New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations

New Polymer Synthesis by Nitroxide Mediated Living Radical Polymerizations

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I. Introduction

A. Background

At first glance, radical polymerization may be considered a mature technology with millions of tons of vinyl based homo- and copolymers being produced annually. This perception of maturity is based on the fact that free radical polymerization is so widely used industrially and in research laboratories for the synthesis of a wide variety of polymeric materials. This widespread adoption is due to its versatility, synthetic ease, and compatibility with a wide variety of functional groups, coupled with its tolerance to water and protic media. These features make possible the development of emulsion and suspension techniques, which greatly simplifies the experimental set up and has led to wide commercial adoption.

Tonny Bosman (left) was born in Nijmegen, The Netherlands, in 1970 and studied chemistry at the University of Nijmegen. His undergraduate research (1994) was done in the group of Roeland Nolte concerning chiral mesogenic phthalocyanines after which he undertook his Ph.D. with Bert Meijer at Eindhoven University of Technology (1999) in the area of dendritic molecules and functional materials. He is currently undertaking postdoctoral research at the IBM Almaden Research Center with Jean Fréchet and Craig Hawker on combinatorial/high-throughput chemistry and its application to developing new methods in living free radical procedures.

Eva Harth (center) was born in Cologne, Germany and studied chemistry at the University of Bonn and the University of Zurich, Switzerland under the supervision of Prof. A. Vasella, ETH Zurich, where she worked on the synthesis and application of glycosylidene fullerenes derivatives. In 1994 she joined the group of Prof. K. Muellen at the MPI for Polymer Research in Mainz, obtaining her Ph.D. in 1998 for work in the area of fullerene adducts and polymers. She is currently undertaking postdoctoral research at the IBM Almaden Research Center focusing on the development of new living free polymerization techniques and novel approaches to nanoscopic materials.

Craig Hawker (right) was born in Toowoomba, Australia, in 1964. He received a B.Sc. degree in chemistry from the University of Queensland in 1984 and a Ph.D. degree in bio-organic chemistry from the University of Cambridge in 1988 under the supervision of Prof. Sir Alan Battersby. Jumping into the world of polymer chemistry, he undertook a postdoctoral fellowship with Prof. Jean Fréchet at Cornell University from 1988 to 1990 and then returned to the University of Queensland as a Queen Elizabeth II Fellow from 1991 to 1993. He is currently a Research Staff Member at the IBM Almaden Research Center and an investigator in the NSF Center for Polymer Interfaces and Macromolecular Assemblies and was recently awarded the 2001 Carl S. Marvel Award in Creative Polymer Science. His research has focused on the interface between organic and polymer chemistry with emphasis on the design, synthesis, and application of unusual macromolecular structures in microelectronics and nanotechnology.

It is therefore surprising that the study of radical polymerization has witnessed a renaissance in terms of both synthetic possibilities and mechanistic understanding in recent years. One of the driving forces for this renaissance has been the growing demand for functionalized, well-defined materials as building blocks in nanotechnology applications. In the preparation of well-defined macromolecules, traditional

free radical procedures have a significant drawback, which is related to the reactivity of the propagating free radical chain end and its propensity to undergo a variety of different termination reactions. The materials obtained are therefore polydisperse with very limited control over macromolecular weight and architecture.[1] Until recently, ionic polymerizations (anionic or cationic) were the only "living" techniques available that efficiently controlled the structure and architecture of vinyl polymers. Although these techniques ensure low polydispersity materials, controlled molecular weight and defined chain ends, they are not useful for the polymerization and copolymerization of a wide range of functionalized vinylic monomers. This limitation is due to the incompatibility of the growing polymer chain end (anion or cation) with numerous functional groups and certain monomer families.[2] In addition, these polymerization techniques require stringent reaction conditions including the use of ultrapure reagents and the total exclusion of water and oxygen. The necessity to overcome all these limitations emboldened synthetic polymer chemists to develop new concepts, which would permit the development of a free-radical polymerization procedure possessing the characteristics of a living process. This field has witnessed explosive growth in recent years and a number of specialized reviews have been published in this general area.[3−6]

B. Scope of Review

This review covers the scientific literature from 1980 to the present concerning nitroxide-mediated living free radical polymerization. Strategies for controlling polymeric structure and macromolecular architecture will be discussed in detail with special emphasis placed on the synthesis of functionalized polymers. Other important synthetic considerations such as the design of nitroxides with improved performance and the development of new synthetic approaches to alkoxyamine initiators will be examined in an effort to provide a basis for future development in the field. While mechanistic and kinetic details of the polymerization process will be examined, for a more detailed treatment the reader is directed to the review article by Fischer in this issue.[7] Similarly, the relationship between nitroxide-mediated and other living free radical techniques, such as atom transfer radical polymerization (ATRP) and radical addition, fragmentation and transfer (RAFT) will be discussed and examples given for each of these novel techniques; however, for an in depth analysis, the reader is directed to the review by Sawamoto in this thematic issue.[8]

II. Historical Perspective

The first detailed attempt to use initiators that control radical polymerization of styrene and methyl methacrylate was reported by Werrington and Tobolsky in 1955.[9] However, the specific dithiuram disulfides that were employed lead to high transfer constants, which resulted in retardation of the polymerization. This promising concept was subsequently overlooked for close to 30 years until the use

of "iniferters" (*ini*tiator−trans*fer* agent−termina*tor*) was introduced by Otsu in 1982 which is arguably the first attempt to develop a true LFRP technique.[10] In this case, disulfides, **1**, including diaryl and dithiuram disulfides, were proposed as photochemical initiators where cleavage can occur at the C−S bond to give a carbon-based propagating radical, **2**, and the mediating thio radical **3** (Scheme 1). While the

Scheme 1
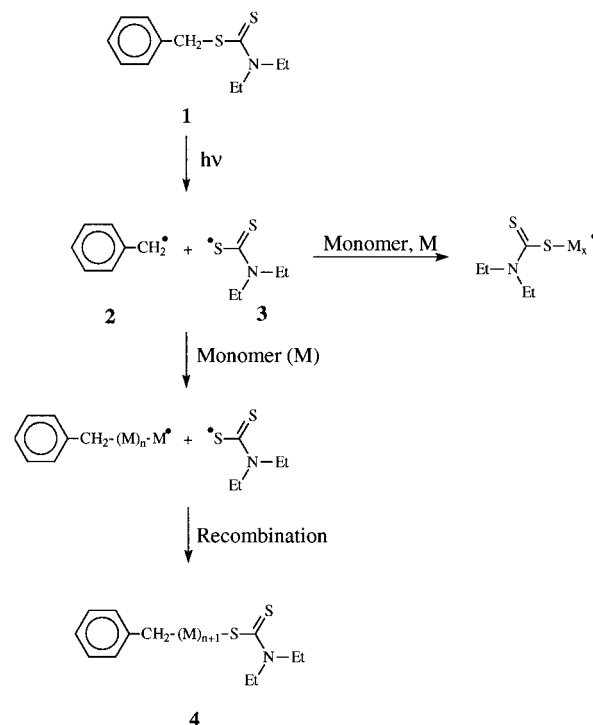
propagating radical **2** can undergo monomer addition followed by recombination with a primary sulfur radical, **3**, to give a dormant species, **4**, it may also undergo chain transfer to the initiator itself. As opposed to conventional free-radical polymerization, which results in chain termination, even at low conversion, this technique provides rudimentary characteristics of typical living systems, such as a linear increase in molecular weight with conversion. In addition, the monofunctional, or α,ω-bifunctional chains, can be considered as telechelic polymers, giving the possibility to prepare block copolymers. Nevertheless, other features of a true living system such as accurately controlled molecular weights and low polydispersities could not be obtained since a thio radical, **3**, can also initiate polymerization. As will be discussed below, one of the primary requirements for a mediating radical is that it undergoes reversible termination of the propagating chain end ***without*** acting as an initiator. Subsequently, a wide range of stabilized radicals has been examined as mediating radicals for the development of a living free radical system.[11−13] As with the preliminary iniferter work of Otsu, they suffer from incomplete control over both the initiation and reversible termination steps and lead to poorly controlled polymerizations; however, their structures do point to interesting features that may be relevant in the future development of this technology (Figure 1). Delocalized systems, the pres-
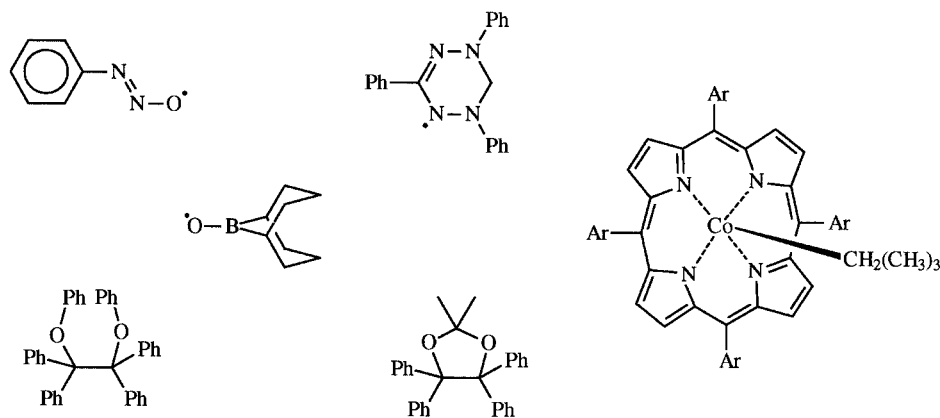
Figure 1.

ence of heteroatoms and in many examples, steric hindrance all play key roles in determining the success of the mediating radical. Of particular note to the nitroxide work described below, is the ability of radicals such as the verdazyl and borinate derivatives to control the polymerization of methacrylates. The tendency of the radical species in these examples to abstract α-hydrogens is obviously decreased for methacrylate polymerizations when compared to nitroxides and an understanding of the difference between these systems may permit the design of improved nitroxides for methacrylate polymerization.

## III. Nitroxide-Mediated Living Free Radical Polymerizations

The pioneering iniferter work provided the basis for the development of LFRP and it is interesting to note the similarity between the iniferter mechanism outlined in Scheme 1 and the general outline of a *successful* living free radical mechanism (Scheme 2). In this general mechanism, the reversible termi-

Scheme 2

R $\bullet$ = mediating radical
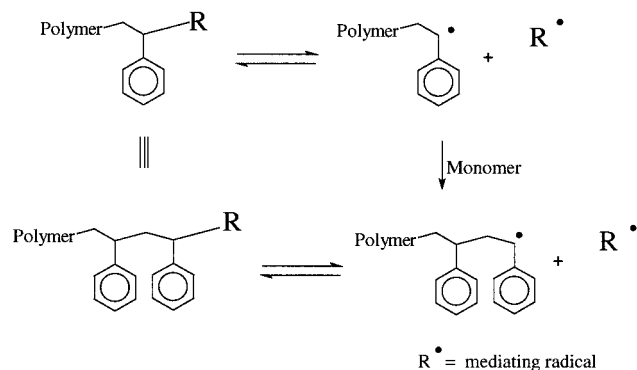
nation of the growing polymeric chain is the key step for reducing the overall concentration of the propagating radical chain end. In the absence of other reactions leading to initiation of new polymer chains (i.e., no reaction of the mediating radical with the vinylic monomer), the concentration of reactive chain ends is extremely low, minimizing irreversible termination reactions, such as combination or disproportionation. All chains would be initiated only from

the desired initiating species and growth should occur in a living fashion, allowing a high degree of control over the entire polymerization process with well-defined polymers being obtained.

The identity of the mediating radical, R$\bullet$, is critical to the success of living free radical procedures and a variety of different persistent, or stabilized radicals have been employed. These range from (arylazo)oxy,[14] substituted triphenyls,[15] verdazyl,[16] triazolinyl,[17] nitroxides,[18] etc. with the most widely studied and certainly most successful class of compounds being the nitroxides and their associated alkylated derivatives, alkoxyamines. Interestingly, the development of nitroxides as mediators for radical polymerization stems from pioneering work into the nature of standard free radical initiation mechanisms and the desire to efficiently trap carbon-centered free radicals. Solomon, Rizzardo, and Moad were able to demonstrate that at the low temperatures typically associated with standard free radical polymerizations, 40−60 °C, nitroxides such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), **5**, reacted at near diffusion controlled rates with carbon-centered free radicals, **6**, generated from the addition of initiating radicals, **7**, to vinyl monomers.[19] The resulting alkoxyamine derivatives, **8**, were essentially stable at these temperatures and did not participate in the reaction further, thus acting as radical traps (Scheme 3).

Scheme 3
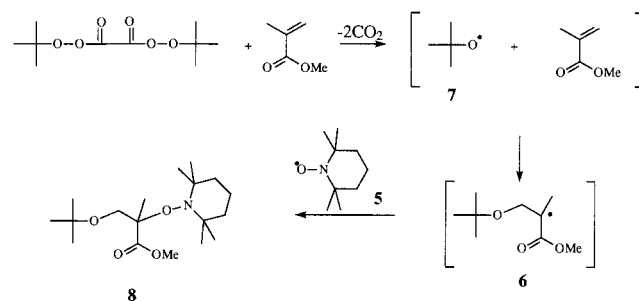
The same workers then applied a similar concept, albeit at increased temperatures (80−100 °C) to the synthesis of low molecular weight polymers and oligomers, primarily with acrylates and hindered

nitroxides.[20] While the polymerization of acrylates cannot be considered living at these low temperatures, this seminal piece of work did provide the foundation for many of the ensuing studies in the whole field of living free radical polymerization.

A. Bimolecular Process

The second seminal contribution which demonstrated to a wide audience that living free radical polymerizations are a viable synthetic methodology was a report from the group of Georges at XEROX describing the preparation of low polydispersity polystyrene.[21] The key feature of this work was the preparation of high molecular weight, low polydispersity materials. By increasing the temperature to 130 °C and conducting the polymerizations in bulk, a system comprising benzoyl peroxide, **9**, and a stable nitroxide, TEMPO (**5**), in a molar ratio of 1.3:1, gave polystyrene derivatives, **10**, by a living process in which the molecular weight increased in a linear fashion with conversion (Scheme 4). Even more

Scheme 4

9

5

130°C

10
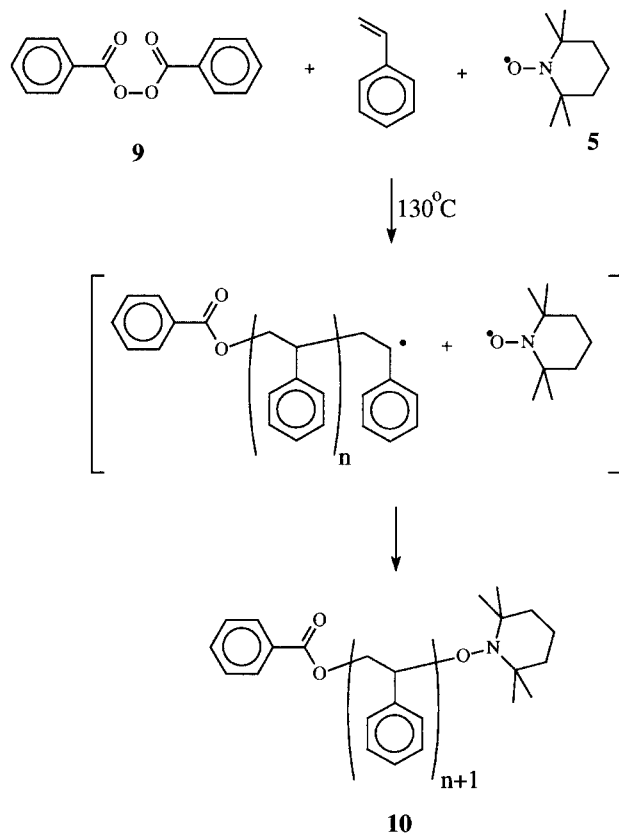
startling were the polydispersity values for **10** (PDI = 1.2−1.3), which were significantly lower than the theoretical lower limit for a free radical process of 1.5 and the typical values of ca. 2.0 for free radical systems. At these elevated temperatures the C−ON bond becomes unstable, releasing the nitroxide which can now act as a polymerization mediator, not as an inhibitor as they are low temperatures, hence their use by Solomon to trap polymerization intermediates.

