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Well-Architectured Poly(dimethylsiloxane)-Containing Copolymers Obtained by Radical Chemistry

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1. Introduction

Polyorganosiloxanes have been produced industrially since the early 1940s, with the development of methylchlorosilane synthesis (Rochow−Muller direct synthesis) at the industrial scale. This was the basis for a rapid increase in sales worldwide, beginning in the United States. In 1992, the total production of silicone was estimated to be up to 600 000 tons per year for a business volume estimated to 5.5 billion dollars.[1] In 2002,[2] the overall production was estimated to be 2 million tons (Western Europe 33%, North America 34%, Asia 28%) for a total value of 8 billion euros. In Western Europe, the production of silicone has been estimated to be 139 000 tons of fluids, 210 000 tons of sealants, 20 000 tons of resins, and 139 000 tons of elastomers. One reason for the high development of these silicon-based polymers and materials is the diverse molecular structures of polyorganosiloxanes and the intimate relationship between structure and properties not easily achievable by other classes of polymers. Thousands of industrial products have been commercialized ranging from linear chains (fluids) to slightly (rubbers) and highly (resins) cross-linked networks, leading to a wide range of applications. Silicone fluids are applied in areas like proceeding aids (26%), personal care (24%), paints and coatings (10%), paper coatings (15%), mechanical fluids (7%), and textile (5%). Due to their exceptional properties, silicone elastomers and resins have found applications in automotive (20%), electrical fitting (15%), medical/health (14%), appliances (9%), consumer goods (9%), textile coating (7%), business machines (5%), coatings (7%), and moldmarking (7%) areas.[2]

Polyorganosiloxanes exhibit exceptional properties as a result of the constitutive unit Si−O−Si of the polymer backbone. The value of the Si−O bond length is equal to 1.64 ± 0.03 Å,[3] substantially smaller than that of the Si−O

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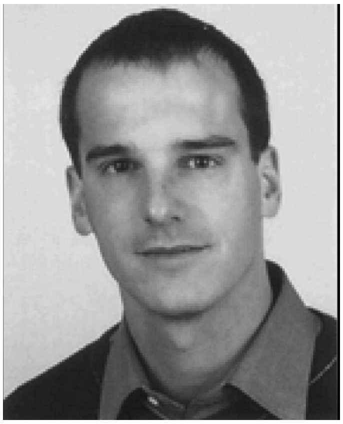
Emmanuel Pouget was born in Montpellier, France, in 1981. He graduated from the National School of Chemistry of Montpellier in 2004. He obtained his Ph.D. degree in 2007 at the University of Montpellier II, working under the direction of Professor B. Boutevin and the cosupervision of Dr. F. Ganachaud and Dr. P. Lacroix-Desmazes in the laboratory of Macromolecular Engineering and Chemistry (IAM) led by Professor B. Boutevin. His research covered silicone modifications (by radical polymerization or chemical grafting in mass, solvent, or dispersed aqueous media) to obtain nanostructured materials. In 2008, he joined BLUESTAR Silicones, where he is currently working as a research manager in the chemistry of silicones.



Jeff Tonnar was born in Luxembourg, in 1979. He graduated from the National School of Chemistry of Montpellier in France in 2004. He obtained his Ph.D. degree in 2007 at the University Montpellier II, working under the direction of Dr. P. Lacroix-Desmazes in the laboratory of Professor Bernard Boutevin. His research covered iodine-mediated polymerization [(reverse) ITP], especially in dispersed aqueous media (suspension, miniemulsion, and ab initio emulsion polymerization). In 2007, he obtained a postdoctoral research position in the laboratory of Professor S. Armes (Sheffield University, U.K.). There he worked on the synthesis of polymer−silica nanocomposites in emulsion polymerization. In 2008, he joined CIBA, where he is currently working as a project manager on emulsion polymerization for paper coatings. In 2008 he received the Thesis Award from Groupe Français d'Etudes et d'Applications des Polymères.

Patrice Lucas was born in Versailles, France, in 1978. He graduated from the National School of Chemistry of Clermont-Ferrand in France in 2002. He obtained his Ph.D. degree in 2007 at the University Montpellier II, working under the direction of Professor J.-J. Robin in the laboratory of Professor Bernard Boutevin. His research dealt with silicone and polyamide thermoplastic elastomer and the compatibilization of these two polymers during reactive extrusion using a radical pathway. In 2006, he joined NANOLEDGE (Montreal, Canada), where he is currently working as a project manager on nanoparticles functionalization and integration in thermosets polymers for high-performance structural materials. He is a member of TRFA (Thermoset Resin Formulators Association).

Patrick Lacroix-Desmazes was born in Caen, France, in 1968. He graduated from the National School of Chemistry of Montpellier, France, in 1992. He obtained his Ph.D. degree in 1996 at the University Claude-Bernard Lyon I, working in the laboratory of Professor Alain Guyot on the use of macromonomers as stabilizers in dispersion polymerization in polar media. After postdoctoral research on suspension polymerization, done with BP Chemicals in Wingles in 1997, he joined the laboratory of Professor Bernard Boutevin as a CNRS research scientist. In 1999, he developed RITP, a promising method for controlled/living radical polymerization. He received his Habilitation Degree in 2004. He was awarded the 2004 Innovative Research ADER Award in collaboration with Solvin Co. His research interests cover living radical polymerizations (photoiniferters, NMP, ATRP, RAFT, ITP, RITP), including in dispersed media (emulsion, dispersion, suspension polymerization), as well as the synthesis and use of polymers in liquid or supercritical carbon dioxide.

bond length calculated from the additivity of the atomic radii (1.83 Å). This is, on one hand, indebted to the partial double-bond character of the Si−O bond[3] and, on the other hand, to the substantial ionic character (40−50%) of the Si−O bond (electronegativity of Si = 1.8 and O = 3.5). This is the reason why polyorganosiloxanes are considered to be "organic−inorganic" elastomers compared to pure organic elastomers (polybutadiene, polyisoprene). The main drawback that arises from the polarity of the Si−O bond is the sensitivity of polysiloxanes to hydrolysis in acidic or basic conditions. The high value of the Si−O−Si angle (140°) and the value of the Si−O bond length partly explain the exceptionally low glass transition temperature observed for polyorganosiloxanes. For instance, PDMS exhibits a glass transition temperature of −123 °C due to torsional motion along the backbone. It has been demonstrated that this very low intermolecular force results in a large molar volume (75.5 $cm^3 mol^{-1}$)[4] and a low cohesion energy density.[5] The low surface tension, surface energy, solubility parameter, and dielectric constant observed for PDMS can also be ascribed to the low intermolecular forces between PDMS chains. The presence of apolar methyl groups around the Si−O−Si polymer backbone explains their high lipophilic and hydrophobic characters. The value of the Si−O bond dissociation energy (BDE) (110 kcal mol^{-1})[3] is high, compared to the

François Ganachaud, 40 this year, studied chemistry at CPE Lyon, where he graduated as an engineering chemist. During his Ph.D work, granted in 1997 from the University Claude-Bernard Lyon I, he proposed new polymer latex/oligonucleotide complexes, under the supervision of Christian Pichot. After a one-year postdoctoral position in Sydney at the KCPC headed by Professor Robert G. Gilbert, he returned in France to take a CNRS research position in Paris with Professor Hémery from 1999 to 2003. He then moved to Montpellier in the laboratory of Professor Bernard Boutevin, where he completed his habilitation in 2004. His current research interests are (i) polymer synthesis in aqueous dispersed media via ionic polymerization, (ii) synthesis of functional silicones and related materials, and (iii) emulsification of various solutes by Ouzo effect.

Bernard Boutevin earned his Chemical Engineering degree from the School of Chemistry in Montpellier (France) and then received his Ph.D. degree in 1975 from Montpellier University, where he became a CNRS researcher. The topics of his research first concerned telomerization: kinetics, chemical modifications, and their use in architectured polymers (block and grafted copolymers). The concept was first applied to fluorinated monomers, and it represents almost one-half of his scientific articles. Nowadays, his research is directed toward telechelic oligomers, and all of the methods of living radical polymerization are investigated (NMP, ATRP, ITP, RITP, and RAFT) in order to prepare original architectured polymers such as block, grafted, gradient, or alternated. In addition, phosphonated and silicone-based monomers and (co)polymers are of increasing interest. He has supervised more than 100 Ph.D. students and published 2 books, more than 450 peer review articles, 25 reviews or chapters of books, has been invited to more than 35 international conferences, and is coinventor of more than 100 patents. In addition, more than 10 products coming from his research group have been or are marketed by companies. He is also a consultant for many companies, including Arkema, and he was a consultant for Dow Corning (United States) and Daikin (Japan). He is a member of the American Chemical Society and Groupe Français d'Etudes et d'Applications des Polymères.

BDE of the C−O bond (85.5 kcal mol^{-1}), C−C bond (82.6 kcal mol^{-1}), and Si−C bond (76 kcal mol^{-1}),[6] which explains the excellent thermal stability of polyorganosiloxanes. In addition, PDMS has a good gas permeability[7] and is transparent to visible and UV light (the methyl groups do not absorb radiation above 300 nm). Polyorganosiloxanes are also resistant to ozone and corona discharge,[3,8] exhibit an excellent film-forming ability, and, among other properties, show some release action, surface activity, and chemical and physiological inertness.[8,9]

This review focuses on PDMS copolymers because they are the most common polyorganosiloxane copolymers. However, the well-developed chemistry of silicone enables one to replace the methyl groups by a wide variety of functional groups (e.g., phenyl or 1,1,1-trifluoropropyl). This can be done either randomly or all along the polysiloxane backbone. Tailored properties can be achieved by judicious choice of the substituents, depending on the targeted properties and applications.

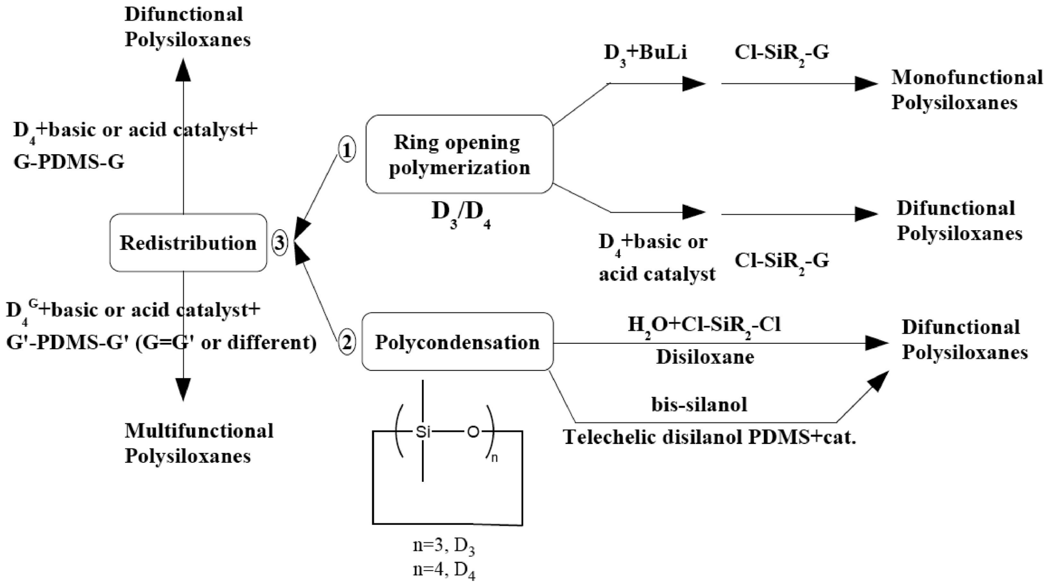
Despite their unique properties, PDMS rubbers require extremely high molecular weights to develop useful mechanical properties. Also, chemical cross-linking is not sufficient, and it is necessary to add finely divided high surface area silica to obtain interesting properties.[8,10–18] Recently, the use of physical cross-linking (hydrogen-bond formation between two complementary groups attached to the silicone backbone) allowed the synthesis of PDMS rubbers owning exceptional properties without addition of silica.[19–21] These assemblies are thermoreversible and sometimes dissolve by adding a polar solvent. Another way of preparing silica-free silicone rubbers is to prepare copolymers that associate elastomeric segments (low T_g polymers, such as PDMS) with thermoplastic segments (high T_g) to generate thermoplastic elastomers (TPE) with improved mechanical properties.[22,23]

Due to the exceptional properties of PDMS, interest indeed has grown in associating PDMS with other polymeric entities to obtain new materials. This strategy implies the synthesis of copolymers with various well-controlled architectures: block, multiblock, or graft copolymers. In the literature, the elastomeric property is undoubtedly the most desired characteristic to be conferred to copolymers. In addition, amphiphilic copolymers can be obtained by associating PDMS with a hydrophilic polymer. The incorporation of a polysiloxane block in another polymer is also utilized to modify the properties of the other polymer, making its surface more hydrophobic, tuning the gas permeability or flexibility of the material.

Many different synthesis routes exist to prepare polyorganosiloxane block or graft copolymers. Anionic polymerizations and coupling reactions between a polysiloxane block and another polymer have largely been treated in several reviews[24,25] and will not be examined here. On the other hand, radical polymerization involving a polysiloxane backbone has not been extensively described in the literature. Radical polymerization has the advantage that it does not require the same purity of reagents as anionic polymerization, which makes it widely used at an industrial level. Moreover, radical polymerization is applicable to a large range of monomers: styrenics, acrylates and methacrylates, vinyl esters (including vinyl acetate (VAc)), acrylamides, halogenated vinyl monomers, and so on. In addition, radical polymerization can be used in dispersed aqueous media, limiting the use of organic solvents. Lastly, radical polymerization has also already been used to prepare a wide range of different copolymer architectures: diblock, triblock, multiblock, graft, or star copolymers.

The aim of this review is thus to give a complete overview of polysiloxane-containing block or graft copolymers pre-

Scheme 1. General Scheme of the Synthesis of Mono-, Di-, and Multifunctional Polysiloxanes[a]



[a] D_3 and D_4 holds for hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane, respectively, whereas G holds for a functional group.

pared by radical polymerization of vinylic monomers. Following this introduction, we give a brief overview of the chemistry of polysiloxanes needed for a good understanding of the following sections. The third part deals with conventional radical polymerization (PDMS macroinitiators, PDMS macromonomers, and PDMS macrotransfer agents) followed in the fourth part by controlled radical polymerization (IniFerTer, NMP, ATRP, ITP, RAFT). The last section summarizes some properties and applications of polysiloxane-containing copolymers from studies quoted in this review.

2. Brief Overview of Synthesis Routes to Functionalized Polysiloxanes

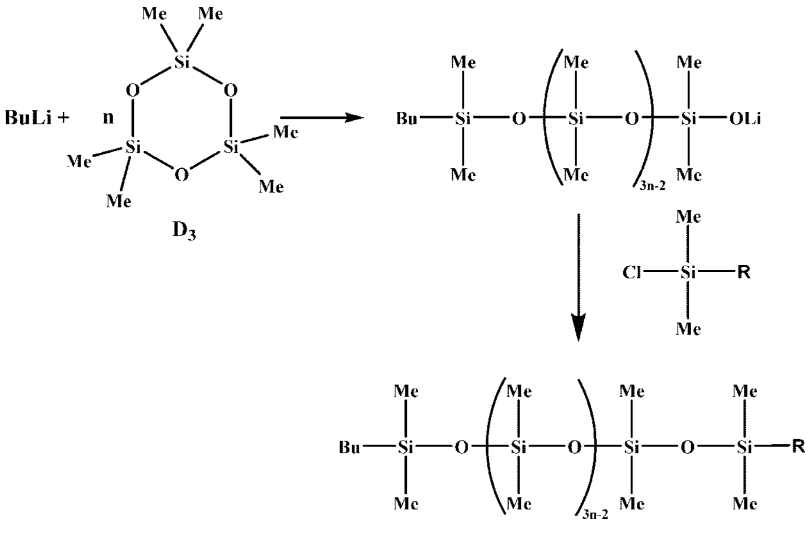
The rich chemistry of polysiloxanes offers many possibilities to tailor the synthesis of well-controlled functionalized polysiloxanes. The amount, nature, and position of the functional groups in the polysiloxane backbone determine the architecture of the final copolymers. Since the synthesis of polysiloxanes with controlled end groups and molar masses has been reviewed by several groups,[24–30] we will only give a brief summary of the most popular synthesis routes.

2.1. Synthesis Routes to Polysiloxane

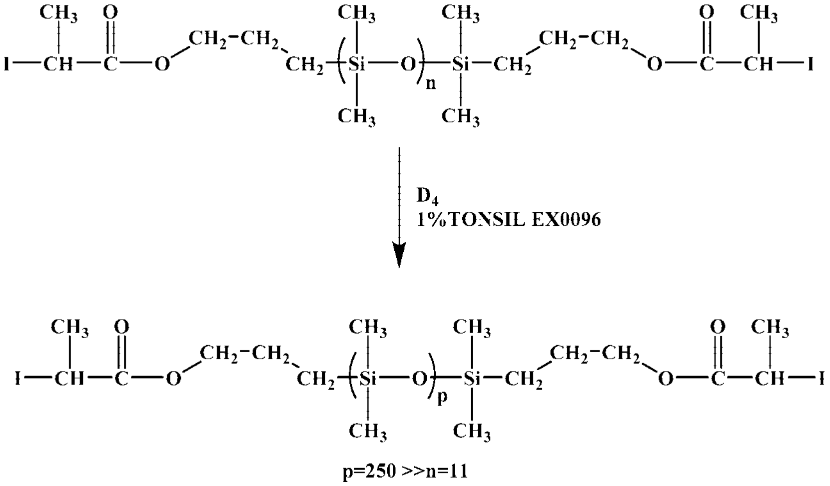
Polysiloxanes are synthesized using three principal routes: ring-opening polymerization (ROP), polycondensation, and redistribution (Scheme 1). The ring-opening polymerization of cyclosiloxanes enables one to synthesize high molecular weight siloxanes with better precision than the polycondensation and redistribution methods. The most common cyclic siloxane monomers are octamethylcyclotetrasiloxane $(Me_2SiO)_4$ (D_4) and hexamethylcyclotrisiloxane $(Me_2SiO)_3$ (D_3).

The living anionic polymerization of D_3 (Scheme 1, route 1),[26] leading to ω-monofunctional polysiloxanes, is initiated by strong inorganic, organic, or organometallic bases. Typically, butyllithium (BuLi) initiates the polymerization by first forming a silanolate anion which further propagates by addition of D_3 (Scheme 2). The counterion is usually an alkali metal (here Li^+), but it can also be a tertiary ammonium or phosphonium cation. The functional group is introduced during the deactivation of the silanolate ion using a functional chlorosilane (Scheme 2).[25] This technique enables a good control of the molecular weight and the chain-end functionality. Here, a promoting solvent such as tet-

Scheme 2. Synthesis of Monofunctional PDMS by Butyllithium-Initiated Ring-Opening Polymerization of D_3



Scheme 3. Synthesis of an α,ω-Diiodo-Functionalized Poly(dimethylsiloxane) with an Increased Degree of Polymerization by Redistribution of D_4 in the Presence of TONSIL EX0096 (sulfonic-acid-modified diatom clay) as Catalyst



rahydrofuran is required to initiate the polymerization of D_3. As will be depicted in the present review, it is possible to initiate the polymerization of D_3 with chemical entities of larger interest than the butyl anion.

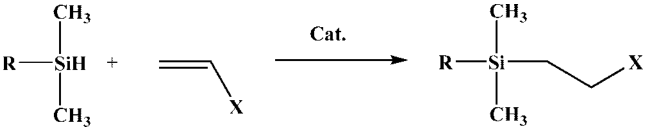
In comparison with D_3, the controlled ring-opening polymerization of D_4 has not been widely studied, mainly because of the lower reactivity of D_4 and a less efficient control over molecular weights and functionality. The main technique of ring-opening polymerization of D_4 involves cheap mineral acid or base catalysts to prepare difunctional polysiloxanes, which can be further used to prepare triblock or multiblock copolymers. Nevertheless, the introduction of pendant reactive side groups into a polysiloxane backbone is quite easy by copolymerizing D_4 with a functionalized D_4 monomer, for which one or both methyl groups on the D unit are substituted by reactive groups. Number-average molecular weights can be easily controlled by adjusting the molar ratio of D_4 over disiloxane transfer agent.[24]

Another way to prepare α,ω-difunctional polysiloxanes is to hydrolyze dichloro- or dialkoxysilanes and to tune the water content to control the molecular weight of the product (Scheme 1, route 2).[25] Silanol end groups are obtained by the controlled hydrolysis of the chloro end groups. Hydrogenopolysiloxanes are prepared by condensation reactions of dichlorodimethylsilane in the presence of chlorodimethylsilane. This process is only applied in industry as a basis for the synthesis of intermediaries in the silicone industry. Generally, a mixture of cyclic and linear silicone is obtained which is then polymerized to obtain longer silicone oils.[31]

Polycondensation of bis-silanol is also a powerful technique to obtain telechelic functional PDMS, again using acid or base catalysts. The use of a functional end blocker allows the preparation of functional telechelic polymers. For instance, Graiver et al.[32] emulsified silanol-terminated oligomers in water with dodecylbenzene sulfonic acid (DBSA) acting as both surfactant and acid catalyst. A minimum of 25 h of reaction at 22 °C yielded very high molecular weight macromolecules.

The last technique used to obtain functional polysiloxanes is to polymerize D_4 and/or D_4^G in the presence of a functionalized chain stopper or a α,ω-functionalized polysiloxane and a small amount of acidic or basic catalyst. Both ROP of the cyclosiloxanes and subsequent redistribution of the chains are necessary to exert a relatively good control of molecular weights and functionality.[33,34] As an example, our group recently carried out the redistribution of D_4 with an α,ω-diiodo-functionalized poly(dimethylsiloxane) to obtain a functional poly(dimethylsiloxane) with a longer chain length (Scheme 3).[35] Redistribution has also been used to prepare α,ω-dicarboxypropyl-,[36] diaminopropyl-,[37] and dihydroxybutyl-[38]functionalized poly(dimethylsiloxane). It is performed by reacting D_4 and the corresponding M_2^X (X-$SiMe_2$-O-$SiMe_2$-X) under acidic (α,ω-dicarboxypropyl-functionalized PDMS) or basic conditions (diaminopropyl- and diaminobutyl-functionalized PDMS).

Scheme 4. General Scheme of the Hydrosilylation Reaction



2.2. Functionalization of Polysiloxane

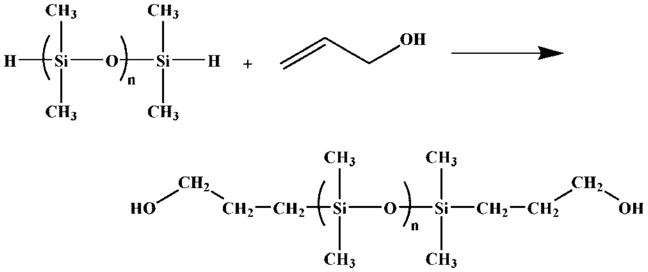
For a more complete overview of the transformation of the polysiloxane chain ends, the reader is redirected to the very complete review of Yilgor et al.[24] The main reactions used to transform the polysiloxane chain ends are hydrosilylation, esterification, amidification, and nucleophilic substitution reactions, all of which are rapidly presented here.

Hydrosilylation is the most popular reaction for functionalizing polysiloxanes owing to the ease of synthesis of starting materials: mono-, di-, or multifunctional PDMS containing Si−H groups. Hydrosilylation is the reaction between a hydridosilyl function and either a C=C double bond or another π bond. It is catalyzed by various metals, such as chloroplatinic acid, by radical precursors, such as di-*tert*-butyl peroxide, in some cases by amine complexes or aluminum chloride, or other catalysts used for more specific reactants.[39] The general scheme of hydrosilylation is given in Scheme 4.

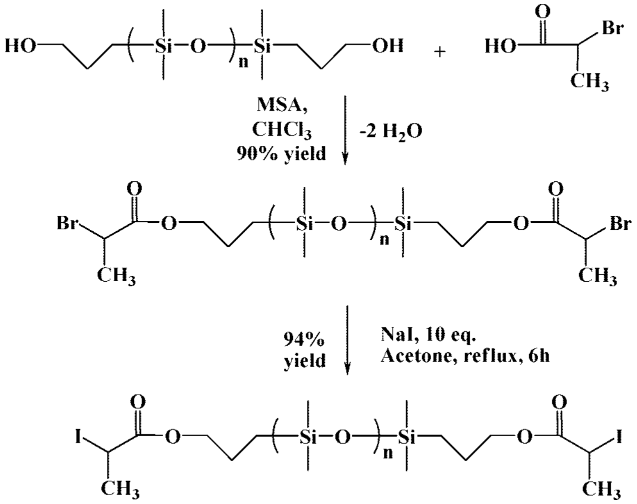
For instance, to obtain α,ω-dihydroxypropyl PDMS, one can hydrosilylate allyl alcohol with α,ω-dihydridosilyl PDMS (Scheme 5).[40] One might note here that some functional groups require protection (typically acid, amine, or alcohol).

Besides hydrosilylation, conventional reactions of organic chemistry like esterification, amidification, or nucleophilic substitution can be used to transform the polysiloxane chain ends (Scheme 6, routes 1−3). The reaction between an isocyanate-functionalized molecule and an amino- or a

Scheme 5. Hydrosilylation of Allyl Alcohol onto a SiH Functional PDMS[40]



Scheme 7. General Mechanism of the Synthesis of the α,ω-Diiodo PDMS Macrotransfer Agent Useful for ITP Polymerization of Styrene and VAc (MSA is methane sulfonic acid)



hydroxy-functionalized polysiloxane is also widely used (Scheme 6, route 4).

For instance, our group[41] carried out the esterification of 2-bromopropionic acid on α,ω-dihydroxypropyl PDMS. Bromine was afterward substituted by iodine to yield an active macrotransfer agent involved in iodine-transfer polymerization of VAc and styrene[41] (Scheme 7).

Amidification is a common route to prepare azo macroinitiators.[42] Typically, α,ω-diaminopropyl PDMS is reacted with 4,4′-azobis-4-cyanopentanoyl chloride (Scheme 8).

Nucleophilic substitution of chlorine by sodium diethyldithiocarbamate in a poly(chloromethylheptamethyltetrasiloxane) was carried out by Inoue et al.[43] to prepare a macroiniferter (initiation transfer termination) (Scheme 9).

The reaction of an excess of diisocyanate with an α,ω-diaminopropyl PDMS gives an α,ω-diisocyanato PDMS which can be further reacted with *tert*-butyl hydroperoxide to obtain a peroxycarbamate macroinitiator (Scheme 10; see section 3.1.5 for details and references).

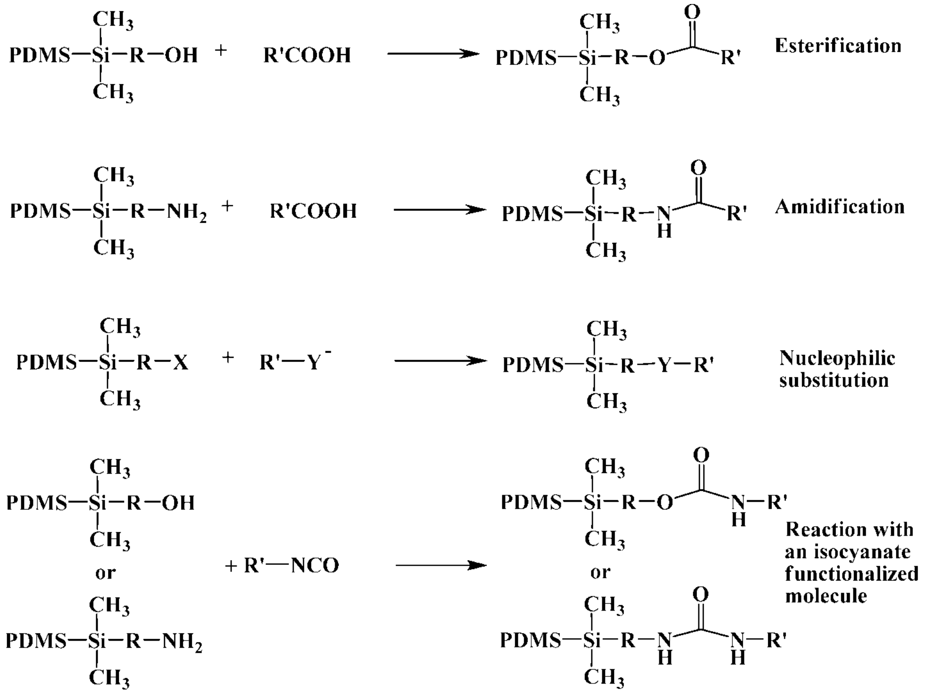
The authors are not willing to make an exhaustive listing of polysiloxane functionalization. More specific reactions of functionalization exist and will be described when required all along this review.

In conclusion, synthesis of the polysiloxane backbone and of course the technique of functionalization have to be well selected depending on the desired reactivity of the PDMS macroreagent. Different types of precursors used in conventional radical polymerization or controlled radical polymerization are presented in the following sections.

