphenylmethane resin. *J Appl Polym Sci* 2008;107:554-61.

- [295] Prolongo SG, Cabanelas JC, Baselga J. Reactive compatibilization of epoxy/polyorganosiloxane blends. *Macromol Symp* 2003;198:283-93.
- [296] Li WW, Liu F, Wei LH, Zhao T. Synthesis, morphology and properties of polydimethylsiloxane-modified allylated novolac/4,4'-bismaleimidodiphenylmethane. *Eur Polym J* 2006;42:580-92.
- [297] Hao JJ, Wang WY, Jiang BB, Cai XX, Jiang LX. Preparation, solubility and thermal behaviour of new bismaleimides containing silicone linkages. *Polym Int* 1999;48:235-43.
- [298] Kuang WF, Cai XX, Jiang LX. Synthesis of a new silicone-containing bismaleimide copolymer resin. *Chin J Polym Sci* 1997;15:231-5.
- [299] Hou SS, Graf R, Spiess HW, Kuo PL. An investigation into PEO/crosslinked-silicone semi-interpenetrating polymer network using H-1 solid-state NMR spectroscopy under fast MAS. *Macromol Rapid Commun* 2001;22:1386-9.
- [300] Hou SS, Kuo PL. Morphological, thermal and solid-state NMR study on a novel PMMA/crosslinked silicone semi-IPN. *Polymer* 2001;42:9505-11.
- [301] Bischoff R, Cray SE. Polysiloxanes in macromolecular architecture. *Prog Polym Sci* 1999;24:185-219.
- [302] Hedrick JL, Yilgor I, Jurek M, Hedrick JC, Wilkes GL, McGrath JE. Chemical modification of matrix resin networks with engineering thermoplastics 1. *Polymer* 1991;32:2020-32.
- [303] Riffle JS, Yilgor I, Tran C, Wilkes GL, McGrath JE, Banthia AK. Elastomeric polysiloxane modifiers for epoxy networks: Synthesis of functional oligomers and network formation studies. In: Bauer RS, editor. *Epoxy Resin Chemistry II*. ACS Symposium Series, Vol 221. Washington DC: ACS, 1983. p. 21-54.
- [304] Yilgor E, Yilgor I. 1,3-bis(gamma-aminopropyl)tetramethyldisiloxane modified epoxy resins: curing and characterization. *Polymer* 1998;39:1691-5.
- [305] Sobhani S, Jannesari A, Bastani S. Effect of Molecular Weight and Content of PDMS on Morphology and Properties of Silicone-Modified Epoxy Resin. *J Appl Polym Sci* 2012;123:162-78.
- [306] Huang W, Yao Y, Huang Y, Yu YZ. Surface modification of epoxy resin by polyether-polydimethylsiloxanes-polyether triblock copolymers. *Polymer* 2001;42:1763-6.

- [307] Guo QP, Chen F, Wang K, Chen L. Nanostructured thermoset epoxy resin templated by an amphiphilic poly(ethylene oxide)-block-poly(dimethylsiloxane) diblock copolymer. *J Polym Sci Part B Polym Phys* 2006;44:3042-52.
- [308] Gong W, Zeng K, Wang L, Zheng SX. Poly(hydroxyether of bisphenol A)-block-polydimethylsiloxane alternating block copolymer and its nanostructured blends with epoxy resin. *Polymer* 2008;49:3318-26.
- [309] Rath SK, Chavan JG, Sasane S, Srivastava A, Patri M, Samui AB, Chakraborty BC, Sawant SN. Coatings of PDMS-modified epoxy via urethane linkage: Segmental correlation length, phase morphology, thermomechanical and surface behavior. *Prog Org Coat* 2009;65:366-74.
- [310] Hou SS, Chung YP, Chan CK, Kuo PL. Function and performance of silicone copolymer. Part IV. Curing behavior and characterization of epoxy-siloxane copolymers blended with diglycidyl ether of bisphenol-A. *Polymer* 2000;41:3263-72.
- [311] Ochi M, Shimaoka S. Phase structure and toughness of silicone-modified epoxy resin with added silicone graft copolymer. *Polymer* 1999;40:1305-12.
- [312] Hameed N, Guo QP, Xu ZG, Hanley TL, Mai YW. Reactive block copolymer modified thermosets: highly ordered nanostructures and improved properties. *Soft Matter* 2010;6:6119-29.
- [313] Hameed N, Guo QP, Hanley T, Mai YW. Hydrogen Bonding Interactions, Crystallization, and Surface Hydrophobicity in Nanostructured Epoxy/Block Copolymer Blends. *J Polym Sci Part B Polym Phys* 2010;48:790-800.
- [314] Xu ZG, Zheng SX. Morphology and thermomechanical properties of nanostructured thermosetting blends of epoxy resin and poly(epsilon-caprolactone)-block-polydimethylsiloxane-block-poly(epsilon-caprolactone) triblock copolymer. *Polymer* 2007;48:6134-44.
- [315] Jones JA, Dadsetan M, Collier TO, Ebert M, Stokes KS, Ward RS, Hiltner PA, Anderson JM. Macrophage behavior on surface-modified polyurethanes. *J Biomater Sci Polym Ed* 2004;15:567-84.
- [316] Ha CS, Gardella JA. X-ray photoelectron spectroscopy studies on the surface segregation in poly(dimethylsiloxane) containing block copolymers. *J Macromol Sci Part C* 2005;45:1-18.
- [317] Mahoney CM, Gardella JA, Rosenfeld JC. Surface characterization and adhesive properties of poly(imidesiloxane) copolymers containing multiple siloxane segment lengths. *Macromolecules* 2002;35:5256-66.