While this original work by the XEROX group displays many of the fundamental aspects of a living

Scheme 5

11

130°C

12

5

n

13
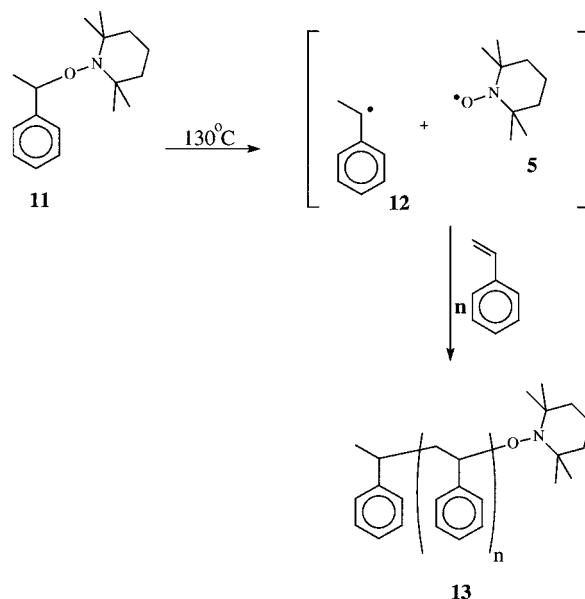
polymerization process, and subsequent studies have confirmed and reinforced these original observations, it must be emphasized that these are not *true* living systems.[22−26] While the concentration and reactivity of radicals at the propagating chain end have been significantly reduced, it is still not negligible and therefore termination reactions can still occur. By the strictest definition, nitroxide-mediated and in fact all versions of LFRP are not living polymerizations; however, the best systems do display all of the characteristics of a living system and so the term, *living* will be used throughout this chapter. For an excellent discussion of the many varied opinions on the correct terminology for living free radical polymerizations the reader is directed to a special, "living or controlled" thematic issue of *J. Polym. Sci.*[27]

B. Unimolecular Initiators

While successful, the poorly defined nature and unknown concentration of the initiating species in the bimolecular process prompted the development of a single molecule initiating system which would permit control over molecular weight, architecture, etc. Borrowing the concept of well-defined initiators from living anionic and cationic procedures, unimolecular initiators for nitroxide-mediated living free radical polymerizations have been developed.[28,29] The structure of these initiators was based on the alkoxyamine functionality that is present at the chain end of the growing polymer during its dormant phase. The C−O bond of the small molecule alkoxyamine derivative **11** is therefore expected to be thermolytically unstable and decompose on heating to give an initiating radical, i.e., the α-methylbenzyl radical **12** as well as the mediating nitroxide radical **5** in the correct 1:1 stoichiometry (Scheme 5). Following initiation the polymerization would proceed as described previous for the bimolecular case to give the polystyrene derivative **13**.

Scheme 6

18
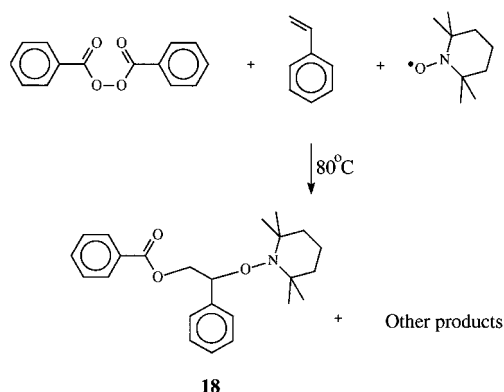
IV. Nitroxides Development

While the above strategies proved that the concept of a living free radical procedure was a viable process there were a large number of problems with the use of TEMPO, as the mediating radical.[29] In addition, the available synthetic methods for the preparation of alkoxyamines were poor and not amenable to the preparation of functionalized initiators in high yield.[30] These included the necessity to use high polymerization temperature (125−145 °C), long reaction times (24−72 h) and an incompatibility with many important monomer families. While it was shown that random copolymers of styrene and either butyl acrylate or methyl methacrylate could be readily prepared with TEMPO,[31] at high incorporations of the comonomer (ca. 50%+) the copolymerization and homopolymerization of (meth)acrylates are no longer living. Before becoming a routine synthetic procedure for the preparation of well-defined polymers, these issues needed to be addressed.

To overcome these deficiencies it was apparent that changes in the structure of the nitroxide were needed. Unlike the initiating radical, which is involved only at the beginning of the polymerization, the mediating radical is involved in numerous reversible termination and activation steps and so changes in its structure would be expected to have a substantial effect on the polymerization. Initial efforts to develop new mediating nitroxides relied on TEMPO based derivatives. The XEROX group were able to polymerize acrylates at elevated temperatures (145−155 °C) in the presence of 4-oxo−TEMPO, **14**, as the mediating nitroxide, and while this is a significant improvement when compared to TEMPO, polydispersities were still between 1.40 and 1.67 and the living nature of the polymerization was questionable.[32] Similarly, Matyjaszewski observed that the rate of polymerization of styrene could be significantly enhanced by the use of a TEMPO derivative, **15**, substituted in the 4-position with a phosphonic acid group (Figure 2). Presumably the ability to form an intramolecular H-bond in **15** leads to a change in mediating ability.[33] This prompted the investigation of a wide range of other TEMPO-like structures, such as di-*tert*-butyl nitroxides, and in the use of additives.[34] All of these approaches lead to an increase in the rate of polymerization, especially for
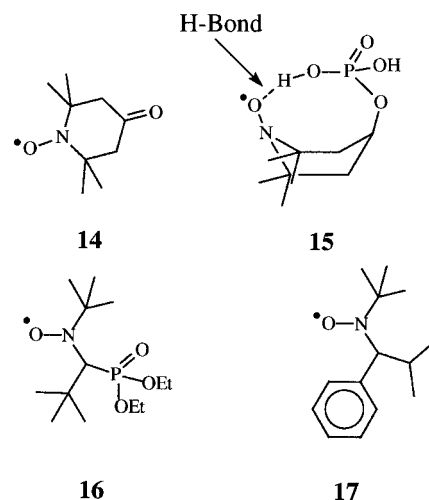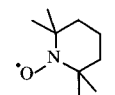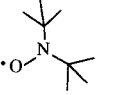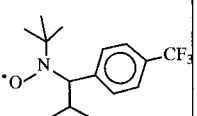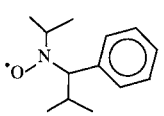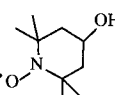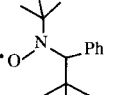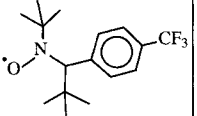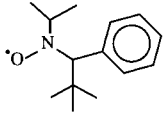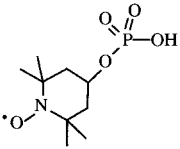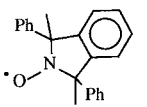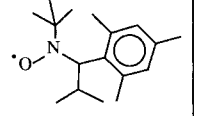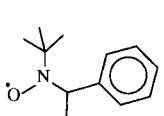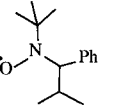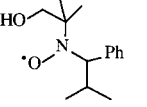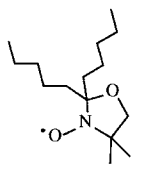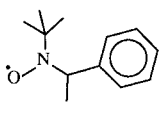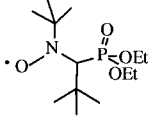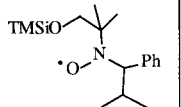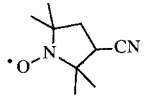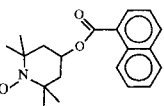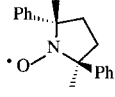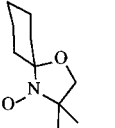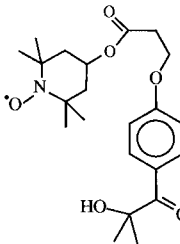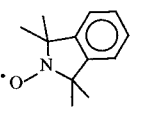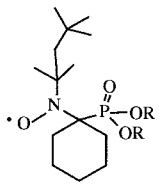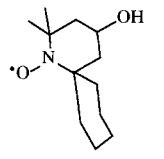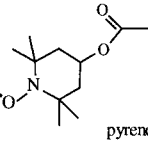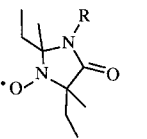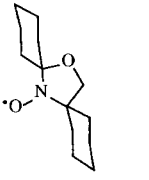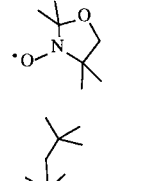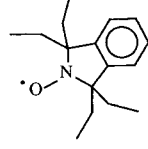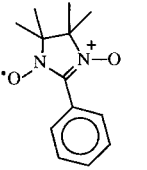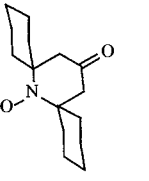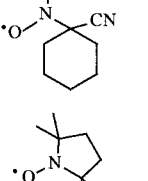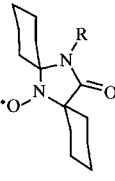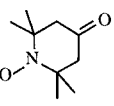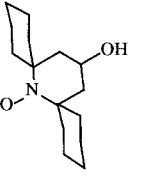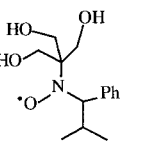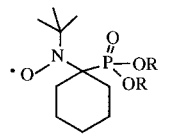

Figure 2.

additives such as camphorsulfonic acid[35] or acetic anhydride,[36] however, the improvements were not significant enough to make nitroxide-mediated polymerizations a viable competitor to other living techniques.

The most significant breakthrough in the design of improved nitroxides was the use of alicyclic nitroxides, which bear no structural resemblance to TEMPO. In fact, their most striking difference was the presence of a hydrogen atom on one of the α-carbons, in contrast to the two quaternary α-carbons present in TEMPO and all the nitroxides discussed above. Interestingly this feature is traditionally associated with unstable nitroxide derivatives and may have some bearing on the success of these compounds. The best examples of these new materials are the phosphonate derivative, **16**, introduced by Gnanou and Tordo[37] and the family of arenes, **17**, introduced by Hawker (Figure 2).[38] These nitroxides have subsequently been shown to be vastly superior to the original TEMPO derivatives, delegating the latter to a niche role for select styrenic polymerizations. The use of nitroxides such as **16** and **17** now permits the polymerization of a wide variety of monomer families. Acrylates, acrylamides, 1,3-dienes and acrylonitrile based monomers can now be polymerized with accurate control of molecular weights and polydispersities as low as 1.05.[39] The versatile nature of these initiators can also be used to control the formation of random and block copolymers from a wide selection of monomer units containing reactive functional groups, such as amino, carboxylic acid, glycidyl. The universal nature of these initiators overcomes many of the limitations typically associated with nitroxide-mediated systems and leads to a level of versatility approaching atom transfer radical polymerization (ATRP) and radical addition fragmentation and transfer (RAFT) based systems.[40−42] The applicability of these systems to other monomers families will be described and demonstrated in the following sections on block copolymers and macromolecular architectures. A list of nitroxides that have been employed as mediators in living free radical polymerizations are included in Table 1 with accompanying references.[43−76]

Table 1. Structure of Nitroxides Employed in Living Free Radical Polymerizations

Structure	Reference	Structure	Reference	Structure	Reference	Structure	Reference
(structure)	43 51 52 57-59 67	(structure)	47 48 50	(structure, CF₃)	38 54	(structure, Ph)	38 54
(structure, OH)	44 49 53 56 66	(structure, Ph)	38	(structure, CF₃)	38 54	(structure, Ph)	38 54
(structure, P=O, OH)	72	(structure, Ph, Ph)	38	(structure)	38 54	(structure, Ph)	38 54
(structure, Ph)	38 39 54 73	(structure, HO, Ph)	38 71	(structure, O)	38 54	(structure, Ph)	38 54
(structure, P=O, OEt, OEt)	37 38 55	(structure, TMSiO, Ph)	38	(structure, CN)	38 54	(structure, O, naphthalene)	63 69
(structure, Ph, Ph)	38 61 62	(structure, O)	38 58				

Structure	Reference	Structure	Reference	Structure	Reference	Structure	Reference
(structure, HO)	69	(structure)	46	(structure, P=O, OR, OR)	65	(structure, OH)	67
(structure, pyrene)	73	(structure, R, O)	76	(structure, O)	67	(structure, O)	67
(structure)	76	(structure, N⁺–O)	64	(structure)	68	(structure, CN)	68
(structure, R, O)	76	(structure, O)	74 75	(structure, O)	67	(structure, CN)	68
		(structure, P, OR, OR)	65	(structure, OH)	67	(structure, HO, OH, HO, Ph)	70 71

Scheme 7

V. Approaches to Alkoxyamines

The development of stable, readily functionalized initiators, which mimic the growing chain end for living free radical systems, is one of the significant achievements and advantages of LFRP. Not only does it allow the greatest degree of control over the final polymeric structure, but also the ready functionalization permits the development of new areas of research in polymer science and nanotechnology. In the case of nitroxide-mediated systems, the dormant chain end is an alkylated nitroxide derivative, also termed an alkoxyamine. Unfortunately, as a class of compounds, alkoxyamines are poorly studied and the initial exploitation of their potential was limited by the lack of versatile and efficient synthetic procedures for their preparation.[77−79]

The growing importance of alkoxyamines for LFRP has motivated organic chemists to pursue new and more versatile synthetic approaches for their preparation. Initially the majority of synthetic approaches to alkoxyamines relied on the generation of carbon-centered radicals followed by the trapping of these radicals by a nitroxide derivative. Initial examples include the reaction of benzoyl peroxide with an excess of styrene to give a benzylic radical followed by trapping of the radical intermediate with TEMPO to give the benzoyl peroxide adduct, **18**. Problems with this synthesis include the relative poor yield (30−40% yield) and the wide range of byproducts,

which complicated purification (Scheme 6).[28] In an effort to both improve the yield of the desired alkoxyamine and simplify purification, a variety of other strategies for generation of the radical intermediate have been studied. Howell has taken advantage of the low reactivity of nitroxides with oxygen-based radicals to prepare benzylic alkoxyamines, **11**, by hydrogen abstraction from ethyl benzene, **19**, followed by nitroxide trapping (Scheme 7).[80,81] Generation of the intermediate radical has also been accomplished photochemically using a di-*tert*-butyl peroxide reaction system and irradiation with 300 nm light. In this case, the mild nature of the reaction conditions allows the yields to be increased to over 90% and more importantly permits thermally unstable alkoxyamines such as the α,α-dimethyl-substituted derivative **20** to be isolated. Under traditional thermal conditions, **20** would decompose on formation due to the inherent instability of the quaternary C−ON bond.[82]

Alternative approaches have also been recently developed which rely on the controlled generation of carbon-centered radicals followed by trapping of the radical-like intermediates. Jahn[83] has employed single electron transfer in the highly efficient generation of radicals from ester enolates, **21**, by treatment of lithium salts with ferrocenium ions, **22**, at −78 °C. These radicals are then trapped by nitroxides to provide functionalized alkoxyamines, **23**, in moderate to high yields. Reduction with LiAlH$_4$ gives the hydroxy derivative **24** in good yield with no attack at the alkoxyamine group, demonstrating the stability of alkoxyamines to a variety of reaction conditions (Scheme 8). Similarly, Braslau has employed Cu^{2+}-promoted single electron-transfer reactions with enolate anions to provide carbon-centered free radicals which can be trapped by nitroxides at low temperatures.[84] Matyjaszewski has applied techniques from atom transfer radical procedures to develop a facile, low-temperature approach to alkoxyamines involving the treatment of suitable ATRP-based initiators, **25**, with copper complexes in the presence of a nitroxide,