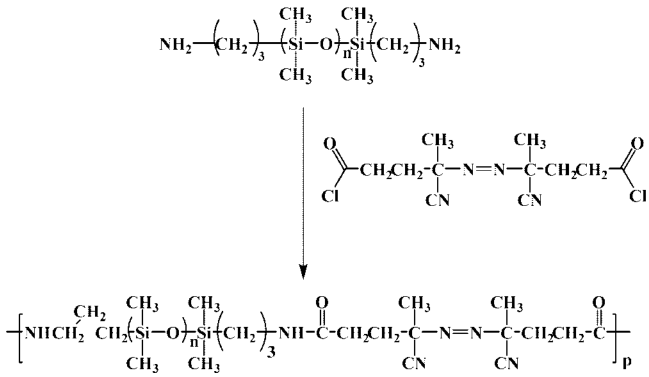
3. Copolymers Obtained by Conventional Radical Polymerization

Conventional radical polymerization involving silicone polymers can follow various strategies. The first section is dedicated to the numerous examples of studies making use of PDMS macroinitiators, the decomposition of which leads to the formation of block and graft copolymers. The second section is an overview of the synthesis of silicone macromonomers and their reactivity and copolymerization. In the last section, grafting through some "transfer to PDMS"

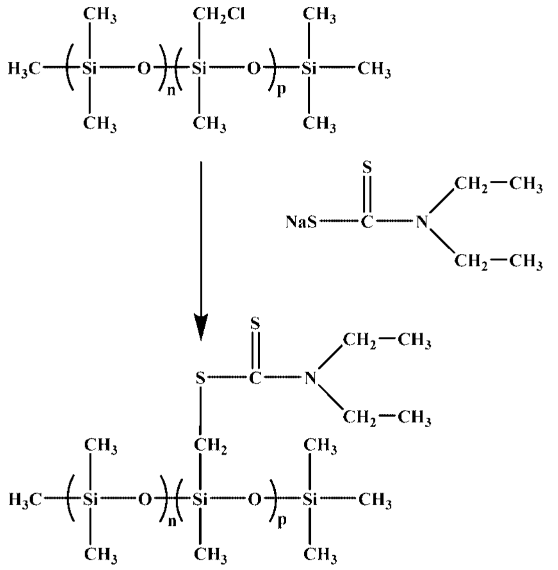
Scheme 6. General Scheme of the Esterification, Amidification, Nucleophilic Substitution, and Functionalization with an Isocyanate Functionalized Molecule



Scheme 8. Synthesis of an Azo Macroinitiator by Reaction of an α,ω-Diaminopropyl PDMS with 4,4′-Azobis-4-cyanopentanoyl Chloride



Scheme 9. Synthesis of a PDMS Macroiniferter by Nucleophilic Substitution of Chlorine by Sodium Diethyldithiocarbamate



(in other words the random generation of radicals onto the silicone backbone to initiate a polymerization) and telomerization will be discussed, including processes implemented in aqueous media to prepare core−shell particles.

3.1. Polysiloxane Macroinitiators

3.1.1. Redox-Initiated Polymerization

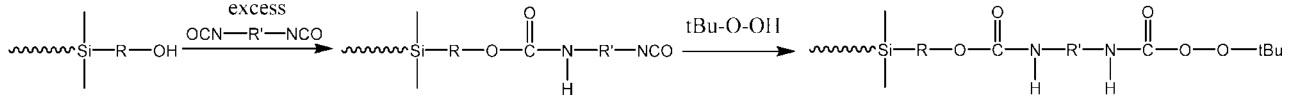
The first step of the redox-initiated polymerization is the formation of an active radical on the PDMS chains followed by the polymerization of the monomer from the so-called PDMS macroinitiator. This technique allows the synthesis of graft and block copolymers containing PDMS.

Most of the studies were carried out by Graiver et al.[44–51] The method is based on a redox initiator system that generates free radicals from enolates of aldehydes and ketones using copper(II) salts (typically copper(II) 2-ethyl hexanoate or copper(II) octanoate). This particular redox system is known to yield α-acyl carbon-centered radicals (Scheme 11).[52,53] Graiver et al.[44–51] found that in the presence of vinyl monomers, these radicals can initiate polymerization, leading to homopolymers with useful chain-end functionality as well as block and graft copolymers.[54–56] The first step of the synthesis is the preparation of carbonyl functional polysiloxanes achieved by ozonolysis of a hexenyl-containing PDMS copolymer.[45] The ozonide intermediate was reacted with zinc and acetic acid to obtain the aldehyde functionality (Scheme 12).

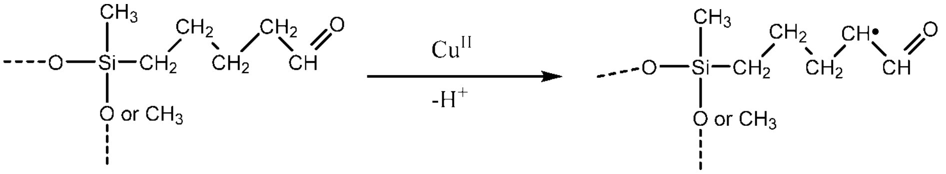
The polymerization of the vinyl monomer starting from the carbonyl functionality of the polysiloxane is initiated by a redox system: a soluble organic salt of Cu^{II}, a tertiary amine such as triethylamine and dimethylphenylamine, a stabilizer for Cu^{II} ions such as pyridine, and a stabilizer for Cu^{I} ions such as triphenylphosphine. This strategy enabled the authors to synthesize a PEA-*b*-PDMS-*b*-PEA (PEA = poly(ethyl acrylate)) in 1 h at 70 °C[44] and other different block and graft PDMS copolymers: PMMA-*b*-PDMS-*b*-PMMA,[46,47,49] PS-*b*-PDMS-*b*-PS,[46,47,49] PVPy-*b*-PDMS-*b*-PVPy,[50,51] PDMS-*g*-PS, PDMS-*g*-PtBuMA,[48] PDMS-*g*-PtBuA,[48] PDMS-*g*-PMAA,[46] PDMS-*g*-PAA,[46] PDMS-*g*-PMMA,[48] and PDMS-*g*-PVPy.[50,51]

The polymerization of *N*-isopropylacrylamide (NIPAM) initiated by the $(NH_4)_2Ce^{IV}(NO_3)_6$ -α,ω-dihydroxyalkyl(polydimethylsiloxane) redox pair was also studied to obtain a thermosensitive triblock copolymer PNIPAM-*b*-PDMS-*b*-PNIPAM.[57] This polymerization was performed at 30 °C in hexane containing a small amount of 1,2-dichloroethane to increase the solubility of NIPAM (heterogeneous solution

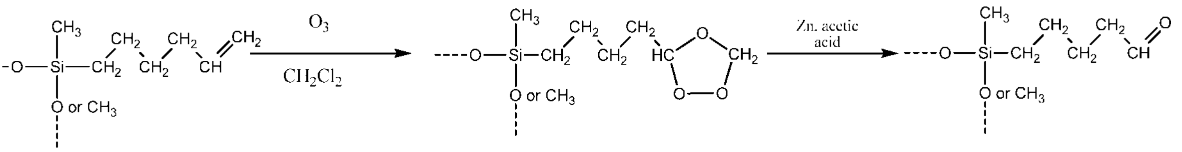
Scheme 10. General Mechanism of the Synthesis of PDMS Peroxycarbamate Macroinitiator



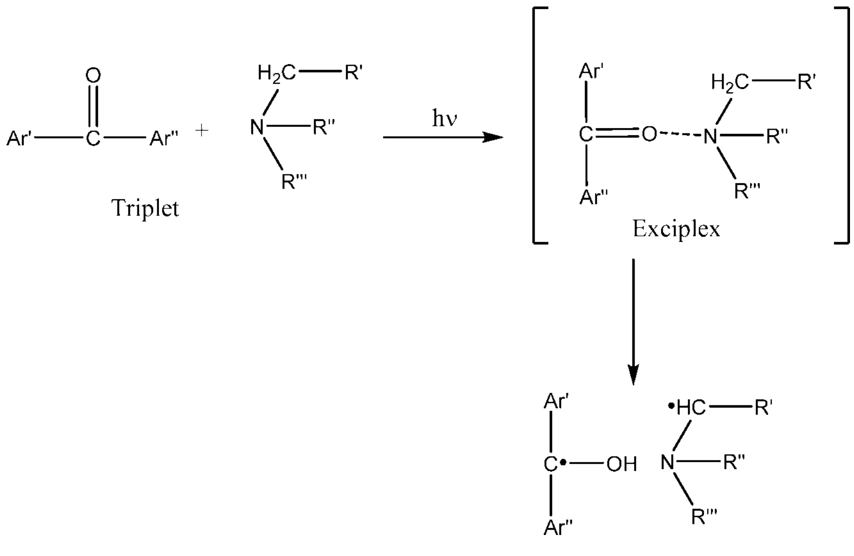
Scheme 11. Generation of α-Acyl Carbon-Centered Radical



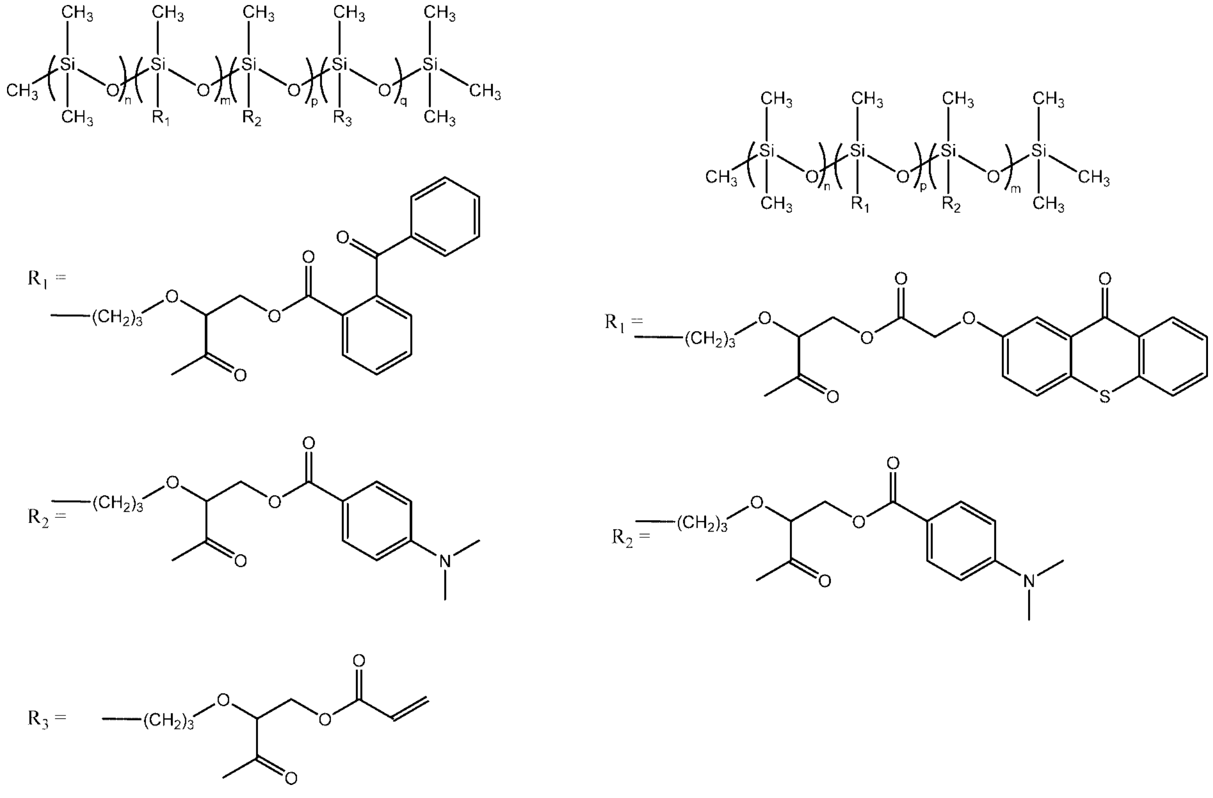
Scheme 12. General Scheme for the Synthesis of Aldehyde Functional Polysiloxanes



Scheme 13. Mechanism of Formation of Alkyl Radicals by Type II Photoinitiators



Scheme 14. Macro-Photoinitiators Used by Pouliquen et al.[62,63]



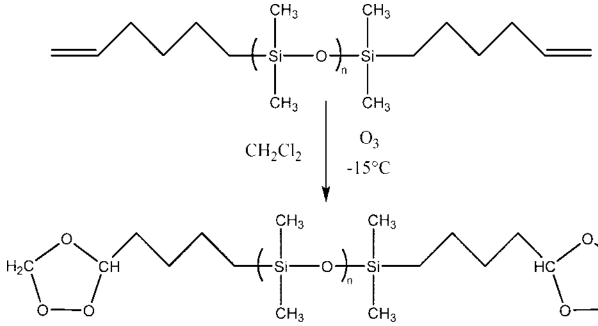
polymerization). Low conversions (<30%) were obtained after 48 h of reaction. The formation of PNIPAM homopolymer chains initiated and/or terminated by the free radicals generated from monomer−Ce^{IV} complexes and the presence of unreacted PDMS oligomers were observed.

3.1.2. Photoinitiated Polymerization

Photoinitiated polymerization is accomplished by incorporating light-sensitive initiators in the polymer structure: photoreactive chromophores such as azo initiator[58] (see azo macroinitiator, section 3.1.7) or diethyldithiocarbamate[43] (see iniferter, section 4.1). Such initiators can be classified in two groups: type I photoinitiators lead to active radicals by monomolecular cleavage (e.g., benzoin ethers),[43,58-61] whereas type II photoinitiators[62,63] generate active radicals by hydrogen photoabstraction, preferably induced by exciplex formation in the presence of an amine co-initiator (e.g., benzophenone/tertiary amine system).[64-67] The mechanism of primary alkyl radicals formation for type II photoinitiators is depicted in Scheme 13.

To the best of our knowledge, only two studies dealt with radical photopolymerization using type II photoinitiators. They were carried out by Pouliquen et al.,[62,63] who synthesized the photoinitiators given in Scheme 14. The photocross-linking of PDMS was performed by copolymerizing a monoacrylate (2-ethylhexyl acrylate) and a diacrylate (1,6-hexanediol diacrylate). By comparing the single molecules to the polymeric system, an increase in initiation efficiency was noticed for the polymer. This "macromolecular effect" was even greater when using a polysiloxane containing only

Scheme 15. Synthesis of Ozonide-Functionalized Polysiloxane



2-benzoyl-benzoic ester groups associated with free 4-dimethylaminobenzoic ester in a photosensitive composition (first photoinitiator in Scheme 14).

Photoinitiated polymerization has been only scarcely studied to obtain PDMS-containing copolymers. For instance, photopolymerization of acceptor−donor systems containing a PDMS backbone has never been investigated. Likely, recent developments in photoinitiator-free photopolymerization[68,69] could be easily adapted to the synthesis of novel photocurable compositions containing polysiloxane.

3.1.3. Ozonide Macroinitiators

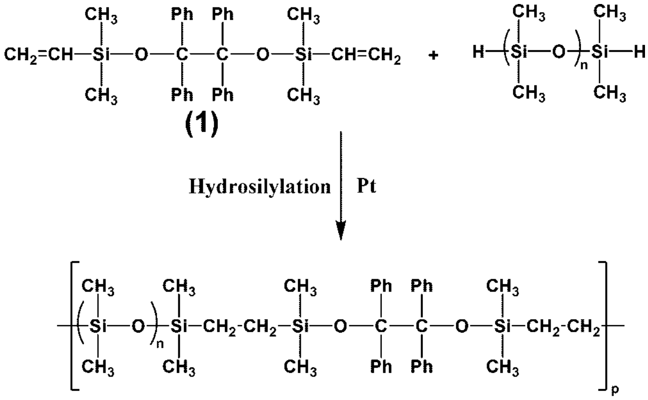
To our knowledge, the use of ozonide-functionalized polysiloxanes to prepare silicone/organic copolymers by radical polymerization is described in only one patent assigned to Dow Corning Corp.[70] The first step of the synthesis is the preparation of the ozonide-containing polysiloxane, accomplished by ozone bubbling through a solution of polysiloxane containing a reactive double bond. As an example, a 5-hexenyl-terminated polysiloxane was dissolved in dichloromethane at −15 °C and ozone was introduced at the bottom of the solution. The structure of the ozonide (Scheme 15) was confirmed by ^{13}C NMR. The second step consists of the radical polymerization of a vinyl monomer such as ethyl acrylate or acrylamide. The former monomer was polymerized at 70 °C for 1 h in the presence of the ozonide-terminated polysiloxane to obtain a poly(ethyl acrylate)-*b*-PDMS-*b*-poly(ethyl acrylate) triblock copolymer. Furthermore, the siloxane chain appeared to moderate the decomposition rate of the ozonide group: the ozonide obtained from 1-hexene with the same method as before was found to be quite unstable and rapidly decomposed through an uncontrolled exothermic reaction.

3.1.4. Bis-(silyl pinacolate) Macroinitiators

Bis(silyl benzopinacolate)s have been introduced as macroinitiators by Crivello et al.[71−77] through the hydrosilylation of the bis(dibenzylvinylsilyl)pinacolate with α,ω-hydride-terminated PDMS (Scheme 16).

The authors studied the kinetics of thermolysis of bis(silyl pinacolate), depending on the nature of the groups (phenyl or methyl) of the thermolyzable moiety. The cleavage between pinacolate groups creates two active radicals which initiate the radical polymerization of styrene,[73] methyl methacrylate (MMA),[73] and *tert*-butyl methacrylate.[77] Moreover, the absence of homopolymer was evidenced by chromatography.[72] The major drawback of this method is the formation, in the final copolymer, of Si−O−C bonds known to be prone to hydrolysis.[78,79]

Scheme 16. Synthesis of Benzopinacolate Macroinitiator by Hydrosilylation



3.1.5. Peroxycarbamate Macroinitiators

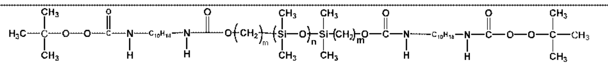
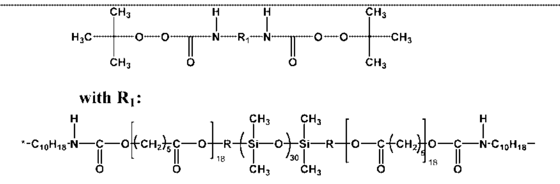
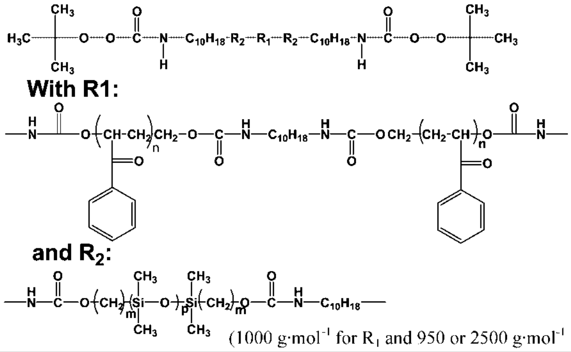
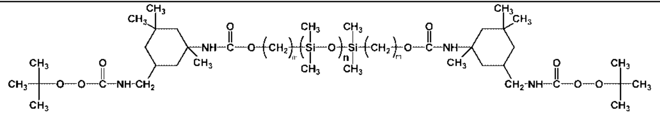
The two-step synthesis of peroxycarbamate-based macroinitiators consists of (i) the reaction of a diisocyanate with either a hydroxy-terminated PDMS or a hydroxy-terminated block copolymer containing a PDMS segment and (ii) the reaction of *tert*-butyl hydroperoxyde with the unreacted isocyanate chain ends (Scheme 10). The different structures reported in the literature are given in Table 1.

The first synthesis of PDMS-containing copolymers using peroxycarbamate macroinitiators has been performed by Baysal et al.[80,81] They polymerized styrene in bulk or in toluene solution at 80 °C for 5 days using a peroxycarbamate-terminated PDMS (Table 1, entry 1). A very high content of homopoly(styrene) was observed at low macroinitiator concentration. Unexpectedly, the polymerization yield decreased when the macroinitiator concentration increased; no explanation was given by the authors. The high content of homopoly(styrene) is essentially due to the presence of an active small radical created by the decomposition of the macroinitiator (i.e., *t*-Bu-O$^\bullet$). The same authors in another study[82,83] used similar peroxycarbamate macroinitiator **1** (Table 1) to prepare PMMA-*b*-PDMS-*b*-PMMA, poly(dibutyl itaconate)-*b*-PDMS-*b*-poly(dibutyl itaconate), poly(dicyclohexyl itaconate)-*b*-PDMS-*b*-poly(dicyclohexyl itaconate),[83] poly(monobutyl itaconate)-*b*-PDMS-*b*-poly(monobutyl itaconate), and poly(monocyclohexyl itaconate)-*b*-PDMS-*b*-poly(monocyclohexyl itaconate).[82] Since the authors could not achieve the synthesis of high molecular weight block copolymers, resulting materials exhibited poor mechanical and physical properties.

More recently, Taskiran[84] carried out the synthesis of PS-*b*-PDMS-*b*-PS copolymers to modify the properties of expandable PS. PDMS-filled expandable PS was synthesized using siloxane-containing peroxycarbamate macroinitiator **1** (Table 1) by suspension polymerization. The final products showed better thermal resistance and surface properties than the non-modified expandable PS.

Uyanik[85] prepared a five-block copolymer PVP-*b*-PCL-*b*-PDMS-*b*-PCL-*b*-PVP (PVP = poly(vinyl pyrrolidone) and PCL = poly(caprolactone)) using a telechelic peroxycarbamate macroinitiator composed of PCL and PDMS (Table 1, entry 2). This macroinitiator was prepared from a commercial PCL-*b*-PDMS-*b*-PCL triblock copolymer and using the synthesis procedure described by Baysal et al.[80] The resulting copolymers showed higher thermal resistance and increased toughness characteristics than the corresponding homopolymers.

Table 1. Peroxycarbamate Macroinitiators and Monomers Used to Prepare Hybrid Copolymers

Entry	Macroinitiator (molecular weight)	Synthesis method	Monomers	Refs
1	 (2500 g.mol^{-1})	1) Diol + diisocyanate 2) tBuOOH	Styrene, MMA, dibutyl itaconate, dicyclohexyl itaconate	80-84
2	 (2200 g.mol^{-1}) R is not defined	1) Diol + diisocyanate 2) tBuOOH	Vinyl pyrrolidone	85
3	 (1000 g·mol^{-1} for R$_1$ and 950 or 2500 g·mol^{-1} for R$_2$)	Multiple step procedure	Styrene, vinyl pyrrolidone	86
4	 (M$_n$≈2500 g.mol^{-1})	Two steps procedure	Vinyl pyrrolidone	87

Five block copolymers of acetophenone-formaldehyde resins (AFR), PDMS, and PVP or PS were synthesized by Uyanik et al.[86] They first prepared a triblock copolymer PDMS-*b*-AFR-*b*-PDMS which was functionalized by reaction of an excess of diisocyanate to the hydroxy chain ends of the central block followed by the reaction of the isocyanate-terminated central block with *tert*-butyl hydroperoxide to obtain a macro-peroxycarbamate initiator (Table 1, entry 3). The monomer (styrene or *N*-vinyl pyrrolidone) was polymerized using this macroinitiator. The authors showed that the solubility of the five-block copolymer is dominated by the middle resin block even though its block length is much smaller than those of the vinyl polymer blocks.

Uyanik et al.[87] also prepared poly(vinyl pyrrolidone)-*b*-PDMS-*b*-poly(vinyl pyrrolidone) triblock copolymers using the peroxycarbamate macroinitiator **4** (Table 1). These copolymers were characterized by differential scanning calorimetry (DSC) and stress−strain tests (see section 5 of this review).

In conclusion, the synthesis of peroxycarbamate macroinitiators is easy and relatively inexpensive. The main drawback of this method is the undesired formation of homopolymer concomitant to the copolymerization due to the presence of free *tert*-butoxy radicals.

3.1.6. Peroxyester Macroinitiators

Peroxyester PDMS macroinitiators were exclusively used by the Nippon Oils and Fats (NOF) Corp.[88−91] The authors prepared PDMS-containing block copolymers using peroxyester-terminated PDMS (Scheme 17).

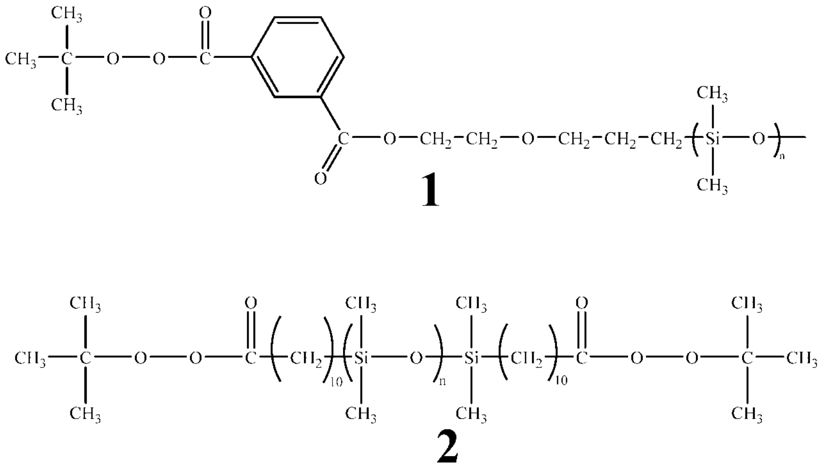
For instance, the polymerization of MMA initiated by a peroxyester-terminated PDMS (Scheme 17 structure **1**) resulted in the formation of a triblock copolymer which can be incorporated in a polyurethane resin to form water-repellent coatings.[91] Again, as for the peroxycarbamate macroinitiators presented in the previous section, *tert*-butoxy radicals resulting from the macroinitiator decomposition initiate the homopolymerization of the vinyl monomers to yield a mixture of homopolymers and copolymers.

3.1.7. Azo Macroinitiators

Azo-containing polymers are interesting materials for the synthesis of block and graft copolymers. These compounds were used in several studies to prepare new materials with enhanced properties.[92] The synthesis of azo macroinitiators based on PDMS is generally easy. Most often, it is accomplished by a condensation (esterification, amidification) or a hydrosilylation reaction between a functionalized azo precursor and a PDMS-containing reactive group (see section 2).

The first synthesis of siloxane-vinyl block copolymers using an azo macroinitiator of PDMS was reported in a Japanese patent.[93] Inoue et al. condensed 4,4′-azobiscyanopentanoyl chloride with α,ω-diaminopropyl PDMS to prepare an azo macroinitiator **1** (Table 2, entry 1, $m = 3$), which was used for the synthesis of triblock copolymers of poly(methyl methacrylate) (PMMA), poly(vinyl acetate), or polystyrene and PDMS.[42] The condensation reactions were

Scheme 17. Examples of Peroxyester-Terminated PDMS Used by the NOF Corporation[88,90,91]



found to proceed almost quantitatively. Depending on the desired properties, various types of polysiloxanes could be used: PDMS, poly(methyl-phenyl siloxane), or poly(methyl-3-trifluoropropyl siloxane). The authors found that the azo macroinitiators have a high polymerization activity, although somewhat lower than that of 2,2′-azobisisobutyronitrile (AIBN), as expected from previous results obtained with other polymeric azo macroinitiators.[94,95]

The reactivity of azo macroinitiator **2** (Table 2, entry 2, $m = 4$) was studied by Chang and co-workers in a series of articles[58,111-113] where block copolymers of PDMS and PMMA were prepared under UV[58,113] or thermal[112] initiations. In the case of thermal initiation, the macroinitiator decomposition followed an expected first-order reaction rate.[121] Decomposition rate constants of the macroinitiator were 4.5×10^{-5}, 12.5×10^{-5}, and 30.5×10^{-5} s^{-1} at 70, 78, and 85 °C, respectively. In the case of UV-initiated polymerization of MMA,[58,113] a higher polymerization rate was observed when using the macroinitiator compared to AIBN. The termination rate constant (k_t) in the MMA/PDMS photoinitiator system was smaller than in the equivalent MMA/AIBN system (4.5×10^7 versus 9.1×10^7 mol L^{-1} s^{-1}). The propagation rate constants k_p for the MMA/PDMS photoinitiator system and the MMA/AIBN system were, respectively, 495.2 and 445.8 L mol^{-1} s^{-1}.

Simionescu[107] prepared polystyrene, PMMA, poly(acrylonitrile), poly(butyl acrylate), or poly(butyl methacrylate)-silicone block copolymers in bulk and solution (toluene) using azo macroinitiator **2** (Table 2, entry 2, $m = 3$). As expected, increasing the monomer/azo group ratio resulted in an increase of molecular weights. PMMA-*b*-PDMS copolymers were also synthesized using azo macroinitiator **3** (Table 2, entry 3).[108] The influence of the polymerization temperature, macroinitiator molecular weight, composition of the initial mixture (vinyl/azo and vinyl/siloxane ratios), and initiator and monomer concentrations was studied. Due to the low content of azo-ester groups, the thermal decomposition of these azo macroinitiators **3** was not studied. However, their efficiency in radical polymerization of vinyl monomers was proved.[110,114]

The thermal decomposition of azo macroinitiator **2** (Table 2, entry 2, $m = 3$) in toluene solution was studied by measuring the decrease of the intrinsic viscosity vs time at 80 °C.[108] A plateau was reached after 7−8 h corresponding to the total decomposition of the azo macroinitiator. Decomposition rate constants k_d were found in the range from 8.1 to 9.8×10^{-5} s^{-1} and decreased with the PDMS chain length (between 1700 and 7100 g·mol^{-1}). These values are similar to those measured by nitrogen release titration for 4,4′-azobis(cyanopentanoic) acid (9.1×10^{-5} s^{-1}).[122] High conversion in solution polymerization demonstrated a higher efficiency with low-siloxane chain-length initiators (high azo molar content). Homo-PMMA was not formed with azo macroinitiator **3** (Table 2, entry 3), which was explained by the fact that *tert*-butyl radicals formed through decomposition of the azo initiator are very reactive and recombine immediately. However, we noticed that this explanation is not in agreement with the results of Fischer et al.[123-125] and Hammond et al.,[126] who established that $R_1 \gg R_t$ (R_1 and R_t, respectively, refer to the rate of the reaction tBu$^\bullet$ + MMA and of the coupling reaction tBu$^\bullet$ + tBu$^\bullet$).