- [318] Gardella JA, Mahoney CM. Determination of oligomeric chain length distributions at surfaces using ToF-SIMS: segregation effects and polymer properties. *Appl Surf Sci* 2004;231:283-8.
- [319] Lee JW, Jeong ED, Cho EJ, Gardella JA, Hicks W, Hard R, Bright FV. Surface-phase separation of PEO-containing biodegradable PLLA blends and block copolymers. *Appl Surf Sci* 2008;255:2360-4.
- [320] Chen X, Gardella JA, Ho T, Wynne KJ. Surface composition of a series of dimethylsiloxane-urea-urethane segmented copolymers studied by electron spectroscopy for chemical analysis. *Macromolecules* 1995;28:1635-42.
- [321] Zhao J, Rojstaczer SR, Gardella JA. Surface composition and morphology of polyimidesiloxane copolymers with short polydimethylsiloxane segments studied by electron spectroscopy for chemical analysis and time-of-flight secondary ion mass spectrometry. *J Vac Sci Technol A* 1998;16:3046-51.
- [322] Jarvis NL, Fox RB, Zisman WA. Surface Activity at Organic Liquid-Air Interfaces. In: Fowkes FM, editor. *Contact Angle, Wettability and Adhesion. Advances in Chemistry, Series, Vol 43.* Washington DC: ACS, 1964. p. 317-31.
- [323] Gaines Jr GL, Bender GW. Surface concentration of a styrene-dimethylsiloxane block copolymer in mixtures of polystyrene. *Macromolecules* 1972;5:82-6.
- [324] Gaines Jr GL. Diffusion and surface activity of block copolymers in polystyrene melts: Effects of copolymer molecular weight and morphology. *Macromolecules* 1979;12:1101-2.
- [325] Dwight DW, McGrath JE, Riffle JS, Smith SD, York GA. ADXPS/STEM studies of surface and bulk microphase behavior in block copolymers and graft copolymers and their blends. *J Electron Spectrosc Relat Phenom* 1990;52:457-73.
- [326] Shaaban AK, McCartney S, Patel N, Yilgor I, Riffle JS, Dwight DW, McGrath JE. ESCA studies on polydimethylsiloxane-urethane copolymers and their blends with segmented polyether urethanes. *Polym Prepr Am Chem Soc Div Polym Chem* 1983;24(2):130-3.
- [327] Kim YS, Yang JL, Wang S, Banthia AK, McGrath JE. Surface and wear behavior of bis-(4-hydroxyphenyl) cyclohexane (bis-Z) polycarbonate/polycarbonate-polydimethylsiloxane block copolymer alloys. *Polymer* 2002;43:7207-17.
- [328] Gordin C, Delaite C, Bistac S, Rusu D, Rusu M. DSC studies of poly(vinyl chloride)/poly(epsilon-caprolactone)/poly(epsilon-caprolactone)-b-poly(dimethylsiloxane) blends. *Polym Bull* 2009;63:517-29.