Scheme 8
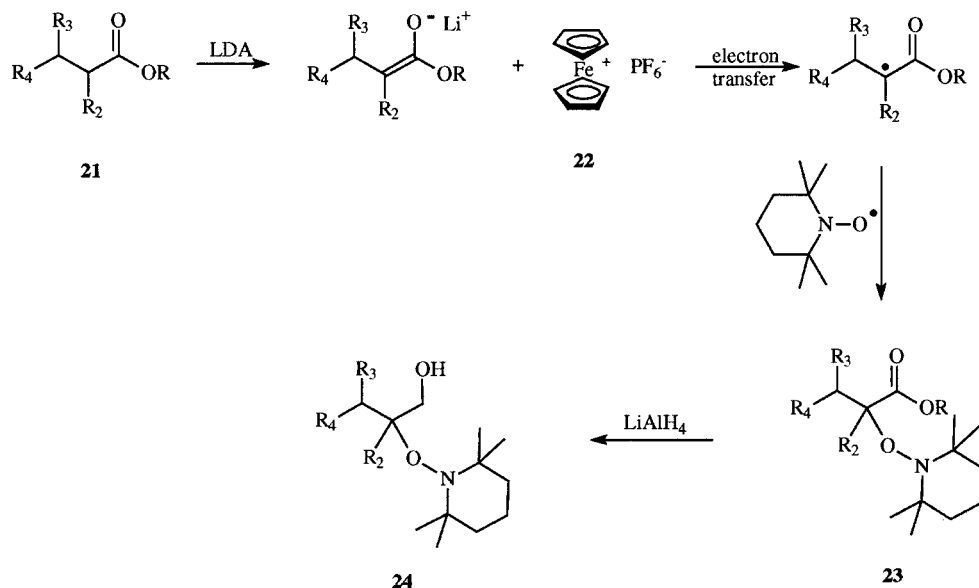
Scheme 9
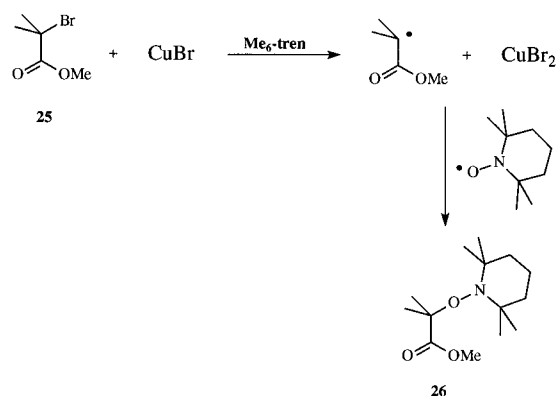
the resulting alkoxyamine **26** being obtained in very high yields (Scheme 9).[85] The use of lead oxide for the oxidation of alkyl hydrazides has also been shown to be an efficient method for the synthesis of alkoxyamines and if chiral nitroxyl radicals are employed a degree of stereochemical control can be obtained.[86] Finally in a novel application of single electron-transfer chemistry, Priddy[87] has employed oxoaminium salts to add across the double bond of styrenic derivatives leading to functionalized alkoxyamine initiators. In the proposed mechanism, the oxoaminium salt **27** undergoes a disproportionation reaction with associated electron transfer to give the corresponding nitroxide, TEMPO, and a chlorine radical. The chlorine radical then adds across the styrenic double bond to give the carbon center radical **28** which is then efficiently trapped by TEMPO to give the chloromethyl-substituted alkoxyamine **29** (Scheme 10). The advantage of this strategy is the facile

Scheme 10
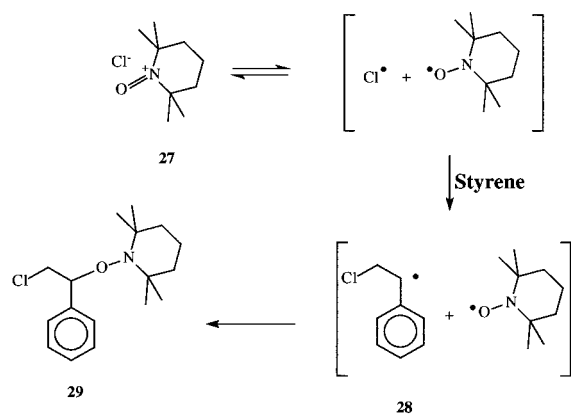
preparation of the alkoxyamine **29**, which can be subsequently transformed into a myriad of functionalized initiators.

Alternate strategies to the trapping of carbon-centered radicals has been developed by a variety of groups in an effort to extend the range of functionalities that can be incorporated into the alkoxyamine structure. Taking advantage of the rich oxidation chemistry of nitroxides, Catala[88] has demonstrated that oxidation to the hydroxyamine followed by proton abstraction with sodium hydride gives the anion which can nucleophilically displace alkyl halides to give the desired alkoxyamine. This is espe-

cially useful for multifunctional alkoxyamines such as **30**, whose synthesis from the corresponding diradical by trapping strategies is not practical (Scheme 11).

Scheme 11
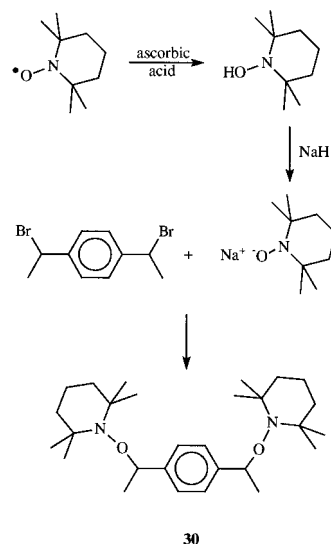
In an interesting application of classical organic chemistry, Bergbreiter employed a Meisenheimer rearrangement of allyl *N*-oxides as a route to alkoxyamines.[89] As shown in Scheme 12, 2,2,6,6-

Scheme 12
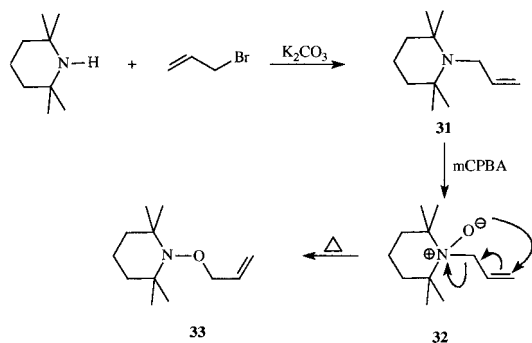
tetramethylpiperidine is initially alkylated with allyl bromide to give the tertiary amine, **31**, which can be oxidized at low temperatures with *m*-chloroperbenzoic acid. The resulting *N*-oxide **32** is not isolated but allowed to undergo rearrangement on warming to give the allyl−TEMPO derivative **33** in moderate yield (Scheme 12). An attractive feature of this synthetic approach to alkoxyamines is the ready availability and low cost of starting materials which is in contrast to the high cost of many nitroxides. In addition, the controlled nature of polymerizations initiated with **33** demonstrates that an α-methylbenzyl group is not necessary for efficient initiation in these systems and a simple allyl group can be used in its place without any detrimental performance.

The use of transition metal complexes for the synthesis of alkoxyamines has also been exploited by Dao.[90] In this case, Jacobsen's reagent, manganese-(III) salen, **34**, is employed to promote the addition of nitroxides across the double bond of olefinic derivatives, specifically activated double bonds such

as styrenics, leading to alkoxyamines suitable for use as initiators in living free radical procedures. While the mechanism for the Jacobsen epoxidation of olefins is still controversial, a substantial body of evidence has been accumulated that supports direct attack of the olefin at the oxomanganese center to generate a radical intermediate followed by collapse to give the desired epoxide.[91] It is anticipated that a similar mechanism is involved during the synthesis of alkoxyamines with evidence suggesting that an intermediate organomanganese derivative, **35**, is involved, which on reduction with sodium borohydride gives the alkoxyamine **36** (Scheme 13). The advan-

Scheme 13
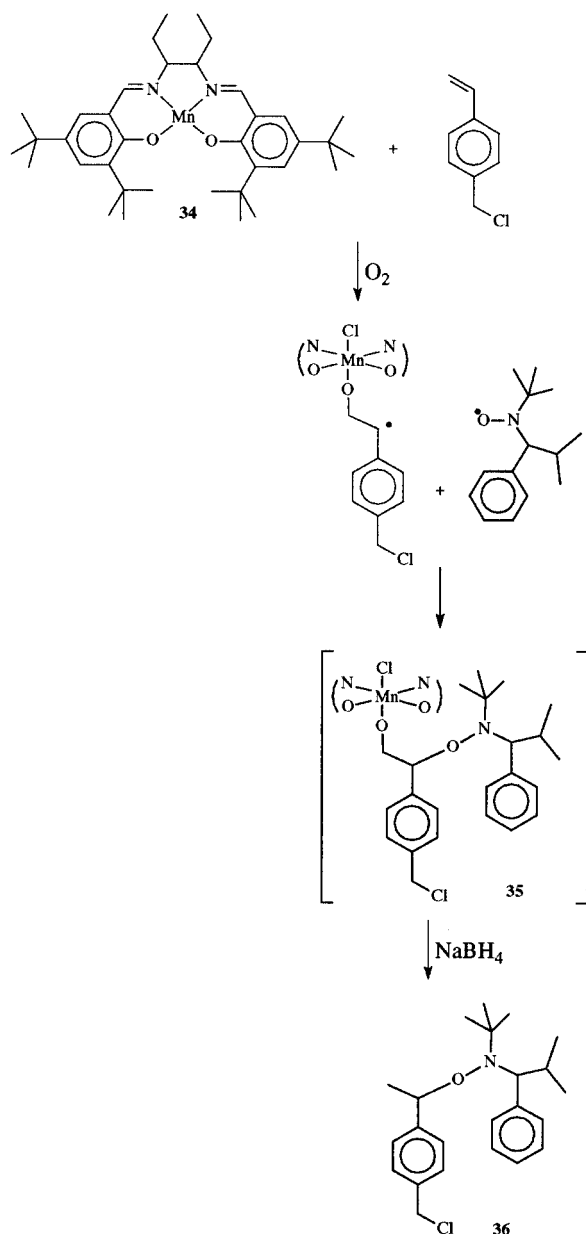
tages of these methods are that a variety of functional groups can be readily introduced, large excesses of reagents are not required to trap the extremely reactive free radical intermediates and near stoichiometric amounts of the alkene and nitroxide are required. Finally, the reactions are high yielding and

produce very few unwanted side products, which greatly facilitates isolation and purification.

VI. Mechanistic and Kinetic Features

A. Nitroxide Exchange

The key kinetic feature of nitroxide-mediated living free radical polymerization is the operation of a special kinetic phenomenon, termed the persistent radical effect. Fischer has developed the equations for the polymerization rates and for the polydispersities of the resulting polymers that have been shown to effectively model LFRP.[92,93] In the initial stages of the polymerization, a small fraction of the initiating radicals **37** formed from decomposition of the unimolecular initiator **38** undergo radical−radical coupling. This leads to a terminated small molecule or oligomer, **39**, and the resulting elimination of two initiating radicals. At this early stage of the polymerization, this is a facile reaction since the diffusing radicals are sterically not congested and the reaction medium is not viscous. However, by its nature, the mediating radical, or persistent radical, **40** does not undergo coupling and so a small increase in the overall concentration of **40** relative to the propagating/initiating radical **37** occurs. This increased level of **40** is self-limiting since a higher concentration leads to more efficient formation of the dormant chain end **41** and a decrease in the amount of radical−radical coupling (Scheme 14). This interplay between

Scheme 14
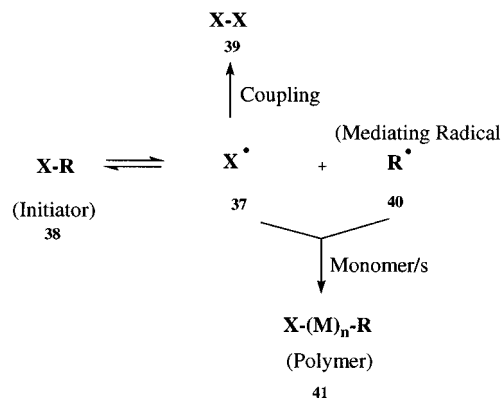
termination and mediation leads to a small amount of excess mediating free radical, giving rise to the persistent radical effect (PRE) and to eventual control over the polymerization process.

The nature of the equilibrium between the dormant system **41** and the pair of radicals **37** and **40** has been probed and exploited by a number of groups. The exact nature of the radical pair, caged pair of radicals, or freely diffusing radicals was probed by a series of crossover experiments.[94] This is an important synthetic issue: the nitroxide counter-radicals are associated with the same polymeric chain end during the course of the polymerization, or do they diffuse freely to the reaction medium, which affects the ability to insert functional groups at the chain ends. In these experiments, the potential diffusion of the mediating radical from the propagating chain end

Scheme 15
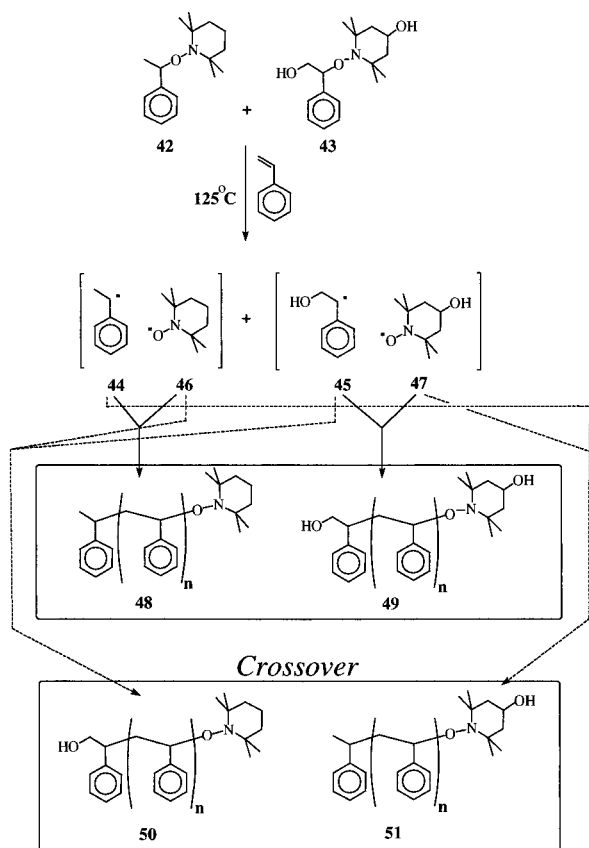
was probed by the use of two structurally similar alkoxyamines, which differ in the presence or absence of functional groups. One derivative is unfunctionalized, **42**, while the other alkoxyamine, **43**, contains two hydroxy groups, one attached to the TEMPO unit while the second is located at the beta-carbon atom of the ethylbenzene unit. If a 1:1 mixture of **42** and **43** is used to initiate the "living" free radical polymerization of styrene, homolysis of the carbon−oxygen

bond of **42** and **43** will lead to four radical species. Each of the radicals produced are chemically different and comprise a pair of initiating, or propagating radicals, **44** and **45**, and a pair of structurally similar mediating nitroxide radicals are produced, TEMPO, **46**, and 4-hydroxy−TEMPO, **47**. If no escape of the mediating nitroxide radical from propagating chain end occurs, only two polystyrene derivatives will therefore be formed, **48** and **49**. In contrast, if radical crossover does occur and the mediating nitroxide radicals are free to diffuse to the polymerization medium, four polystyrenes having different substitution patterns, **48**−**51**, will be obtained. Significantly, the experimental result from these crossover experiments revealed a statistical mixture of all four products, even at low conversions (ca. 5%), implying freely diffusing radicals (Scheme 15).