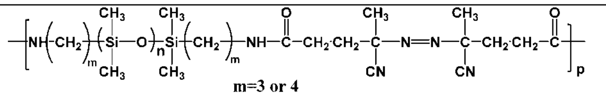
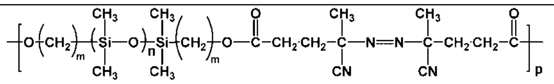
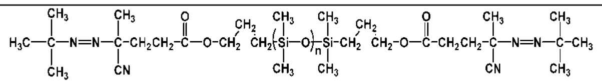
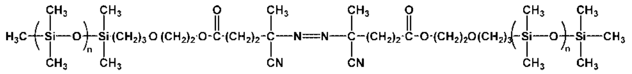
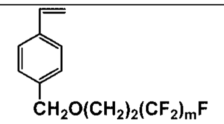
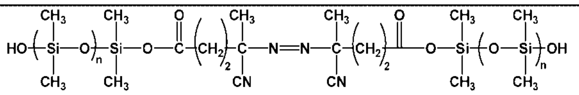
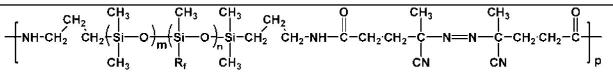
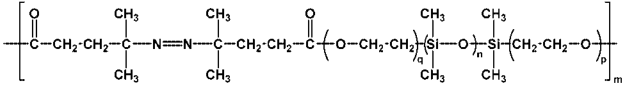
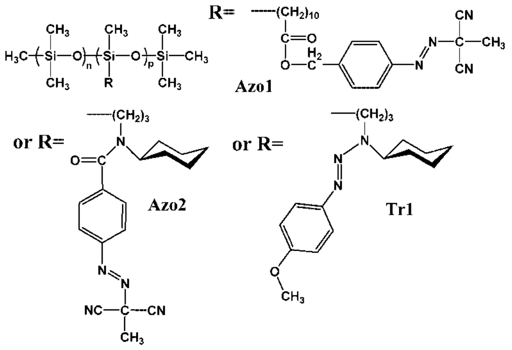
The azo macroinitiator **1** (Table 2, entry 1, $m = 3$) and the azo macroinitiator **2** (Table 2, entry 2, $m = 3$) were also used in different processes of polymerization: dispersion polymerization (organic media, supercritical CO_2 (scCO$_2$)), emulsion polymerization, and precipitation polymerization. PDMS-PMMA block copolymers using azo macroinitiator **1** were prepared by dispersion polymerization.[99] The azo macroinitiator acts as both a stabilizer and an initiator for the dispersion polymerization of MMA in a good solvent of PDMS, typically, *n*-heptane or cyclohexane, which have solubility parameters in the range of 7.4−8.2 cal$^{1/2}$ cm$^{-3/2}$, close to the solubility parameter of PDMS (around 7.3 cal$^{1/2}$ cm$^{-3/2}$).[127] The polymerization produced nanospheres with diameters in the range of 170−270 nm by controlling the concentration of the azo macroinitiator.

More recently, Okubo et al.[101] produced submicrometer PMMA particles by dispersion polymerization with azo macroinitiator **1** (Table 2, entry 1, $m = 3$) in scCO$_2$. The PDMS chains operated as a steric barrier. The number-average particle diameter measured by scanning electron microscopy (SEM) was 210 nm.

Noguchi et al.[106] prepared latexes by aqueous miniemulsion polymerization of azo macroinitiator **1** (Table 2, entry 1, m: unknown) and MMA, butyl acrylate (BuA), methacrylic acid (MAA), and hydroxyethyl methacrylate (HEMA) in water. The resulting copolymers were useful for coatings and as additives for paper, fibers, and films, which showed improved water repellency, weatherability, sliding property, and gas permeation.

Precipitation polymerization with azo macroinitiators **1** and **2** (Table 2, $m = 3$) in toluene was carried out by Szajdzinska-Pietek et al.[102] and Pinteala et al.[109] to prepare PMAA-*b*-PDMS copolymers. Pyrene was used as a fluorescent probe

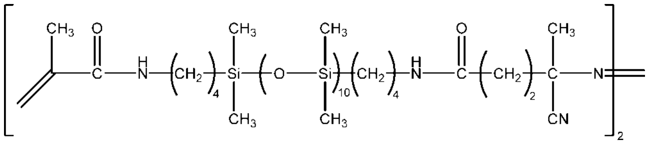
Table 2. Azo Macroinitiators and Monomers Used To Prepare Hybrid Copolymers

Entry	Azo macroinitiator (molecular weight)	Synthesis method	Monomers	Refs
1	 $\mathrm{\left[NH\left(CH_2\right)_m\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n\overset{CH_3}{\underset{CH_3}{Si}}\left(CH_2\right)_m-NH-\overset{O}{\overset{\Vert}{C}}-CH_2CH_2-\overset{CH_3}{\underset{CN}{C}}-N{=}N-\overset{CH_3}{\underset{CN}{C}}-CH_2CH_2-\overset{O}{\overset{\Vert}{C}}\right]_p}$ m=3 or 4 (M$_n$(PDMS blocks)=250, 770, 1050, 2100, 4000, 5000, 10000 g.mol^{-1})	Amidification	MMA, VAc, Styrene, butadiene, vinyl chloride, BuA, MAA, HEMA	42,93,96-106
2	 $\mathrm{\left[O\left(CH_2\right)_m\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n\overset{CH_3}{\underset{CH_3}{Si}}\left(CH_2\right)_m-O-\overset{O}{\overset{\Vert}{C}}-CH_2{\cdot}CH_2-\overset{CH_3}{\underset{CN}{C}}-N{=}N-\overset{CH_3}{\underset{CN}{C}}-CH_2{\cdot}CH_2-\overset{O}{\overset{\Vert}{C}}\right]_p}$ m=3 or 4 (M$_n$(PDMS)=1700, 4100, 5700, 7000, 7100 g.mol^{-1})	Esterification	Styrene, AN, MMA, BuA, BuMA, MAA, NVP	58,107-113
3	 (M$_n$(PDMS)= 3800, 6400, 10500 g.mol^{-1})	Esterification	Styrene, MMA, BuMA, BuA	108,114
4	 $\mathrm{H_3C\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n\overset{CH_3}{\underset{CH_3}{Si}}(CH_2)_3O(CH_2)_2O-\overset{O}{\overset{\Vert}{C}}-(CH_2)_2-\overset{CH_3}{\underset{CN}{C}}-N{=}N-\overset{CH_3}{\underset{CN}{C}}-(CH_2)_2-\overset{O}{\overset{\Vert}{C}}-O-(CH_2)_2O(CH_2)_3\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n\overset{CH_3}{\underset{CH_3}{Si}}-CH_3}$ (M$_n$(PDMS)=1000 g.mol^{-1})	Esterification	 m=6 or m=8	115
5	 $\mathrm{HO\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n\overset{CH_3}{\underset{CH_3}{Si}}-O-\overset{O}{\overset{\Vert}{C}}\left(CH_2\right)_2\overset{CH_3}{\underset{CN}{C}}-N{=}N-\overset{CH_3}{\underset{CN}{C}}\left(CH_2\right)_2\overset{O}{\overset{\Vert}{C}}-O-\overset{CH_3}{\underset{CH_3}{Si}}\left(O-\overset{CH_3}{\underset{CH_3}{Si}}\right)_nOH}$ (M$_n$(PDMS)= 500 g.mol^{-1})	Esterification	Styrene, MMA	116
6	 R$_f$= $\mathrm{CH_2CH_2CF_3}$ m=0, n=14 R$_f$= $\mathrm{CH_2CH_2(CF_2)_5CF_3}$ m=59, n=9 R$_f$= $\mathrm{CH_2CH_2(CF_2)_7CF_3}$ m=49, n=9 (M$_n$(PDMS)= 9800 g.mol^{-1}) 3,3,3-trifluoropropyl (TFP), tridecafluoro-1,1,2,2-tetrahydrooctyl (TFO) and heptadecafluoro-1,1,2,2-tetrahydrodecyl (HFD)	Amidification	MMA	117
7	 $\mathrm{\left[\overset{O}{\overset{\Vert}{C}}-CH_2{\cdot}CH_2-\overset{CH_3}{\underset{CH_3}{C}}-N{=}N-\overset{CH_3}{\underset{CH_3}{C}}-CH_2{\cdot}CH_2-\overset{O}{\overset{\Vert}{C}}\left(O-CH_2{\cdot}CH_2\right)_q\left(\overset{CH_3}{\underset{CH_3}{Si}}-O\right)_n\overset{CH_3}{\underset{CH_3}{Si}}\left(CH_2{\cdot}CH_2-O\right)_p\right]_m}$ (M$_n$(PDMS)=12000 g.mol^{-1})	Esterification	Styrene	118
8		**Azo1**: Hydrosilylation **Azo2**: amidification **Tr1:** electrophilic substitution	MMA, BuMA, Styrene	119,120

to study the conformational changes of this block copolymer in aqueous solutions (see section 5).

PB-*g*-PDMS and PDMS-*b*-PS were synthesized in bulk using azo macroinitiators **1** (Table 2, entry 1, $m = 4$).[103,104] In the case of the PB-*g*-PDMS, the reaction proceeds by radical addition to pendent vinyl groups of poly(butadiene) (PB) chains. It was observed that an increase in macroinitiator concentration up to 52% w/w in the PB solution resulted in a cross-linked graft copolymer. Molecular weights of soluble graft copolymers were between 450 000 and 600 000 g·mol^{-1}. In both PB-*g*-PDMS and PDMS-*b*-PS cases, the molecular weights increased when the macroinitiator con-

Scheme 18. Structure of the Macromonomeric Initiator (macroinimer) Used by Hamurcu[104]



centration decreased. Hamurcu[104] also carried out the cross-linking of PS using a macroinimer, the structure of which is given in Scheme 18.

Azo macroinitiator **1** (Table 2, entry 1, $m = 3$) was also used to synthesize poly(vinyl chloride) (PVC)/PDMS block copolymers[105] containing only 4.5% of PDMS. The material obtained showed better processability properties than pure PVC and exhibited a contact angle of 100° instead of 85° in the case of pure PVC.

The synthesis of styrene-, MMA-, butyl methacrylate (BuMA)-, and BuA-containing block copolymers was performed in toluene using azo macroinitiator **3** (Table 2, entry 3).[114] By size exclusion chromatography (SEC) analysis and careful extraction of unreacted azo macroinitiator, it was shown that the obtained block copolymers are of ABA type when polymerizing MMA (due to the termination by disproportionation)[128] and of multiblock copolymers $(AB)_n$ type when styrene was polymerized (due to the termination by recombination).[128,129]

More recently, Bertolucci et al.[115] carried out the synthesis of PDMS-*b*-poly(semifluorinated styrene)-*b*-PDMS in trifluorotoluene using the azo macroinitiator **4** (Table 2, entry 4). A triblock copolymer was formed showing that the termination occurred by recombination. Even for short PDMS chains ($n = 8$), the authors observed a thermotropic mesophase which was attributed to the self-assembly of fluorinated segments in microphase-separated domains.

Azo macroinitiator **5** (Table 2, entry 5) was synthesized by a condensation reaction between an α,ω-hydroxy-PDMS and 4,4′-azobis(4-cyanopentanoyl chloride) with an excess of PDMS.[116] It was used to prepare block copolymers with styrene and MMA in a mixture of methyl ethyl ketone/dichloromethane. The major drawback of such an azo macroinitiator is the sensitivity of the Si−O−C linkage toward hydrolysis.[78,79]

In 1990, Inoue's team published a study[117] on the preparation of fluoroalkylsilicone-poly(methyl methacrylate) block copolymers and their PMMA blends using the azo macroinitiator **6** (Table 2, entry 6). The fluoroalkyl silicone contained three kinds of fluoroalkyl side chains: 3,3,3-trifluoropropyl (TFP), tridecafluoro-1,1,2,2-tetrahydrooctyl (TFO), and heptadecafluoro-1,1,2,2-tetrahydrodecyl (HFD) groups. The formation of triblock copolymers containing PMMA and fluoroalkylsilicone was observed. The results concerning the surface properties of this triblock copolymer are detailed in the section dedicated to the copolymer properties (section 5).

In a Japanese patent of Wako Pure Chemicals Industries,[118] Shiraki described the synthesis of polyorganosiloxane-polyoxyalkylene block copolymers azo macroinitiators. For instance, an azo macroinitiator was manufactured by esterification of α,ω-bis(polyoxyethylene)-polydimethylsiloxane with 4,4′-azobis(4-cyanopentanoic acid) (Table 2, entry 7). Then, this azo macroinitiator was reacted with styrene in toluene to obtain a multiblock copolymer containing PEO, PDMS, and PS.

Kollefrath and co-workers[119,120] used azo- and triazene-modified polysiloxanes (Table 2, entry 8) as macroinitiators for graft copolymerization with MMA, BuMA, and styrene. **Azo1** and **Azo2** showed similar thermal behaviors as AIBN. Two different radicals are formed: an aryl radical connected to the polymer backbone which acts as the initiator and a 1,1-dicyanoethyl radical which is known to be very stable and unable to promote initiation of free radical polymerization.[130] With **Azo1** and **Azo2**, the polymerizations were performed at 80 °C, giving high monomer conversion. Nevertheless, the authors also observed the presence of unreacted PDMS macroinitiator which could be separated by precipitation. With **Tr1**, yields were below 50% and additional degradations of the PDMS backbone were observed at 95 °C.

To conclude this section, the polymerization initiated by azo macroinitiators is a convenient way to obtain both graft and block copolymers. The major drawback of azo macroinitiators is their low initiation efficiency (30−40%). Hence, the resulting structures are not well controlled, and their compositions present various proportions of diblock, triblock, and multiblock copolymers as well as homoPDMS and homopoly(vinyl monomer). Azo macroinitiators recently appeared to be of great interest in controlled radical polymerization. For example, they could be coupled with a control agent such as $Co(Acac)_2$ for controlling the polymerization of VAc as published by Jerôme et al.,[131] a cobalt−porphyrin complex developed by Wayland et al. to control the polymerization of acrylates,[132–134] an organostibine compound developed by Yamago et al.[135–137] to control a wide variety of monomers, or molecular iodine I_2 to perform reverse iodine-transfer polymerization (RITP) developed by Lacroix-Desmazes et al.[138–143] (see section 4).

3.2. Polysiloxane Macromonomers

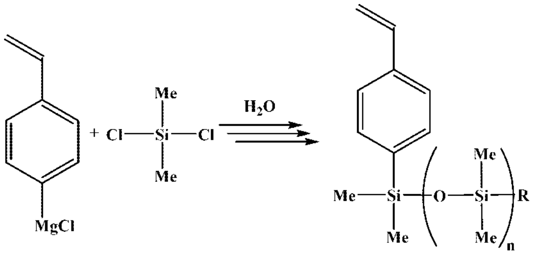
In the field of copolymerization, macromonomers represent an important class of precursors. They are composed of a macromolecular chain that bears a polymerizable group at one chain end. Thanks to this functionality, they are able to copolymerize with common vinylic monomers to generate graft copolymers via a "grafting through" mechanism. The key points of this strategy are the synthesis of the macromonomers and their reactivity.

3.2.1. Synthesis of Polysiloxane Macromonomers and Copolymerization

Some synthesis pathways to silicone macromonomers bearing usual polymerizable functions such as (meth)acrylic and styrenic groups were reported a long time ago. To our knowledge, the first synthesis of a styrene-based silicone macromonomer was described in the early 1960s.[144] The reaction of a Grignard reagent (*p*-vinylphenylmagnesium chloride) with dimethyldichlorosilane followed by hydrolysis led to a silane macromonomer. This macromonomer was condensed with α,ω-dichloropolysiloxane, which enabled Greber et al. to prepare polysiloxane macromonomers with various chain lengths (Scheme 19).

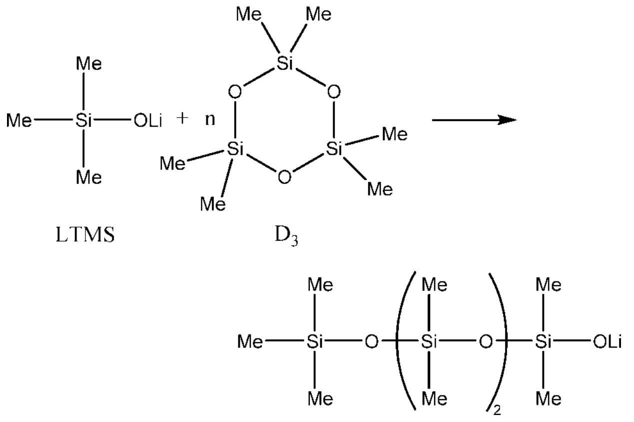
The same styrenic chlorosilane was later used by Kawakami et al.[145] to prepare polydimethylsiloxane styrenic macromonomers. Instead of a chain elongation by silane condensation, they first polymerized D_3 starting from lithium trimethylsilanolate (LTMS) (Scheme 20). Then, this living polydimethylsiloxane was end-capped with the styrenic

Scheme 19. Silane and Polysiloxane Macromonomers Synthesized by Greber et al.[144]



n=1, R = Cl as product
n=1, R = OH as hydrolyzed product (2nd step)
n=2 to 50 as polysiloxane macromer

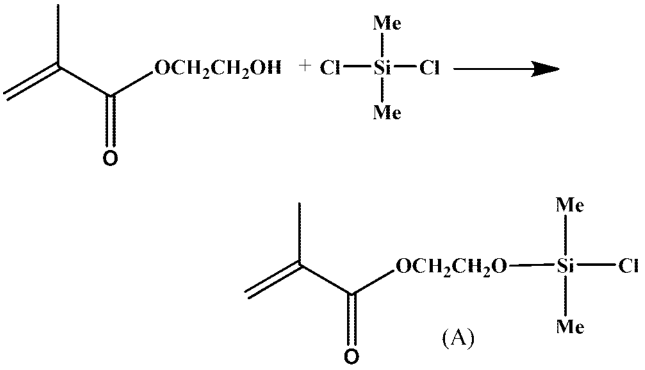
Scheme 20. Preparation of a Living Polydimethylsiloxane by Kawakami et al.[145]



chlorosilane to lead to the suitable polysiloxane macromonomer. They also used a methacrylated chlorosilane prepared by hydrosilylation of **I** and **II** by dimethylchlorosilane (Scheme 21).[145] It is worth noting that hydrosilylation yields were, respectively, 27% and 75%.

The styrenic polysiloxane macromonomer (M_n = 3000 g·mol^{-1}) was involved in a copolymerization with styrene to prepare a grafted copolymer.[145] The initial proportions were 15.8 wt % of macromonomer and 84.2 wt % of styrene. The resulting copolymer ($M_n \approx$ 40 000 g·mol^{-1}) was grafted with 15 wt % of siloxane component, indicating a similar reactivity between the styrenic macromonomer and styrene. They also copolymerized methacrylate siloxane macromonomer, issued from a polysiloxane end capped by **I′** (see Scheme 21) (M_n = 5200 g·mol^{-1}, 21.1 wt %) with MMA (78.9 wt %). The resulting copolymer (M_n = 32 000 g·mol^{-1}) was grafted with 21 wt % of siloxane, indicating a similar reactivity between the methacrylate macromonomer and MMA.

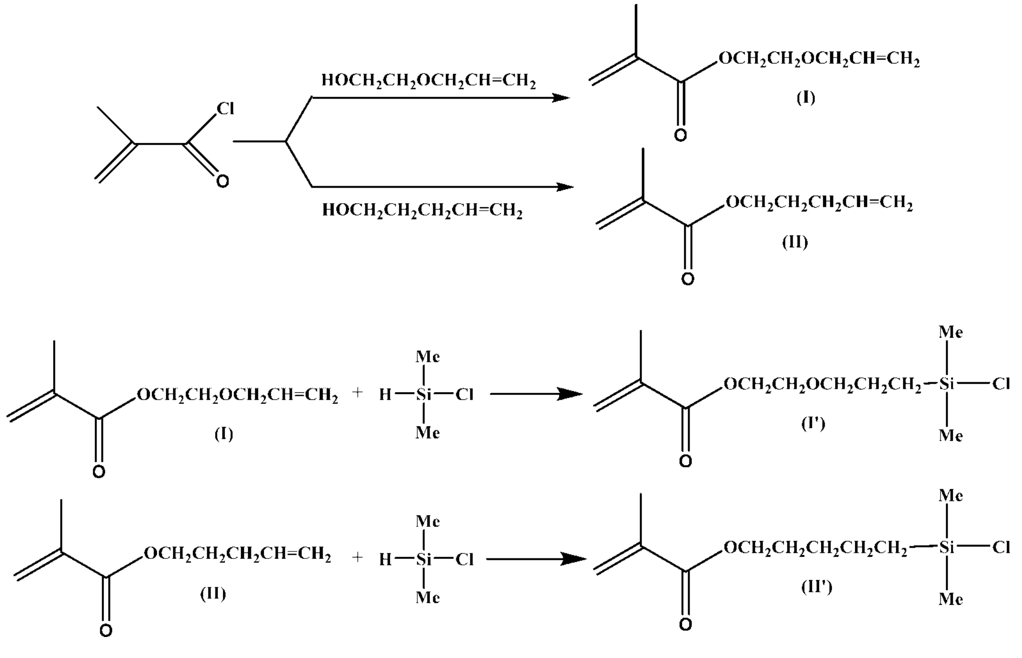
Scheme 22. Synthesis of a Methacrylate Chlorosilane for End Capping



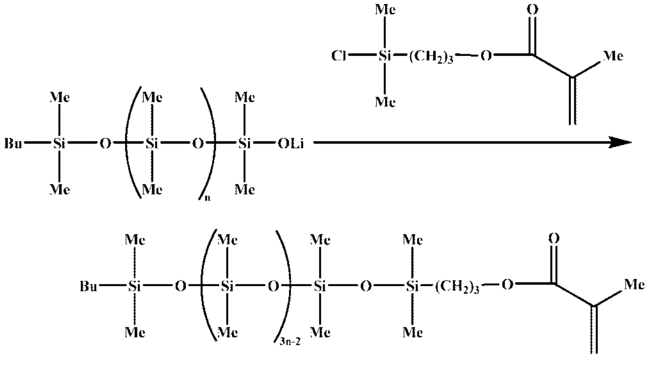
Kawakami et al.[146] thus developed one of the first methods to prepare methacrylic polysiloxane macromonomers (Scheme 21). Both styrenic and methacrylic terminating agents led to macromonomers with a narrow molecular weight distribution ($M_w/M_n \leq$ 1.14) and hydrosilylation yield close to 100%. It is worth noting that the end capping with A (Scheme 22) led to a macromonomer with a functionality of 0.38. According to the authors, this low value should be attributed to the weakness of the C−O−Si bond, which is believed to cleave during the synthesis.

Considering the initiation step of D$_3$ by an organolithium reagent, DeSimone et al.[147] pointed out that it is better to control the first addition step of the reaction in a nonpolar solvent such as cyclohexane. In this manner, the obtained siloxanolate−lithium pair is not easily separated. The actual polymerization begins when a polar solvent, such as THF,

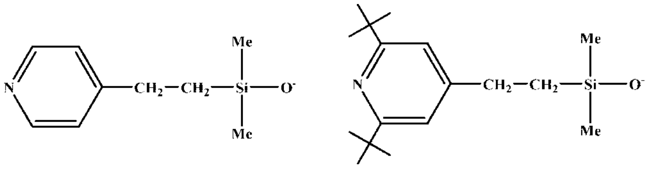
Scheme 21. Synthesis of Macromonomers by Kawakami et al.[146]



Scheme 23. Termination of D_3 Polymerization with 3-Methacryloyloxypropyldimethylchlorosilane



Scheme 24. Pyridyl Derivative Silanolate Anion for the Initiation of D_3 Polymerization



(I) (II)

is added. Hence, polymers of high and relatively well controlled molecular weight are obtained.

Later, 3-methacryloyloxypropyldimethylchlorosilane became commercially available, and it is nowadays preferred as a terminating agent in ROP (Scheme 23).[147]

Aoyagi et al.[148] prepared novel initiators by starting the polymerization of D_3 with the 2-(4-pyridyl ethyl) or 2-(2,6-di-*tert*-butyl-4-pyridyl)ethyl silanolate anion (Scheme 24). After the polymerization, addition of methacryloxypropyldimethylchlorosilane led to the corresponding functionalized macromonomers. The copolymerization of these macromonomers with MMA or BMA conferred to the obtained materials an enhanced gas permeability thanks to the pyridyl groups.

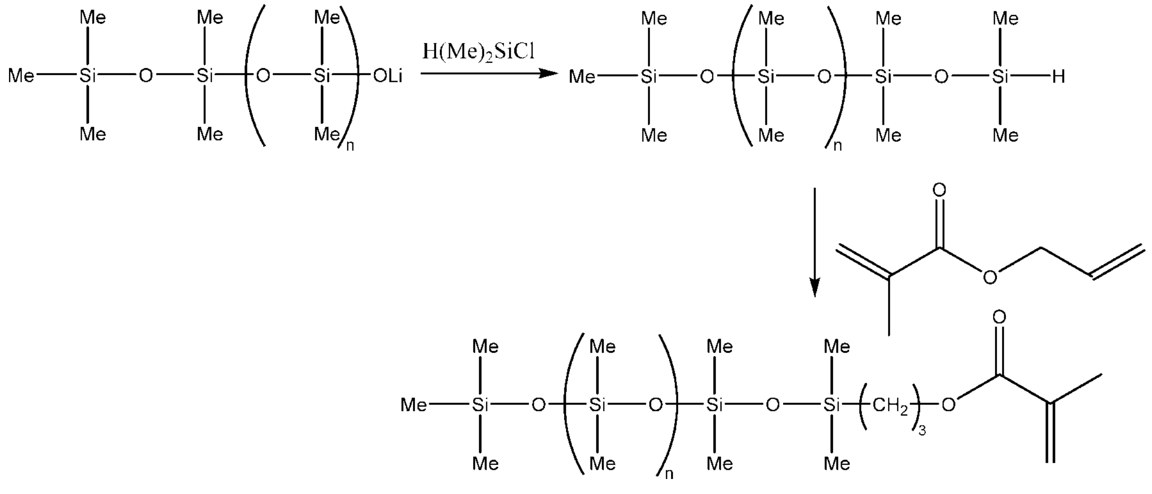
Another way to obtain methacrylic polysiloxane macromonomer is to terminate the polymerization of D_3 with chlorodimethylhydrogenosilane and then to run the hydrosilylation of allyl methacrylate onto this hydride-terminated polysiloxane (Scheme 25).[149] This synthetic pathway is close to the one developed by Kawakami et al.[145,146] except that hydrosilylation is carried out after termination. Nevertheless, the authors concluded that this method leads to an unsatisfactory functionality of the macromonomer (less than unity).

Lastly, vinyl polysiloxane macromonomers were also synthesized by termination with chlorodimethylvinylsilane (Scheme 26).[150–152] Here, the vinylsilane group was used afterward as a polymerizable function. For instance, Maynard et al.[152] copolymerized this macromonomer with VAc to reach a PVAc-*g*-PDMS copolymer (M_n = 94 800 g·mol^{-1}) with an average of three PDMS branches per chain. The final content of PDMS in the copolymer was less than expected whatever the initial feed in macromonomer. According to the authors, this low incorporation is due to a segregation effect during copolymerization. This conclusion is in agreement with previous observations by Tezuka et al.[150]

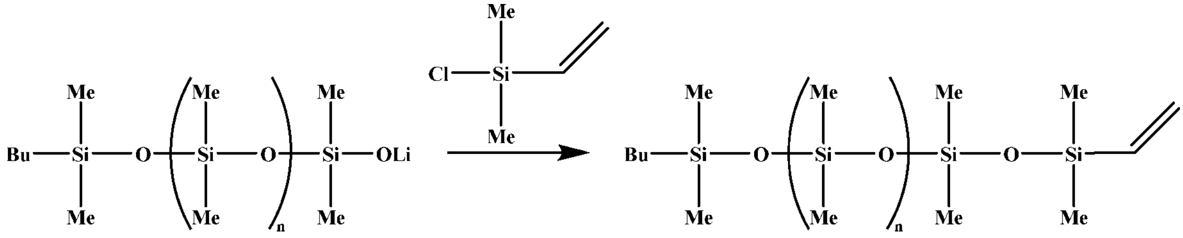
3.2.2. Multifunctional Macromonomers

Different ways to obtain multifunctional polysiloxane macromonomers were developed depending on the targeted application. Yu et al.[153] modified an amino-terminated polysiloxane with isocyanatoethyl methacrylate (IEM). The urea linkage formed in the macromonomer backbone made it more soluble in polar reactive diluents used in the study described hereafter. This technique of preparation was not really attractive until recently, when aminopolysiloxanes with suitable purity allowed reinvestigating this subject.[154] Its reaction with *m*-isopropenyl-α,α-dimethyl benzyl isocyanate

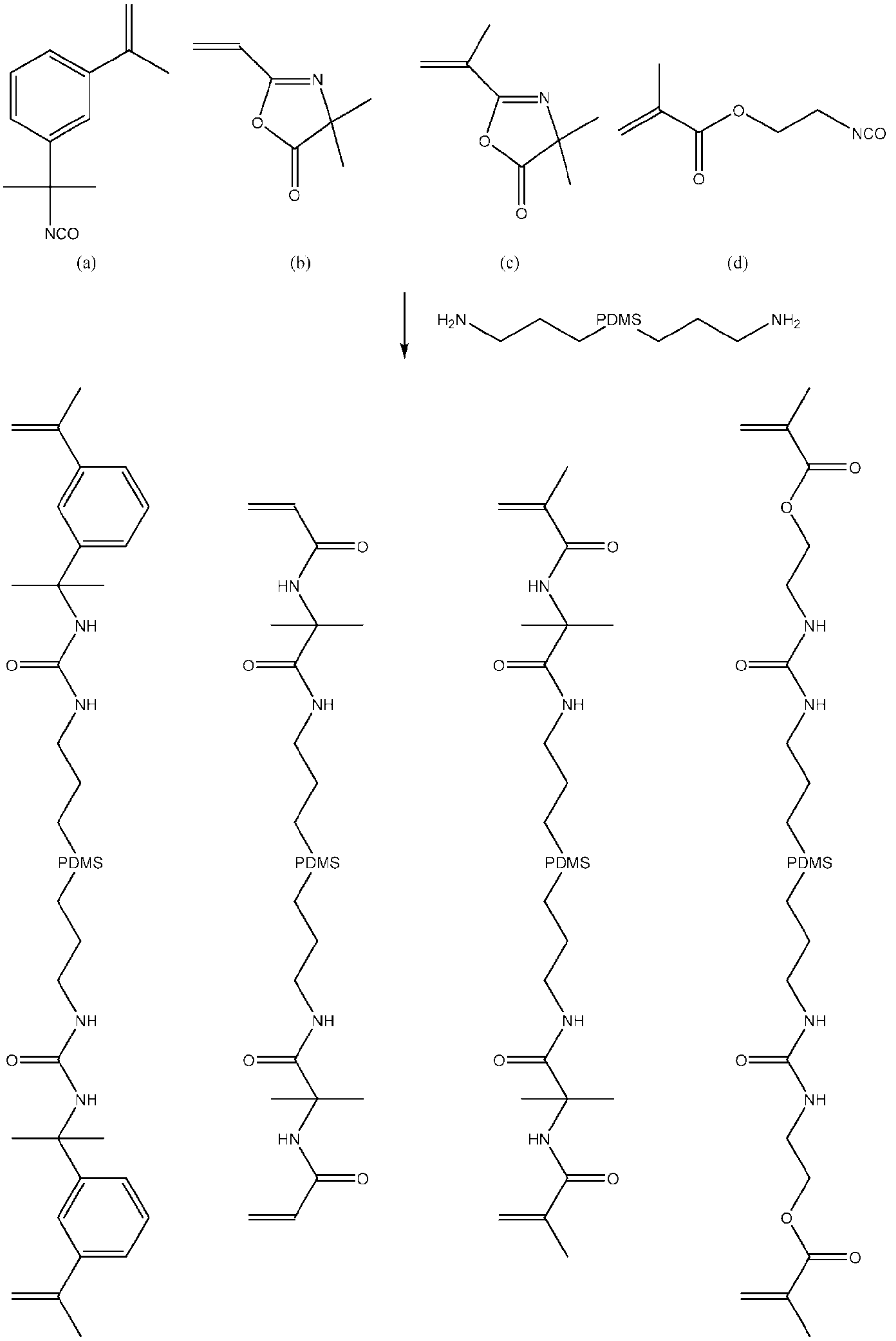
Scheme 25. Methacrylate Polysiloxane Macromonomer Synthesis by Cameron et al.[149]



Scheme 26. Termination of a Silanolate Polymers with Chlorodimethylvinylsilane



Scheme 27. Structures of (a) m-TMI, (b) VDMAz, (c) IDMAz, and (d) IEM and Their Corresponding Macromonomers after Reaction with an Amino-Terminated Polydimethylsiloxane

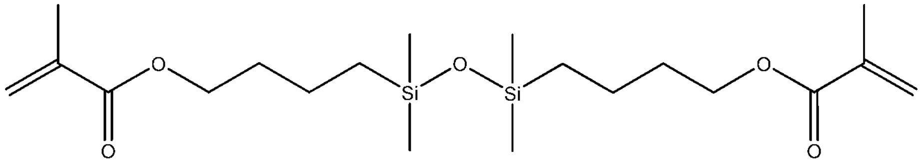


(*m*-TMI), vinyldimethyl-azlactone (VDMAz), isopropenyl dimethyl azlactone (IDMAz), or isocyanatoethylmethacrylate (IEM) (Scheme 27) led to the corresponding macromonomers with styrenic, acrylamide, methacrylamide, or methacrylate functions, respectively.

