Application of Nitroxide Mediated Polymerization in Different Monomer Systems

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Abstract: Nitroxide mediated polymerization (NMP) is one of the main reversible de-activation radical polymerization (RDRP) techniques and was one of the earliest discovered. However, other RDRP processes like atom transfer radical polymerization (ATRP) and reversible addition fragmentation transfer polymerization (RAFT) surpassed NMP, as it was largely restricted to styrenic polymerizations. Recently, with second-generation nitroxides, controlled homopolymerizations (predictable degree of polymerization with conversion, high chain end fidelity and narrow molecular weight distributions) of acrylates, acrylamides and dienes are now possible. Methacrylic ester homopolymerizations have remained somewhat elusive with commercially available alkoxyamines, but with a low concentration ~ 1-10 mol% of a controlling co-monomer, methacrylate-rich polymers are accessible. Recent reports have shown promising possibilities for methacrylate homopolymerizations. This review will summarize the progress made in the diversity of monomers polymerizable by NMP and an outlook of the ability of NMP to polymerize new families of monomers or to use under-utilized monomers for emerging applications will be given.

Keywords: nitroxide mediated polymerization; styrenics, acrylates, methacrylates, acrylamides, dienes

1. INTRODUCTION

Nitroxide mediated polymerization (NMP) has arrived at an interesting juncture in its development. As one of the main reversible de-activation radical polymerization (RDRP) processes (also known more colloquially as controlled radical polymerization (CRP) or living free radical polymerization), it was one of the first reported in the early 1990s [1-5]. However, it was rapidly surpassed by atom transfer radical polymerization (ATRP) [6,7] and reversible addition fragmentation transfer polymerization (RAFT). [8,9] NMP with first-generation nitroxides such as 2, 2, 6, 6, tetramethylpiperidinyl-1-oxy (TEMPO) was restricted to the polymerization of styrenics largely. In contrast, ATRP and RAFT readily polymerized acrylic and methacrylic monomers in a controlled fashion. However, NMP began to catch up in the early 2000s with the advent of N-*tert*-butyl-N-[1-diethylphosphono-(2,2 dimethylpropyl)] nitroxide (the so-called SG1 type of initiator and its subsequent commercially available unimolecular initiator BlocBuilder-MA) [10] and 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyl nitroxide (TIPNO) [11,12] type of unimolecular alkoxyamine initiators which permitted acrylates and acrylamides to be readily polymerized in a controlled manner. Methacrylates remained largely elusive generally, but a co-monomer approach indicated a promising way to obtain largely methacrylic copolymers [13]. Methacrylate homopolymerizations have remained a target and *in situ* NMP using nitrones was effective for homopolymerization of various methacrylates [14-16]. Additionally, recently developed alkoxyamines have indicated some promise for methacrylate homopolymerizations [17-22]. Although there seems to be a wide consensus of the suitability of NMP to produce styrenic, (meth)acrylic, (meth)acrylamidic and diene-based homopolymers and copolymers, \ some families are not fully explored, such as vinyl esters, vinyl azlactones and cyclic ketene acetals, that are have not been studied thoroughly by NMP.

Several excellent reviews summarize succinctly the history of NMP in terms of initiator development, polymerization mechanisms and corresponding multi-scale modeling, monomer types, reaction media, and applications [23-31]. In the following review, I will chronologically focus exclusively on the kinds of monomers that NMP has been successfully applied to, along with potential new directions in materials development. I hope this updated review will encourage the exploration of new monomer polymerizations or improved polymerizations of existing monomers by NMP in terms of chain end fidelity, molecular architecture, and process latitude.

2. STYRENIC POLYMERIZATIONS

NMP of styrenic monomers was first reported using TEMPO [1,5]. Although this structural motif seems limited, styrenic-based polymers by NMP exhibited a wide variety of properties amenable to many applications. For example, p-acetoxy-functional styrenics were polymerized by TEMPO for photolithographic resist materials [32,33], sodium-sulfonate styrene was polymerized to make water-soluble polyelectrolytes [34-36], as was lithium styrenesulfonyl(trifluoromethanesulfonyl) imide (SSTFSILi) using BlocBuilder-MA [37], 2,5-bis[(4-methoxyphenyl) oxycarbonyl]styrene for liquid crystal materials [38], and phenylenevinylene-functional monomers for luminescent polymers [39]. In the following sections, TEMPO and similar ring-bearing structural motifs will be defined as first-