Moreover, this crossover or exchange of mediating radical can be exploited as a synthetic tool to introduce functional groups at the polymer chain end/s. Turro[95] has elegantly taken advantage of this feature of nitroxide-mediated living free radical procedures to develop a strategy for the facile preparation of chain end functionalized macromolecules. In this approach a precursor polymer, **52**, is prepared from a standard unfunctionalized initiator, such as **42**, purified, and then redissolved in a high boiling point solvent such as chlorobenzene and heated at 125 °C in the presence of a large excess of functionalized nitroxide, **54**. At this temperature the equilibrium between **53** and the two radicals is established and since the released nitroxide, **46**, is free to diffuse into the solution, exchange with the functionalized nitroxide, **54**, can occur leading to the desired chain end functionalized macromolecule, **55** (Scheme 16). This strategy presents a number of advantages, reactive functional groups can be introduced under mild conditions, from the same precursor polymer a variety of differently tagged macromolecules can be prepared, and the same strategy can be applied to

Scheme 16
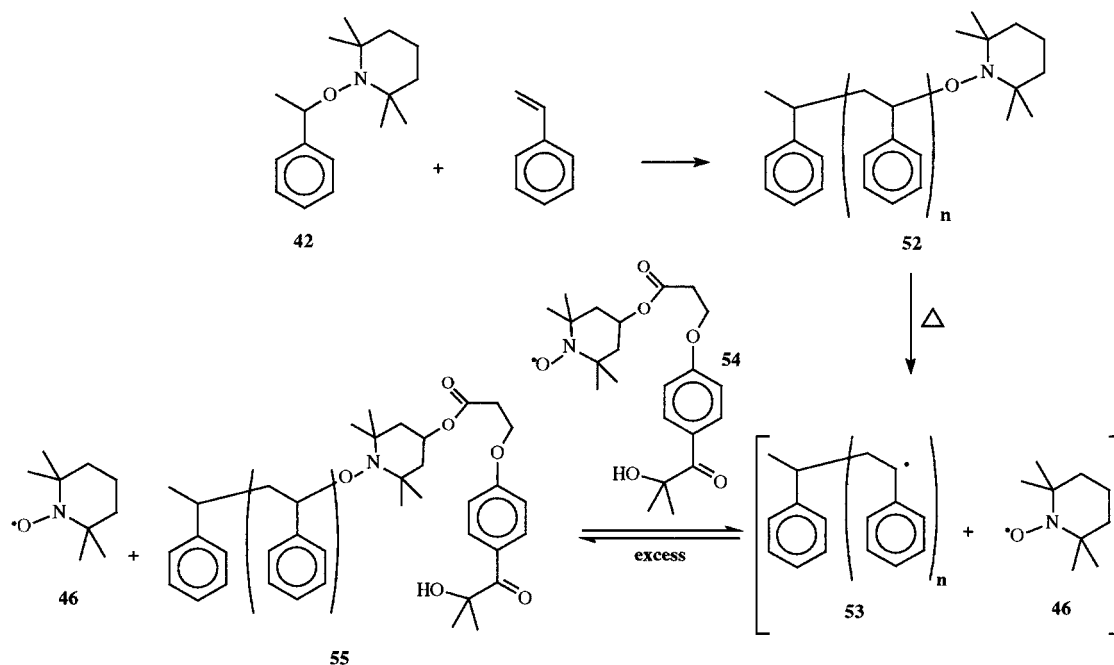
macromolecules of different architectures. It should however, be noted that the primary driving force for this functional interconversion is statistics and so under normal laboratory conditions with nitroxide excesses of 10−20 equiv complete exchange of the chain end does not occur.

B. Additives

From the above discussion it is obvious that the persistent radical effect relies on a subtle interplay between the mediating nitroxide radicals and propagating radical chain ends. The rate of polymerization and extent of termination reactions such as radical coupling can however, be manipulated by changing the balance between all of these competing reactions and kinetic equations which are present during the persistent radical effect. This has been accomplished by a number of groups in different ways. One of the most well-studied strategies is to continuously add initiator or have a very slowly decomposing initiator also present in the polymerization mixture.[96] This continuously supplies initiating radicals to the system and results in the reaction continuously trying to obtain a steady state, persistent radical effect situation. The stationary concentration of the nitroxide is therefore reduced and correspondingly, the rate of deactivation is decreased. This should lead to an increase in the rate of polymerization with a concomitant increase in the polydispersity of the polymers obtained. Indeed this has been shown to be the case in a number of studies. The addition of either dicumyl peroxide and *tert*-butyl hydroperoxide has been shown to lead to rate enhancements of up to 300% with only moderate increases in polydispersity. In a related study, continuous slow addition of a standard low-temperature free radical initiator, AIBN, was also shown to give similar results.[97] These findings are important from a commercial viewpoint since they may allow the long reactions times and high temperatures normally associated with nitroxide-mediated polymerizations, especially those involving TEMPO, to be alleviated without compromising the gross characteristics of the product.

These experiments are also relevant to the polymerization of styrenic derivatives. As discussed above, styrenics were the first and still arguably the easiest monomer family to polymerize under living conditions using nitroxides. One of the primary reasons for the facile polymerization of styrenics is thermal polymerization. Unlike acrylates and other vinyl monomers, which do not readily undergo self-initiation to generate radicals, it has been shown that thermal self-initiation of styrene provides a low concentration of propagating radicals.[98,99] This is sufficient for obtaining a rate enhancement similar to the addition of excess initiator and allows a reasonable rate of polymerization under the persistent radical effect. Another consequence of autopolymerization is that the rate of polymerization of styrene in the presence of nitroxides is independent of the concentration of the alkoxyamine and remarkably close to the rate of thermal polymerization under the same conditions.[100]

C. Chain End Degradation

Another side reaction in nitroxide-mediated living free radical polymerization that affects the kinetics and structural integrity of the products is decomposition of the alkoxyamine chain ends. One potential pathway that has been studied in detail is the facile reduction of the mediating nitroxide radical to give the corresponding hydroxyamine **56** by H-transfer. As illustrated in Scheme 17 for polystyrene, this results in a dead polymer chain, **57**, containing an unsaturated chain end. Hydroxylamine **56** can then be involved in H-transfer back to a growing radical chain end to regenerate the nitroxide while at the same time leading to a second H-terminated dead polymer chain, **58**. These termination reactions decrease the living character of the polymerization and if they are significant enough will alter the overall kinetics and lead to a nonlinear system. To understand the system in more detail, Priddy has investigated the decomposition of alkoxyamine initiators in a variety of solvents.[101] The results clearly show that alkoxyamines undergo significant decomposition at the temperatures normally associated with living free radical polymerization. In 1,2,4-trichlorobenzene, ca. 50% decomposition has occurred after 2 h leading to H-abstraction and the identification of styrene as a major decomposition product (cf. Scheme 17). The authors conclude that significant decomposition of the alkoxyamine chain ends should occur during polymerization due to the competitive rates of polymerization and decomposition. However, significant decomposition is not observed experimentally and may be due to the absence of monomer in the model studies coupled with the decreased rate of H-abstraction from a polymer chain end compared to a small molecule. While reduced, this reaction is not completely absent from nitroxide-mediated polymerizations and simulations and theoretical treatments have shown that its effect on the polymerization kinetics is slight but does result in an increase in molecular weights distribution.[102] This also explains the lower polydispersities observed for the second-generation nitroxides **17** (ca. 1.05−1.10) compared to TEMPO (1.15−1.25) for polystyrene polymerizations. The shorter reaction times and lower temperatures associated with **17** leads to a decreased amount of alkoxyamine decomposition and associated broadening of the molecular weight distribution. This feature also explains the observed difference in the polymerization of styrenics and methacrylates under nitroxide-mediated conditions. Styrenics are able to undergo living polymerization under the influence of minor amounts of thermal initiation/hydrogen transfer reactions and the effect of these side reactions on the "livingness" of the system and the structure of the final products is not significant and cannot be detected in most cases. In contrast, for methacrylates there is no thermal initiation and the contribution from hydrogen transfer is significantly greater. The majority of chains therefore undergo termination reactions and effectively *"die"* leading to an uncontrolled, nonliving system. This has been observed experimentally with significant amounts of

Scheme 17
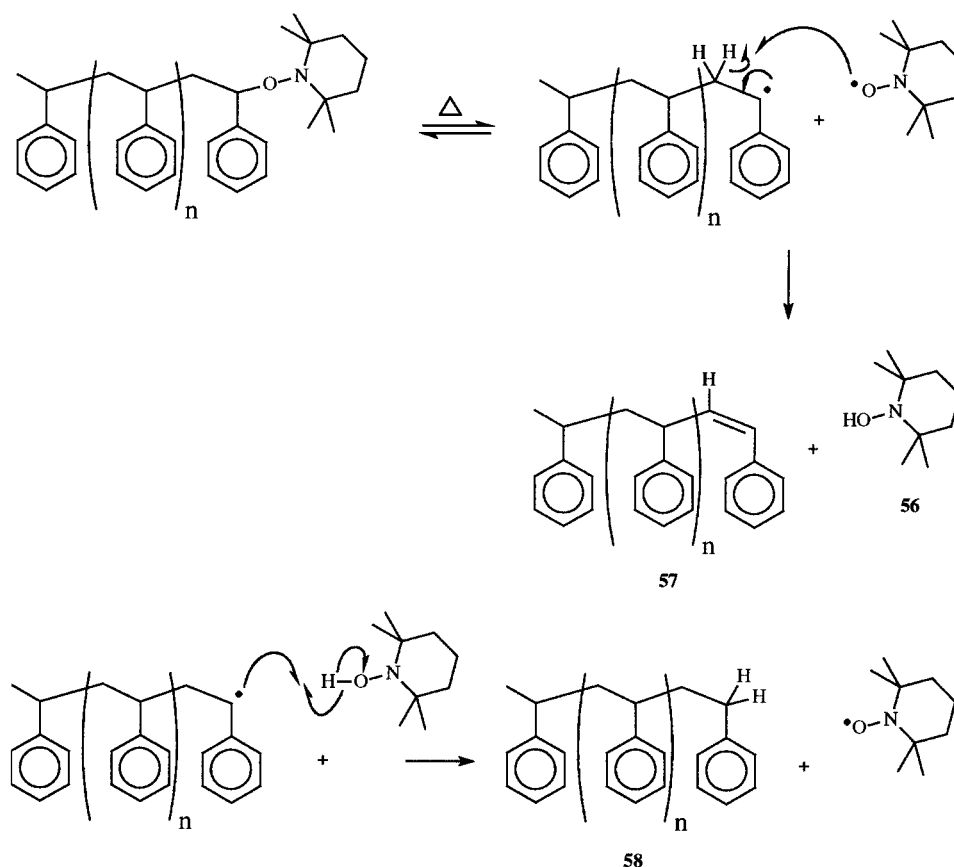
alkene-terminated polymer chains detected by MAL-DI mass spectrometry as well as NMR and UV−vis studies.[103,104]

D. Elucidation of Living Nature

For monomer families other than methacrylates, the low occurrence of these side reactions and the essentially living nature of these polymerizations can be demonstrated by a variety of different techniques. A preliminary guide to the "livingness" can be obtained by examining the relationship between the evolution of molecular weight and conversion. As shown in Figure 3, the polymerization of n-butyl acrylate (250 equiv) in the presence of **59** (X = Y = H) (1.0 equiv) and **17** (0.05 equiv) at 123 °C for 16 h results in a linear relationship.[38] This demonstrates that all of the chains are initiated at the same time and grow at approximately the same rate. Following this initial screening, the efficiency of initiation and the degree of control during the polymerization can be accurately gauged by determining the correlation between the experimental molecular weight and the theoretical molecular weight. As for all living polymerizations, the theoretical molecular weight is determined by the molar ratio of monomer to initiator, taking into account the conversion of the polymerization. For an initiation efficiency of 100%, the relationship between experimental molecular weight and theoretical molecular weight should be a straight line with a slope of 1.0. Indeed, evolution of experimental molecular weight, M_n, with theoretical MW
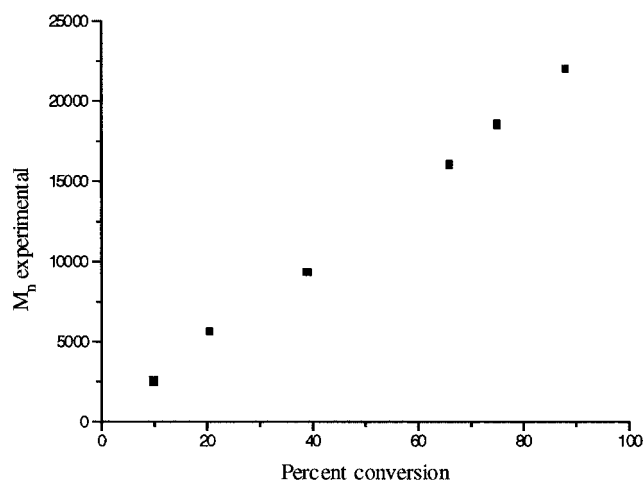
Figure 3. Evolution of molecular weight, M_n, with percent conversion for the polymerization of n-butyl acrylate (250 equiv) in the presence of **42** (X, Y = H) (1.0 equiv) and **17** (0.05 equiv) at 123 °C for 16 h.

for the polymerization of styrene and **59** (X = Y = H) at 123 °C for 8 h with no degassing or purification is a straight line. This suggests that initiating efficiencies are 95% or greater (Figure 4). The ability to obtain polydispersities of between 1.10 and 1.20 for these polymerization is further support for a controlled/living process. Figure 4 also demonstrates a critically important feature of nitroxide-mediated living free radical polymerizations that is also true for ATRP and RAFT, no purification of monomers or rigorous polymerization conditions are required to obtain very well-defined polymers, thereby opening
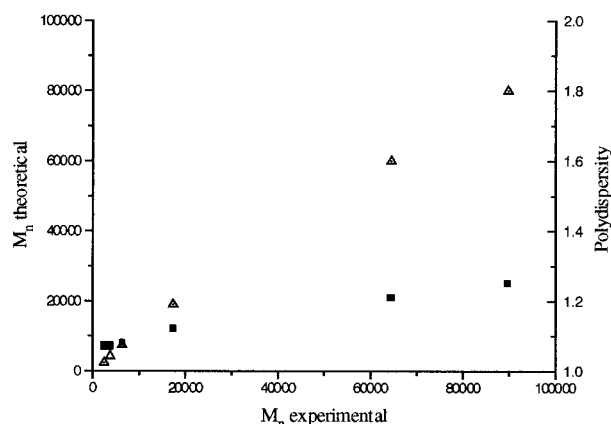
Figure 4. Evolution of experimental molecular weight, M_n, and polydispersity with theoretical MW for the polymerization of styrene and **42** at 123 °C for 8 h with no degassing or purification.

these synthetic techniques up to a much wider range of researchers.

As will be discussed below, the final piece of evidence that is needed to conclusively prove the living nature of a nitroxide-mediated process is to use the alkoxyamine chain end to prepare a block copolymer. Again if the polymerization is living, efficient reinitiation of the second block should be observed to give a block copolymer with no homopolymer contamination (care should be taken in analyzing homopolymer content by GPC, especially using RI detection). While this is a desired goal, it should be realized that the efficiency of reinitiation for the second block is monomer dependent and in select circumstances inefficient reinitiation may be obtained even though ca. 100% of the starting blocks contain an alkoxyamine chain end. This feature will be further discussed in the following section on structural control.

E. Emulsion and Related Processes

Until recently, living radical polymerizations have been predominantly studied in homogeneous systems, i.e., bulk or solution polymerizations. While simplified systems, they are less attractive to industry, which prefers to employ aqueous dispersed media and emulsion procedures in particular. A considerable amount of effort has therefore been directed to the development of nitroxide-mediated polymerizations under heterogeneous conditions such as suspension, dispersion, seeded emulsion, batch emulsion, and miniemulsion.[105-108] The difficulty with many of these studies is that TEMPO or similar derivatives were employed as the mediating radical. This necessitated the use of temperatures greater than the boiling point of water and so high-pressure reaction setups were required and stabilization of the latex/emulsion particles at these elevated temperatures was problematic. Even with these difficulties a basic understanding of the process is starting to emerge. The choice of the nitroxide is critical and the compatibility of the nitroxide with water and the partition coefficients between the various phases are all critical factors.[109] Recent work by Charleux[110] has also shown that the choice of second-generation nitroxides, which

operate at lower temperatures (<100 °C), may alleviate many of these difficulties and permit a viable emulsion process to be developed.