In order to obtain cross-linked materials, Tenhu and Heino[155] and later O'Shea and George[156,157] copolymerized α,ω-methacrylate-terminated polysiloxane with styrene. The macromonomer was obtained by hydrosilylation of allyl methacrylate on hydride-terminated polydimethylsiloxane. The first team showed that the degree of cross-linking was a function of the macromonomer's content. The second team showed that cross-linking was only possible as long as the macromonomer chain length was not too high (3700 g·mol^{-1}) and that homopolymerization of the macromonomers occurred during the formation of the network. However, more surprisingly, they also demonstrated that when the PDMS chain was longer ($M_n \approx 21\,000$ g·mol^{-1}) neither cross-linking nor homopolymerization of the macromonomer was taking place. This result was consistent with the finding that, on average, only one methacrylate group per macromonomer chain reacted, which was attributed to a shielding of the reactive group due to the adopted coil conformation of the macromonomer.

Künzler and Ozark[158] also prepared α,ω-methacrylate-terminated polysiloxane by redistribution of **III** with D_4 and 2,4,6,8-tetramethylcyclotetrasiloxane (D_4^H) (Scheme 28). This macromonomer was hydrosilylated with fluorinated allylic compounds to yield fluorinated siloxane macromonomers. Methacrylate functions were used to cross-link the

Scheme 28. Methacrylate Siloxane Involved in a Redistribution with D_4 and D_4^H



(III)

material using UV cure during the macromonomer copolymerization with hydrophilic dimethylacrylamide or *N*-vinyl pyrrolidone to prepare hydrogels with water content ranging from 18 to 44 wt % and high oxygen permeability. Fluorinated groups were introduced in order to get a better resistance to lipid, but it turned out that the CF_2H terminal group improved the solubility of the siloxane in polar solvents and in hydrophilic monomers. The properties of the resulting film are discussed in the final section of this review (section 5).

Thanks to the initiator method, Suzuki et al. prepared PDMS bearing both ethynylene and polymerizable functionalities[159] or both alkenyl and methacrylate groups.[160,161] The last one was prepared by polymerization of D_3 initiated by a vinylsilanol activated by BuLi. The reaction of the resulting product with a methacrylic chlorosilane gave the desired macromonomer. After its copolymerization with styrene or MMA, the alkenyl function enabled the authors to cross-link the obtained copolymer thanks to hydrosilylation or via photoactivated thiol−ene reaction. The sequential aspect of this preparation renders it particularly elegant and attractive for applications like photolithography.

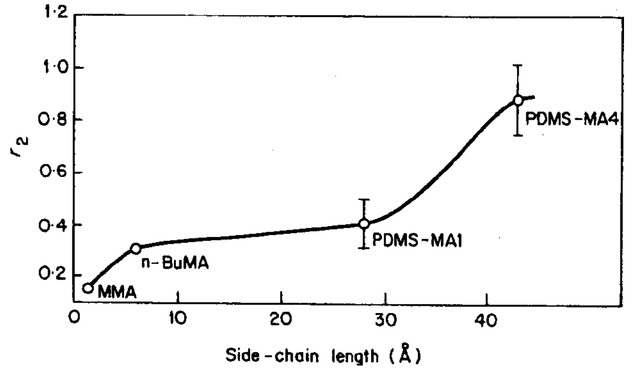
Another UV-cured cross-linked system with acrylate-terminated polysiloxane and various reactive diluents (ethyl methylacrylate (EMA), 2-hydroxyethylmethacrylate (HEMA), butyl acrylate (BA), acrylic acid (AA), and 4-vinylpyridine (4 VP)) was studied.[153] Here, the functionalized polysiloxane acts as the cross-linker. An increase in the reactive diluent quantity decreased the cross-link density, whereas elongation at break, Young's modulus, and ultimate tensile strength increased. Moreover, the reactive diluents were classified according to the increase of the dynamic and tensile moduli they generated (4 VP > HEMA > BA-AA > EMA > BA). Mazurek et al.[154] thoroughly described synthesis, morphologies, and mechanical properties of silicone bearing various terminal functions such as methacrylate, styrene, acrylamide, or methacrylamide copolymerized with various acrylate monomers by UV cure and led to similar conclusions as Yu et al.[153]

To sum up the macromonomer issue, it can be seen from this overview that silicone macromonomers with various functionalities have been available for a long time. It emerges that siloxane macromonomers are essentially obtained thanks to D_3 ROP to reach monofunctional macromonomers. Besides, bifunctional macromonomers obtained by a simple one-step method allow preparing cross-linked polymeric materials. Both mono- and bifunctionalized PDMS are more and more extensively used thanks to their commercial availability.[162]

3.2.3. Macromonomers Reactivity in Copolymerization

In general, the copolymerization parameters of a monomer and a macromonomer, r_1 and r_2, are assumed to be close when bearing a similar polymerizable group. This was the conclusion of Greber et al.,[144] who determined in the copolymerization of styrenic macromonomers (Scheme 19) with styrene reactivity ratios $r_1 \approx r_2 \approx 1$ using the Mayo−Lewis method.[163] Kawakami et al.[145] also estimated that the reactivity ratios of both styrenic and methacrylic macromonomers were quite the same as those of the corresponding monomers but without measuring them accurately.

Scheme 29. Values of r_2 vs Length of the Side Chain for the Copolymerization of AN (M_2) with Various Methacrylates[a]



[a] M_1: MMA, BuMA, or methacrylic polysiloxane macromonomers PDMS-MA1 500 g mol^{-1} and PDMS-MA4 1110 g mol^{-1}. Reprinted with permission from ref 166. Copyright 1966 Elsevier Ltd.

Cameron and Chisholm[149] determined the ratios r_1 and r_2 for the copolymerization of methacrylic polysiloxane macromonomers (M_1) with styrene (M_2). Despite the use of two different methods to reach these coefficients (Fineman−Ross[164] and Kelen−Tudos[165]), experimental errors prevented them from any meaningful values for macromonomer ratio r_1. Nevertheless, a tendency was drawn: the value of r_2 increases (from 1.06 to 1.55) as the molecular weight of the macromonomer increases (from about 500 to 10 000 g·mol^{-1}). According to the authors, this behavior is due to steric effects. In another study,[166] under similar conditions except that the comonomer was acrylonitrile (AN), the authors reached the same conclusion as illustrated in Scheme 29.

DeSimone et al.[147,167,168] compared the copolymerization of methacrylic polysiloxane macromonomer with MMA by different polymerization processes: free radical, group transfer (GTP), and anionic polymerizations. They determined that the molecular weight distributions were logically narrower in GTP and anionic polymerization than in free radical polymerization. In addition, they nicely obtained the chemical composition distribution (CCD) using supercritical fluid fractionation (SCFE) in supercritical chlorodifluoromethane, which is far less laborious and time consuming than other techniques such as solvent demixing fractionation[169] or reversed-phase high-performance liquid chromatography.[170] It appeared that CCD is much narrower in GTP and anionic polymerization than in free radical polymerization.

Vinylsilane has been previously considered as a radically polymerizable monomer, although it rather behaves like a transfer agent as discussed later in this review (section 3.3.1). Nevertheless, it is worth mentioning in this part that vinylsilane-terminated silicone macromonomers were found to copolymerize with VAc, to our knowledge the only monomer depicted in the literature able to copolymerize with vinyl silane.[150–152] Vinylsilanes otherwise do not homopolymerize but only form oligomers, which may be ascribed to the alpha silyl radical being too stable, i.e., unreactive toward the propagation step, thus only promoting transfer and/or termination reactions. Considering macromonomers, their low reactivity was additionally attributed to a macrophase separation during the polymerization process, since increasing the macromonomers feed did not generate chains with a higher graft density.

3.3. Polysiloxane Macrotransfer Agents

3.3.1. Transfer to PDMS

Radicals are known to react onto the methyl of the PDMS backbone (by hydrogen abstraction) from which polymerization can occur. Nevertheless, preparing copolymers this way is extremely challenging since the silylmethyl radicals thus formed can also recombine to yield a cross-linked material. Therefore, the resulting architectures are typically not well-defined copolymers but either grafted cross-linked silicone, when using common bulk and solution processes, or core–shell particles, when using a seeded emulsion polymerization process.

Two main radical generator families are generally quoted in the literature. “Nonvinyl-specific radical generators” produce radicals onto a PDMS backbone, without the need for any reactive functions, to cross-link the materials. The most famous nonvinyl-specific vulcanizing agent is benzoyl peroxide. “Vinyl-specific radical generators”, such as di-*tert*-butyl peroxide, normally only react on PDMS functionalized with vinyl functions. Depending on the authors, this latter peroxide can proceed in different ways: either it is unable to generate a radical on a permethyl PDMS backbone[171,172] or it generates a silylmethyl radical on a permethyl PDMS backbone, which however very quickly recombines with radicals derived from di-*tert*-butyl peroxide decomposition.[173–175] Whatever the type of radical generator used, PDMS cross-linking is induced by the reaction of radicals generated on the backbone of the silicone polymer, via a vinyl group or a methyl group, yielding interchain links, respectively composed of 3 or 2 methylene groups.

Apart from this vulcanization process, it was shown recently that it is possible to use these generated radicals for copolymer synthesis thanks to a “grafting from” method. Vinylic siloxanes, cyclosiloxanes, or polysiloxanes exposed to a radical generator generally only lead to the formation of a dimer or more hardly to a trimer; we thus considered these vinyl-functionalized molecules as transfer agents rather than (co)polymerizable entities as often quoted in the literature. Some reports dealt with the radical copolymerization of vinylic monomers in the presence of vinyl-functionalized polysiloxane, but none of them focused on the characterization of the resulting copolymers. For example, toughened thermoplastics such as PMMA or PS were synthesized by polymerization initiated by radicals generated on the vinyl functions of PDMS.[176] Dong et al.[177] prepared PS-modified silicone elastomers in a similar manner. In a first step, a vinyl containing hydroxyl-terminated polysiloxane was first reacted with styrene and benzoyl peroxide, and in a second step, cross-linking of the PDMS phase proceeded thanks to a trialkoxysilane. Using extraction techniques, the authors showed experimentally that soluble fractions were less important than the theoretical ones. They noticed that either formation of PDMS-*g*-PS during the first step of styrene polymerization could occur or PS could be so entangled in the PDMS network that it could not be extracted. Analyses only focused on the final cured blends, so that no information is available on the copolymer structures formed during the first stage of the protocol. Indeed, whereas abstraction of hydrogen on vinyl-PDMS is possible, it has not been extensively studied in bulk or in solvent media. As in the case of transfer to nonvinylic polysiloxane, this may be due to the difficulty encountered to control the resulting material architecture.

A series of patents from the same assignee described first the polymerization from a radical generated on a PDMS backbone and the generation of cross-linked materials from hydroxyl groups of the polydimethylsiloxane. Actually, as described in the examples, hydroxy-terminated PDMS was mixed with di-*tert*-butyl peroxide and various monomers such as styrene, butyl acrylate, or acrylonitrile. Afterward, the mixture was heated to lead to the corresponding grafted copolymers prior to cross-linking thanks to trichlorosilane or tri- or tetra-alkoxysilane and so forth.[178,179] This was done in solvent media[180] to obtain coatings by casting, in bulk in a reactor,[181,182] or in extruders[183] to give materials. A surprising fact is the use of di-*tert*-butyl peroxide, a “vinyl-specific radical generator”, which is claimed to be preferred to benzoyl peroxide; the latter however falls in the scope of the invention. Enhanced mechanical properties such as tensile strength, elongation, and hardness were claimed, and coatings were more abrasion resistant. Thanks to this method, thixotropic polymers such as poly(dimethylsiloxane)-*g*-poly(methacrylic acid) were also obtained.[184,185]

To sum up this part, transfer to PDMS was not an intensive field of research following the early studies on that topic in the 1970s, undoubtedly because of the difficulty to control polymerization reactions especially with nonfunctionalized PDMS. This process however remains attractive in the latex field thanks to the ease of process and its versatility as will be described in the following section.

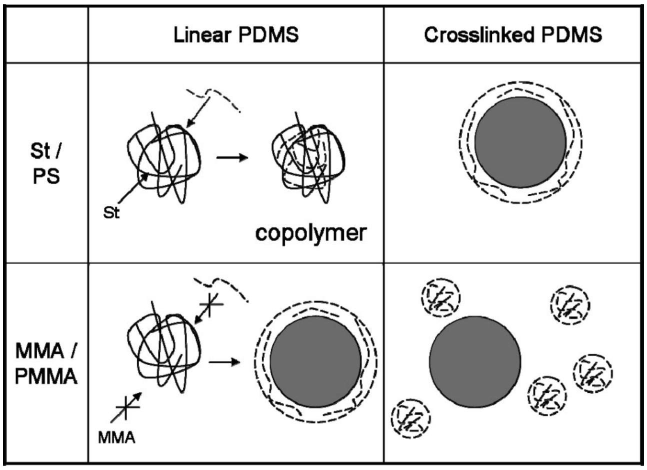
3.3.2. Silicone Containing Core–Shell Particles via Radical Polymerization

Core–shell latex particles resulting from seeded emulsion polymerization are of high interest given their numerous applications such as coating modification, rubber strengthening, or thermoplastic and thermosetting polymer toughening. This last application generally involves a thermoplastic shell and an elastomeric core, the latter explaining the interest for the silicone field. In direct emulsion, it is thermodynamically favored that the most hydrophobic polymer, in most cases PDMS, will form the core of the structure. However, some strategies have been developed to obtain core–shell structures where PDMS surrounds the particles. Note that most systems involve a polymerization of the shell around the core without any chemical links between them. Some of them will be considered as reference samples, but formation of a shell linked to the core through radical reactions is the purpose of this section.

We first discuss the formation of copolymers where unfunctionalized PDMS is used as the seed. Okaniwa and Ohta[186,187] prepared PDMS-*g*-PS and PDMS-*g*-PAN copolymers by forming a radical by hydrogen abstraction from the silylmethyl group of the silicone polymer in emulsion. The efficiency of the grafting reaction was correlated to the initiator properties: its ability to generate an oxyradical, its oil solubility, and the absence of potentially abstractable protons in its structure which may consume the radical. Among the studied initiators, *tert*-butyl perlaurate reduced by $FeSO_4$ led to the best grafting ratio. In addition, Okaniwa[188] also investigated core−shell materials using PDMS/polybutadiene as the core and poly(styrene-*co*-acrylonitrile) as the shell. Polybutadiene is widely used for its elastomeric properties in the core−shell field, and its grafting with thermoplastic polymers is relatively easy; its major drawback arises from its sensitivity to oxidation. Okaniwa overcame this disadvantage from the association of PB with PDMS which is especially oxidation resistant. The author showed that the modification of the PDMS with PB remained efficient (still using *tert*-butyl perlaurate/$FeSO_4$ redox initiator). Thanks to such PB/PDMS seeds, Okaniwa could graft SAN more easily than on pure PDMS seeds. As already mentioned, initiation of polymerization from unfunctionalized silicone polymers is scarcely used because of the challenging control of the reaction.

To the best of our knowledge, the first introduction of vinyl-containing PDMS seed copolymerized with acrylic or styrenic monomers appeared in patents[189–191] which claimed improved thermal or mechanical properties. An increase of the vinyl content in the seed led to enhanced elongation at break and tensile strength of the resulting materials. He et al.[192,193] studied more deeply core−shell particles with vinyl-PDMS as the starting material (resulting from the copolymerization of D_4 and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (D_4^V)). Actually, they compared two strategies in order to obtain core−shell materials. The vinyl-functionalized PDMS was either cross-linked before its use as a seed for the polymerization of the shell or directly used as the seed. In this latter case, cross-linking and polymerization occurred simultaneously. The authors observed that the formation of a core−shell structure was influenced by (i) the reactivity ratios of the monomers and polysiloxane, (ii) the mobility of the species in the emulsion, (iii) the hydrophilicity of the monomers (the authors used a hydrosoluble initiator), and (iv) the compatibility of the vinyl monomers and their polymers with PDMS. For instance, using an emulsion polymerization with linear vinyl PDMS as the seed, they were able to prepare core−shell particles with BMA and MMA but not with styrene. By contrast, core−shell particles were obtained with cross-linked PDMS (i.e., in the absence of vinyl functions) with styrene but not with MMA. In a more complete study,[194] the authors demonstrated that since styrene and poly(styrene) were compatible enough with the PDMS seed, they were able to penetrate the seed as long as PDMS was not cross-linked and consequently formed a nonsegregated copolymer latex. When PDMS is cross-linked, it acts as a shield and yields a PDMS-PS core−shell structure. On the contrary, MMA and PMMA are much less compatible with PDMS. Consequently, when the seed consisted of cross-linked PDMS, MMA was rejected and homopolymerized away from PDMS (Scheme 30).

Scheme 30. Morphologies of Core−Shell Latexes Depending on the Nature of the PDMS Seed and the Miscibility of the Comonomers with PDMS



Kong and Ruckenstein[195] prepared PDMS-poly(St-MMA-AA) core−shell particles thanks to a similar seeded emulsion polymerization process. Five weight percent of D_4^V was added during the preparation of the PDMS seed by anionic or cationic polymerization of D_4. Using transmission electron microscopy (TEM), they observed that core−shell particles exhibited a more uniform particle size distribution than without D_4^V. 3-(Trimethoxysilyl)propyl methacrylate was also added to D_4 during the polymerization to cross-link the seed whose diameter decreased. Unfortunately, its effect on the properties of the final material was not extensively discussed. Analogous PDMS-PMMA or PDMS-PBuA core−shell particles using vinyl polysiloxane were obtained by Dai et al.,[196] where polymerization was initiated by ^{60}Co γ-ray irradiation. Films formed from these materials showed higher decomposition temperatures, enhanced pendulum hardnesses, lower water absorptions, but decreased tensile strengths as the PDMS concentration increased. Zou et al.[197,198] observed that the particle size greatly influences the film properties such as mechanical performance, water absorption, and transparency. For instance, increasing the vinyl content from 1.1×10^{-3} to 2.2×10^{-3} mol per gram of seed emulsion led to a decrease of particle size and a 20% enhancement of the tensile strength of a PDMS-P(MMA-co-BA) film. On the other hand, the evolution of the elongation at break was negligible. Lin et al.[199] also prepared PDMS-poly((meth)acrylate) (MMA and BuA) core−shell particles, but they observed much more complex morphologies when 10 wt % of D_4^V were added to D_4 during ROP of the PDMS seed. Actually, this led to a multiglobular shell surrounding a shapeless PDMS core. As demonstrated by Soxhlet extraction of the particles, the structure was indebted to cross-linking occurring by copolymerization of acrylate monomers with vinyl groups. Contact angle measurements showed the more hydrophobic character of the film resulting from the D_4^V-containing seeds, giving evidence for a partial shell formation.

In order to obtain a core−shell structure with PDMS as the shell, Kong et al.[200] prepared first a cross-linked PMMA seed using ethylene glycol dimethacrylate (EGDMA) and then a D_4^V/ammonium persulfate mixture was added at the end of the MMA polymerization. D_4^V vinyl functions were supposed to react with residual MMA of the PMMA seed in formation. Afterward, the shell was obtained by polymerizing D_4. The authors compared a film made from the obtained latex with one formed from a similar core−shell latex which did not involve D_4^V. TEM observations showed that PDMS containing vinyl groups formed a continuous phase in the first film (in presence of D_4^V). Consequently,

Scheme 31. Chemical Initiation Mechanism of Telomerization[a]

$$\begin{array}{llcll}
\text{Initiation} & \text{Initiator} & \xrightarrow{k_d} & R^\bullet & (1) \\
 & R^\bullet + YZ & \xrightarrow{k_{tr1}} & RZ + Y^\bullet & (2) \\
 & Y^\bullet + M & \xrightarrow{\quad} & YM^\bullet & (3) \\
\text{Propagation} & YM_n^\bullet + M & \xrightarrow{k_p} & YM_{n+1}^\bullet & (4) \\
\text{Chain transfer} & YM_n^\bullet + YZ & \xrightarrow{k_{tr}} & YM_nZ + Y^\bullet & (5) \\
\text{Termination} & Y^\bullet + Y^\bullet & \xrightarrow{k_t} & Y_2 & (6) \\
 & YM_n^\bullet + YM_p^\bullet & \xrightarrow{\quad} & \text{polymer} & (7)
\end{array}$$

[a] YZ is the telogen, and M is an unsaturated monomer that can react by radical polymerization.

its hardness was lower than the reference sample without D_4^V. It should be noticed that 3-methacryloxypropyl trimethoxysilane (MATS) was also used to prepare such core−shell architectures. This molecule can copolymerize with MMA[201,202] or styrene[203] when added in the last moments of the seed polymerization. Afterward, methoxysilane groups reacted with D_4 to give the core−shell structure.

To summarize this core−shell section, radical polymerization allowed researchers to obtain small and fine particles with well-defined morphologies, which is a key issue for the properties of the resulting materials.

3.3.3. Chemical-Initiated Telomerization

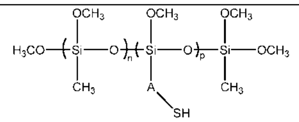
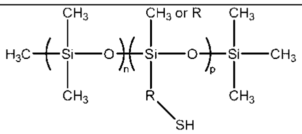
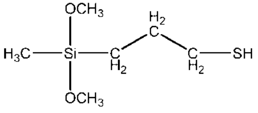
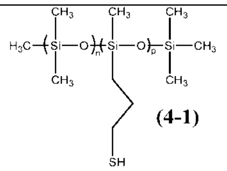
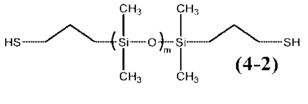
The telomerization process consists of reacting, under polymerization conditions, a molecule YZ, which is called a telogen, with more than one unit of a compound M containing an unsaturated group, called a taxogen, to form products called telomers $Y(M)_nZ$.[204,205] The general mechanism of telomerization by chemical initiation is given in Scheme 31. By functionalizing a PDMS chain, it is possible to transform it into a macrotelogen.

Telomerization differs from polymerization in the following issues: the fragments of the initiator mainly induce the rupture of the telogen, whereas in polymerization they add onto the monomer; the number of M units in the final product is larger than 1 but lower than 100; the functional groups on both chain ends can be easily transformed thanks to the low molecular weights of the resulting polymers.

Several authors carried out the synthesis of block or graft copolymers using a PDMS macrotelogen, as summarized in Table 3. They all carry a thiol function except the one used by Tezuka that bears a Si−H functionality (Table 3, entry 5).[206]

The first synthesis of PDMS graft copolymers using telomerization has been carried out by the Dow Corning Corp.[207] in 1969 using two different emulsion pathways. In the first step, siloxanes **1** (Table 3, entry 1) were prepared by emulsion copolymerization of the corresponding trimethoxysilane as described by Hyde[208] and Findlay.[209] The second step is the addition of the vinyl monomer and ammonium persulfate to the nitrogen-purged emulsion to perform the polymerization by heating. In a second approach, the polysiloxane that has been previously prepared by bulk

Table 3. Telogens and Monomers Used To Make Block and Graft PDMS-Based Copolymers by Telomerization

Entry	Telogen	Synthesis method of the telogen	Monomers	Refs
1	 with A = arylene or alkylene moiety	Emulsion polymerization of corresponding trimethoxysilane	Styrene, MMA, EA	207
2	 with R = a secondary or tertiary saturated aliphatic hydrocarbon chain with 1 to 8 carbon atoms.	Cationic polymerization of cyclic siloxane	Styrenic, acrylic, methacrylic monomers, vinyl halides and VAc.	22,23,210-212
3		Commercial product (used in telomerization, followed by condensation)	MMA	213
4	 (4-1)  (4-2)	Commercial product	Styrene, MMA and chloroprene	(1)[214], (2)[214,215]
5	$H\text{-}Si(CH_3)_2\text{-}Cl$	Commercial product	VAc	206

or solution techniques is emulsified, the second step being identical to the one described above.

Falender et al.[22,23,210,211] from the Dow Corning Corp. also performed the telomerization of many different monomers (acrylic, methacrylic, styrenic monomers) using a PDMS macrotelogen (Table 3, entry 2). For example, they carried out the synthesis of PDMS-*g*-poly(styrene-*co*-acrylonitrile) of high impact strength using a mercaptopropyl PDMS as a telogen in water suspension or in bulk with benzoyl peroxide as radical initiator.

Saam and Tsai[212] carried out the dispersion polymerization of methyl methacrylate in aliphatic hydrocarbons containing poly(dimethylsiloxane) modified with mercaptoalkyl side groups (Table 3, entry 2). They observed the formation of particles stabilized by a protective layer of solvated poly(dimethylsiloxane). The evolution of particle size was studied while polymerizing MMA. In the very early stage of polymerization, a large number of very small particles of broad size distribution was formed. These particles contained a relatively high amount of silicone stabilizer in the form of graft copolymers. As the conversion increased, the particles tended to agglomerate to give some larger particles and a broad size distribution. Between 5% and 10% conversion, a critical point was reached: the smaller particles were absorbed by the larger particles present in the system. From this point, new particles were no longer formed (end of nucleation) and polymerization occurred within the swollen monomer particles. This was evidenced by a steady particle growth and a final narrow size distribution.

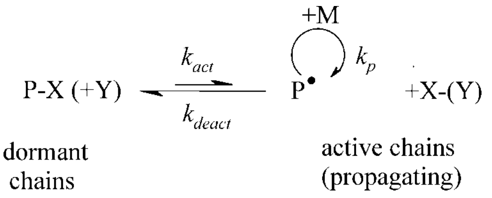
Our group also performed the synthesis of triblock cooligomers of poly(methyl methacrylate)-*b*-PDMS-*b*-poly(methyl methacrylate)[213] by telomerization. The first step consisted of the synthesis of a macromonomer containing a PMMA chain using γ-mercaptopropylmethyldimethoxysilane as telogen (Table 3, entry 3), MMA as monomer, and AIBN as initiator. The second step was the condensation reaction between the macromonomer and the silanol-terminated PDMS at 100 °C for 20 h in the presence of a catalyst (2-ethylhexanoic acid/tetramethylguanidine complex). The presence of small amounts of diadduct (reaction of the second methoxy silyl group with a silanol-terminated PDMS) has been observed.

More recently, Fawcett et al.[214] carried out the telomerization of different monomers (styrene, MMA, chloroprene) (Table 3, entry 4) using mercaptopropyl-functionalized PDMS and AIBN as radical initiator. The authors observed that the thiol/monomer ratio controls the reaction type: for a low monomer/macrotelogen ratio, only one monomer unit reacted with the SH group (thiol−ene reaction), whereas a higher concentration ratio resulted in graft and block copolymers.