generation nitroxides, although there have been newer, more effective ones developed recently [40-41]. Alkoxyamines like the TIPNO and SG1 families are termed second-generation nitroxides herein. Figure 1 shows the structures of the most common or noteworthy nitroxides.
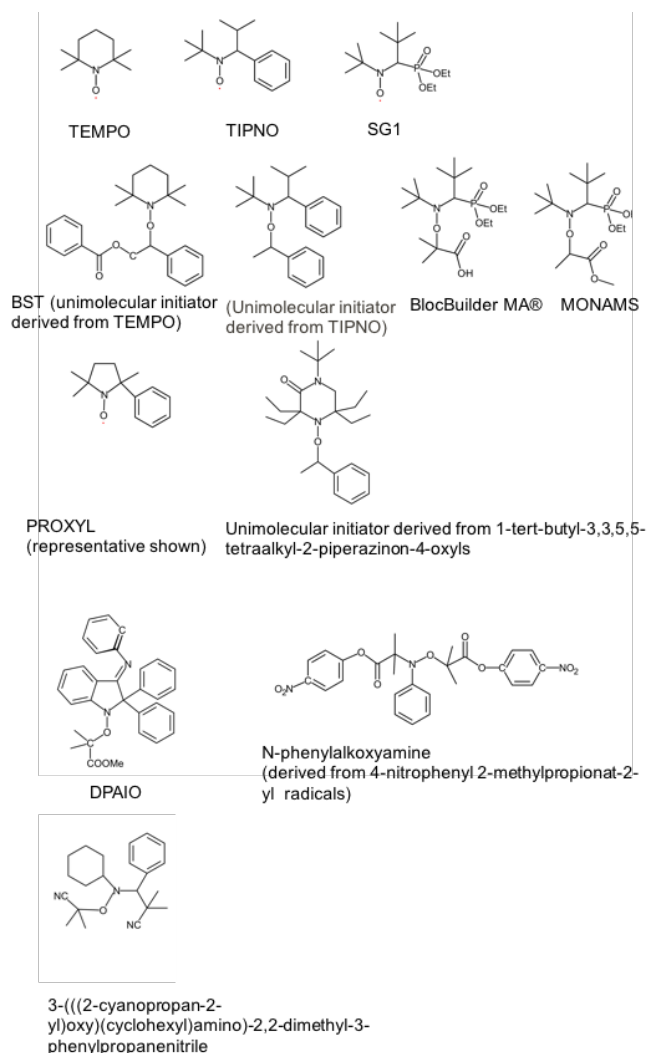

Figure 1: Structures of common nitroxides used to date along with pertinent features. TEMPO (and the derived BST) was developed initially and was limited to polymerization of styrenic monomers; second-generation nitroxides like SG1 (and the derived BlocBuilder-MA and MONAMS) and TIPNO-based initiators could polymerize acrylates, acrylamides and methacrylates with the aid of a co-monomer. PROXYL and the hindered alkoxyamines derived from Studer's group could polymerize acrylates at much lower temperatures. The last three entries correspond to alkoxyamines that can homopolymerize methacrylates.

2.1. Bulk styrenic polymerizations

The earliest styrenic NMPs were conducted in bulk for simplicity [1,2]. Recipes typically consisted of a two-step process where the TEMPO, styrenic monomer and conventional radical initiator such as benzoyl peroxide were used to form the adduct at low temperature (~ 100 °C), which serves effectively as a unimolecular initiator (the so-called BST, as shown in Figure 2). Subsequently increasing