VII. Toward New Materials

It is obvious from the above discussion that under the correct conditions and with the appropriate mediating nitroxide free radical, living polymerization conditions can be achieved. On the basis of this realization, numerous groups have demonstrated that the degree of structural control normally associated with more traditional living processes, such as anionic procedures, can be equally applied to nitroxide-mediated living free radical polymerizations.

A. Molecular Weight Control

The initial work of Hawker[28] on the use of alkoxyamines as unimolecular initiators demonstrated that the molecular weight of polystyrene could be accurately controlled up to M_n values of ca. 75 000 using the assumption that one molecule of the TEMPO-based alkoxyamine **11** initiates the growth of one polymer chain and the length, or degree of polymerization, of that chain is governed by the molar ratio of styrene to **11**. Subsequent work by others, especially with the second-generation alkoxyamines, such as **59**, have conclusively proved this ability and, especially in the case of **59**, the upper molecular weight limit (M_n) for controlled molecular weights has been increased to between 150 000 and 200 000.[38] For typical monomers and polymerization conditions, values of ca. 200 000 may represent an upper limit for nitroxide-mediated, ATRP, and RAFT-based living free radical systems. At higher molecular weights the small amount of extraneous radicals and terminating species quickly become significant when compared to the low concentration of initiating and propagating radicals present in the system. This leads to a loss of control and an increasingly nonliving process.

B. Telechelic Polymers

The ability to control molecular weights provides good evidence that the basic reaction scheme for alkoxyamine initiated polymerizations does operate. By analogy, it should therefore be possible to prepare telechelic polymers in a fashion similar to living anionic procedures. However, a major difference is that elaborate schemes for the efficient transformation of the anionic chain ends to the desired functionality does not need to be developed since living free radical procedures can tolerate a wide variety of functional groups. The ability exists to prepare functionalized alkoxyamines such as **59**, in which functional groups can be placed at either the initiating chain end, **Y**, or the nitroxide-mediating chain end, **X** (Scheme 18). The range of functional groups that have been introduced into telechelic polymers such as **60** is wide and include many useful reactive groups, e.g., CO_2H, NH_2, etc. A recent study has shown that at molecular weights of up to 50 000–75 000 the level of incorporation is very high, i.e., greater than 95%.[73,111] This high level of incorpora-

Scheme 18

59

60

Scheme 19

Reaction 2

Reaction 3

Reaction 4
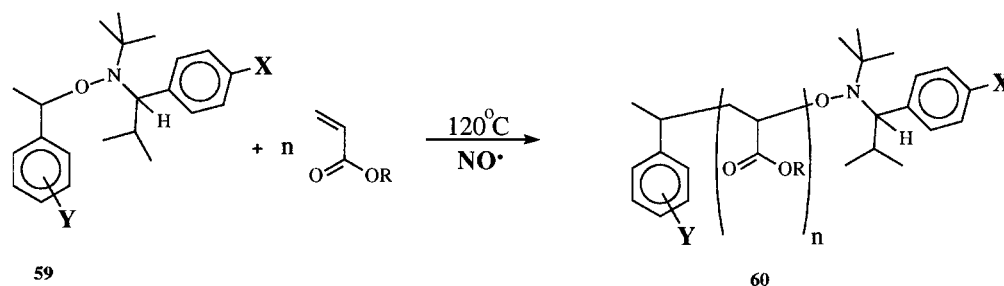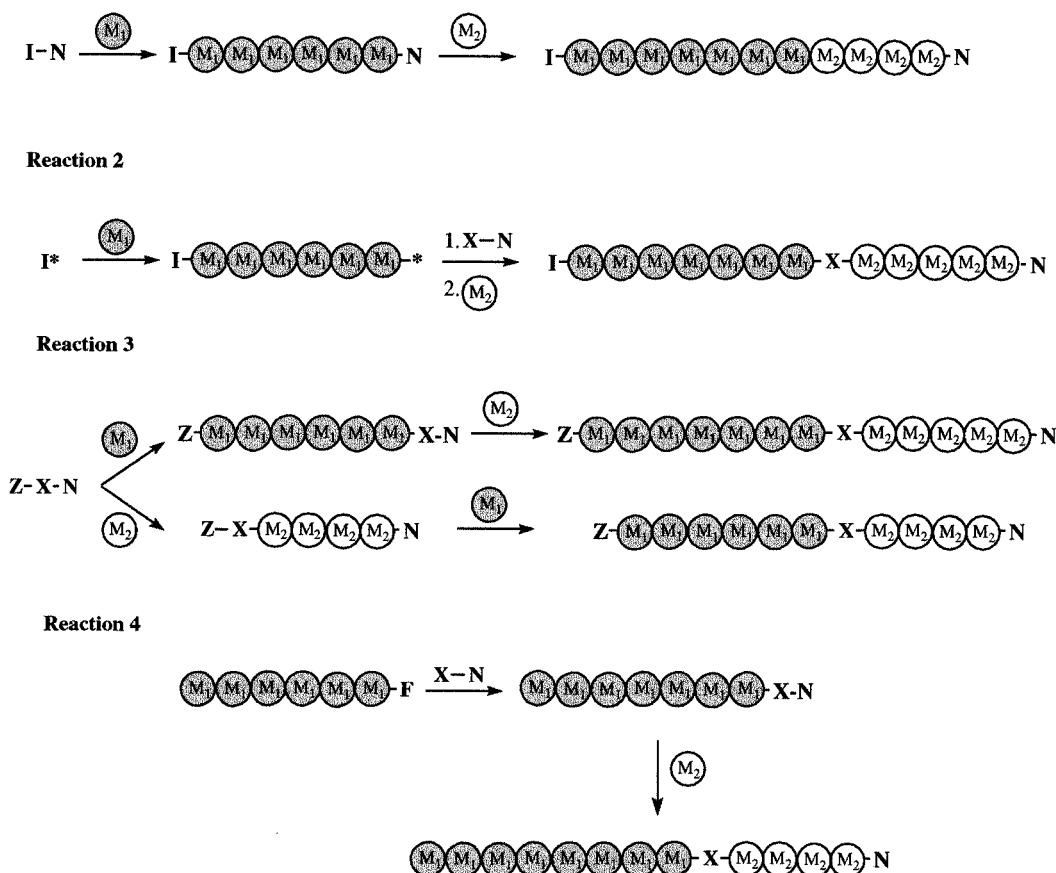
tion is a direct result of having the functional groups built into the initiator, coupled with the necessity for no functional group transformations at the chain ends. It should also be realized that functional group interconversions are possible based at the propagating chain end on alkoxyamine chemistry and a number of groups have exploited this in the design of telechelic systems.[112-115]

C. Block Copolymers

One of the primary driving forces behind the interest that living radical procedures have received in recent years is the ability to prepare block copolymers. Not only may existing block copolymers be prepared more efficiently and in some case with a greater degree of control, but also novel block copolymers, which were not accessible using existing techniques, may also be prepared. The synthetic versatility associated with alkoxyamine initiators and the ability to introduce a wide variety of functional

groups allows block copolymers to be prepared in at least four different ways. As shown in Scheme 19, vinyl block copolymers can be prepared in a traditional sequential fashion by the polymerization of one monomer followed by a second monomer (reaction 1). Alternatively, a functionalized alkoxyamine can be used to terminate polymerization of an initial monomer under conditions other than living free radical. The alkoxyamine-terminated macromolecule can then be used as a macroinitiator to prepare block copolymers. The interesting feature of this process is that it permits the facile introduction of a functional group or chromophore at the junction point between the two blocks (reaction 2). In reaction 3, a dual, or double-headed, initiator is prepared which has both an alkoxyamine initiating fragment and an initiating group for a different polymerization contained in the same molecule. Depending on the compatibility of the initiating groups, the polymerization processes and the desired structure of the block copolymer, the

order of polymerization can be varied to give the desired block copolymer. Finally, a preexisting telechelic polymer can be mono- or difunctionalized with the appropriate alkoxyamine to give a macroinitiator from which a vinyl block can be grown under living radical conditions. While not an extensive list of all possible procedures, the multitude of synthetic strategies that have currently been explored for nitroxide-mediated living radical procedures does give an indication of the extreme versatility in block copolymer formation which is possible using this novel technique. To give a greater insight into the myriad possibilities, a list of linear block copolymers that have been prepared using nitroxide-mediated processes is detailed in Table 2 and a number of actual examples discussed below.[116−172]

As discussed above, one synthetic strategy relies on the coupling of a functionalized alkoxyamine with a telechelic or mono-functional nonvinylic polymer to give a macroinitiator. This macroinitiator can then be used in standard living free radical procedures. Such an approach is best illustrated by the preparation of poly(ethylene glycol)-based block copolymers[129,136,150,167] by initial reaction of a mono-hydroxy terminated poly(ethylene glycol) with sodium hydride followed by the chloromethyl-substituted alkoxyamine **36**. The PEG-based macroinitiator (PDI = 1.05−1.10) **61** can then be used to polymerize a variety of vinyl monomers, such as styrene, to give amphiphilic block copolymers, **62**, which have accurately controlled molecular weights and very low polydispersities, 1.05−1.10 (Scheme 20).[167] The extremely low poly-

Scheme 20
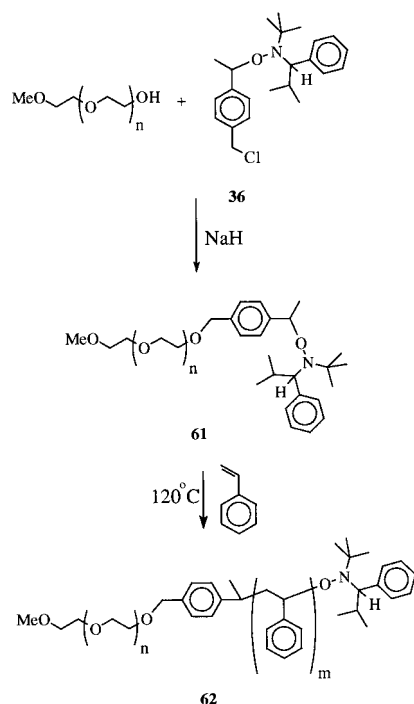
dispersities may be due to the use of a macroinitiator in contrast to typical small molecule initiators. In the latter case, mobility and reactivity of the initiating radicals is high leading to radical−radical coupling. For the macroinitiator, diffusion and reactivity is

decreased, leading to reduced radical coupling and a more controlled polymerization.

The second strategy for nonvinylic block copolymer formation involves the combination of living free radical techniques with other polymerization processes either to form linear block copolymers or graft systems. All of these processes take advantage of the compatibility and stability of alkoxyamines and their associated nitroxide-mediated polymerization procedures with a wide range of reaction conditions. For example, this permits the alkoxyamine initiating group to be copolymerized into a poly(olefin) backbone under metallocene conditions[169] or into a vinyl backbone under anionic[170] or normal free radical conditions.[171] The latter is an interesting application of the specificity of nitroxide-mediated living free radical polymerizations. Since the cleavage of the C−ON bond is thermally activated, reactions at lower temperatures (ca. <80 °C) can be performed without any initiation occurring from the alkoxyamine group/s. Therefore normal free radical polymerizations, ATRP, and RAFT procedures can be performed in the presence of alkoxyamines. Subsequent activation of the alkoxyamine permits the facile synthesis of graft and block copolymers.

The synthetic versatility associated with combining different polymerization techniques can also be demonstrated by the preparation of poly(caprolactone)-*b*-(styrene) copolymers by a combination of living ring opening polymerization with nitroxide-mediated free radical procedures using a hydroxy-substituted alkoxyamine as a dual, or double-headed, initiator, **63**.[173] The primary alcohol is used as the initiating group for the ring opening polymerization of caprolactone to give the alkoxyamine-terminated macroinitiator **64**, which can then be used to initiate the living polymerization of styrene to afford the well-defined block copolymer **65**. Alternatively, the alkoxyamine group of **63** can be used to initiate the polymerization of styrene, and in turn, the hydroxy-terminated polystyrene **66** allows the ring opening polymerization to be initiated from the hydroxy group to give the analogous block copolymer **65** (Scheme 21). The significant feature of this approach is that either sequence of living polymerizations gives the same polymeric structure, the ultimate choice being dictated primarily by the block copolymer composition. In a similar vein, Sogah has combined living free radical polymerization with the cationic ring opening of oxazolines, and anionic ring opening into the same multifunctional initiator. This trifunctional system has been shown to be highly effective leading to well-defined block copolymers and can even be combined into a one-pot, one-step block copolymerization by simultaneous free radical and either cationic ring opening or anionic ring opening procedures.[174]

The advantages of living free radical polymerizations are not restricted to the synthesis of block copolymers, which contain a nonvinylic block/s, i.e., caprolactone. The compatibility with functional groups and the inherent radical nature of the process also permits significant progress to be made in the synthesis of block copolymers based solely on vinyl monomers. While a number of these structures can

Table 2. Structure of Monomer Employed in the Synthesis of Block Copolymers by Nitroxide Mediated Living Free Radical Procedures

Scheme 21

be obtained from other living processes, such as anionic procedures, in many cases they can be prepared more readily by living free radical techniques and the special attributes of living free radical chemistry do allow a range of new materials to be prepared. For example, Bignozzi and Ober have reported the synthesis of a series of side chain LC-coil diblock copolymers by living free radical polymerization. Interestingly these materials were shown to possess a smectic mesophase and a lamellar microstructure by X-ray diffraction.[168]

While the block copolymers available from "living" free radical procedures may not be as well defined as the best examples available from anionic techniques, they have the advantage of greater availability and a significantly enhanced tolerance of functional groups. Technological applications that have been examined for these block copolymer include dispersants for pigments,[175] precursors to shell cross-linked nanoparticles for drug delivery,[176,177] supports for combinatorial chemistry,[178] and resist materials for photolithography.[179]

The advent of second-generation alkoxyamines, which are suitable for the polymerization of a range of monomer families, has significantly enlarged the range of block copolymers that can be prepared using nitroxide-mediated processes. For example, block copolymers such as poly(styrene-*b*-isoprene), poly-(*tert*-butyl acrylate-*b*-N,N-dimethylacrylamide), etc. can be readily obtained by polymerization of the first monomer to give the starting block, which is either isolated or used in situ.[38] The second monomer is then added, with or without the presence of a solvent to aid solubility, and on heating the second block is grown. One of the interesting features of preparing block copolymers by nitroxide-mediated, ATRP, or RAFT procedures is that initial block can be char-

acterized and stored before proceeding to the second block. This is totally unlike anionic procedures and is extremely useful from a synthetic viewpoint. In many respects, it is actually fortuitous since the conversions obtained in living free radical procedures do not typically reach 100%; therefore, the in situ approach actually affords an impure second block, which is contaminated with the first monomer.

One drawback that nitroxide-mediated polymerizations have in common with anionic procedures is that they both suffer from a monomer sequence issue when preparing specific block copolymers. The classic example for living free radical systems is the preparation of styrene-acrylate block copolymers. If a starting polystyrene macroinitiator, **67**, is used to polymerize *n*-butyl acrylate to give the block copolymer **68**, a significant amount of a low molecular weight shoulder is observed.[38] The exact nature of this shoulder, whether it is unreacted, or terminated starting polystyrene block is unknown. Attempts to overcome this unexpected lack of reactivity by the addition of solvent, etc., have been unsuccessful and are related to the relative rates of polymerization and initiation for styrene and acrylates. The initiating ability of the starting polystyrene block is however, not an issue since it can be used to initiate the polymerization of isoprene extremely efficiently leading to well-defined block copolymers, **69**, with no homopolymer or lower molecular weight contamination (Scheme 22).