- [329] Gordin C, Delaite C, Bistac S, Schuller AS, Rusu D, Rusu M. PDMS migration at poly(vinyl chloride)/poly(epsilon-caprolactone)/poly(epsilon-caprolactone)-b-poly(dimethylsiloxane) blends surfaces. *Polym Test* 2009;28:446-51.
- [330] Karal O, Hamurcu EE, Baysal BM. Blends of polycaprolactone-poly(dimethylsiloxane)-polycaprolactone triblock copolymer with poly(vinyl chloride): preparation and characterization. *Polymer* 1997;38:6071-8.
- [331] Anonymous, Wacker Chemie AG. Silicone-based thermoplastics. http://www.wacker.com/cms/media/publications/downloads/6320_EN.pdf Accessed August 2013. 10 pp.
- [332] Stein J, Truby K, Wood CD, Stein J, Gardner M, Swain G, Kavanagh C, Kovach B, Schultz M, Wiebe D, Holm E, Montemarano J, Wendt D, Smith J, Meyer A. Silicone foul release coatings: Effect of the interaction of oil and coating functionalities on the magnitude of macrofouling attachment strengths. *Biofouling* 2003;19:71-82.
- [333] Martinelli E, Sarvothaman MK, Alderighi M, Galli G, Mielczarski E, Mielczarski JA. PDMS Network Blends of Amphiphilic Acrylic Copolymers with Poly(ethylene glycol)-Fluoroalkyl Side Chains for Fouling-Release Coatings. I. Chemistry and Stability of the Film Surface. *J Polym Sci Part A Polym Chem* 2012;50:2677-86.
- [334] Martinelli E, Sarvothaman MK, Galli G, Pettitt ME, Callow ME, Callow JA, Conlan SL, Clare AS, Sugiharto AB, Davies C, Williams D. Poly(dimethyl siloxane) (PDMS) network blends of amphiphilic acrylic copolymers with poly(ethylene glycol)-fluoroalkyl side chains for fouling-release coatings. II. Laboratory assays and field immersion trials. *Biofouling* 2012;28:571-82.
- [335] Martinelli E, Suffredini M, Galli G, Glisenti A, Pettitt ME, Callow ME, Callow JA, Williams D, Lyall G. Amphiphilic block copolymer/poly(dimethylsiloxane) (PDMS) blends and nanocomposites for improved fouling-release. *Biofouling* 2011;27:529-41.

Figure 1. General structure of silicone or siloxane polymer backbone.

Figure 2. Most stable conformations of (a) hexahydrogensiloxane, (b) dimethyl ether, and (c) hexamethyldisiloxane determined by quantum mechanical calculations.

- Figure 3. Chemical structures of some important silicone polymer backbones with non-reactive substituents: (a) dimethylsiloxane, (b) methylphenylsiloxane, (c) diphenylsiloxane, (d) 3,3,3-trifluoropropylmethylsiloxane.
- Figure 4. Chemical structures of some important silicone polymer backbones with chemically reactive substituents: (a) methylvinylsiloxane, (b) methylhydrogensiloxane, (c) methylglycidoxypropylsiloxane, (d) methylaminosiloxane.
- Figure 5. Preparation of monofunctional PDMS oligomers through anionic polymerization.
- Figure 6. General structures of α,ω -difunctionally terminated “telechelic” siloxane oligomers. (a) Si-X terminated oligomers, (b) Si-R-X terminated oligomers.
- Figure 7. Preparation of telechelic (Si-R-X) terminated silicone oligomers by hydrosilylation reactions.
- Figure 8. Preparation of telechelic silicone oligomers through equilibration reactions ($x=3-5$).
- Figure 9. Chemical structures of (a) polycaprolactone-b-PDMS (PCL-PDMS-PCL) and (b) poly(2-ethyloxazoline)-b-PDMS (POX-PDMS-POX) triblock copolymers.
- Figure 10. Synthesis of poly(γ -benzyl-L-glutamate)-PDMS-poly(γ -benzyl-L-glutamate) (PBLG-PDMS-PBLG) triblock copolymers by the ring-opening polymerization of γ -benzyl-L-glutamate-*N*-carboxyanhydride using α,ω -aminopropyl terminated PDMS oligomers as macroinitiators(53).
- Figure 11. Preparation of polystyrene-b-polydimethylsiloxanetriblock copolymers (PS-PDMS-PS) by ATRP polymerization (68).
- Figure 12. Preparation of polydiphenylsiloxane-b-polydimethylsiloxanetriblock copolymers (PDPD-PDMS-PDPS) through Pt catalyzed hydrosilylation reactions of vinyl terminated PDPS macromonomers and α,ω -siliconehydride terminated PDMS oligomers (35, 39).
- Figure 13. Loss of end-group functionality due to back biting reactions in hydroxybutyl terminated PDMS oligomers (90).
- Figure 14. Reaction scheme for the preparation of silicone-urethane copolymers by two-step polymerization usually termed as the “prepolymer method”.
- Figure 15. Modulus-temperature and $\tan \delta$ -temperature curves for silicone-urea copolymer based on PDMS-7000 with a hard segment content of 18% by weight(89).