Thermal-initiated telomerization was also carried out in $scCO_2$ to prepare PMMA particles.[215] Okubo and co-workers used a triblock copolymer PMMA-*b*-PDMS-*b*-PMMA as colloidal stabilizer, prepared in situ by telomerization using a mercaptopropyl telechelic PDMS as telogen with AIBN as initiator (Table 3, entry 4). The particle diameter could be controlled by the concentration of the telogen which serves as steric stabilizer, with sizes ranging from submicrometers to micrometers. A very small consumption of telogen was observed, albeit producing sufficient copolymers to stabilize the PMMA particles.

Tezuka et al.[206] used telogen **5** (Table 3, entry 5) to prepare poly(vinyl alcohol)-*b*-PDMS-*b*-poly(vinyl alcohol) (PVA-*b*-PDMS-*b*-PVA) block copolymers. The first step was the telomerization of VAc in the presence of dimethylchlorosilane as telogen and AIBN as radical initiator in benzene. The second step was the coupling reaction of the chlorosilane-terminated poly(vinyl acetate) (PVAc) prepolymer with a α,ω-telechelic silanolate-terminated PDMS. Finally, PVA-*b*-PDMS-*b*-PVA block copolymers were obtained by saponification of the PVAc-*b*-PDMS-*b*-PVAc block copolymer using a 10% aqueous sodium hydroxide solution in methanol. However, due to the sensitivity of PDMS to basic conditions, a loss of more than 15 wt % of siloxane was observed during this last hydrolysis step.

Scheme 32. General Scheme of Reversible Activation−Deactivation in Controlled Radical Polymerization[217]



The literature already largely described telomerization of a wide range of monomers.[204,205] To date, mainly thiol-type PDMS were used as telogens. Using PDMS as a macrotelogen is an easy way to prepare silicone-containing copolymers, keeping in mind that the final product does not exhibit high molecular weights. Moreover, chemical-initiated telomerization is compatible with dispersed aqueous or $scCO_2$ media (suspension, emulsion, dispersion polymerizations).

4. Copolymers Obtained by Controlled Radical Polymerization

The controlled radical polymerization (CRP)[216] process includes a group of radical polymerization techniques that have attracted much attention over the past decade since they provide simple and robust routes to the synthesis of well-defined polymers, low-dispersity polymers, and preparation of novel functional materials. The general principle of the reported methods relies on a reversible activation−deactivation process between dormant chains (or capped chains) and active chains (or propagating radicals) with different rate constants k_{act} and k_{deact}, respectively (Scheme 32).[217,218]

The past few years have witnessed rapid growth in the development and understanding of new CRP methods. The most popular CRP methods treated in the following text are iniferters,[219] nitroxide-mediated polymerization (NMP)[220] that requires alkoxyamines, atom-transfer radical polymerization (ATRP)[221] involving alkyl halides, metallic salts, and ligands, iodine-transfer polymerization (ITP) using alkyl iodides,[141] and reversible addition−fragmentation chain transfer polymerization (RAFT)[222] using dithiocarbonyl derivatives.

4.1. Iniferter

Iniferters[219] are specific agents that proceed in a radical polymerization via initiation, propagation, primary radical termination, and transfer to initiator (Scheme 33). Because bimolecular termination and other transfer reactions no longer dominate the polymerization, these polymerizations are performed by insertion of the monomer molecules into the iniferter bond, thus generating polymer chains with two initiator fragments at the chain ends. These thermal iniferters give controlled molecular weights but do not present a living chain end (i.e., no possibility of further chain extension). PDMS-based macroiniferters are given in Table 4 (entries 1 and 2).

Scheme 33. Main Steps Involved in the Mechanism of Iniferter Polymerization

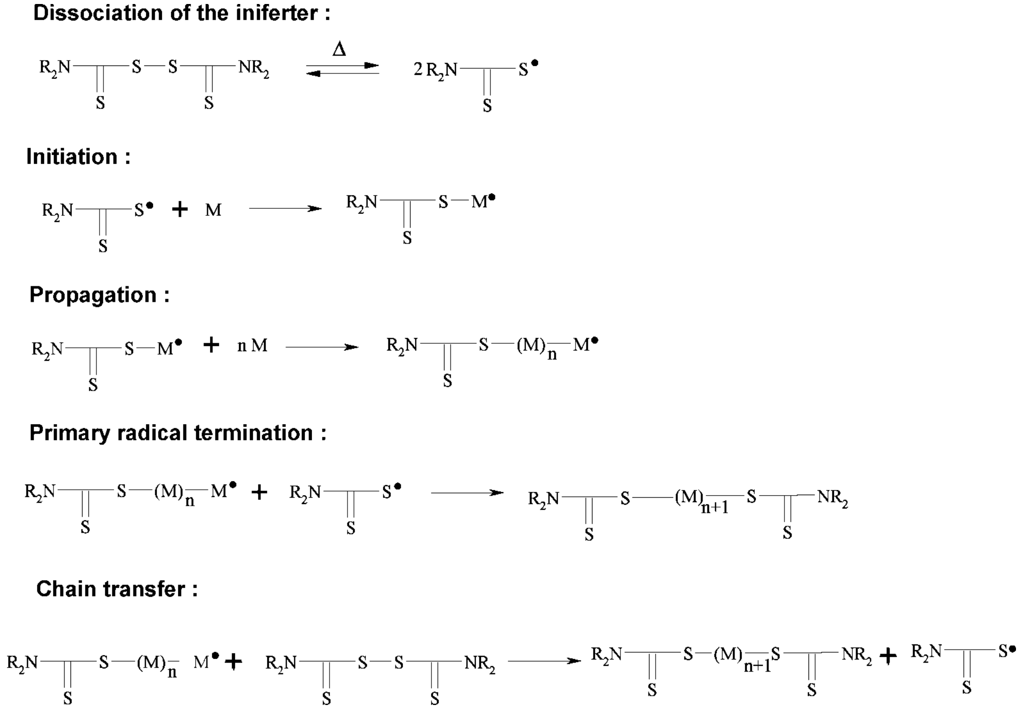
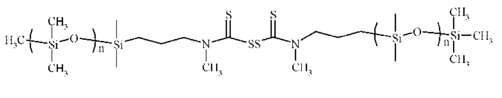
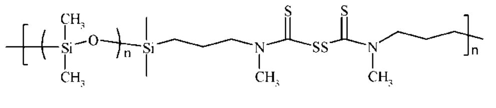
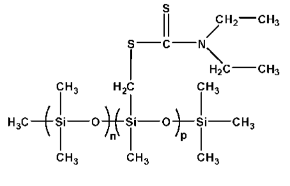
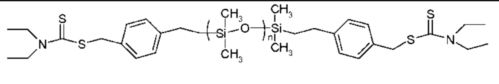
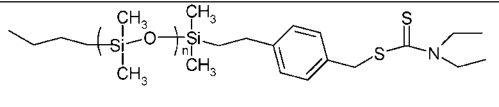


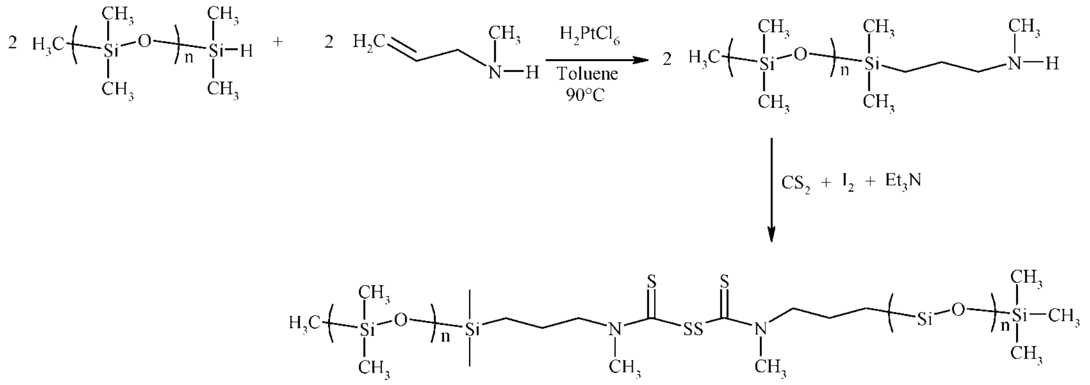
Table 4. PDMS Thermal- and Photo- Macroiniferters

Entry	Transfer Agent	Synthesis method	PDMS M_n range ($g.mol^{-1}$)	Controlled Monomers	Ref.
1		Hydrosilylation + thiocarbamylation	2 300 2 800 4 200	MMA, Styrene	223-227
2		Hydrosilylation + thiocarbamylation	400 1 070 3 050	MMA, Styrene, Acrylamide	228
3		Nucleophilic substitution of chlorine by $KSC(S)N(C_2H_5)_2$	crosslinked PDMS	HEMA, Acrylamide, AMPS, DMAEMA, NaSS, NVP, MAA	43
4		Hydrosilylation + Nucleophilic substitution	-	MMA, MeA, AA, HEA	229-231
5		Hydrosilylation + Nucleophilic substitution	26 800	VAc, FOA	232

Macroiniferter **1** (Table 4, entry 1) was synthesized by a hydrosilylation reaction between Si−H-terminated PDMS and allyl-*N*-methylamine. Subsequent chain extension of the macrodiamine by the thiocarbamylation reaction using CS_2 and oxidative coupling using I_2 led to the formation of the polymeric iniferters (Scheme 34).

Macroiniferter **1**, when used under thermal initiation in the presence of vinylic monomers, gives a triblock copolymer with a central vinylic polymer block and a PDMS segment at both ends. This macroiniferter was used for styrene and MMA polymerization between 60 and 100 °C in bulk or in toluene solution.[223,224] When the polymerization of styrene or MMA was carried out in concentrated solutions or in bulk, a slight microsegregation was observed due to the incompatibility of the PDMS segment with the propagating polymer chain. This polymer demixtion led to a decrease of the macroiniferter efficiency.[223] Moreover, the authors observed a decrease in chain transfer with increasing PDMS chain

Scheme 34. Synthesis of Macroiniferter 1 (Table 4, entry 1)



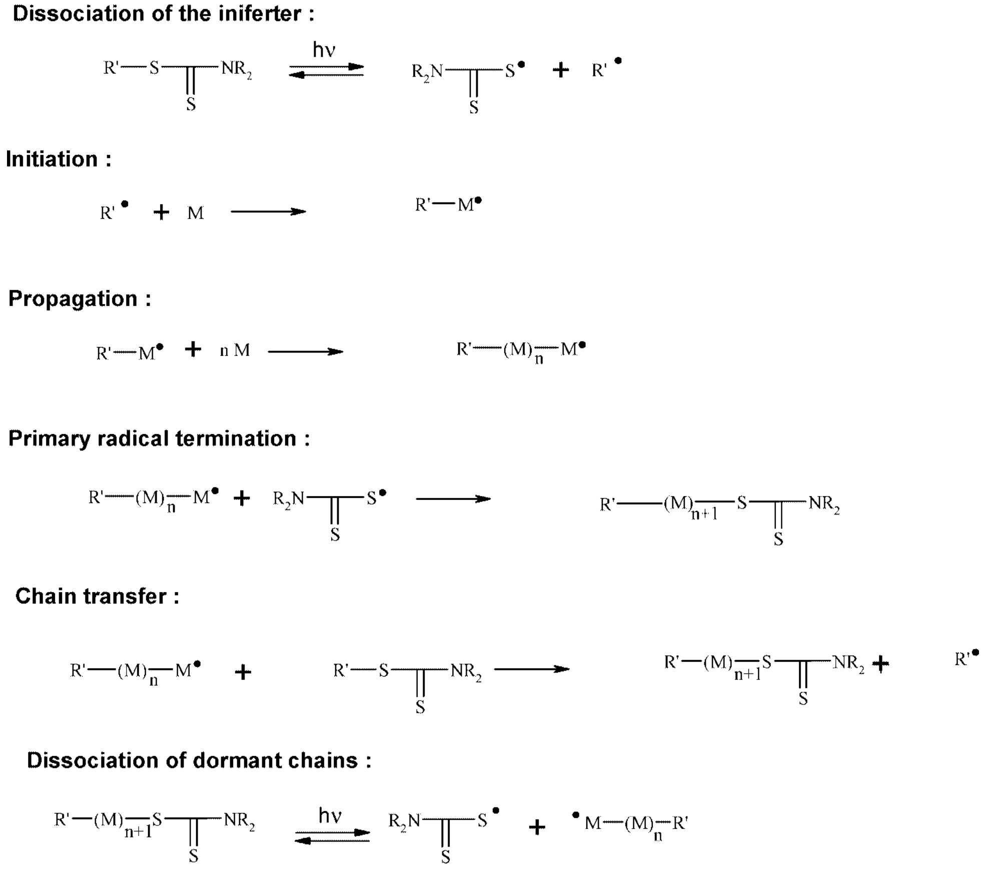
length (M_n = 2800−4200 g·mol^{-1}), which also suggested the occurrence of some phase segregation.[224] The azeotropic temperatures of the iniferter, where $k_{tr} = k_p$ or $C_{tr} = k_{tr}/k_p = 1$, were determined to be 125 °C for MMA and 110 °C for styrene. When $C_{tr} = 1$, the molecular weight remains constant during the polymerization. When the temperature is lower than the azeotropic temperature, the polymerization is not controlled and M_n decreases as the conversion proceeds (i.e. $C_{tr} < 1$). The authors found that for this macroiniferter $C_{tr(styrene)} = 1.5 \times C_{tr(MMA)}$.

Macroiniferter **2** (Table 4, entry 2) is the equivalent of macroiniferter **1** but starting from a difunctionnal PDMS chain. When a vinylic monomer is polymerized in the presence of this particular transfer agent, a multiblock copolymer is formed. In the polymerization of MMA, Nair et al.[228] showed that when the concentration of the macroiniferter increased, a retardation effect due to the participation of thiuramyl radicals in termination reactions was observed. The molecular weight increased linearly with conversion, and the final PDIs of the multiblocks were around 2−2.5. These authors thus reported the successful synthesis of PS-PDMS and PMMA-PDMS multiblock copolymers, whereas when polymerizing acrylamide to obtain amphiphilic copolymers, a strong phase segregation occurred and led to an insoluble material due to some physical cross-linking.

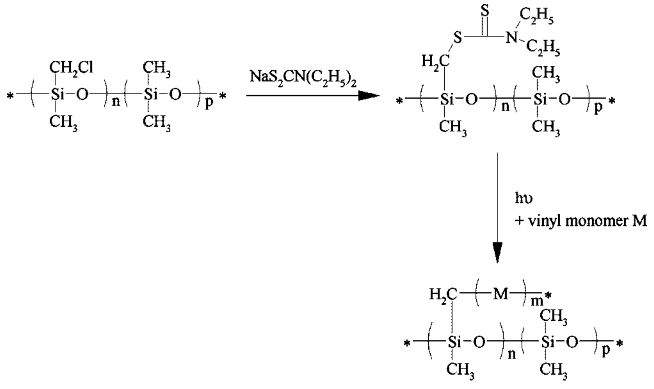
Photoiniferters are iniferters that are activated under UV radiation. These iniferters have the advantage that they lead to living chains. Indeed, the polymer chain resulting from termination can be reactivated by cleaving the C−S bond under UV radiation (Scheme 35). The different PDMS-based macrophotoiniferters reported here are quoted in Table 4 (entries 3−5).

The first study on photoinitiated polymerization was carried out by Inoue et al.[43] They modified the surface of a cross-linked poly(dimethylsiloxane-*co*-methyl chloromethylsiloxane) by photopolymerizing hydrophilic monomers

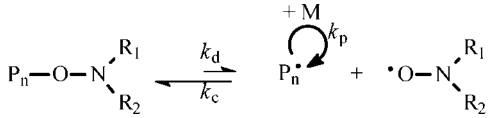
Scheme 35. Main Steps Involved in the Mechanism of Photoiniferter Polymerization



Scheme 36. Synthesis of the PDMS Photoiniferter and Grafted Polymer Obtained



Scheme 37. General Mechanism of Nitroxide-Mediated Polymerization



(Table 4, entry 3) using diethyldithiocarbamated PDMS as photoiniferter. The synthesis of this photoiniferter and the grafted polymer obtained is described in Scheme 36. By this method, they successfully prepared hydrophilic surfaces which could find applications in biomedical devices.

Macrophotoiniferter **4** (Table 4, entry 4) was successfully used for the controlled polymerization of MMA and copolymerization of methyl acrylate and acrylic acid under UV radiation.[230] Moreover, the living character of the chain ends was demonstrated by further growing two blocks of poly(2-hydroxyethylacrylate) (PHEA) from the PMMA-*b*-PDMS-*b*-PMMA triblock copolymer. Finally, VAc and 1,1-dihydroperfluorooctyl acrylate (FOA) were successfully polymerized by macrophotoiniferter **5** (Table 4, entry 5) under UV radiation.[232] In the case of VAc, diblock copolymers with PDI = 1.4 (at 30% monomer conversion) were obtained.

Until now, PDMS-based macroiniferters were used for the controlled polymerization of styrene, MMA, methyl acrylate (MeA), acrylamide, AA, MAA, HEMA, HEA, AMPS, DMAEMA, sodium styrene sulfonate (NaSS), *N*-vinyl pyrrolidone (NVP), and FOA. Iniferters allow the controlled polymerization of a wide range of monomers,[219] but the control over the molecular weights is poorer than by other PRC methods and photoactivation is required to achieve living character.

4.2. NMP: Nitroxide-Mediated Polymerization

In nitroxide-mediated polymerization (Scheme 37),[220] the reversible termination is the key step to keep a low concentration of propagating radicals in the reaction medium. All polymer chains should only be initiated by the alkoxyamine, leading to well-controlled polymer architectures. The nature of the counter radical is essential for the controlled character of the polymerization.

The alkoxyamine has a rather labile C−O bond which cleaves homolytically upon heating to liberate the radical on the polymer chain, which propagates, and the counter radical, which is only able to end cap the propagating chains. The equilibrium is overwhelmingly shifted to the left (dormant chains), and the control is ensured thanks to the persistent radical effect (i.e., accumulation of nitroxides).[233,234] Table 5 summarizes the different precursors used in the synthesis of PDMS-based copolymers by NMP techniques.

Styrene has been the most widely studied monomer for nitroxide-mediated polymerization from a PDMS precursor. As for conventional free radical polymerization, azo macroinitiators can be used to initiate the polymerization. Yoshida et al.[235,236] used a bicomponent system consisting of a multiblock azo macroinitiator **1** (Table 5, entry 1) (M_n = 30 800 g·mol^{-1} with PDMS segments M_n = 5000 g·mol^{-1}) and 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl (MTEMPO) (Scheme 38). As soon as the azo macroinitiator decomposed, the formed radicals were trapped by MTEMPO to create the active macroalkoxyamine in situ. Styrene was polymerized in bulk at 130 °C for 72 h. Due to the low initiator efficiency, the resulting copolymer exhibited an AB diblock structure rather than the expected ABA triblock one. A chain extension with *p*-methoxystyrene showed the living character of the polymer chain end.

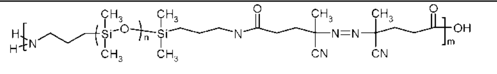
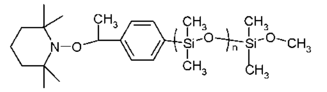
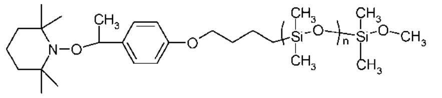
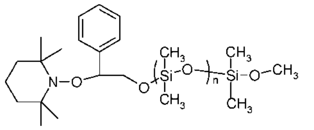
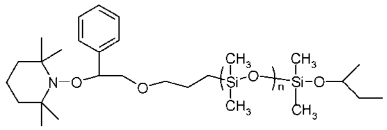
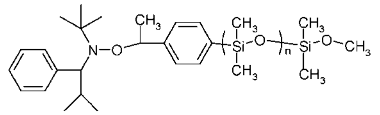
Macroinitiator **1** (Table 5, entry 1) was also used by Ryan et al.[237] in the dispersion polymerization of styrene in scCO$_2$ using SG1 (*N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl)nitroxide) (Scheme 38) as a control agent at 110 °C. A rather broad bimodal molecular weight distribution (MWD) was obtained. The use of AIBN as co-initiator and the reduction of the number of azo moieties in the azo macroinitiator tended to reduce the bimodality while introducing sufficient siloxane units to stabilize the dispersion in scCO$_2$. The azo moieties were partially consumed by heating the macroazo initiator before adding the monomer to reach a new precursor with M_n= 21 800 g·mol^{-1} and only 25% remaining azo moieties. A chain extension showed the high livingness of the polymer chains. The broad MWD was ascribed to polysiloxane chains bearing SG1 moieties at one or two chain ends, leading to di- or triblock copolymers, respectively.

When a bicomponent system is used (azo macroinitiator + nitroxide), the low initiator efficiency leads to an ill-defined architecture and a mixture of homopolymers and diblock and triblock copolymers.[220] To obtain a well-defined di- or triblock copolymer, it is better to use a monocomponent system, assuring a better controlled architecture. Therefore, several organolithium alkoxyamines were used as initiators for the anionic polymerization of D$_3$, leading to PDMS alkoxyamines. These macroalkoxyamines were further used for the nitroxide-mediated polymerization of styrene, leading to well-defined diblock copolymers. This method was first applied by using macroalkoxyamine **2** (Table 5, entry 2 and Scheme 39) for the bulk polymerization of styrene[238] at 120 °C. The controlled polymerization proceeded up to 20% conversion, giving the desired diblock copolymer. However, above 20% styrene conversion, SEC analysis showed a bimodality, indicating the formation of homopoly(styrene) along with low molar mass diblock copolymer.

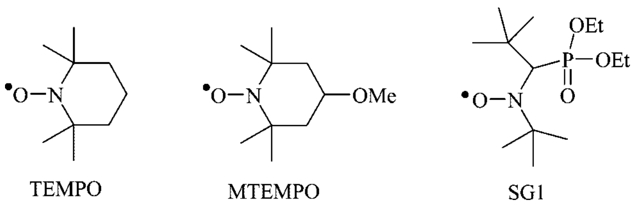
Macroalkoxyamine **3** (Table 5, entry 3) was used to polymerize styrene in bulk at 120 °C.[239] The macroalkoxyamine reacted quantitatively to form diblock copolymers, and a linear evolution of molecular weight with conversion proved the controlled character of the polymerization. A final PDI of 1.3 above 25% conversion was obtained. However, maximum monomer conversion was limited to 42%.

Macroalkoxyamine **4** (Table 5, entry 4) was used for bulk and solution polymerizations of styrene[240] at 120 °C where some discrepancies between the molecular weights determined by SEC and NMR were observed. Moreover, the

Table 5. PDMS Macroalkoxyamines and PDMS Macroinitiators Used in Nitroxide-Mediated Polymerization

Entry	Macroalkoxyamine	Synthesis method	PDMS M_n range ($g.mol^{-1}$)	Controlled Monomers	Ref.
1	 +MTEMPO or SG1	Amidification and initiator decomposition in the presence of MTEMPO or SG1	PDMS block 5 000 Azo Macroinitiator 30 800	Styrene	235-237
2		Anionic polymerization of D_3 from TEMPO-CH(CH$_3$)-Ph-Li	7 600	Styrene	238
3		Anionic polymerization of D_3	6 900	Styrene	239
4		Anionic polymerization of D_3	12 100 46 800	Styrene	240
5		Hydrosilylation	2 000 4 200 10 200	Styrene	241,242
6		Anionic polymerization of D_3	4 000	Styrene, MeA, Isoprene	243

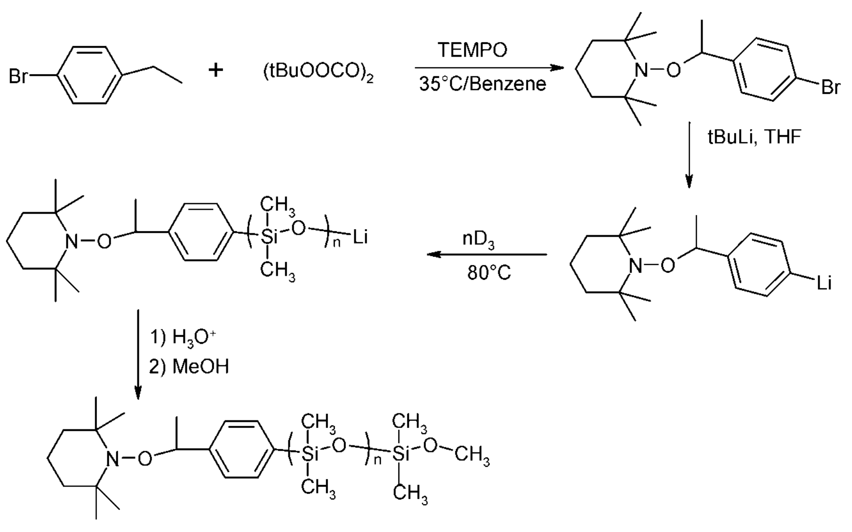
Scheme 38. Formulae of TEMPO, MTEMPO, and SG1



resulting copolymer did not have the expected composition from the monomer feed.

Macroalkoxyamine **5** (Table 5, entry 5) was synthesized by hydrosilylation,[241,242] thus avoiding the presence of the rather fragile Si—O—C bond.[78,79] This macroalkoxyamine was used for the solution polymerization of styrene,[241] leading to a mixture of homopoly(dimethylsiloxane), homopoly(styrene), and diblock copolymer. The presence of homoPDMS proved the incomplete reaction of the macroinitiator, while homoPS resulted from some thermal autoinitiation. However, by optimizing the reaction conditions, the amount of homopolymers was reduced, leading to a practically pure diblock copolymer.[242] Nevertheless, some inhomogeneity in SEC could be attributed to diblocks with varying PS and PDMS content. Moreover, NMR analysis only showed around 30% of remaining TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) units on the chain ends. The difference was attributed to some hydrogen transfer,[220,244] leading to —CH=CH—Ph and —CH$_2$—CH$_2$—Ph chain ends.

Scheme 39. Synthesis of Macroalkoxyamine 2 (Table 5, entry 2)



Because TEMPO has no ability to control the radical polymerization of vinyl monomers other than styrene and styrene derivatives, Miura et al.[243] used macroalkoxyamine **6** (Table 5, entry 6) to polymerize styrene and other monomers. The TIPNO (*N*-*tert*-butyl 1-phenyl-2-methylpropylaminoxyl)-based alkoxyamine has been reported to act as an excellent mediator for a wide range of vinyl monomers including styrene. Styrene was polymerized in bulk at 120 °C. A linear evolution of the molecular weight with conversion was observed, and SEC showed a monomodal MWD with a PDI of 1.2, a value lower than those obtained at similar conversion with TEMPO-bearing control agents.[238,239] TIPNO, like SG1, is a better control agent than the commercially available TEMPO. The TIPNO-based alkoxyamine **6** (M_n = 4000 g·mol^{-1}, PDI = 1.09) was further used for the polymerization of methyl acrylate (MeA) in bulk at 120 °C.[243] A linear evolution of molecular weights with conversion was observed with a final PDI value below 1.2 at 50% conversion. A good correlation between experimental and theoretical molecular weights was observed. Moreover, to show the living character, the PDMS-*b*-poly(MeA) diblock copolymer was further used as a macroalkoxyamine in the polymerization of styrene, leading to an ABC triblock copolymer with PDI = 1.4. Alkoxyamine **6** was also used for the controlled polymerization of isoprene (IP) in bulk at 120 °C.[243] The final diblock copolymer presented a PDI of 1.15 and a good agreement was noticed between experimental and theoretical molecular weights. The diblock copolymer was further used in the polymerization of styrene to synthesize a PDMS-*b*-poly(IP)-*b*-PS triblock copolymer with a monomodal MWD (PDI = 1.37).

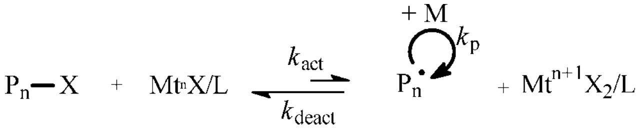
To date, NMP from PDMS macroalkoxyamines was essentially used for styrene polymerization. Only Miura et al.[243] polymerized methyl acrylate and isoprene from a PDMS macroalkoxyamine. It is known that nitroxide-mediated polymerization allows the controlled polymerization of a wide range of monomers.[220] Among others, the controlled polymerization of acrylates (such as *tert*-butyl acrylate (tBuA), nBuA, or MeA), styrenics (such as styrene, *p*-bromostyrene, *p*-chlorostyrene, *p*-epoxystyrene, *p*-methoxystyrene, *p*-acetoxystyrene, *p*-chloromethylstyrene, *p*-*tert*-butoxy styrene, or styrene *p*-sulfonic acid sodium salt), isoprene, 4-vinyl pyridine, acrylonitrile, maleic anhydride, isopropylacrylamide, and *N*,*N*-dimethylacrylamide could be considered in the future. Indeed, all these monomers can be potentially polymerized using nitroxide-mediated polymerization from a poly(dimethylsiloxane) macroalkoxyamine, giving a wide range of different properties to the second block, which could lead to a variety of new applications. Furthermore, NMP of PDMS macromonomers has not been reported yet to yield graft copolymers. This is probably due to the limited range of commercially available PDMS macromonomers, since those based on methacrylates could not be easily controlled by NMP. Recent progress in NMP of methacrylates now makes it possible.[245,246]

4.3. ATRP: Atom-Transfer Radical Polymerization

4.3.1. Main Features

The mechanism of ATRP[221] is described in Scheme 40. The control is achieved by an equilibrium between active (or propagating) and dormant species. This equilibrium is defined by the rate constants k_{act} and k_{deact}. The lower the concentration of active species ($k_{act} \ll k_{deact}$), the better the control and the lower the extent of irreversible termination. Irreversible termination occurs as in conventional free radical polymerization by combination or disproportionation.