Scheme 22
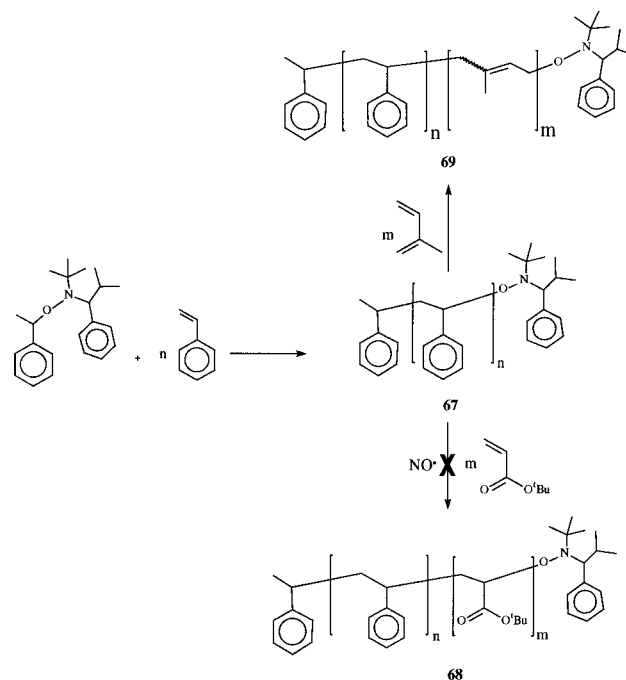
The reverse strategy, polymerization of the acrylate block followed by styrene, has been successful and has allowed the preparation of well-defined block copolymers with levels of control comparable to ATRP procedures. In this strategy, an alkoxyamine functionalized poly(*n*-butyl acrylate) block, **70,** is initially grown and then used to polymerize styrene at 123 °C under argon for 8 h. This results in 92% conver-

sion to give the block copolymer **71**, analysis of which revealed the expected increase in molecular weight, while the polydispersity remained very low (PD. = 1.06−1.19) and there were no detectable amount of unreacted starting poly(acrylate) block (Scheme 23).

Scheme 23

70

71

The radical nature of nitroxide-mediated processes also allows novel types of block copolymers to be prepared in which copolymers, not homopolymer, are employed as one of the blocks. One of the simplest examples incorporate random copolymers[124] and the novelty of these structures is based on the inability to prepare random copolymers by living anionic or cationic procedures. This is in direct con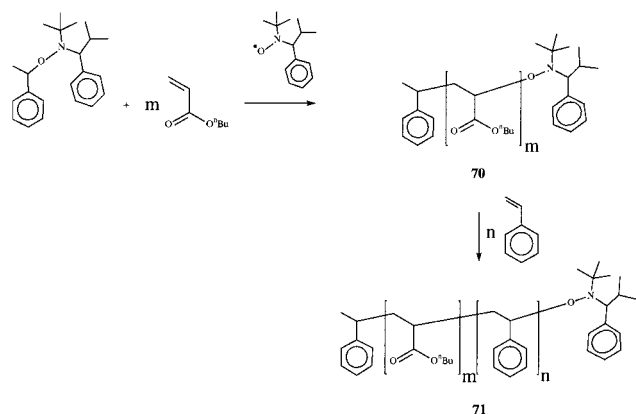trast to the facile synthesis of well-defined random copolymers by nitroxide-mediated systems. While similar in concept, random block copolymers are more like traditional block copolymers than random copolymers in that there are two discrete blocks, the main difference being one or more of these blocks is composed of a random copolymer segment. For example, homopolystyrene starting blocks can be used to initiate the copolymerization of styrene and 4-vinylpyridine to give a block copolymer consisting of a polystyrene block and a random copolymer of styrene and 4-vinylpyridine as the second block.[166]

The potential for these materials can be better appreciated if the synthesis and application of the functionalized block copolymer **72** is considered. An initial random copolymer of methyl acrylate and glycidyl methacrylate, **73**, is prepared by nitroxide-mediated living free radical polymerization and then used to initiate the polymerization of isoprene leading to the random block copolymer **72** (Scheme 24). The design of these macromolecules incorporates a random block which is not only miscible with thermosetting epoxies, but also can undergo reaction leading to covalent linking between the copolymer microstructure and the cross-linked epoxy resin. The polyisoprene block is immiscible and so drives the formation of a nanoscopic phase separated structure and leads to modification of the physical and mechanical properties of the thermosetting epoxy. The facile synthesis of **72**, which combines reactive epoxy functionalities with both a block and random copolymer structure, demonstrates the far reaching potential of living radical procedures.

D. Random Copolymers

One of the major advantages of living radical procedures compared to living anionic or cationic polymerizations is the ability to prepare well-defined random copolymers. In traditional anionic or cationic procedures, there are numerous problems which normally preclude the successful synthesis of random copolymers. For example, reactivity ratios can be extremely large in anionic systems, and so true random copolymerizations do not occur and blocky structures are obtained. Alternatively, the polymerization conditions for one monomer or functional group are not compatible with the second monomer and an uncontrolled polymerization is obtained. This lack of synthetic versatility has prompted numerous groups to examine the synthesis of well-defined random copolymers via living radical techniques. While early work with TEMPO did demonstrate that random copolymers can be prepared under nitroxide-mediated conditions the inability to control the homopolymerization of monomers other than styrene limited the range of monomer units and possible random copolymer structures.[31,174,180] With the advent of second-generation nitroxides, such as **17**, the realm of well-defined random copolymers have been dramatically opened. For example, while the homopolymerization of methacrylates does not give controlled polymers, random copolymers of methacrylates with up to 90 mol % of methacylate incorporation can be prepared in a living fashion.[38] The actual rationale for this stark contrast is not known at the moment and deserves further study since it may provide insights into controlling H-abstraction and in turn methacrylate polymerization in these systems. The ultimate aim of these studies would be to develop a living polymerization of methacrylates that leads to well-defined materials, one of the major challenges in this general area.

The finding that the reactivity ratios for monomers under living free radical conditions are essentially the same as under normal free radical conditions is also fundamentally important. As a consequence of this, random copolymers prepared by living free radical processes are different on a molecular level to those prepared by normal free radical methods, even though they may appear the same on the macroscopic level (Scheme 25). In the case of traditional free radical polymerization, continuous initiation leads to chains initiating and terminating at different stages of the polymerization. Therefore, chains that are initiated and terminated at low conversion experience a different monomer feed ratio compared to chains initiated later in the polymerization. The polymerization product is therefore a complex mixture of random copolymers with different monomer compositions and different molecular weights. For living radical systems, all chains are initiated at the same time and grow at approximately the same rate, as a consequence all of the growing chains experience the same change in monomer concentrations. As a result the random copolymers have approximately the same composition coupled with a low dispersity of molecular weights. This is depicted graphically in Scheme 25; however, it should

Scheme 24

73

74
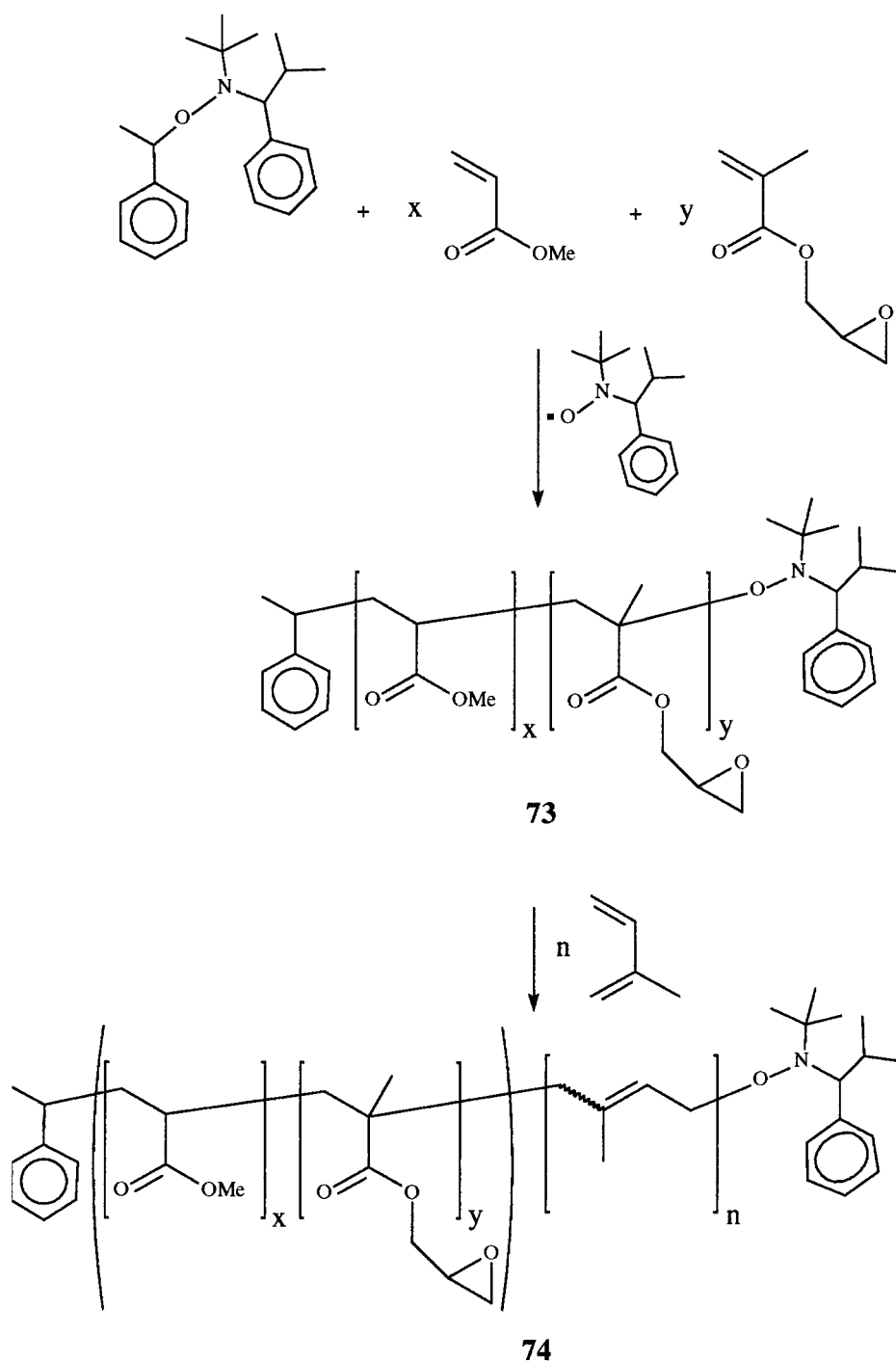
also be pointed out that while the graphical representation suggests that all the chains are the same length, this is not the case especially for the tradition free radical case where polydispersities of 2.0 are typically obtained (cf. 1.1 for nitroxide systems). The structural variation between chains is therefore further exacerbated in traditional systems.

An excellent example of using reactivity ratios and the synthetic versatility of nitroxide systems to prepare unusual block copolymers is the copolymerization of styrene/maleic anhydride mixtures.[181] When an excess of styrene is used, the copolymerization leads to preferential and finally total consumption of maleic anhydride at conversions of styrene signifi-

Scheme 25

Living Free Radical
Initiation at T = 0,
compositionally similar

$M_1 + M_2$

Traditional Free Radical
Continuous Initiation,
compositionally different
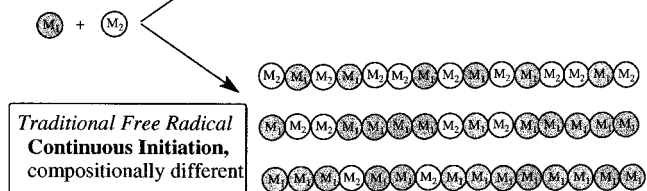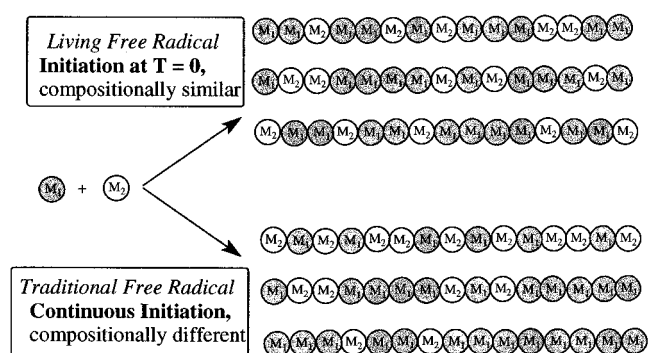
cantly less than 100%. As a result, the growing polymer chains experience an initial monomer feed of styrene and maleic anhydride which gradually changes during the course of the polymerization to a monomer feed of neat styrene. This has been experimentally demonstrated, and as can be seen in Figure 5, after 1.5 h, no detectable amounts of maleic
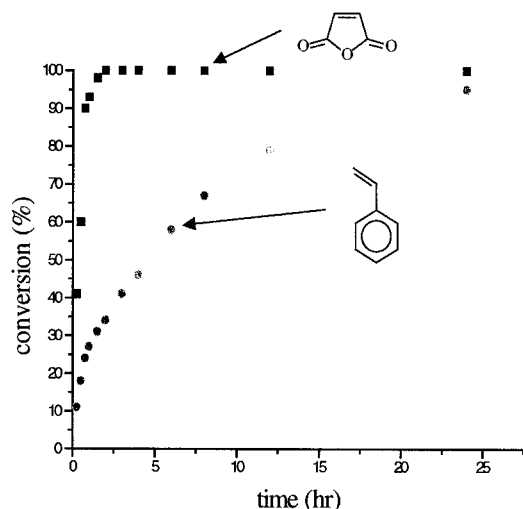
Figure 5. Evolution of conversion with time for the polymerization of a 9:1 mixture of styrene and maleic anhydride mediated by **42** and 0.05 equiv of **17** at 123 °C.

anhydride could be observed in the polymerization of a 9:1 mixture of styrene and maleic anhydride. Significantly, the conversion of styrene at this stage was only ca. 25−30% and the random copolymer of styrene and maleic anhydride **74** that is formed in situ now experiences a monomer feed that is neat styrene. Further polymerization now involves growth of a homopolystyrene block. This results in the formation of a functionalized block copolymer, **75**, in a single step, consisting of an initial ca. 1:3 copolymer of maleic anhydride and styrene, respectively, followed by a block of polystyrene which is roughly twice the molecular weight of the initial anhydride functionalized block (Scheme 26). These materials can be considered to be a limiting example of gradient copolymers and by carefully choosing reactivity ratios, structures intermediate between statistically random copolymers and one-step block copolymers can be prepared by living free radical techniques.[182] Other examples include the controlled polymerization of termonomer mixtures of styrene, maleimides, *n*-butyl methacrylate, though in this example the polydispersity is moderate (i.e. 1.5−1.6) due to the use of TEMPO as the mediating radical.[183]

VIII. Complex Macromolecular Architectures

A. Star and Graft Polymers

The reduced concentration of radical centers at the chain ends of living radical polymerizations opens up a number of possibilities in the synthesis of complex macromolecular architectures due to the very low

Scheme 26

occurrence of side reactions such as radical−radical chain coupling. While the use of polyfunctional initiators under normal free radical conditions gives cross-linked networks due to radical coupling reactions, under living radical conditions a polyfunctional initiator may be expected to lead to the desired graft, or star polymer with little, or no, unwanted coupling products, provided the number of grafts/arms is not too high (less than 10−20). When compared to ATRP, this is one area is which nitroxi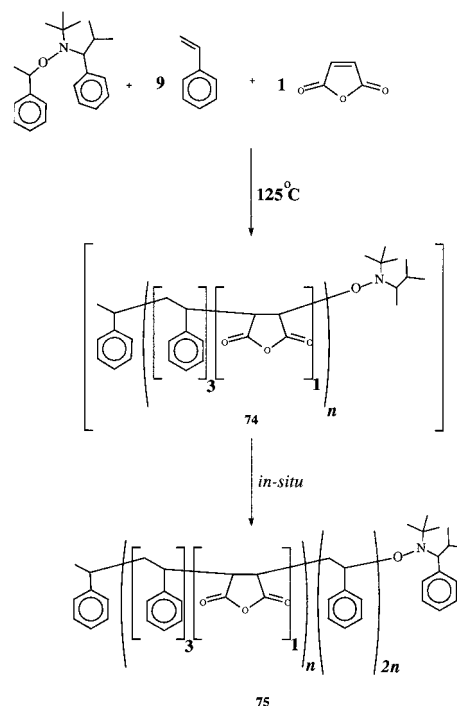des systems do suffer from a drawback. The actual concentration of radicals is dictated by the nitroxide systems and cannot be readily controlled by external means. This is in direct contrast to ATRP where the radical concentration can be varied by the level of catalyst added.