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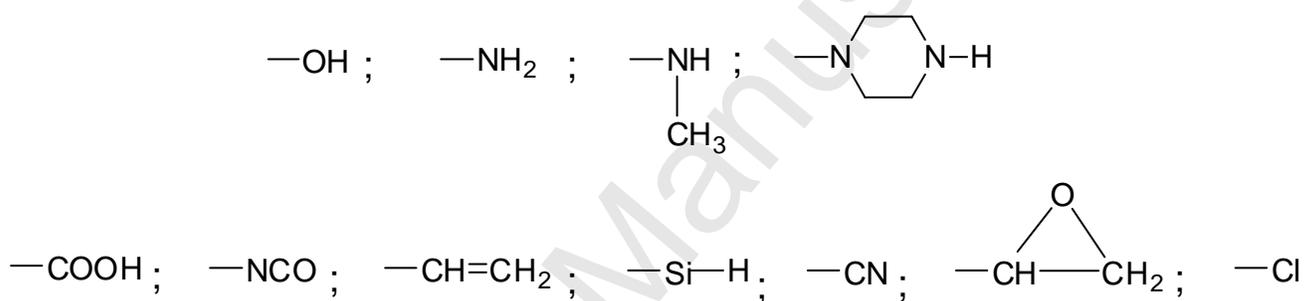
- Figure 16. Dependence of ultimate tensile strengths of silicone-urea copolymers as a function of urea hard segment content PDMS segment length and diamine chain extender. (●) PDMS-2500-E, (□) PDMS-2500-D, and (Δ) PDMS-3200-D (E: Ethylene diamine, D: 2-methyl-1,5-diaminopentane) (89). Copyright 2003. Reproduced with permission from Elsevier Science Ltd. Oxford, UK.
- Figure 17. TEM micrograph of PDMS-PPO-urea polymer. PDMS phases appear as dark in the micrograph (131). Copyright 2001. Reproduced with permission from Taylor and Francis, London, UK.
- Figure 18. (A) SEM image, (B) Si map of SEM image and (C) tapping mode topographical AFM image of PDMS-PCL-urethane coating containing 37% by weight PCL-PDMS-PCL copolymer (10% by weight PDMS) (108). Copyright 2005. Reproduced with permission from American Chemical Society, Washington DC, USA.
- Figure 19. Reaction scheme for the preparation of PDMS-aramid segmented copolymers by a two-step, solution polycondensation method (180).
- Figure 20. Chemical structures of a linear and a graft PDMS-imide copolymer prepared by Voit (204).
- Figure 21. Chemical structures of (a) PDMS-polyethersulfone (PDMS-PSF) and (b) PDMS-aromatic polycarbonate (PDMS-PC) segmented copolymers.
- Figure 22. Extruder output as a function of the type and amount of silicone copolymer additive in PP blends. (○) PCL-PDMS-PCL, (●) PDMS-PU additive (26). Copyright 2002. Reproduced with permission from Elsevier Science Ltd. Oxford, UK.
- Figure 23. Influence of annealing on the surface hydrophobicity of polyamide-6 modified with a silicone-urea copolymer. Change in water contact angles as a function of the amount of silicone copolymer in the blend before (□) and after (■) annealing at 110 °C for 2 hours (27). Copyright 2003. Reproduced with permission from Elsevier Science Ltd. Oxford, UK.

Table 1. Glass transition temperatures of random poly(dimethyl-diphenylsiloxane) copolymers (3, 10)

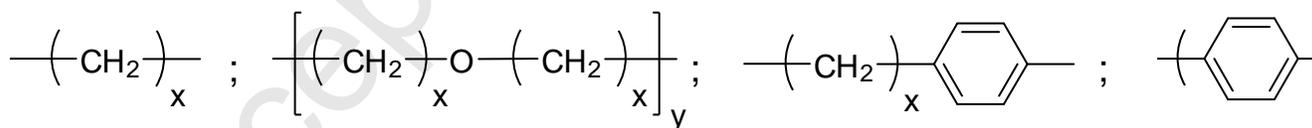
Diphenylsiloxanecontent		T _g (°C)
(weight %)	(mole %)	
0	0	-123
11.9	4.8	-115
21.5	9.4	-105
43.4	22.4	-79
59.6	35.3	-49
78.3	58.0	-35

Table 2. Chemical structures of reactive end groups and hydrocarbon bridges on (Si-R-X) terminated telechelic silicone oligomers

Reactive end groups (X)



Chemical structures of typical hydrocarbon bridges (R)



$$X = 1 - 6 ; y = 1 - 3$$