Scheme 40. Mechanism of Atom-Transfer Radical Polymerization



Several reviews from Matyjaszewski[247–251] treat of the synthesis of organic–inorganic hybrid materials using atom-transfer radical polymerization. They all deal with the general synthesis routes used to obtain such hybrid materials, but none of them gives an extensive overview of the existing state of the art. Note that a patent from Matyjaszewski et al. covers the synthesis of poly(dimethylsiloxane)-containing block and graft copolymers by ATRP.[252]

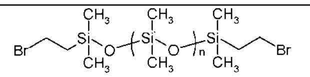
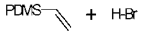
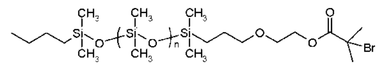
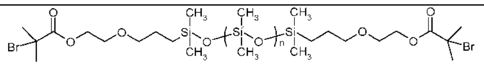
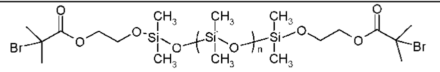
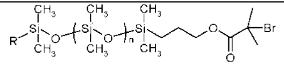
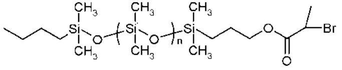
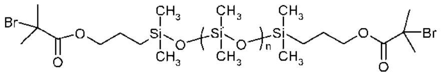
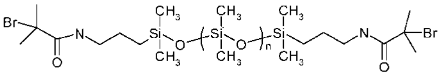
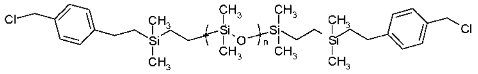
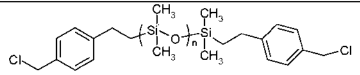
4.3.2. Block Copolymers

Various PDMS macroinitiators have been used for the synthesis of di- and triblock copolymers (Table 6). Most of them were prepared by hydrosilylation, even though several other routes have been explored. The most widespread macroinitiators bear a chlorobenzyl or bromo-isobutyrate end group.

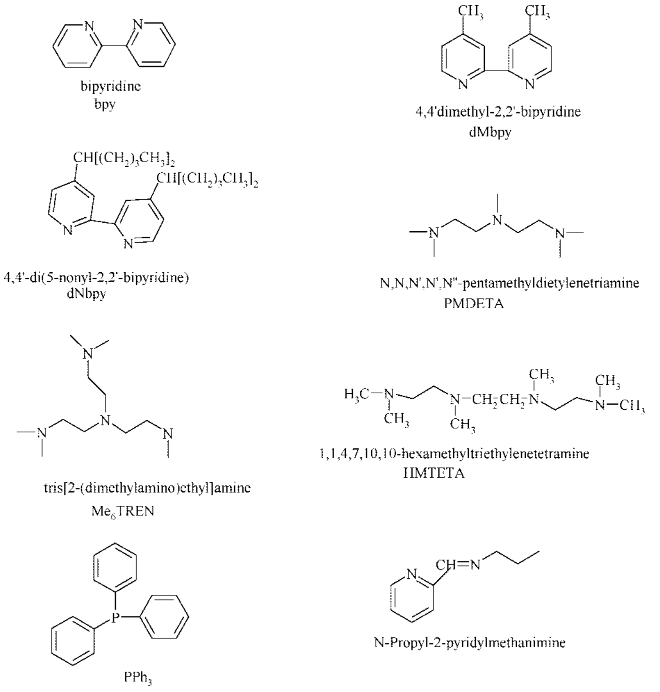
In ATRP, ligands are used to favor the homolytic scission of the carbon–halogen bond. The formula of the most commonly used ligands are given in Scheme 41. Macroinitiator **1** (Table 6, entry 1) (M_n = 1800–10 000 g·mol^{-1}) was used by Peng et al. for the controlled polymerization of styrene[253,254] and butyl methacrylate.[255] PS-*b*-PDMS-*b*-PS triblock copolymers were obtained using the CuCl/dNbpy (4,4′-di(5-nonyl-2,2′-bipyridine)) catalyst system (Scheme 41) in phenyl ether at 130 °C. The molecular weight increased with conversion, and the final polydispersity index was 1.33. The influence of the polysiloxane chain length was also investigated.[253] When using higher molecular weight polysiloxane chains (1800–10 000 g·mol^{-1}), styrene conversion and the rate of polymerization diminished whereas the polydispersity index increased. When the catalyst concentration was increased, the rate of polymerization, the final monomer conversion, and the polydispersity index also increased.

Macroinitiators **2** and **3** (Table 6, entries 2 and 3) were prepared in similar ways, macroinitiator **2** from a monofunctional PDMS and macroinitiator **3** from a difunctional PDMS, opening the way to di- and triblock copolymers, respectively. Zhang et al.[257] used both macroinitiators (8000 g·mol^{-1}) to synthesize AB and ABA block copolymers in bulk at 120 °C with $NiBr_2(PPh_3)_2$ as catalyst. Successfully polymerized monomers included MMA, *n*-BuA, *t*-BuA, trimethylsilyl methacrylate (TMSMA), trimethylsilyl acrylate (TMSA), and trimethylsiloxy-ethyl acrylate (TMSEA). *t*-BuMA and 1-ethoxyethyl methacrylate (EEMA) were also polymerized, but a deactivation of the catalyst led to a low monomer conversion (<20%). The polymerization of *t*-BuA, which exhibits a higher reactivity than *t*-BuMA, continued up to high monomer conversions. Deprotection of the hydroxyl group in the case of poly(trimethylsiloxyl-ethyl acrylate) and of carboxylic acid in the case of poly(trimethylsilyl methacrylate) and poly(trimethylsilyl acrylate) was carried out in the presence of aqueous dichloroacetic acid as catalyst in a THF–acetone–methanol solvent mixture at room temperature, leading to new and original block copolymers containing PHEA, poly(acrylic acid) (PAA) or

Table 6. PDMS Macroinitiators Used for the Synthesis of Di- and Triblock Copolymers by Atom-Transfer Radical Polymerization

Entry	Macroinitiators	Synthesis method	PDMS M_n range (g.mol^{-1})	Controlled Monomers	Ref.
1			1 800, 6 400, 10 000	Styrene, BuMA	253-255
2		Esterification	6 200, 8 000, 9 500	MMA, tBuMA, nBuA, tBuA, TMSMA, TMSEA, EEMA, TMSA	256-259
3		Esterification	2 100, 5 000	MMA, DMAEMA	256,260-262
4		-Si-Cl + HO-R-Br	8 200	BMA	263
5	 with R = *n*-Bu or poly(styrene)	Hydrosilylation	670-5 800	MMA+nBuA, OEGMA, nBuA, Styrene, MMA, HEMA-TMS	264-268
6		Hydrosilylation	8 800	MMA	266
7		Hydrosilylation	8 200	MMA, HEMA-TMS	265
8		Amidification	2 200	MMA, DMAEMA	269
9		Hydrosilylation	4 500, 9 800	Styrene, MMA, nBuA, iBnA	265,270,271
10		Hydrosilylation	885, 6 200	MMA, Styrene, iBnA, nBuA	272-274

Scheme 41. Structure of the ATRP Ligands Used in the Studies Involving PDMS Macroinitiators



poly(methacrylic acid) (PMAA). However, one could wonder whether the PDMS chain is not degraded in such acidic media. The *tert*-butyl ester groups were partially hydrolyzed (40%) using a NaI/SiMe$_3$Cl two-step technique without altering the PDMS segment.

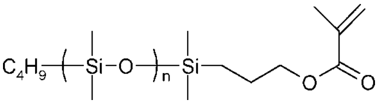
Macroinitiator **2** (Table 6, entry 2) (6200 g$\cdot$mol^{-1}) was used by Minami et al.[258] as IniStab (initiator + stabilizer) for the dispersion polymerization of methyl methacrylate in scCO$_2$. The polymerization was carried out using the CuBr/HMTETA (1,1,4,7,10,10-hexamethyltriethylenetetramine) catalyst system at 65 °C. Monomer conversions above 70% were obtained and increased when increasing the initiator concentration (i.e., decreasing the targeted molecular weight). Good initiator efficiency was observed, and although the molecular weight distributions had a slight tailing of low molecular weights, a correct polydispersity index of 1.25 was obtained.[259] Huan et al.[256] synthesized PMMA and poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) containing di- and triblock copolymers by using macroinitiators **2** and **3** (5000 g$\cdot$mol^{-1}) at 90 °C in toluene and the CuBr/*n*-propyl-2-pyridinalmethanimine catalyst system. In both cases, a linear evolution of the molecular weight with conversion was observed and monomodal MWDs were obtained. Similarly, Bes et al. polymerized MMA[260,261] and 2-dimethylaminoethyl methacrylate (DMAEMA)[262] from macroinitiator **3** (2100−5000 g$\cdot$mol^{-1}) and obtained the expected triblock copolymer with good control over the molecular weights. The same group used macroinitiator **8** (Table 6, entry 8) for the polymerization of MMA and DMAEMA in toluene.[269]

Macroinitiator **4** (Table 6, entry 4) (8200 g$\cdot$mol^{-1}) bears the same bromo-isobutyrate chain ends as macroinitiator **3** but was synthesized differently. Thus, macroinitiator **4** has a rather fragile Si−O−C[78,79] bond between the different blocks. It was used to polymerize butyl methacrylate at 110 °C in diphenyl ether using the CuCl/dNbpy catalyst system.[263] Complete initiator efficiency and monomodal MWDs were obtained. When the macroinitiator concentration was increased, the polymerization rate and monomer conversion increased. Moreover, when the catalyst concentration was increased, the rate of polymerization as well as the PDI increased. The rate of polymerization was found to be proportional to [catalyst]$^{0.82}$ and to [macroinitiator]$^{0.67}$.

Macroinitiator **5** (Table 6, entry 5) (R = *n*-Bu) exhibits the same chain end as macroinitiator **2**, although it was synthesized by hydrosilylation. The bulk polymerization of oligo(ethylene glycol) methyl ether methacrylate (OEGMA)[264] using macroinitiator **5** (640−3950 g·mol^{-1}) and CuBr/Me$_6$TREN (tris[2-(dimethylamino)ethyl]amine) or CuBr/PMDETA (*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine) at 20 °C or CuBr/N(*n*-propyl)-2-pyridylmethanimine at 90 °C showed a poor control of the molecular weights, explained by an incompatibility between the PDMS macroinitiator and OEGMA. Upon addition of benzene to compatibilize the reagents, good control was achieved, especially when using PMDETA as ligand at 20 °C. The activity of ATRP ligands progresses in the order N1 < N2 < N3 < N4 (where 1, 2, 3, 4 refer to the number of N atoms in the ligand).[221] *N*-(*n*-Propyl)-2-pyridylmethanimine ensured a very good control of the molecular weights at 90 °C in *n*-propanol. It was suggested that a high temperature led to a higher compatibilization of the reaction mixture. The same macroinitiator **5** (R = *n*Bu) was used for the controlled polymerization of MMA[265] at 90 °C in xylene using a CuBr/dNbpy catalyst system. The molecular weight increased with conversion, and the final PDI was 1.17. Moreover, BuA was successfully polymerized, giving the desired diblock copolymer with a monomodal MWD. Macroinitiator **5** was also used by Pyun et al.[268] to polymerize styrene. Chain extension of the PDMS-*b*-PS macroinitiator with 3-(dimethoxymethylsilyl)-propyl acrylate (DMSA) by ATRP yielded an ABC triblock copolymer. The latter reactive segment was covalently attached to a silicon wafer. They used the equivalent difunctional macroinitiator **7** (8200 g·mol^{-1}) to successfully polymerize MMA and 2-trimethylsilyoxyethyl methacrylate (HEMA-TMS). Macroinitiator **5** (R = PS) was used to synthesize PS-*b*-PDMS-*b*-PBuA and PS-*b*-PDMS-*b*-PMMA triblock copolymers.[265,267]

Hong et al.[266] compared the different reactivities of a 2-bromoisobutyrate-terminated PDMS (macroinitiator **5** in Table 6 (5800 g·mol^{-1})) and a 2-bromopropionate-terminated PDMS (macroinitiator **6** in Table 6 (8800 g·mol^{-1})) using the (CuBr/PS8-dMbpy)/(CuBr$_2$/Me$_6$TREN) hybrid catalyst system. In this catalyst system, 4,4′-dimethyl-2,2′-bipyridine (dMbpy) was immobilized on a cross-linked PS. The polymerization of methyl methacrylate with the 2-bromopropionate-terminated PDMS was faster than with the 2-bromoisobutyrate-terminated PDMS; this result was unexpected, since the isobutyrate group is more reactive than the 2-bromopropionate group because of the more labile C−Br bond. It was suggested that the better dissociation properties of bromoisobutyrate led to a higher amount of formed radicals and therefore a higher amount of CuBr$_2$ deactivator (persistent radical effect)[233,234] resulting in retardation. The bromopropionate-terminated PDMS presented a low initiator efficiency and produced polymers with a large, bimodal MWD. Moreover, MMA and BuA were copolymerized using macroinitiator **5** and the previously described hybrid catalyst system in toluene to avoid a phase segregation. The rate of polymerization increased with increasing BuA concentration. Like in conventional free radical polymerization, MMA was incorporated faster than BuA. The reactivity ratios were specifically calculated for this system ($r_{\mathrm{MMA}} = 2.16$ and $r_{\mathrm{BuA}} = 0.42$).

Scheme 42. Structure of the PDMS Methacrylate Macromonomer



Macroinitiator **9** in Table 6 (9800 g·mol^{-1}) was used by Nakagawa et al.[270,271] to successfully polymerize styrene in diphenyl ether or in bulk at 130 °C using the CuCl/dNbpy catalyst system. Styrene conversions around 70% were obtained, and the linearity of the first-order kinetic plot confirmed the constant concentration of growing radicals throughout the polymerization. The whole molecular weight distribution was shifted toward higher molecular weights. The same macroinitiator **9** was used for the polymerization of MMA[265] in toluene at 90 °C using the same CuCl/dNbpy catalyst system. It was shown that the molecular organic benzyl chloride initiator had a higher efficiency than the PDMS macromolecular initiator. Moreover, the macroinitiator was used for the polymerization of styrene, isobornyl acrylate, and BuA.[265]

Macroinitiator **10** in Table 6 was used for the polymerization of isobornyl acrylate,[274] styrene,[272–274] and MMA.[273] In the polymerization of MMA,[273] when using the CuCl/bpy catalyst system at 130 °C in xylene, a low initiator efficiency was observed. The living character of the resulting block copolymer was demonstrated by resuming the polymerization with 1-(dimethoxymethylsilyl)propyl acrylate to give the desired ABC triblock copolymer.[272]

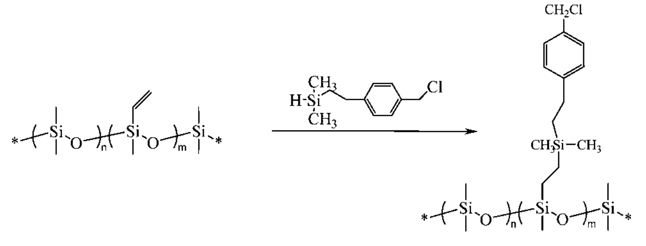
4.3.3. Graft Copolymers

4.3.3.1. Macromonomer Route. The use of CRP allows all the chains to grow simultaneously to ensure that they have the same composition. When a macromonomer is used, the spacing between the side chains is determined by the reactivity ratios of the macromonomer and the comonomer. These reactivity ratios are determined by (i) the reactivity of the macromonomer and the comonomer based on their chemical structure, (ii) the rather slower diffusion of the large macromonomer, and (iii) the possible incompatibility due to repulsive interactions between the growing polymer chain and the macromonomer.[275,276]

When copolymerizing the methacrylate-terminated PDMS ($M_n = 2200$ g·mol^{-1}, PDI = 1.18) (Scheme 42) and MMA (5/95 mol %) by ATRP (ethyl 2-bromoisobutyrate as initiator),[275] the proportion of PDMS in the copolymer was kept close to the feed composition regardless of the monomer conversion. Therefore, the branches were distributed homogeneously all along the polymer backbone. When using ethyl 2-bromoisobutyrate as initiator and CuCl/dNbpy as catalyst at 90 °C in bulk, a phase segregation was observed[276] due to the incompatibility between the PDMS macromonomer and the growing PMMA radical. This phase segregation could be diminished by working in xylene.[277] Moreover, when ethyl 2-bromoisobutyrate was replaced by a PDMS macroinitiator, a better compatibilization of the growing polymer chain with the macromonomer was observed.[276]

Lutz et al.[278] used the macromonomer route to synthesize PMMA gradient graft copolymers containing poly(D-lactic acid) (PLA) and poly(dimethylsiloxane) side chains. Moreover, they synthesized (PMMA-*g*-PLA)-*b*-(PMMA-*g*-PDMS) diblock copolymers by using ethyl 2-bromoisobutyrate as initiator and CuCl/dNbpy as catalyst at 90 °C in a solvent mixture of *p*-xylene and diphenyl ether. When using a hybrid

Scheme 43. Preparation of the Macroinitiator for the Graft Polymerization from Pendant ATRP Initiators



catalyst system (where the catalyst CuBr/PS8-dMbpy was immobilized onto cross-linked PS) in toluene, MMA was consumed faster than with the homogeneous catalyst system.[279]

Double comb copolymers of poly(ethylene glycol) methyl ether methacrylate and poly(dimethylsiloxane)-terminated methacrylate (Scheme 42) were synthesized[280] by using ethyl 2-bromoisobutyrate as initiator and CuCl/Me$_6$TREN as catalyst at 70 °C. The copolymer formed statistical hetero-grafted brushes due to similar reactivity ratios between the two macromonomers.

4.3.3.2. Pendant Side Groups. Several publications dealt with graft copolymerization by ATRP from pendant side groups. In all cases the macroinitiator was prepared by hydrosilylation of a pendant vinyl-functionalized PDMS with a 2-(4-chloromethylphenyl)ethyldimethylsilane (Scheme 43).[270,274,281,282] Styrene was polymerized in bulk or in toluene with the macroinitiator, showing a good efficiency (>97%). However, the variable number of initiating sites per PDMS chain was responsible for a rather high PDI (between 2 and 3).

4.3.3.3. Surface Initiation. In addition to the bulk or solution graft copolymerization, the vinyl polymerization by ATRP can also be initiated from the PDMS surface. It is well known that ATRP initiators are conveniently grafted onto the surface of silicon wafers by self-assembly of 2-bromoisobutyryl-functionalized trichlorosilane.[267] In a similar manner, ATRP initiator could also be tethered onto PDMS films by creating a reactive group at the surface of the PDMS film by UV/ozone treatment (Scheme 44).[283] This reactive group would further be used to graft an ATRP initiator onto the surface. Thus, acrylamide in water solution was grown from the PDMS film surface by this technique.[283]

4.3.3.4. Star Copolymers. Star copolymers are prepared from multifunctional ATRP initiators. Tetramethylcyclotetrasiloxane was first hydrosilylated with *p*-vinylbenzyl chloride (Scheme 45). This four-arm siloxane ATRP initiator was used to polymerize styrene[284,285] in bulk using CuCl/dNbpy as catalyst. To achieve appreciable conversions (72%), the reaction had to be conducted at 130 °C. An almost pure star copolymer was obtained, although some thermal initiation of styrene produced a small fraction of low molecular weight dead chains. The same macroinitiator was used with Cu(0)/bpy and CuCl/bpy catalyst systems[282] in the polymerization of styrene. However, since the siloxane content in these star copolymers is very low, one can assume that the resulting copolymer does not have properties inherent to PDMS.

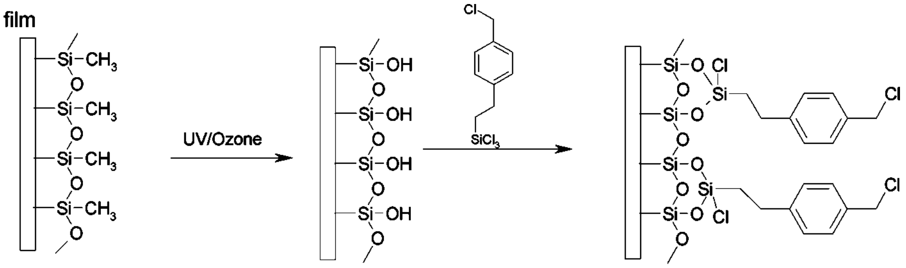
In summary, ATRP from PDMS macroinitiators or with PDMS macromonomers was the most widely studied route among CRP methods. It has been applied to the polymerization of a wide range of monomers. ATRP has given interesting results for the controlled synthesis of complex architectures from PDMS chains and gave the desired copolymer architectures with relatively low PDI and acceptable monomer conversions. However, the insolubility of certain catalyst systems can present a problem to achieve good initiator efficiency and correct control over the molecular weights.

4.4. ITP: Iodine-Transfer Polymerization

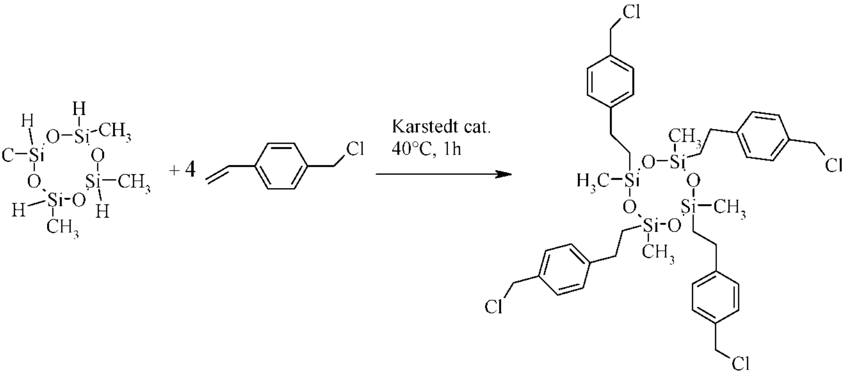
Iodine-transfer polymerization[141] was developed in the late 1970s by Tatemoto[286,287] and relies on the use of alkyl iodides as transfer agents. The mechanism of ITP with alkyl iodide is shown in Scheme 46.

The initiating radical, A$^•$, is generated by decomposition of a radical initiator, such as 2,2′-azobisisobutyronitrile, in

Scheme 44. Preparation of the Macroinitiator for the Surface-Initiated Graft Polymerization by ATRP



Scheme 45. Preparation of a Four-Arm Siloxane ATRP Initiator



Scheme 46. Reactions in Degenerative Transfer Polymerization with Alkyl Iodides

$$\text{Initiator} \xrightarrow{k_d} 2\text{A}^\bullet \qquad (1)$$

$$\text{A}^\bullet + \text{M} \xrightarrow{k_{i1}} \text{P}_1^\bullet \qquad (2)$$

$$\text{P}_n^\bullet + \text{M} \xrightarrow{k_p} \text{P}_{n+1}^\bullet \qquad (3)$$

$$\text{P}_n^\bullet + \text{R-I} \underset{k_{-I}}{\overset{k_I}{\rightleftharpoons}} \text{P}_n\text{-I} + \text{R}^\bullet \qquad (4)$$

$$\text{R}^\bullet + \text{M} \xrightarrow{k_{i2}} \text{P}_1^\bullet \qquad (5)$$

$$\text{P}_m^\bullet + \text{P}_n\text{-I} \underset{k_{-ex}}{\overset{k_{ex}}{\rightleftharpoons}} \text{P}_n^\bullet + \text{P}_m\text{-I} \qquad (6)$$

$$\text{P}_m^\bullet + \text{P}_n^\bullet \xrightarrow{k_t} \text{P}_{n+m} \ / \ \text{P}_n^{=} + \text{P}_m^{\text{H}} \qquad (7)$$

step 1. $A^\bullet$ adds to monomer in step 2, and the resulting radical propagates as shown in step 3. The transfer of iodine from the transfer agent, R−I, to the propagating radical, $P_n^\bullet$, results in the formation of the dormant chain P_n−I and a new initiating radical, $R^\bullet$ (step 4). Large differences in the stability of the reactants and products involved in step 4 (i.e., relative values of k_I and k_{-I}) could result in shifting the equilibrium overwhelmingly to the right ($k_I \gg k_{-I}$) or to the left ($k_I \ll k_{-I}$). The case where the structure of $R^\bullet$ closely resembles the structure of the propagating radical results in a thermodynamically neutral transfer step (i.e., $k_I \approx k_{-I}$). In step 5, $R^\bullet$, generated from the alkyl iodide, adds to a monomer unit. The exchange process described in step 6 is thermodynamically neutral (i.e., degenerative transfer: $k_{ex} = k_{-ex}$, $K = k_{ex}/k_{-ex} = 1$) because the propagating chains and dormant chains have the same structure on both sides of the equilibrium. The ratio between transfer rate coefficients and propagation, namely, the transfer constant, gives the reactivity of the transfer agent ($C_T = k_I/k_p$) and the exchange constant gives the reactivity of the dormant chains ($C_{ex} = k_{ex}/k_p$). As in any radical process, conventional termination occurs in ITP polymerization with alkyl iodides (step 7). Lowering the contribution of the irreversible termination step remains essential to keep a good control over the polymerization. In ITP, the overall concentration of the polymer chains is indeed equal to the sum of the concentrations of the consumed transfer agent and of the consumed initiator. Iodine-transfer polymerization from PDMS macrotransfer agents has been barely studied. The few PDMS-based macrotransfer agents studied in ITP are described in Table 7.

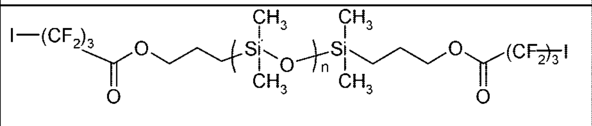
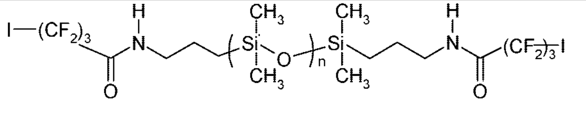
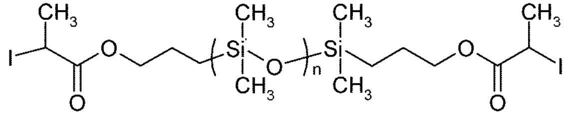
Shinya et al.[288] used transfer agent **1** (Table 7, entry 1) as macrotransfer agent or as photoiniferter (under UV activation) to polymerize tetrafluoroethylene (TFE). Under UV radiation, the iodinated group cleaved homolytically to create a radical on the PDMS chain and an iodine radical. Although the mechanism was not given by the authors, we can assume that the growing polymer chain was reversibly deactivated by reaction with an iodine radical, with iodine (created from the combination of two iodine radicals) or by degenerative chain transfer. They observed a good incorporation of the macrotransfer agent into the triblock copolymer and TFE conversion reached 40%. However, when using vinylidene fluoride (VDF) or chlorotrifluoroethylene (CTFE) as monomers, low monomer conversion and poor transfer agent efficiency were observed. Similar results were obtained by thermal peroxide initiation. The same group used transfer agent **2** (Table 7, entry 2) to copolymerize VDF and TFE (VDF/TFE = 85/15 mol %) under UV radiation. Even though they observed low conversions of monomer and transfer agent, the desired triblock structure was confirmed after extraction.

Our group used macrotransfer agent **3** (Table 7, entry 3) to synthesize PS-*b*-PDMS-*b*-PS triblock copolymers in miniemulsion polymerization.[41] An increase of molecular weights with conversion showed the controlled character of the polymerization. A high styrene conversion of 90% was obtained. NMR and SEC analysis were successfully correlated with the theoretical molecular weight. A chain extension in seeded emulsion polymerization proved the living character of the iodinated chain end. However, a pH drop, attributed to chain-end degradation by HI elimination, was observed during the polymerization. It was demonstrated that the reaction had to be stopped rapidly once high monomer conversion has been reached in order to avoid undesirable chain-end degradation.

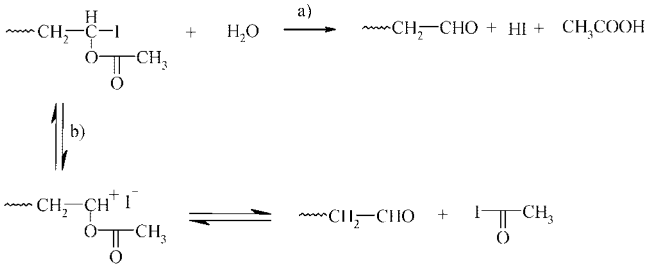
More recently our group used the same macrotransfer agent **3** (Table 7, entry 3) for the controlled synthesis of PVAc-*b*-PDMS-*b*-PVAc triblock copolymers in bulk at 80 °C.[290] The molecular weight evolution proved the controlled character of the synthesis, and high conversions, around 75%, were obtained. However, the PVAc-I chain end was prone to degradation (Scheme 47), as previously demonstrated by Boutevin et al.[291] in the case of PVAc-X chain ends (X = Br or Cl). Iovu et al.[292] showed an identical degradation mechanism by hydrolysis of the PVAc-I chain ends.

A Japanese patent describes the synthesis of poly(dimetylsiloxane)-*g*-poly(ethylacrylate) copolymers.[293] The ma-

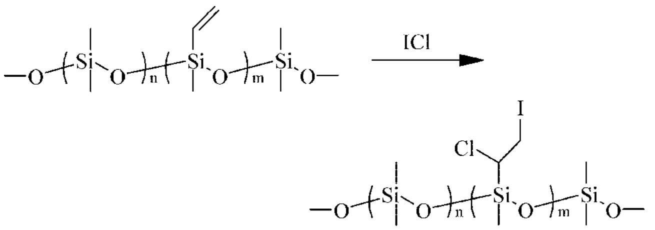
Table 7. PDMS Macrotransfer Agents Used in Iodine-Transfer Polymerization

Entry	Transfer Agent	Synthesis method	PDMS M_n range ($g.mol^{-1}$)	Controlled Monomers	Ref.
1		Esterification	10 000	TFE, VDF/TFE	288
2		Amidification	10 000 100 000	TFE, VDF/TFE	288,289
3		Esterification	1 340	Styrene, VAc	41,290

Scheme 47. Hydrolysis (a) and Decomposition (b) of the Iodo End Group of Poly(vinyl acetate) after Iodine-Transfer Polymerization[292]



Scheme 48. Synthesis of the Macrotransfer Agent Used for Preparing Poly(dimethylsiloxane) Graft Copolymers by Iodine-Transfer Polymerization[293]



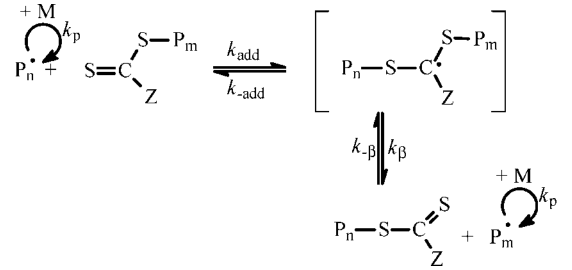
crotransfer agent was prepared by reacting 97:3 dimethylsiloxane−vinylmethylsiloxane copolymer with ICl (Scheme 48). The copolymers were prepared by graft polymerization of iodine-containing silicone polymers with ethyl acrylate in the presence of a radical polymerization initiator and then used as compatibilizers for rubber compounds.