the temperature to 120-130 °C and adding more monomer resulted in chain growth. Similar procedures were followed for a vast array of styrenics polymerized with TEMPO in bulk [42-63].
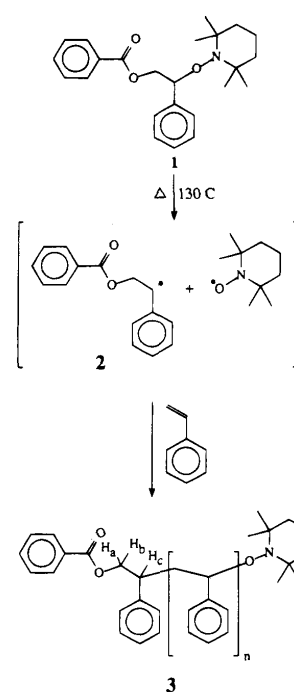
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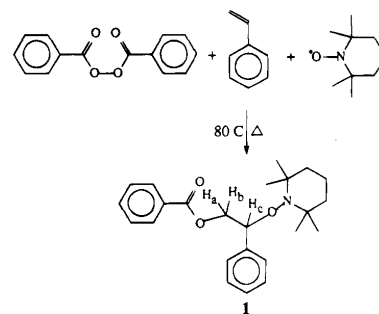
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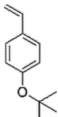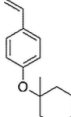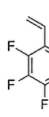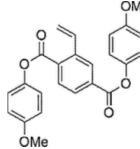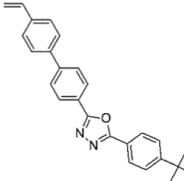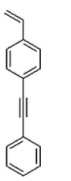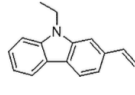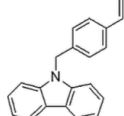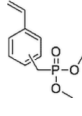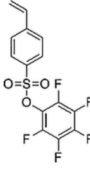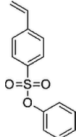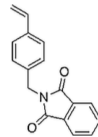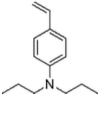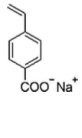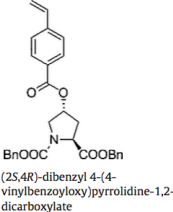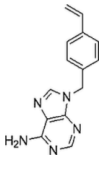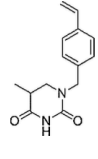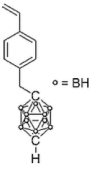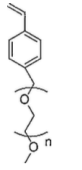
Figure 2: Use of a unimolecular initiator termed BST which is developed from the adduct of benzoyl peroxide, styrene and TEMPO. Reprinted with permission from Hawker, C. J. Molecular weight control by a "living" free-radical polymerization process. *J. Am. Chem. Soc.* 1994, 116, 11185-11186 [3]. Copyright 1994 American Chemical Society.

With the massive experimental thrust towards using TEMPO to control styrenic polymerizations, kinetic modeling studies ensued with the general objective of trying to predict molecular weight distribution and account for side reactions/products that would alter chain end fidelity and microstructure. For example, in bulk polymerization, diffusion controlled processes were added into the kinetic model by Roa-Luna et al [64]. They found that diffusion controlled bimolecular termination enhanced chain end fidelity whereas diffusion controlled activation/reactivation, and propagation worsened it, with the overall effect of providing slightly better predictions compared to

experimental data. Other modeling studies echoed the importance of diffusion-controlled termination in bulk NMP, and added that diffusional limitations are only important in propagation to very high conversion or very low temperature [65]. These researchers also added that bulky mediating agents can impact the activation/deactivation reactions at high conversion, with a significant broadening of the molecular weight distribution.

Table 1: Summary of styrenic monomers polymerized by nitroxide-mediated polymerization.

Reprinted from Reference [29] from *Prog. Polym. Sci.,* 38, Nicolas, J.; Guillaneuf, Y.; Lefay, C.; Bertin, D.; Gigmes, D.; Charleux, B. Nitroxide-mediated polymerization. 63-235, 2013 with permission from Elsevier.

Other studies examined cyclic polymerization effects for styrene/divinylbenzene copolymerizations, as it was expected that more homogeneous networks could be derived using NMP [66-67]. Using a series of models, cyclization reactions were predicted quite well compared to experiments and a combination of several models reasonably predicted gel points [66]. However, ideal network prediction cannot be often realized by NMP due to the presence of cyclization reactions [67]. The effect of other side-reactions such as chain transfer to dimer was examined by modeling of bulk NMP with BlocBuilder-MA systems, indicating lower chain end fidelity and poorer chain length control when chain transfer to dimer was incorporated [68]. An excellent summary of the status of modeling efforts with respect to some of these issues in RDRP is provided by Masan et al [69].

With the development of TIPNO and SG1 nitroxides in the late 1990s, styrenic monomers continued to be applied with the main advantage that such polymerizations could be conducted at much lower temperatures < 100 °C [10-12], which enabled different avenues for NMP. For example, the polymerization of non-equimolar mixtures of styrene with maleic anhydride using BlocBuilder-MA/SG1 led to one-shot block copolymers of poly(styrene-*alt*-maleic anhydride)-*block*-poly(styrene) where the styrene/maleic anhydride were nearly strictly alternating due to the lower temperature being possible (90 °C) [70] whereas with a TIPNO-based system, higher temperatures were required, which made the first S/MA sequence being essentially random [71]. It should be noted that such sequence controlled polymerizations have received much attention in that they encode functionality by the precise controlled sequence employed [72-74]. Further, the development of second-generation nitroxides permitted the use of non-pressurized reactors for dispersed aqueous polymerizations (emulsion, miniemulsion), which facilitates reactor selection for industrial scale-up [75, 76]. Table 1 lists the various styrenic monomers that have been polymerized by NMP.