This principal was first tested by the synthesis and polymerization of the trifunctional unimolecular initiator **76**.[184] Interestingly, no detectable amounts of cross-linked or insoluble material was observed, and degradation of the 3-arm polystyrene star **77** by hydrolysis of the ester links was found to give the individual polystyrene arms **78** (Scheme 27). Analysis of **78** revealed a molecular weight comparable to that expected from the initiator-to-monomer ratio and a narrow polydispersity (ca. 1.10−1.15). These results demonstrate that each of the initiating units in the tris-alkoxyamine is "active" and the individual polystyrene arms grow at approximately the same rate with little or no cross-linking due to radical coupling reactions.

Subsequently, this concept has been extended to more highly functionalized star-initiators as well as polymeric initiators for the synthesis of graft structures. It should however, be appreciated that the polymerization process is still radical in nature and while radical−radical coupling reactions are decreased they are not eliminated and so as the number of initiating sites per molecule increase, the prob-

Scheme 27
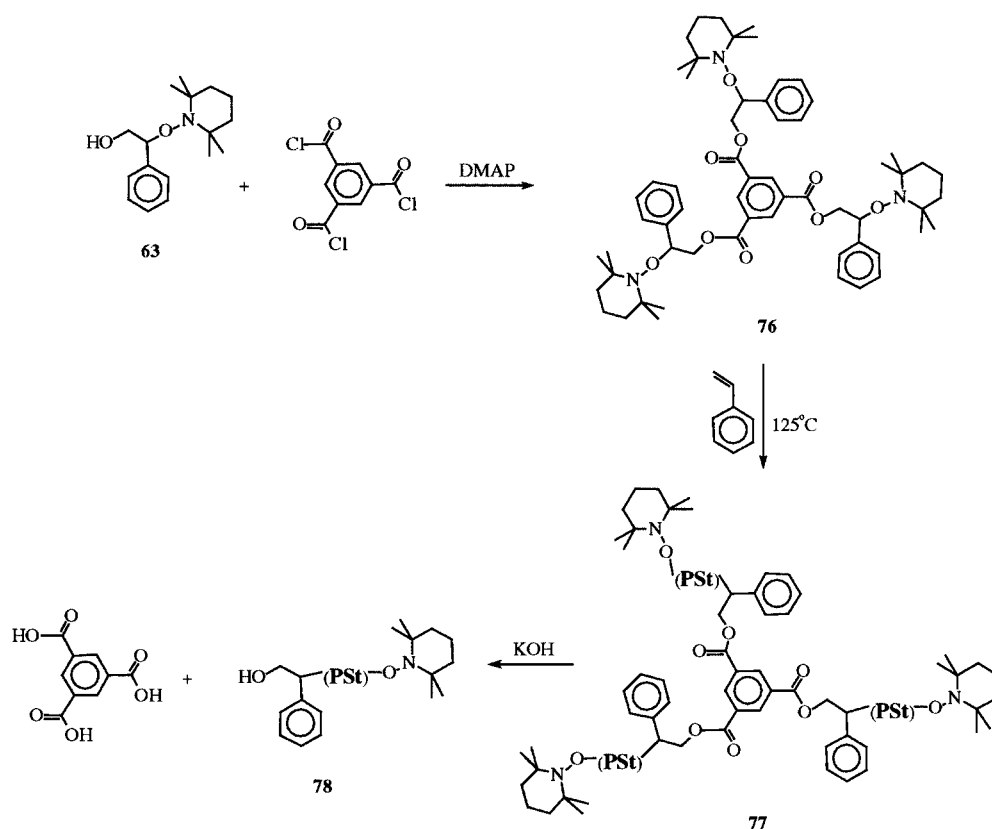
ability of coupling also increases. For example, a mixture of styrene and *p*-chloromethylstyrene can be polymerized under "living" free radical conditions to give a well-defined linear copolymer, **79**, with controlled molecular weight and low polydispersity (ca. 1.10−1.25). Reaction of **79** with the sodium salt of the hydroxy functionalized unimolecular initiator then gives the desired polymeric initiator **80** which is a precursor to a variety of graft copolymers, **81**.[185] At average grafting densities of greater than six initiating sites per backbone, chain−chain coupling becomes apparent by GPC, and at densities greater than 15, it is a major process (Scheme 28).

B. Hyperbranched and Dendritic Structures

As demonstrated by Fréchet[186] in the development of self-condensing polymerizations, the ability to form reactive unimolecular initiators, such as **82**, opens up a number of avenues to unusual macromolecular architectures that are either difficult, or impossible, to prepare using traditional free radical chemistry or living anionic procedures. In the case of the styrenic derivative **82**, a propagating center and an initiating center are combined in the same molecule to effectively create a self-condensing monomer, which is similar to AB$_2$ monomers used for the preparation of hyperbranched and dendritic macromolecules by condensation chemistry. Homopolymerization of **82** under "living" free radical conditions was shown to lead to initial formation of dimers, trimers, etc. and eventually hyperbranched macromolecules, **83**, with the kinetics of growth resembling a step-growth polymerization even though the polymerization occurs by a free radical mechanism

(Scheme 29).[187a] One interesting facet of this polymerization is that the hyperbranched polystyrene derivatives contain numerous initiating centers. These numerous initiating centers have been used to form a unique class of star macromolecules in which the central core is a highly functionalized hyperbranched polymer. Subsequently, Fréchet[187b] and Matyjaszewski[188] have applied a similar technique to the preparation of hyperbranched polystyrene derivatives by the homopolymerization of *p*-chloromethylstyrene using ATRP conditions, though the actual structure of the materials obtained seems to be variable.[189]

The synthesis of these highly branched star polymers has recently attracted much interest and a variety of simplified approaches have been reported. While Yang[190] has discussed the use of mediating nitroxides, which contain a polymerizable double bond and therefore lead to branch points, the majority of work has centered on the coupling, or knitting together, of preformed linear chains by reaction with cross-linkable monomers, a technique which has been extensively used in anionic and cationic procedures. One of the attractive features of this approach, which is unique to living radical systems, is that the starting linear chains, **85**, can be isolated, characterized and stored before subsequent coupling. Additionally, a variety of different chains in terms of molecular weight, composition, etc. can be copolymerized together to give heterogeneous star-block copolymers.[191,192] The basic strategy is outlined in Scheme 30, and involves the preparation of alkoxyamine terminated linear chains **84** and subsequent coupling of these dormant chains with cross-linking agents such as divinylbenzene or a bis(maleimide) deriva-

Scheme 28

79

80

81

Scheme 29

+ trimers,
tetramers, etc.

82

83

Scheme 30

+ vinyl
monomer

Alkoxyamine
functionalization

84

85
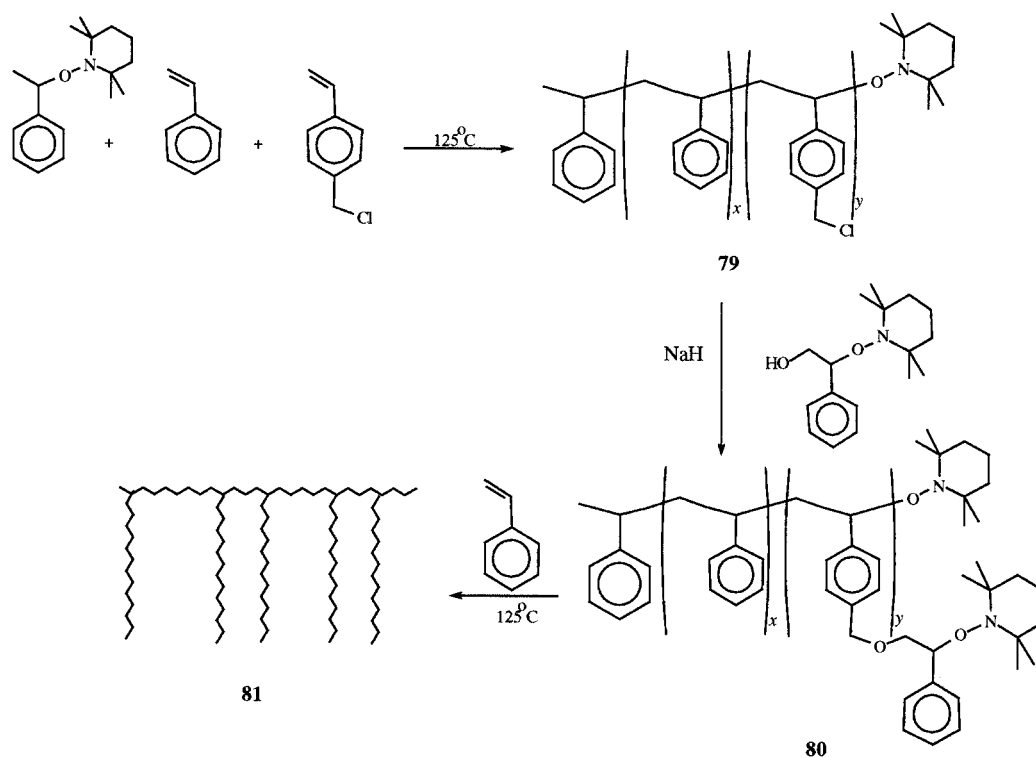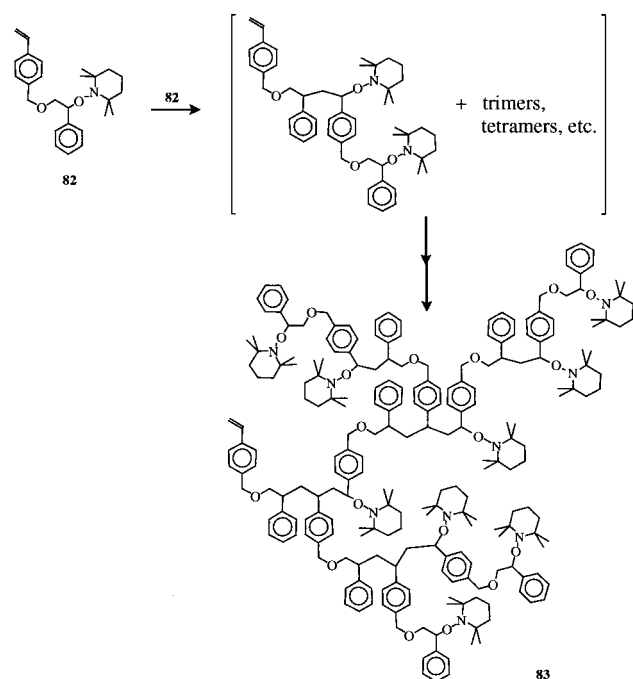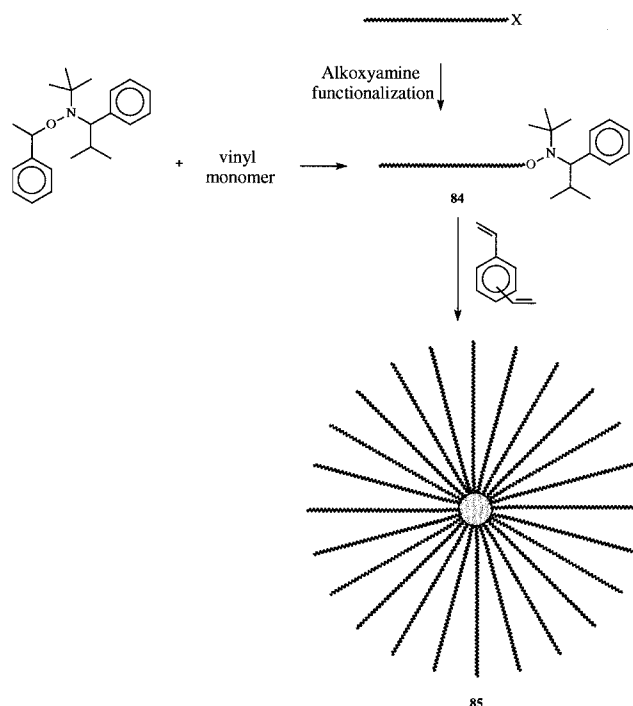
tive. Since the only requirement is an alkoxyamine chain end, the range of starting linear polymers is immense and is not restricted to vinyl polymers or homopolymers. Microgels have also been extensively studied by Solomon using living free radical procedures and their structure has been shown to be subtlely different to that obtained using traditional free radical procedures.[193]

Unique dendritic—linear block copolymers have also been prepared by the coupling of functionalized initiators with dendritic macromolecules prepared by the convergent growth approach.[194] In these ap-

proaches, the dendrimer can be attached to either the initiating fragment of the alkoxyamine or the mediating nitroxide and the dendritic initiator used to initiate the growth of linear vinyl blocks under controlled conditions. As demonstrated in the work of Fréchet and Hawker,[195] these monodisperse dendritic initiators are perfectly suited for the preparation of well-defined block copolymers, for example coupling of the dendrimer **86**, which contains a single bromomethyl group at its focal point with the hydroxy functionalized unimolecular initiators gives the

dendritic initiator **87**. Hybrid dendritic−linear block copolymers, **88**, with well-controlled molecular weights and low polydispersities are then obtained by the reaction of **87** with a variety of styrenic monomers or comonomer mixtures under living free radical polymerization conditions (Scheme 31).[161,195,196] Simi-

Scheme 31
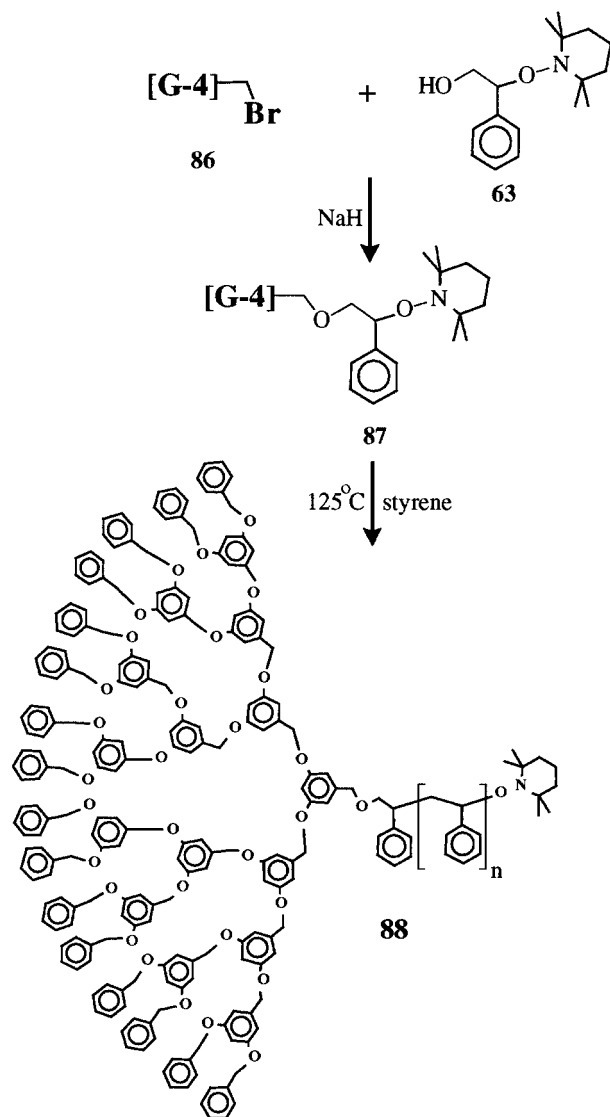
lar structures can also be prepared using ATRP chemistry and in this case the initiating group is simply a focal point chloromethyl, or bromomethyl functionality.[197] While the majority of examples involve the dendrimer being attached to the initiator, there is a single instance where it is attached to the mediating radical. Interestingly, in the case[198] where the dendritic block is attached to the nitroxide, the molecular weights and polydispersities for the block copolymers are not as well controlled as in the case where the dendrimer is attached to the initiating fragment. This difference may be due to the increased steric bulk of the dendritic nitroxide which would be expected to decrease its mobility and hence ability to control the polymerization. While a detailed study has not been performed this result may have important implications especially for complex, functionalized nitroxides whose diffusion characteristics may

be different to the more traditional small molecule nitroxides.