To conclude, the literature extensively describes iodine-transfer polymerization for a wide range of monomers,[141] including styrenics, acrylates, vinyl esters, dienes, fluorinated monomers (TFE, VDF, hexafluoropropylene (HFP)), and chlorinated monomers (vinyl chloride, vinylidene chloride). This leaves a lot of possibilities for ITP from PDMS macrotransfer agents. It should also be possible to synthesize graft copolymers by using PDMS macromonomers with ITP[141] or RITP[138−141,294,295] techniques. Moreover, ITP[41] and RITP[142,143,296−299] are compatible with dispersed aqueous medium, which is of great interest for implementing the technique at an industrial scale.

4.5. RAFT: Reversible Addition−Fragmentation Chain Transfer

RAFT polymerization[300,301] involves dithiocarbonyl-transfer agents of general formula Z−C(S)S−R. The dithiocarbonyl group reacts in two steps: first, addition of a radical (formed by initiator decomposition) to the C=S double bond followed by a beta fragmentation of one of the two C−S bonds of the intermediate radical. Like iodine-transfer polymerization, RAFT is based on a degenerative transfer. When the transfer agent (Scheme 49) involves a xanthate (Table 8, entry 2), various authors sometimes refer to the "MADIX" process as claimed by the Rhodia Co.,[302,303] which stands for MAcromolecular Design through the Interchange of Xanthates. Again, a patent from Matyjaszewski covers the synthesis of poly(dimethylsiloxane) containing block and graft copolymers by RAFT.[252]

Scheme 49. General Mechanism of RAFT/MADIX Polymerization



4.5.1. Block Copolymers

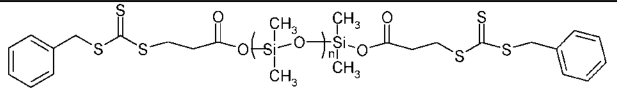
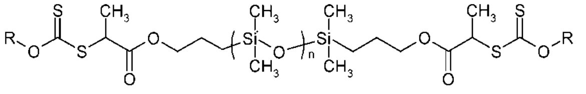
Several different macrotransfer agents were used to synthesize block copolymers by RAFT (Table 8). Pai et al.[304] used transfer agent **1** (Table 8, entry 1) to grow two statistical copolymer blocks from the central PDMS block, comprising units of *N*,*N*-dimethyl acrylamide (*N*,*N*-DMA) and 2-(*N*-butyl perfluorooctanefluorosulfonamido) ethyl acrylate (BFA) leading to an amphiphilic triblock copolymer, however containing fragile Si−O−C bonds.[78,79] The polymerization was conducted in trifluorotoluene, which solubilized the macroRAFT agent and the vinylic copolymer. The molecular weight increased with conversion as expected, leading to the desired triblock copolymer. However, the authors observed that the copolymer composition varied whether a conventional RAFT agent or the corresponding macroRAFT agent was used. They assumed that the hydrophobic PDMS chain favored the incorporation of the hydrophobic BFA, through a preferred solvation in the PDMS phase.

The RHODIA Co. has developed a series of MADIX agents exhibiting the general structure of compound **2** (Table 8, entry 2), the R group allowing tuning the reactivity of the MADIX agent. They used MADIX agent **2** with R = $-C_2H_5$ for the controlled polymerization of VAc,[308] ethyl acrylate,[308] butyl acrylate,[311] and 2-dimethylaminoethyl acrylate,[305] giving well-defined triblock copolymers. One potential drawback of MADIX lies in the fact that the xanthate terminal group, if not deactivated, is likely degraded during the lifetime of the polymer or under some specific application conditions, leading to some low molecular weight malodorous, potentially toxic sulfur-based byproduct.[306,307] Therefore, the RHODIA Co. has developed some methods to eliminate the xanthate end group from the copolymer. MADIX agent **2** was oxidized[306,310] with dilauryl peroxide at 80 °C in isopropanol or with di-*tert*-butyl peroxide at 175 °C in 2-octanol giving the PDMS ethyl ester and *S*-undecyl-*O*-ethyl xanthate which could easily be eliminated by selective precipitation.[312] Moreover, transfer agent **2** with different R groups (isobutyl, cyclohexyl, and phenyl ethyl) was used to study elimination of the xanthate group by dethiocarboxylation,[307,309] giving the thiol-terminated PDMS. All were completely dethiocarboxylated when heated at 180 °C in *o*-dichlorobenzene. The phenyl ethyl derivative even underwent complete dethiocarboxylation when heated for 2 h at 130 °C in chlorobenzene.

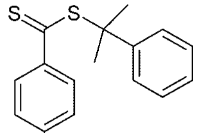
4.5.2. Graft Copolymers

Shinoda et al.[277,313] used cumyl dithiobenzoate (Scheme 50) as a RAFT transfer agent for the copolymerization of MMA and PDMS macromonomer (Scheme 42) (M_n = 2300 g·mol^{-1}). The reaction was conducted at 75 °C with 5 mol % of PDMS-MA. Xylene was added to the reaction medium

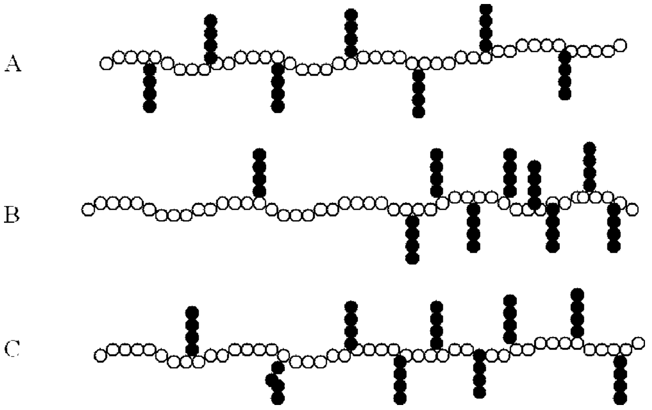
Table 8. PDMS Macrotransfer Agents Used for the Polymerization by RAFT/MADIX

Entry	Transfer Agent	Synthesis method	M_n range (g.mol^{-1})	Controlled Monomers	Ref.
1		Esterification	18 000	DMA, BFA	304
2		Esterification + Nucleophilic substitution	1 300	VAc, EtA, BuA, tBuA,2-dimethyl aminoethylacrylate	305-311

Scheme 50. Cumyl Dithiobenzoate



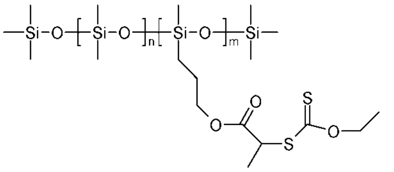
Scheme 51. (A) Homogeneously Distributed Branches, (B) Heterogeneously Distributed Branches (toothbrush structure), and (C) Intermediate Distribution



to favor homogeneous conditions and to lead to a more controlled polymerization. Since the used macromonomer bore a methacrylate end group, the authors expected a similar reactivity of the macromonomer to MMA ($r_{MMA} = r_{macromonomer} = 1$) (Scheme 51A). It was shown that MMA was incorporated slightly faster than the macromonomer into the copolymer. When using the Jaacks method[314] the reactivity ratio r_{MMA} was found to be equal to 1.49.

In a conventional free radical polymerization, r_{MMA} was found around 2.98. This means that when a RAFT agent is used, the incorporation of the macromonomer is more regular all along the copolymerization, leading to a better defined architecture. However, at a lower temperature (60 °C), the incompatibility between PMMA and PDMS increased, leading to a higher r_{MMA} and worse control of the macromonomer incorporation. Therefore, the reaction temperature has to be kept relatively high (75 °C) to reach better control over the copolymerization. Since $r_{MMA} > 1$, incorporation of PDMS-MA is less important in the early stages of the polymerization, leading to a toothbrush structure (Scheme 51B) at low temperature (60 °C) and an intermediate toothbrush-regular distribution structure (Scheme 51C) at higher temperatures (75 °C).

Scheme 52. PDMS with Pendant Xanthate Groups Used To Synthesize Graft Copolymers[308]



The RHODIA Co. has claimed the synthesis of PDMS graft copolymers using a poly(dimethylsiloxane) with pendant xanthate groups (Scheme 52).[308] This macro MADIX agent was synthesized by anionic copolymerization of D_4 and D_4-containing pendant propanol side groups. The primary pendant alcohol was esterified with 2-bromopropionyl bromide. However, the esterification reaction was not complete, and 30% of free OHs were still present according to the ^1H NMR spectrum. The final transfer agent was obtained by nucleophilic substitution of bromine by the xanthate salt (K^+ ^-SCSOEt) in acetonitrile.

Until now, RAFT and/or MADIX from PDMS macrotransfer agents were used for the controlled polymerization of *N*,*N*-DMA, BFA, VAc, EtA, BuA, tBuA, and 2-(dimethylamino) ethyl acrylate. RAFT allows the controlled polymerization of a very wide range of monomers,[300,301] and therefore, many other copolymers could be potentially prepared. For instance, the controlled polymerization of acrylates (BuA, MeA, AA, 2-hydroxyethyl-acrylate,...), styrenics (styrene, styrene *p*-sulfonic acid sodium salt,...), methacrylates (such as MMA and MAA), acrylamides, *N*-vinyl monomers (*N*-vinyl pyrrolidone), vinyl esters (vinyl acetate, vinyl benzoate), vinyl derivatives of pyridine (4-vinyl pyridine, 2-vinylpyridine), halogenated monomers (vinylidene chloride), and acrylonitrile has been described.[315] One drawback of RAFT/MADIX is the potential decomposition of chain ends, giving possible harmful byproducts. Another limitation is the rather complex synthesis of the RAFT/MADIX macrotransfer agents since very few precursors (such as KSC(S)OEt) are commercially available.

4.6. Conclusion on CRP Techniques

Controlled radical polymerization has allowed the controlled synthesis of a large number of PDMS-containing block and graft copolymers with predefined molecular weights. The use of PDMS azo macroinitiators can be combined with different CRP methods. For example, a macroinitiator was used in combination with TEMPO in

Table 9. Advantages and Drawbacks of the Five Main Controlled Radical Polymerization Methods

Polymerization method	Advantages	Drawbacks
Iniferter	large monomer range	large PDI
		photoactivation is required to reach living properties
NMP	low PDI	high reaction temperatures (>100 °C)
		bad control with TEMPO (except for styrenics)
ATRP	low PDI	presence of metallic ions
	large monomer range	neither control of acidic monomers nor VAc
		catalyst partial insolubility
ITP	implemented in dispersed aqueous medium	relatively large PDI
	control of halogenated monomers	no control over methacrylates (except by RITP)
RAFT/ MADIX	control of functional monomers (VAc, AA, etc.)	possible chain-end degradations with harmful byproduct release
	triblock copolymers with vinylic central block	
	control of vinylidene chloride	

NMP. Moreover, it would be possible to polymerize a vinylic monomer by RITP and reverse ATRP. When an azo macroinitiator (or peroxide macroinitiator) is used, the low initiator efficiency is responsible for an important number of dead chains and an ill-defined architecture. The use of macroiniferters, macroalkoxyamines (NMP), macroinitiators (ATRP), or macrotransfer agents (ITP, RAFT/MADIX) leads to a higher initiator efficiency, giving a much better control of the copolymer architecture. The desired block or graft copolymers are obtained with good control of the molecular weights.

Among the five major CRP methods, each one has its advantages and drawbacks (Table 9). Iniferters enable the controlled polymerization of a wide range of monomers, although producing polymers with large PDIs. Moreover, thermal iniferters permit the synthesis of triblock copolymers, with the PDMS blocks being at the extremities, as well as multiblocks. The main drawback of photoiniferters is that irradiation is required to obtain a living character. Nitroxide-mediated polymerization leads to polymers with low PDIs, but the compulsory high temperature of reaction can be problematic if the recipe involves fragile reactants or when one would like to work in dispersed aqueous medium. Moreover, TEMPO has a low efficiency for monomers other than styrene and its derivatives. Therefore, other controlling agents using more efficient counter radicals, such as SG1, must be used to polymerize other monomers and to work in dispersed aqueous medium. ATRP leads to copolymers with low PDIs and controls a large range of monomers. However, acidic monomers or vinyl acetate can not be controlled. Moreover, the presence of metallic ions and the low solubility of the catalyst in the reaction medium can be a problem. Iodine-transfer polymerization is a rather low-cost method which is applicable in dispersed aqueous medium (miniemulsion and potentially suspension polymerization). Moreover, the iodinated transfer agents allow the control of fluorinated and chlorinated monomers. The main drawbacks of ITP are the lack of control of methacrylates (the new RITP method is however able to fill this gap) and the rather large PDIs finally obtained in comparison with other CRP methods (although medium polydispersity is actually not a real drawback for most industrial applications and is even sometimes helpful).[316] The RAFT/MADIX technique enables control of vinylidene chloride, VAc, and functional monomers like AA. However, a potential chain-end degradation produces sulfur-containing side products. Therefore, a chain-end elimination or transformation could be necessary depending on the desired application.

Controlled radical polymerization allows the synthesis of a wide range of block and graft copolymers from PDMS precursors. However, it is important to choose the best method depending on the type of monomer to be polymerized (especially for functional monomers), on the required level of control of the polymerization (low PDI), and on the type of application (for instance, sensitivity to metallic species from ATRP). Moreover, until now, only ITP from PDMS macrotransfer agents has been implemented in dispersed aqueous medium. The synthesis of these copolymers is possible in processes where the PDMS chain does not need to diffuse across the aqueous phase (miniemulsion or suspension polymerization). Indeed, since the PDMS is too hydrophobic to diffuse across the aqueous phase, these copolymers cannot be synthesized in ab initio emulsion polymerization (unless a reverse emulsion would be considered). Thus, the use of CRP to synthesize well-defined copolymer architectures from PDMS precursors leaves a lot of unexplored possibilities like the use of functional monomers (possibly protected monomers), the use of enhanced CRP methods like RITP, and the polymerization in dispersed media.

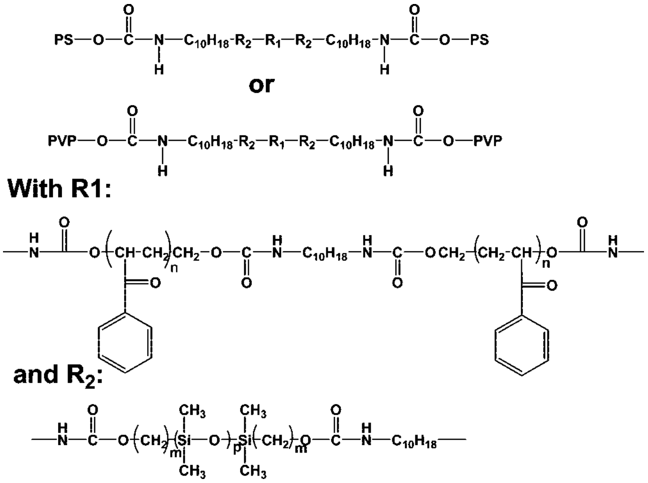
5. Some Properties and Some Applications

The original architectures obtained by radical polymerization of various monomers in the presence of PDMS enable the preparation of hybrid materials having well-controlled properties. The presence of PDMS segments in the materials generally creates a phase demixing, which can change the surface properties of a material or its mechanical and solution properties. The presence of a PDMS block in the material generally enhances the thermal stability compared with the reference organic homopolymer. Some interesting applications found in the literature cited in this review will be briefly detailed in the following discussion.

5.1. Phase Segregation Properties

Cameron et al.[166,317] studied the variation of the glass transition temperature (T_g) by DSC for copolymers of methacrylic polysiloxane macromonomers and styrene (or AN) that naturally demix. Their goal was to highlight the effect of the forced miscibility due to a copolymer architecture. First, they experimentally measured the T_g's of the PS domains versus the size of the macromonomers incorporated in the backbone. Following the Gordon−Taylor equation[318] for totally miscible blends, the authors concluded that an "appreciable degree" of miscibility exists between the domains of the copolymer. They observed that the plasticizing effect of PDMS with PS is much more important than in the case of poly(acrylonitrile) (PAN) where the

Scheme 53. Five-Block Copolymers of AFR, PDMS, and PVP or PS



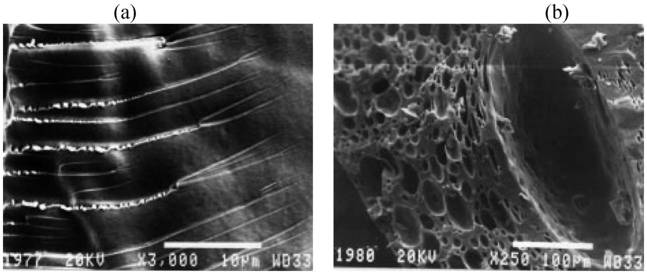
measured T_g's were closer to those of the parent homopolymers. It indicates that, in spite of the chemical bonding in both cases, the forced miscibility is much more efficient with PS-PDMS copolymers than with PAN-PDMS copolymers. Blahovici et al.[319] investigated the miscibility of PMMA-*g*-PDMS copolymers blended with the PMMA parent homopolymer. By DSC measurements, they observed only one T_g versus two T_g's for a blend composed of the two parent polymers (i.e., PDMS and PMMA). This allowed them to conclude that such copolymers were miscible with PMMA.

In another study, Hamurcu et al.[104] observed that networks from block copolymers of PDMS and PS showed a T_g of 45 °C, giving evidence for the plasticizing effect of the flexible PDMS segments ($M_n = 1050\ \mathrm{g \cdot mol^{-1}}$). Fawcett et al.[214] also showed the presence of only one T_g in the silicone graft copolymers with short chains of poly(chloroprene). Hamurcu and co-workers[103,104] carried out the synthesis of PDMS-*b*-PS. Only the T_g of the poly(styrene) (PS) block (90 °C) was observed, otherwise lower than the one of homo-PS (100 °C) because of the plasticizing effect of the short PDMS segments.

Uyanik and co-workers[86] studied different properties of PDMS-containing five-block copolymers based on AFR and PVP or PS (Scheme 53). The T_g of the PS blocks is affected by their chain length, but they are not significantly altered by the presence of the middle blocks. In this five-block copolymer, the domains are well separated and no plasticizing effect was observed.

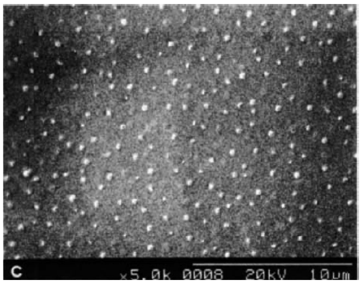
Cvetkovska et al.[82] studied the morphology of poly(monobutyl itaconate)-*b*-PDMS-*b*-poly(monobutyl itaconate) triblock copolymers. The SEM image of the poly(monobutyl itaconate) homopolymer shows a laminated fracture (Scheme 54a), whereas the triblock copolymer shows a porous morphology (Scheme 54b). SEM images carried out by Chang et al.[112] in the case of PMMA-*b*-PDMS copolymers also show a phase separation (Scheme 55). This phase segregation is always observed when the length of the blocks is enough to induce an incompatibility between the two polymers. The surface of the film shows a PDMS ball-like structure (confirmed by Si mapping), the average diameter of the phase domain being around 0.4 μm.

Scheme 54. SEM Image of Poly(monobutyl itaconate) Homopolymer ((a) magnification ×3000) and Poly(monobutyl itaconate)-*b*-PDMS-*b*-poly(monobutyl itaconate) Triblock Copolymer ((b) magnification ×250)[a]



[a] Reproduced with permission from ref 82. Copyright 2000 Wiley-VCH Verlag GmbH & Co. KGaA.

Scheme 55. SEM Micrograph of PDMS-*b*-PMMA Film[a]



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Smith et al.[320,321] studied the bulk properties and monitored the morphology of PMMA-*g*-PDMS. As expected, they observed spherical domains of PDMS in a PMMA matrix for low contents of PDMS. However, for higher contents, e.g. 45 wt % of PDMS, they observed a cylindrical texture. The size of the domains increased with the length of the PDMS side chain (Scheme 56). Smith et al.[322] also observed that the blends of PMMA-*g*-PDMS copolymers with PMMA and PVC changed from a spherical to a bicontinuous morphology when the PDMS content ranged from 25% to 47%, respectively. Incompatible blends with PVC and PMMA were also obtained for higher PDMS contents.

5.2. Surface Properties

From our literature survey, it was possible to extract studies dealing with the surface properties either of the copolymers themselves or of the copolymers embedded in a matrix. It is well known that PDMS exhibits a low surface energy ($20\ \mathrm{mN\ m^{-1}}$). Low energies were also observed for various PDMS-containing copolymers, as investigated by Kawakami et al.,[146,323,324] Smith and McGrath,[325] Lee et al.,[326] or Taskiran et al.[327] As expected, the contact angle measurements revealed that there was a logical increase of the surface hydrophobicity with an increasing PDMS content or molar mass (Table 10).

In another study, Bes et al.[261] performed the synthesis and characterization of PMMA-*b*-PDMS-*b*-PMMA triblock copolymer. DSC measurements revealed a phase segregation (two T_g's) even at low PMMA content (23 wt %). A higher degree of segregation and a high PDMS concentration at the surface were, respectively, observed by TEM and X-ray photoelectron spectroscopy (XPS) for the copolymers containing the highest PDMS content. Logically, the surface tension was higher and the contact angle with water smaller in the case of a high PMMA-containing copolymer (surface tension ranging from $\gamma_S = 19.15$ (41% mol PMMA) to 27.32 $\mathrm{mN \cdot m^{-1}}$ (81% mol PMMA) and a water contact angle ranging from 112.9° to 105.25°). Nakamura[99] also observed a PDMS accumulation at the surface of PMMA particles

Scheme 56. TEM of PMMA-*g*-PDMS with an Increase of Side Chain Length and End View of the Cylindrical Morphology of PMMA-*g*-PDMS (20 000 g mol^{-1})[a]

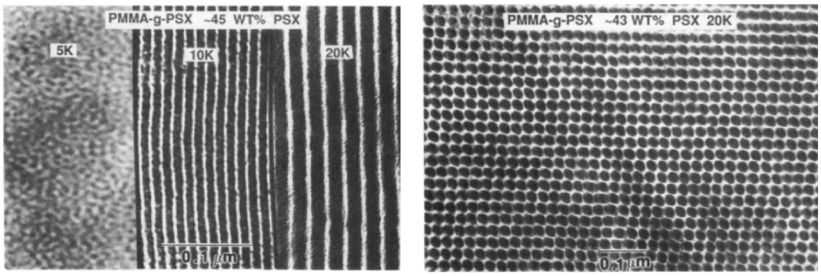

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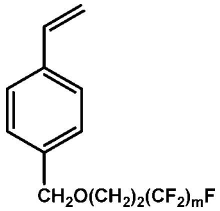
Table 10. Influence of the Siloxane Content and Molecular Weight on Water Contact Angle of PMMA-*g*-PDMS As Measured by Smith and McGrath[325]

macromonomer M_n (g mol^{-1})	wt % (charged)	wt % (via NMR)	contact angle
PMMA homopolymer control			74°
1000	5	4.0	97°
	20	15.0	105°
5000	5	4.3	99°
	20	16.8	107°
10 000	5	5.8	108°
	20	15.9	109°

Scheme 57. Fluorinated Monomers Used by Bertolucci et al.: *m* = 6 (StyF6) and *m* = 8 (StyF8)[115]



prepared by dispersion polymerization in organic media using an azo macroinitiator. This result is in accordance with the fact that the azo macroinitiator is used as a dispersant (steric stabilizer) during the polymerization. Smith and co-workers[320,321] analyzed the surface characteristics of PMMA-*g*-PDMS graft copolymers. Results were in agreement with those obtained by other groups: the presence of PDMS resulted in an increase of water contact angle, i.e., the material was more hydrophobic.

Bertolucci et al.[115] studied the wetting behavior of fluorinated styrene-siloxane block copolymers. The structure of the fluorinated monomers is given in Scheme 57. The hydrophobic behavior in water was not influenced by siloxane or fluoropolymer surface composition. The oleophobic behavior for the copolymer using StyF8 (n = 8) with alcohols (θ_{adv} = 64° and θ_{rec} = 45°) was typical of fluorinated surfaces, while a reference PDMS coating was wetted ($\theta_{adv} = \theta_{rec} = 0°$). The results for the copolymer using the StyF8 from Wilhelmy plate dynamic contact angle analysis were characteristic of fluorinated surfaces (both hydrophobic and oleophobic), in contrast to PDMS surfaces which are only hydrophobic. In addition, the higher surface stability of the copolymer using StyF8 compared to that of the copolymer using StyF6 (n = 6) was attributed to the thermodynamic stabilization imparted by the liquid crystalline mesophase created by the association of fluorinated chains with $n \geq 8$.

Uyanik et al.[86] showed that the solubility of five-block copolymers PVP-*b*-PDMS-*b*-AFR-*b*-PDMS-*b*-PVP or PS-*b*-PDMS-*b*-AFR-*b*-PDMS-*b*-PS is affected by the AFR block, while the surface properties are affected by the PDMS blocks: as expected, the contact angle increased with PDMS content or molecular weight.

Ohata et al.[96,100] found that the excellent ink repellency and ink resistance of silicone acrylic block copolymers films (UV or thermo curable) resulted from their morphology and from the silicone domain spacing within the films. These films were found to be hard enough to form a nozzle face and exhibited over 80° of θ_{adv} and 60° of θ_{rec} when put in an ink, which are superior values from those observed for silicone or fluorinated coating films. Moreover, the durability of the films was outstanding.

Hou et al.[328,329] described the surface composition of the P(HEMA)-*g*-PDMS, an amphiphilic graft copolymer. Thanks to XPS analyses, they could determine that an increase of the length of the grafted PDMS led to an increase of both the concentration of PDMS at the air interface and the surface layer thickness. However, even for high PDMS content in the copolymer, the surface was never saturated with PDMS, as in the case of block copolymers. By copolymerizing the two monomers either by anionic polymerization (yielding a narrow MWD, PDI about 1.1) or by photoinduced polymerization (yielding a broad MWD, PDI about 3.0), the authors did not observe any significant differences under dry conditions. However, under wet conditions, the authors demonstrated the reorganization of the surface to generate a more favorable energetic conformation with a decrease in PDMS content. It is worth mentioning that, in these conditions, MWD plays an important role owing to the shorter chain segments ability to reorganize more easily. In summary, anionic polymerization yielded materials that were more resistant in wet conditions.

Inoue et al.[43] carried out the surface modification of PDMS using hydrophilic monomers. They noticed a decrease of the water contact angle versus the extent of surface grafting. The lowest contact angles were obtained with sodium styrene sulfonate (NaSS) and methacrylic acid monomers (55°). The same group[98] also observed the surface accumulation of PDMS in PDMS-*b*-PMMA/PMMA blends using X-ray photoelectron spectroscopy (XPS), spectroscopy for chemical analysis (ESCA), and water contact angle analysis. The water contact angle increased abruptly with siloxane bulk concentration or siloxane chain length (M_n > 2000 g·mol^{-1}). In another study from this group,[117] the surface characteristics of fluoroalkylsilicone-PMMA block copolymers and their PMMA blends were investigated using XPS, water contact angle analysis, and measurement of the 180° peel strength against pressure-sensitive adhesives. It was observed from film casting of the blends that the contact angles were higher on the air side of the film than on the glass side. Again, the higher the siloxane content, the higher the contact angle. Preferential surface accumulation of siloxane segments was observed for the block copolymers having long siloxane chains and also relatively long fluoroalkyl side chains. Interestingly, the presence of fluoroalkyl groups in the side chains of silicone decreased significantly the 180° peel strength on both air and glass sides. The conclusion of their work was that the fluoroalkyl groups having a relatively long chain length (tridecafluoro and heptadecafluoro) were phase separated from PMMA segments and also enhanced the surface accumulation of methylsiloxane groups.

A very interesting study carried out by Kawakami et al.[330] suggested that the incorporation of PMMA-g-PDMS in a matrix of PMMA changed the contact angle and the composition at the surface. They showed that the graft copolymers phase accumulated on both the air- and glass-side surfaces. Particularly under low surface energy conditions (i.e at the air surface), the siloxane segments caused a large change in the contact angle value and ESCA spectra.

Finally, according to Taskiran et al.,[84,327] microscopy can give indications on the surface properties. Indeed, comparison between expandable poly(styrene) (EPS) and EPS modified by silicone acrylate showed a rough surface for the first one whereas the modified EPS appeared smooth and glossy.

5.3. Mechanical Properties

PDMS is often used to enhance the mechanical properties of materials in terms of deformation at break and impact resistance. The issue that has to be overcome is the compatibility between PDMS and the host material. The following examples illustrate the benefit that can be gained from insertion of PDMS in block copolymers.

The mechanical properties of PDMS-*b*-PS copolymers were studied by Baysal et al.[80,103] Considering PDMS molar content ranging from 12% to 18%, the mechanical properties of the copolymers were quite different from those of PS homopolymer. It was observed that elongation at break for PS was around 2%, whereas the elongations for the copolymers were in the range of 7−26%. In addition to these expected performances, stress at break and Young's moduli were only slightly lower than the PS reference. As expected, the copolymers having the highest PDMS content exhibited the best elastomeric properties. These results were confirmed on similar materials[103,104] observing that the block copolymers had higher elongations (6−8%) than PS homopolymer and that tensile strengths were very close to the values of PS homopolymer (22−50 MPa).