This building block, or modular approach to the synthesis of complex macromolecular architectures can be taken a step further in the rapid synthesis of combburst, or dendritic graft copolymers by a tandem "living" free radical approach.[185,199,200] The underlying strategy in this novel approach to highly branched linear polymers is that each layer, or generation, of linear polymers is prepared by "living" free radical procedures and the initiating groups are either present during the polymerization or introduced in a post-polymerization functionalization step. In this way very large, highly branched combburst copolymers can be prepared in a limited number of steps using mild reaction conditions. As shown in Scheme 32 the initial linear backbone **89** is prepared by nitroxide-mediated "living" free radical polymerization of a mixture of styrene and *p*-chloromethyl styrene. At this stage the polymerization mechanism can be switched from nitroxide mediated to atom transfer "living" free radical conditions to give graft copolymers or TEMPO based initiating groups can be introduced by reaction of the numerous chloromethyl groups with the sodium salt of **63** to give the polymeric initiator **91**. A second layer, or generation, of reactive chloromethyl groups can be introduced on the grafted arms **92** by a second copolymerization of styrene and *p*-chloromethylstyrene. This functionalized graft copolymer can again be used as a complex polymeric initiator for ATRP polymerization that introduces a third layer of linear polymer chains, **93**. In analogy with the divergent growth approach to dendritic macromolecules, this stepwise functionalization/growth strategy can be continued to give larger and larger combburst macromolecules and the mild reaction conditions permit a wide variety of monomer units and functional groups to be used.

The versatility associated with nitroxide-mediated polymerizations, in terms of both monomer choice and initiator structure, also permits a wide variety of other complex macromolecular structures to be prepared. Sherrington[201] and Fukuda[202] have examined the preparation of branched and cross-linked structures by nitroxide-mediated processes, significantly the living nature of the polymerization permits subtlety different structures to be obtained when compared to traditional free radical processes. In addition, a versatile approach to cyclic polymers has been developed by Hemery[203] that relies on the synthesis of nonsymmetrical telechelic macromolecules followed by cyclization of the mutually reactive chain ends. In a similar approach, Chaumont has prepared well-defined polymer networks by the cross-linking of telechelic macromolecules prepared by nitroxide-mediated processes with bifunctional small molecules.[204]

IX. Surface-Initiated Polymerizations

The stability of alkoxyamine initiators is not only a major synthetic advantage when compared to more traditional living polymerization procedures but it also permits opportunities in the area of surface modification. In analogy with the work that has

Scheme 32

89

90

91

92

93

wwww = PS chains
wwww = PBMA chains
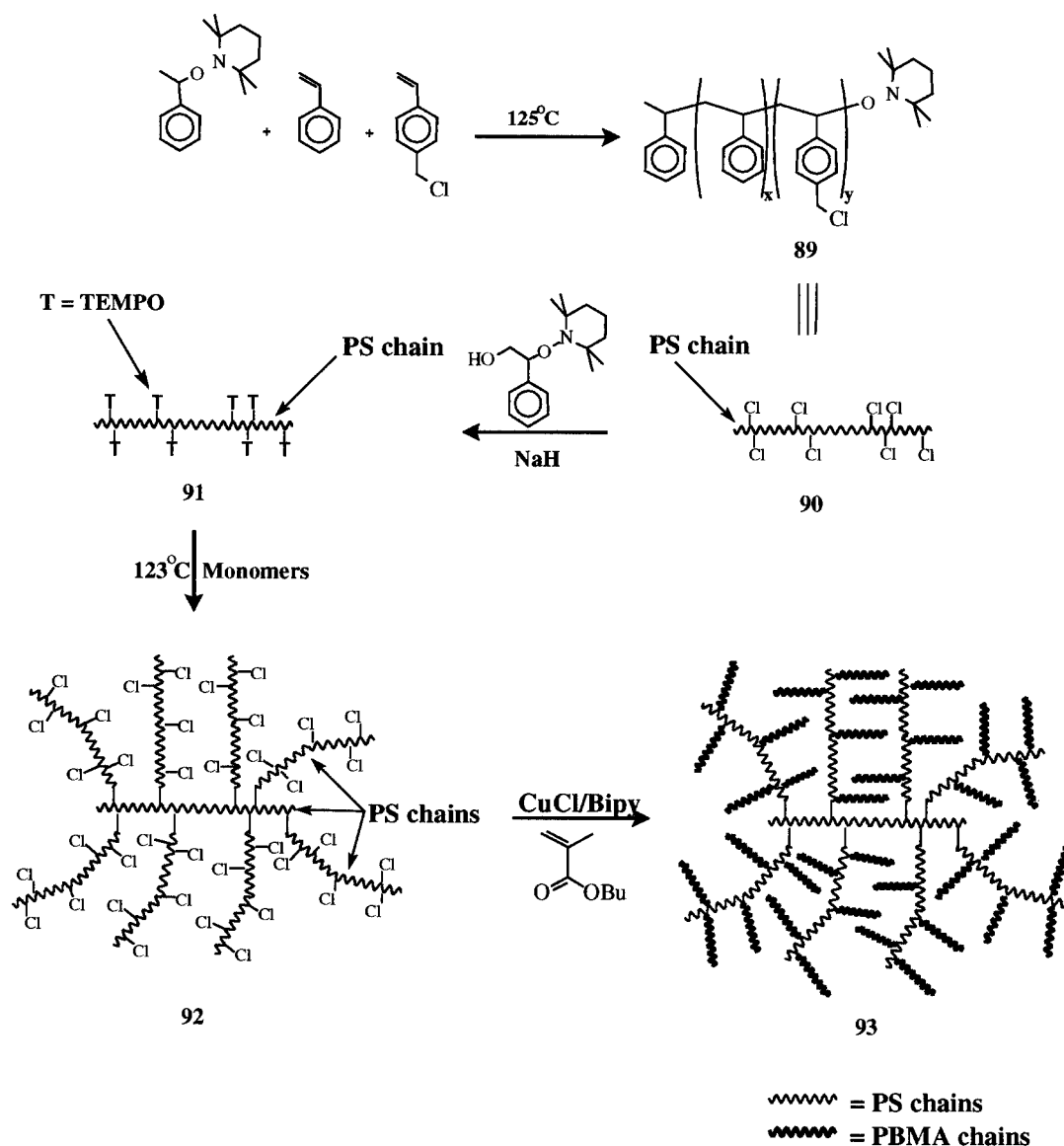
subsequently been done in the area of ATRP, functionalized alkoxyamines were the first example of living radical initiators, prepared and attached to a variety of surfaces and subsequently used to grow covalently attached polymer chains. The living nature of the polymerization provides an unprecedented ability to control the structure, density, functionality, etc. of the surface attached polymer chains and has rapidly become an area of significant importance and growth.[205] Numerous studies have appeared demonstrating the ability to control the degree of polymerization or thickness of the grafted polymer chains, achieve low polydispersities and prepare block copolymers. The covalent nature of the surface attachment also allows either the living free radical initiators themselves to be patterned or the resulting polymer brushes to be patterned (Figure 6).[206,207] This allows the surface chemistry and topology of the polymer brush to be controlled and this ability to control the placement and structure of vinyl polymer chains is an indication of the tremendous potential that both nitroxide-mediated and atom transfer living free radical polymerizations show in the general area

of nanotechnology. Two examples that capture this promise are the preparation of functionalized macroporous monoliths for advanced chromatographic separations and the design of "Rasta-resins". The latter are especially interesting as ultrahigh capacity supports for combinatorial chemistry which not only utilize the increased functionality or amplification afforded by the surface-initiated polymerization concept (one initiating site leads to numerous reactive functional groups) but takes advantage of the more "solution-like" environment of the functional groups attached to the solvated polymer chains when compared to functionalities at a solid–liquid interface or in a cross-linked resin.[208,209] Similar strategies can be performed on alternate particulate substrates such as silica[205] or carbon black[210] or via ATRP techniques.[211]

The potential for surface-initiated polymerizations using nitroxide-mediated living free radical procedures is perhaps best illustrated by the direct synthesis of dispersed nanocomposites by Sogah and Giannelis.[212] In this approach the synthetic versatility of the alkoxyamine group is again exploited to
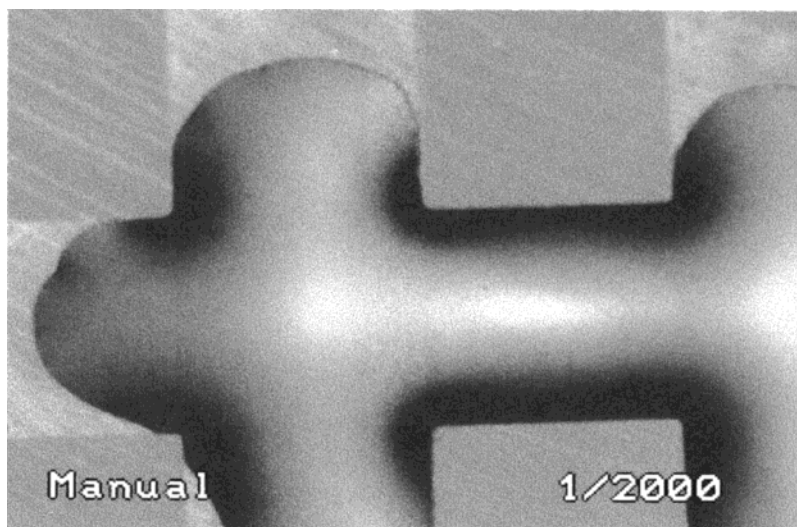
Figure 6. Interaction of a water droplet with 200 micron features of a patterned polymer brush prepared by surface-initiated polymerization. The unusual wetting profile is due to preferential interaction of the water droplet with the poly-(acrylic acid) brush domains (light) and complete non-wetting of the hydrophobic poly(*tert*-butyl acrylate) domains (dark).

prepare the quaternary amine salt **94** which due to its chemistry can intercalate readily into the inter-gallery spaces of a silicate or inorganic matrix. These "anchored" alkoxyamine groups can now be used to initiate the polymerization of a vinyl monomer such as styrene leading to a dispersed silicate nanocomposite. The advantages of this novel approach are that the intercalation of small initiating species such as **94** is orders of magnitude faster than for similar chain end functionalized polystyrene derivatives. In addition, critical polymer characteristics such as molecular weight and polydispersity are controlled while block or random copolymer formation is possible (Scheme 33).

X. Outlook

Even though the first reports of a successful living radical process leading to high molecular weight (>30 000), low polydispersity (1.1−1.2) materials were published in 1993 the impact on the field of polymer chemistry has been immense, opening up possibilities in both polymer synthesis and polymer physics that until recently were either prohibitively difficult or impossible. The development of nitroxide-mediated living free radical polymerizations as an important synthetic tool has been extremely rapid and poses exciting possibilities for the future. However, there are a number of issues that must be addressed to enable the continued evolution of this new technique. A greater understanding of the relationship between nitroxide/alkoxyamine structure and polymerization efficiency needs to be developed. Specifically, mediating nitroxides or strategies must be developed which allow the polymerizations to be conducted at lower temperatures (ca. 60−80 °C) in shorter time periods (2−5 h) and with higher conversions (ca. 99%+). It is also highly desirable to further increase the range of monomers that can be polymerized under living conditions, prime candidates are methacrylates and vinyl acetate based monomers. Finally a complete understanding of block copolymer formation, reinitiation efficiency, etc. needs

to be developed in order to make block copolymer formation a routine procedure for the nonexpert. If these challenges can be overcome the industrial appeal of nitroxide-mediated living free radical procedures will increase significantly, while also providing an extremely powerful synthetic technique for the synthesis of vinyl based polymers.

The power of living free radical procedures as synthetic tools in polymer science can be better appreciated by considering the potential advantages when compared to traditional techniques such as anionic polymerization. The ability to accommodate functional groups and diverse families of monomers permit block, random, and gradient copolymers to be prepared without complicated, multistep reaction schemes. Complex macromolecular architectures can also be prepared, however, the low occurrence of radical−radical coupling reactions does place restrictions on the number of propagating arms per macromolecule. The radical nature of the polymerization process does limit the ability to control the stereochemistry; no evidence has been currently presented to indicate that living free radical processes can lead to tacticity control. Presumably the generation of a planar radical at the propagating chain end during each monomer addition step is the key step in this loss of stereochemical control.

Another significant advantage of living free radical procedures is the stability of the initiating species. In the case of nitroxide-mediated processes, the above discussion clearly demonstrates that a variety of chemical transformations can be performed with no deleterious effect on the initiating ability of the alkoxyamine initiator. Not only does this significantly improve the ability to prepare chain end labeled macromolecules but also permits initiating fragments to be introduced at various surfaces, interfaces, chain ends of dendrimers, along the backbone of a linear polymer chain, etc. As more and more effort is devoted to controlling structure and function on the nanometer scale, the role of well-defined polymeric materials with controlled size, dispersity and func-

Scheme 33
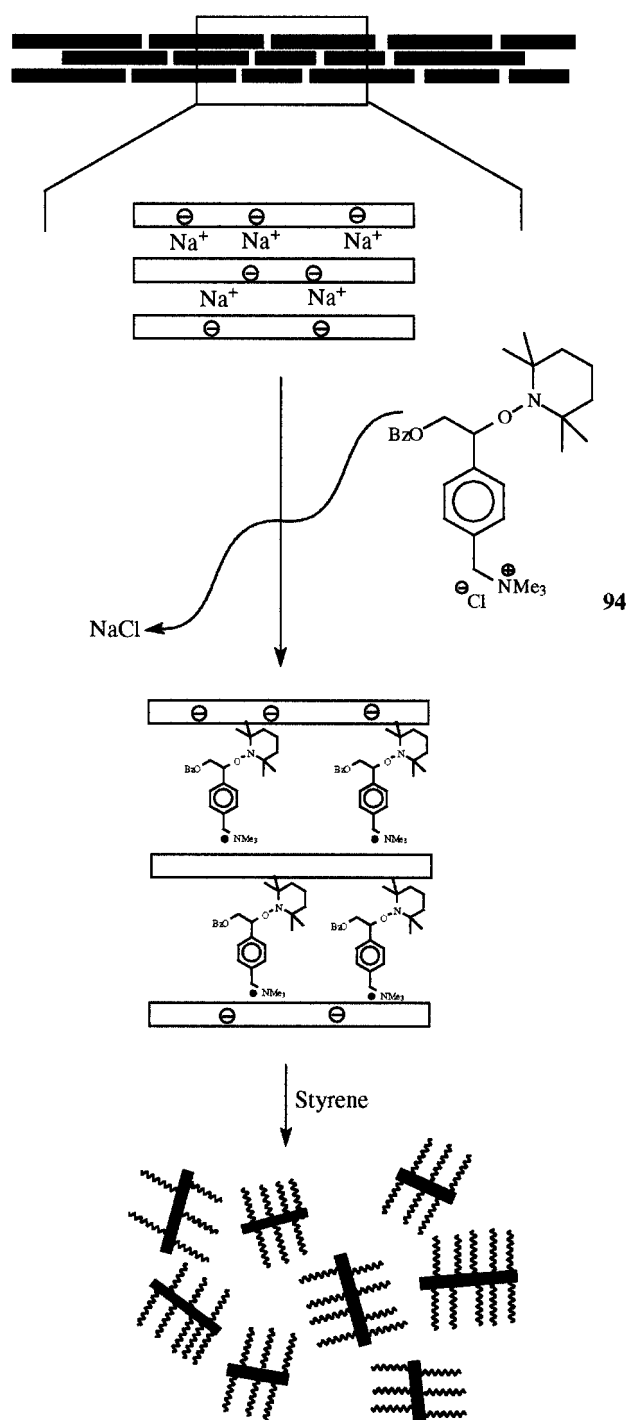
tional group placement will become critical. The further development of nitroxide-mediated, ATRP, and RAFT processes is therefore critical for the preparation of these materials and for the continued evolution of nanotechnology.

XI. Acknowledgments

XII. Note Added after ASAP

References to the paper by Chiefari and Rizzardo have been removed.

XIII. References

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