The enhancement of impact resistance by insertion of PDMS blocks was described by Falender et al.,[22,23] who prepared PDMS-*g*-P(AN-*co*-S) copolymers by telomerization using a thio-functionalized PDMS as macrotelogen. The higher the PDMS content, the higher the impact strength.

Uyanik[85] studied the mechanical properties of a five-block copolymer PVP-*b*-PCL-*b*-PDMS-*b*-PCL-*b*-PVP. The copolymer showed a tensile strength, a Young's modulus, and an ultimate tensile strength lower than the one observed for homo-PVP. On the contrary, the ultimate tensile elongation was higher for the copolymer than for the homo-PVP (Table 11).

Table 11. Mechanical Properties of PVP-*b*-PCL-*b*-PDMS-*b*-PCL-*b*-PVP and Homo-PVP

sample	ultimate tensile elongation (%)	tensile strength (MPa)	ultimate tensile strength (MPa)	Young's modulus (GPa)
homo-PVP	10.5	33.2	20.4	0.75
block copolymer	13.2	22.6	19.6	0.39

Uyanik et al.[87] also studied the behavior of water-soluble PVP-*b*-PDMS-*b*-PVP under tensile stress. The authors surprisingly obtained that the ultimate tensile strength and ultimate tensile elongation of the films of copolymer were lower than PVP's and that their Young's moduli values were higher than PVP's. They also showed by DSC that the thermal characteristics of the copolymers were similar to those of PVP homopolymer.

Neugebauer et al.[280] prepared densely grafted PDMS-PEO copolymers by ATRP using PDMS and PEO macromonomers. Morphology and mechanical analyses revealed the presence of crystalline (PEO) and amorphous (PDMS) phases. The viscous modulus was found to be higher than the elastic modulus ($G'' > G'$), which is typical of a melt state. It was also observed that after cross-linking, caused by annealing at high temperature, the material showed properties typical of elastomers, more precisely of a soft gel ($G' < 10^4$ Pa and $G' \geq G''$).

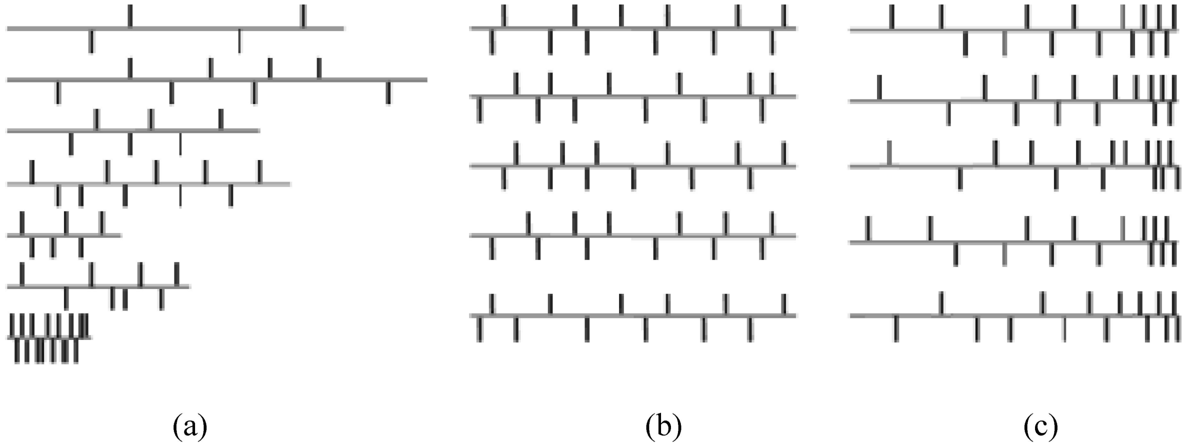
Shinoda et al.[277] carried out the analysis of three graft PMMA-PDMS copolymers prepared by RAFT, ATRP, and conventional radical polymerization. The three graft copolymers show different architectures (Scheme 58). At small deformations, the mechanical properties measured by dynamic mechanical analysis (DMA) did not differ for the different architectures and indicated a thermoplastic−elastomer behavior. This was confirmed by tensile test measurements which showed similar moduli. However, at high deformations, under tensile test, sample (c) exhibited a low elongation at break (1.3 MPa) and a high strength at break (6.4 MPa), sample (b) a high elongation at break (3.8 MPa) and a low strength at break (4.2 MPa), while sample (a) had an intermediate behavior. These results were linked to the sample architectures and consequent morphologies, more or less phase segregated.

5.4. Thermal Stability

Smith et al.[331] observed that copolymers of MMA and silicone methacrylate macromonomers were more thermally stable than the homo-PMMA. Furthermore, the longer the PDMS side chains, the more stable the grafted copolymer (Scheme 59). It was demonstrated[332,333] that when MMA is homopolymerized by free radical polymerization, recombination and disproportionation both occur, leading, on one hand, to a sterically hindered linkage which decomposes at 175 °C and, on the other hand, to an unsaturated end group which degrades at about 225 °C. The other disproportionation product, that is, the saturated product, degrades beyond 300 °C. In the case of a copolymerization with a macromonomer such as silicone methacrylate, irreversible termination of the propagating radical leading to a saturated end group by chain transfer seems to be more favorable, as long as there is enough macromonomer in the medium to end cap each chain. The authors suggested that chain transfer could be favored by longer radical lifetimes of the macromonomers and supported this explanation by SEC data which showed that the higher the macromonomer content, the larger the molecular weight distribution, i.e., the higher the number of chains, finally resulting in an increase of the thermal stability.

Chang et al.[111] observed the same behavior in the case of PMMA-*b*-PDMS block copolymers. The block copolymers

Scheme 58. Schematic Representation of the Three Copolymers Prepared by (a) Conventional Radical Polymerization, (b) ATRP, and (c) RAFT[a]



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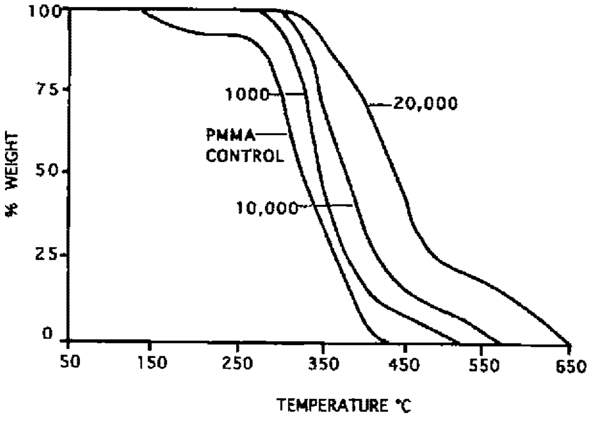
Scheme 59. TGA Analyses of PMMA-*g*-PDMS with Various Siloxane Chain Lengths[a]



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began to degrade at 240 °C, alike PMMA homopolymer, although at a slower rate as the temperature was raised. The temperature at 40% weight loss in PDMS-*b*-PMMA increased with increasing the PDMS content in the copolymers (from 400 to 420 °C while increasing the Si content from 4.1% to 7.3%).

Uyanik[85] studied the thermal properties of a five-block copolymer PVP-*b*-PCL-*b*-PDMS-*b*-PCL-*b*-PVP. Thermogravimetric analysis (TGA) clearly showed an increase in the thermal stability of the copolymer compared to the homopolymers (PVP and PCL). The decomposition temperatures of the homopolymers were all below 440 °C, whereas for the copolymers, a 5 wt % loss was observed at 170 °C, and the decomposition temperatures were all around 440 °C.

5.5. Solution Properties

Poly(*N*-isopropylacrylamide) (PNIPAM) is known to exhibit a well-defined and reversible lower critical solution temperature (LCST) in water, around 32−34 °C, which is close to the body temperature. In a recent study, Uyanik et al.[57] analyzed the solution properties of PNIPAM-*b*-PDMS copolymers by measuring the LCST. The LCST was found to be lower in concentrated solutions (<35 °C at 0.5 wt %) than in dilute solutions (>35 °C at 0.01 and 0.1 wt %), presumably a consequence of the presence of the hydrophobic terminal PDMS group. At higher concentrations (>0.5 wt %), a collapse of the macromolecular coils was observed due to the hydrophobic forces between isopropyl groups. Thus, colloidally stable and hydrophobically modified PNIPAMs carrying PDMS chains at either one or two chain ends exhibited macroscopic solution-phase separation different from homopoly(NIPAM)s.

Bes and co-workers[262] evaluated the surfactant properties of PDMAEMA-*b*-PDMS-*b*-PDMAEMA prepared by ATRP using a PDMS macroinitiator. They carried out surface tension measurements on aqueous solutions of the triblock copolymer versus concentrations and pH. It was observed that the surface tension of the aqueous solution was mostly reduced at basic pH (around 30−40 $mN \cdot m^{-1}$ depending on triblock copolymer concentration). Indeed, protonation of PDMAEMA at acidic pH induces a lower self-association of the amphiphilic copolymer: the predominant species in solution appeared to be unimers, and the surface activity was very low. On the contrary, at basic pH, the charge density (degree of protonation) on PDMAEMA is low and the copolymer behaved as a surfactant. Furthermore, aggregates with a high hydrodynamic diameter were ascribed to polymer "hollow vesicles".

Pinteala et al. studied the conformations of PMAA-*b*-PDMS copolymers in water solutions.[102,109] In dilute solutions, the prevailing associations were intramolecular associations, whereas at higher concentrations, intermolecular associations also arose, resulting in the formation of complex assemblies. Moreover, from low to high pH values, the conformation of the block copolymers also changed from contracted to expanded assemblies.

Graiver's[44,50,51] PVP-*b*-PDMS-*b*-PVP and PDMS-*g*-PVP copolymers properties were analyzed in a 5% HCl aqueous solution containing soap (10 wt %). It was found that the copolymers have a high antifoaming activity.

5.6. Other Applications

5.6.1. Supercritical CO_2

Paisner and DeSimone[334] used PS-*g*-PDMS copolymers as the starting material to obtain well-ordered mesoporous low dielectric materials. Actually, a film of copolymer prepared by spin coating was treated with acetic acid to degrade the PDMS chains: it leaves well-defined mesopores within the PS matrix.

Silicone macromonomers were found to act as steric stabilizers in MMA,[335–339] styrene,[339] or VDF[340,341] dispersion polymerization in $scCO_2$. Tai et al.[341] showed that the PVDF molecular weight was much higher in the presence of the macromonomer than in conventional radical polymerization without macromonomer (up to 600 000 vs 50 000 $g \cdot mol^{-1}$, respectively).

Dinçer et al.[342] prepared PDMS-*b*-PS-*b*-PDMS triblock copolymer in $scCO_2$ using a PDMS azo macroinitiator. The PDMS azo macroinitiator played the role of polymeric azoinitiator for styrene but not as a steric stabilizer as proven by the presence of nonstabilized PDMS-*b*-PS-*b*-PDMS at the end of the polymerization.

Okubo et al.[258] carried out the ATRP of MMA in dispersion in $scCO_2$ using a PDMS macroinitiator as an inistab. The same team observed that the polymerization of styrene[237] in $scCO_2$ was controlled by nitroxide-mediated radical polymerization and stabilized using an "inistab" PDMS macroinitiator. They also produced PMMA particles by dispersion polymerization with mercaptopropyl-terminated PDMS stabilizer.[215]

5.6.2. Solid Electrolyte

Trapa and co-workers[343] prepared a microphase-separated poly[(oxyethylene) methacrylate]-*g*-PDMS, a solid electrolyte material when associated with a lithium salt of high ionic conductivity. The microphase separation generated solid-like mechanical properties even though this material was used at a higher temperature than both components' T_g's. In a previous study, the authors showed that the conductivity was linked to the T_g of the nonconducting block: the lower the T_g, the higher the conductivity. Thus, PDMS was found to be a very good candidate since it is a polymer with one of the lowest T_g's. In conclusion, it was outlined that these copolymers were the best in terms of combination of properties ever made in the salt-doped materials' category.

5.6.3. Polymer Blends

Kollefrath et al.[119,120] used PDMS-*g*-poly(acrylate) copolymers to compatibilize an acrylic and a silicone rubber. They observed that the compatibilizing effect was higher for small PDMS grafts and that the size of the acrylic rubber phases decreased by increasing the percentage of graft copolymer. A similar strategy was applied by Ochi and Shimaoka[344] for epoxy resin. PDMS-*g*-PMMA was obtained by copolymerization of a methacrylate-functionalized PDMS with MMA. Molecular weights of copolymer segments are key points of macromolecular compatibilizers for polymer blends. The authors gained the full benefits of the macromonomer technique by testing various readily tailored copolymers.

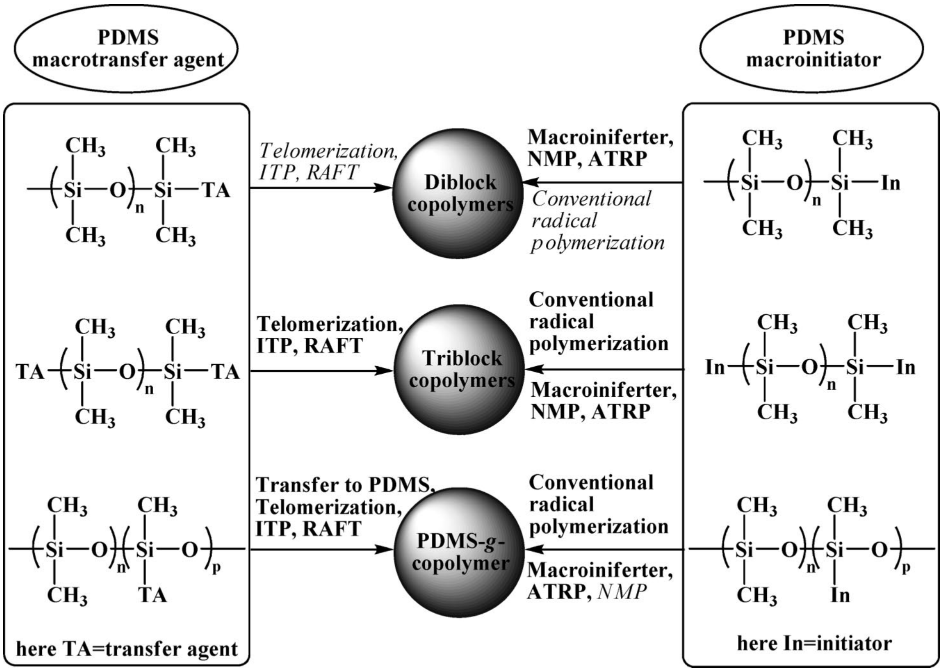
5.6.4. Nanocomposites

Jeong et al.[345] synthesized PS-*b*-PDMS block copolymers in the presence of organoclay nanocomposites. Increasing the PDMS content ($M_n = 5000$ $g \cdot mol^{-1}$) resulted in a better dispersion of organoclay nanocomposites as observed by X-ray diffraction and TEM. It seems that the organoclay lies preferentially in the PDMS domains, which may be interesting for the applications.

6. Conclusion

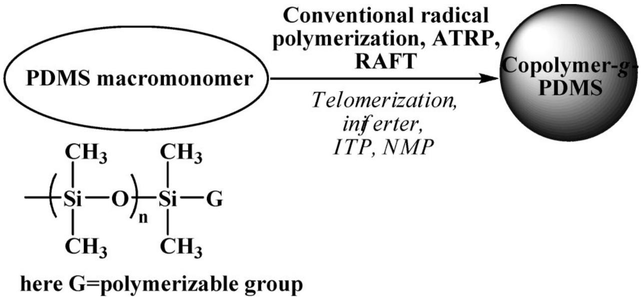
Many synthetic routes have been used for the synthesis of PDMS-containing copolymers: anionic polymerization, cationic polymerization, coupling reactions (for instance, esterification, hydrosilylation), and so on. However, ionic polymerization requires reagents of high purity and strict experimental conditions which are problematic for an industrial process. Even if coupling reactions have given interesting results, their use with high molecular weight polymers is challenging due to the low concentration of reactive groups. The synthesis of PDMS-based copolymers using radical chemistry has been widely studied in recent

Scheme 60. PDMS Precursors Used for Preparing Block and Direct Graft Copolymers[a]



[a] The routes not reported yet are in italics.

Scheme 61. PDMS Precursor for Inverse Graft Copolymers[a]



[a] The routes not reported yet are in italics.

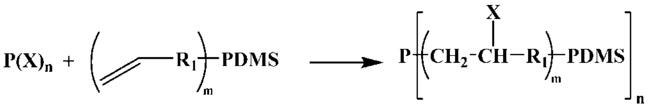
[a] The routes not reported yet are in italics.

years. Advantageously, radical polymerization is a versatile industrial method compatible with a wide range of monomers and with different media like dispersed aqueous media or $scCO_2$. Thus, numerous functional PDMS allowed the synthesis of different architectures such as block, graft, multiblock, or star copolymers as well as the preparation of latex particles with a core−shell morphology.

Results described in this review are summarized in Schemes 60 and 61, where the general structures of the poly(dimethylsiloxane) precursors and the synthetic pathways to reach the desired PDMS-containing architectured copolymers are proposed.

Hence, the targeted architecture can be obtained by selecting the correct polysiloxane macroinitiator or polysiloxane macrotransfer agent (monofunctional, difunctional, or multifunctional to obtain diblock, triblock, or graft copolymers, respectively) and polysiloxane macromonomer (to obtain inverse graft copolymers). Besides, the radical polymerization technique has to be selected depending on the desired level of control over the architecture and the cost of the synthesis. The cheap “radical transfer to PDMS” method gives a poor control over the number of branches and the copolymer molecular weights. However, this can be satisfactory for applications in polymer blends. Core−shell particles have also been widely prepared by transfer to PDMS due to their numerous applications in coating modification, rubber strengthening, or improving the mechanical properties of thermoplastic polymers. The use of polysiloxane azo macroinitiators or peroxy macroinitiators allows a better control of the number of blocks, even if the molecular weight of the resulting copolymers is seldom controlled. In recent years, controlled radical polymerization (CRP) techniques have emerged to allow the precise control of the copolymer

Scheme 62. General Scheme of the Synthesis of Controlled Architectures through Atom-Transfer Radical Addition[a]



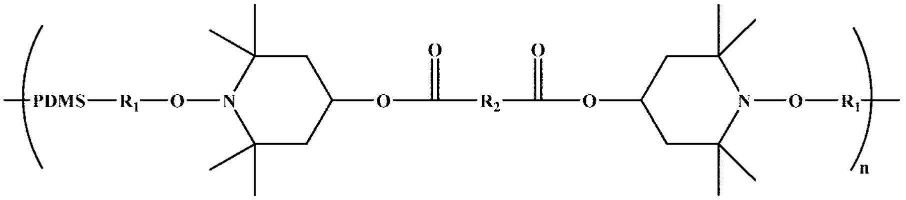
[a] $P(X)_n$ designates a halide-functionnalized polymer chain: $n = 1$, $m = 1$, preparation of diblock copolymers; $n = 1$, $m = 2$ and $n = 2$, $m = 1$ preparation of polymer-*b*-PDMS-*b*-polymer and PDMS-*b*-polymer-*b*-PDMS triblock copolymers, respectively; if halide is grafted on the P polymer chain, Polymer-*g*-PDMS inverse graft copolymers could be obtained with $m = 1$ and crosslinked materials could be obtained with $m \geq 2$; if double bond is grafted on the PDMS backbone, PDMS-*g*-Polymer direct graft copolymers could be obtained with $n = 1$ and crosslinked materials could be obtained with $n \geq 2$. Star copolymers will be obtained with a star precursor.

Table 12. Summary of the Architectures of PDMS-containing Copolymers Obtained Using Radical Chemistry[a]

	Diblock copolymers	Triblock copolymers	Multiblock copolymers	Star copolymers	Graft copolymers		Crosslinked copolymers
					Direct (PDMS-g-Polymer)	Inverse (Polymer-g-PDMS)	
Polysiloxane macroinitiators	*	✓	✓	*	✓	■	✓
Polysiloxane macromonomers	▨	▨	▨	▨	▨	✓	✓
Transfer to PDMS	■	■	■	■	✓	■	✓
Telomerization	*	✓	■	*	✓	*	*
Macroiniferter	✓	✓	✓	*	✓	*	*
NMP	✓	✓	*	*	*	*	*
ATRP	✓	✓	▨	✓	✓	✓	*
ITP	*	✓	▨	*	✓	*	*
RAFT	*	✓	*	*	✓	✓	*

[a] Architectures already obtained using radical chemistry (✓); new conceivable ways for the synthesis of controlled architectures (*); hardly applicable techniques for obtaining the targeted architectures (dashed compartments); not currently applicable techniques for generating the targeted architectures (black compartments).

Scheme 63. General Scheme of Macroalkoxyamine Potentially Useable in NMP To Prepare Multiblock Copolymers (example with hydroxy-TEMPO derivatives)



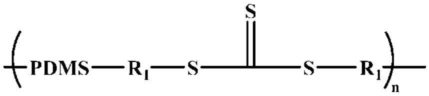
architecture (number of blocks, branches, and control over the molecular weight of each block). They all have a certain number of advantages and drawbacks depending on the nature of the polymerized monomer, the desired level of control, or the use of dispersed aqueous media. However, they allow the synthesis of a wide range of well-defined copolymer architectures with tuned bulk, solution, surface, mechanical, and thermal properties.

Table 12 summarizes the architectures already obtained using radical chemistry (check marks in the table). On the basis of the progress in radical and controlled radical polymerization, we also indicated new conceivable ways for the synthesis of controlled architectures (asterisks in the table). On the contrary, some techniques are hardly applicable (dashed compartments in the table) or not currently applicable for generating some architectures (black compartments in the table).

Concerning the conventional radical polymerization techniques (polysiloxane macroinitiators, polysiloxane macromonomers, transfer to PDMS, and telomerization), many architectures cannot be generated. Polysiloxane macroinitiators have been widely used, but diblock and star copolymers have not been prepared using this technique yet. The use of polysiloxane macromonomers is of great interest in the synthesis of inverse graft copolymers (polymer-*g*-PDMS) and cross-linked materials (by using a di- or multifunctionnal PDMS macromonomer), but the other architectures are hardly attainable. Starting from the macronomer, a slightly different route for the synthesis of diblock, triblock, multiblock, and star copolymers as well as direct PDMS-*g*-Polymer, inverse Polymer-*g*-PDMS and crosslinked materials could lie in the use of atom-transfer radical addition between halide-functionalized polymers $P(X)_n$ (formed by ATRP or ITP/RITP, for instance) and PDMS macromonomers that would not homopolymerize (such as allylic derivatives) (Scheme 62). A similar route based on thiol−ene reactions is also conceivable. Transfer to PDMS is such an uncontrolled technique that well-defined architectures could not be generated. Concerning telomerization, it is quite easy to prepare macrotelogen and, moreover, some commercial products exist. This technique permits control of molecular weights and could advantageously compete with some more expensive techniques such as controlled radical polymerization methods, but there is still some work to carry out.

The controlled radical polymerization methods have been very widely studied, and all the architectures could be generated. Concerning the macroiniferter method, the principal issues concern the synthesis of the macroiniferter and the potential degradation products (CS_2 in the case of use of dithiocarbonyl derivatives). ATRP and ITP cannot be used to get multiblock copolymers directly during the polymerization. However, a two-step route, for example, through the atom-transfer radical coupling of triblock copolymers, could also be a way to reach this architecture. Diblock copolymers could be easily generated by using a monofunctional macrotransfer agent in RAFT and ITP. Multiblock copolymers have never been obtained by CRP techniques even if it is possible by NMP and RAFT. In the first case, it is necessary to use PDMS chains linked by difunctional alkoxyamine (Scheme 63). In RAFT, the use of trithiocarbonate (Scheme 64) would give direct access to multiblock copolymers. Star copolymers could be easily prepared by using a star-functionnalized PDMS as it has been previously reported in ATRP. The preparation of a PDMS with grafted alkoxyamine groups could be a way to obtain direct graft copolymers (PDMS-*g*-polymer). Inverse graft copolymers (polymer-*g*-PDMS) could be synthesized by copolymerization with PDMS macromonomers. Finally, cross-linked copolymers could be prepared by all the techniques provided that a multifunctional monomer (cross-linker) is used.

Scheme 64. General Structure of the Macrotrithiocarbonate That Could Be Used in the Synthesis of Multiblock Copolymers by RAFT



To the best of our knowledge, even if many academic and industrial works have been performed on the synthesis of well-architectured PDMS-containing copolymers via radical polymerization and in spite of their obvious potential, to date, no product is commercially available (unlike polycondensation reactions, e.g., Geniomer). This may be attributed to the fact that many methods are still in their infancy and need more investments. Therefore, upcoming developments should focus on high added value applications such as cosmetics, biomaterials, membrane technologies or surface modification of microfluidic devices, and patterning to name a few.[346−352] All of these applications require a deeper knowledge of the structure−property relationship prior to their industrial developments. Industrial research will also be mandatory to exploit the properties and extend the range of applications.

7. Abbreviations

VP	4-vinylpyridine
AA	acrylic acid
AFR	acetophenone formaldehyde resin
AIBN	2,2′-azobisisobutyronitrile
AMPS	2-acrylamido-2-methylpropanesulfonic acid
AN	acrylonitrile
ATRP	atom-transfer radical polymerization
BDE	bond dissociation energy
BFA	2-(*N*-butyl perfluorooctanefluorosulfonamido) ethyl acrylate
bpy	bipyridine
BuA	butyl acrylate
BuLi	butyllithium
BuMA	butyl methacrylate
C_{ex}	degenerative chain-transfer constant
CRP	controlled radical polymerization

C_T	transfer constant
CTFE	chlorotrifluoroethylene
D_3	2,2,4,4,6,6-hexamethylcyclotrisiloxane
D_4	2,2,4,4,6,6,8,8-octamethylcyclotetrasiloxane
D_{4H}	2,4,6,8-tetramethylcyclotetrasiloxane
D_{4V}	2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane
DMA	dynamic mechanical analysis
DMAEMA	2-dimethylaminoethyl methacrylate
dMbpy	4,4′-dimethyl-2,2′-bipyridine
DMSA	3-(dimethoxymethylsilyl)-propyl acrylate
dNbpy	4,4′-di(5-nonyl-2,2′-bipyridine)
DP_n	number-average degree of polymerization
DSC	differential scanning calorimetry
EA	ethyl acrylate
E_a	activation energy
EEMA	1-ethoxyethyl methacrylate
EMA	ethyl methacrylate
EPS	expandable poly(styrene)
FOA	1,1-dihydroperfluorooctyl acrylate
HEA	2-hydroxyethyl acrylate
HEMA	2-hydroxyethyl methacrylate
HEMA-TMS	2-trimethylsilyloxyethyl methacrylate
HFP	hexafluoropropylene
HMTETA	1,1,4,7,10,10-hexamethyltriethylenetetramine
iBnA	isobornyl acrylate
IDMAz	isopropenyl dimethyl azlactone
IEM	isocyanatoethylmethacrylate
iniferter	initiatior transfer termination
inistab	initiator−stabilizer
ITP	iodine-transfer polymerization
LCST	lower critical solution temperature
LTMS	lithium trimethylsilanolate
MAA	methacrylic acid
MADIX	macromolecular design trough interchange of xanthates
Me_6TREN	tris[2-(dimethylamino)ethyl]amine
MeA	methyl acrylate
MMA	methyl methacrylate
M_n	number-average molecular weight
MTEMPO	4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl
m-TMI	*m*-isopropenyl-α,α-dimethyl benzyl isocyanate
M_w	weight-average molecular weight
MWD	molecular weight distribution
NaSS	sodium styrene sulfonate
N,*N*-DMA	*N*,*N*-dimethyl acrylamide
NIPAM	*N*-isopropylacrylamide
NMP	nitroxide-mediated polymerization
NMR	nuclear magnetic resonance
NVP	*N*-vinyl pyrrolidone
OEGMA	oligo(ethylene glycol) methyl ether methacrylate
PAA	poly(acrylic acid)
PAN	poly(acrylonitrile)
PB	poly(butadiene)
PCL	poly(caprolactone)
PDI	polydispersity index
PDMS	poly(dimethylsiloxane)
PEA	poly(ethyl acrylate)
PLA	poly(lactic acid)
PMAA	poly(methacrylic acid)
PMDETA	*N*,*N*,*N*′,*N*′,*N*″-pentamethyldietylenetriamine
PMMA	poly(methyl methacrylate)
PNIPAM	poly(*N*-isopropylacrylamide)
PS	poly(styrene)
PtBuMA	poly(*tert*-butyl methacrylate)
PVA	poly(vinyl alcohol)
PVAc	poly(vinyl acetate)
PVC	poly(vinyl chloride)
PVP	poly(vinyl pyrrolidone)
PVPy	poly(4-vinylpyridine)
RAFT	reversible addition−fragmentation chain transfer
RITP	reverse iodine transfer polymerization
ROP	ring-opening polymerization
$scCO_2$	supercritical carbon dioxide
SEC	size exclusion chromatography
SEM	scanning electron microscopy
SET	single electron transfer
SG1	*N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethylpropyl)nitroxide
tBuA	*tert*-butyl acrylate
tBuMA	*tert*-butyl methacrylate
TEM	transmission electron microscopy
TEMPO	2,2,6,6-tetramethylpiperidinyl-1-oxy
TFE	tetrafluoroethylene
T_g	glass transition temperature
TGA	thermogravimetric analysis
TIPNO	*N*-*tert*-butyl 1-phenyl-2-methylpropylaminoxyl
TMSA	trimethylsilyl acrylate
TMSEA	trimethylsiloxy-ethyl acrylate
TMSMA	trimethylsilyl methacrylate
TPE	thermoplastic elastomer
UV	ultraviolet
VAc	vinyl acetate
VDF	vinylidene fluoride
VDMAz	vinyldimethylazlactone
XPS	X-ray photoelectron spectroscopy

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