With the wide variety of styrenics polymerized by NMP with TEMPO in bulk, statistical copolymerizations followed of styrenics with various acrylamides, acrylates and methacrylates (the latter at concentrations < 50 mol%; I am defining methacrylic-rich copolymerizations with > 90 mol% in the feed as essentially methacrylates by NMP). All of these copolymerization pairs could be well-controlled up to certain compositions and some pairs included the following: styrene with acrylonitrile [77-81], methyl methacrylate [33, 82], ethyl methacrylate [83], butyl methacrylate [83,84], methyl acrylate [83], ethyl acrylate [83], butyl acrylate [83], 2-hydroxyethyl acrylate [83], vinyl acetate [83], N-acryloyl morpholine [82], 2-ethoxyethyl acrylate [82], isobornyl acrylate [82], vinylferrocene [85], N-vinylcarbazole [86,87], N-cyclohexylmaleimide [88], p-chlorostyrene [89] and vinyl pyrrolidone [90].

2.2. Solution styrenic polymerizations

For solid monomers that are often water-soluble such as styrenic sulfonic acid, sodium salt (SSNa) and others that are often extensively conjugated (eg. for electronic applications),

polymerizations were required to be conducted in homogeneous solution. For example, SSNa was polymerized in water/glycol mixtures by TEMPO [33-35] and subsequently later in purely aqueous solutions by water-soluble TEMPO-derived nitroxides [91], TIPNO-related nitroxides [92] and with BlocBuilder-MA/SG1 systems [93]. Tran et al. polymerized lithium 4-styrenesulfonyl(trifluoromethane sulfonyl) imide (SSTFSILi), as a polyelectrolyte material for lithium batteries, in 10 wt% aqueous solution at 90 °C [37]. When N-vinylcarbazole was copolymerized with styrene, dioxane solvent was required to continue the polymerization [86, 87], while the styrenic 9-(4-vinylbenzyl)-9H-carbazole (VBK) had to be dissolved in dimethylformamide (DMF) to be homo- and copolymerized [94,95]. Vinyl triphenylamine (vTPA) was polymerized in anisole using a TIPNO-based initiator [96]. Liquid crystalline monomers such as 2,5 bis[4-butenylbenzoyl]oxystyrene (BBOS) were polymerized in solution using TEMPO [97-110]. Zhao and co-workers polymerized styrenics attached with oligoethylene glycol (OEG) groups using TIPNO in anisole at 120 °C, yielding polymers with tunable cloud points in water by using different substituent lengths on the (OEG) units [111-113] (Figure 3).
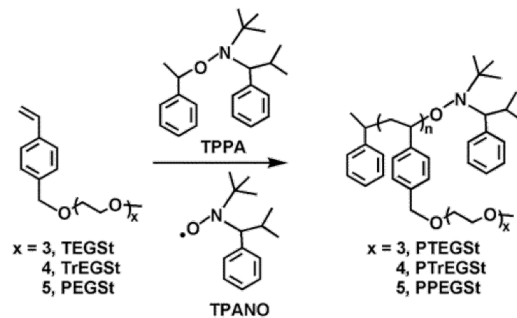
Figure 3: Styrenic monomers with water-soluble oligoethylene glycol chains in the *para* position controlled with TIPNO type of alkoxyamine (TPPA) and some additional free nitroxide (TPANO) to make thermoresponsive polymers. Reprinted with permission from Zhao, B.; Li, D.; Hua, F.; Green, D. R. Synthesis of thermosensitive water-soluble polystyrenics with pendant methoxyoligo(ethylene glycol) groups by nitroxide-mediated radical polymerization. *Macromolecules* **2005**, *38*, 9509-9517 [111]. Copyright 2005 American Chemical Society.

2.3. NMP of styrenics in dispersed aqueous systems

The review of NMP in dispersed aqueous systems (suspension, emulsion, miniemulsion) has been described extensively elsewhere [114-118]. The NMP of styrenics with TEMPO was first reported in the mid-1990s [119], as the salient features of NMP and other RDRP processes presented the possibility of making block copolymers and other more sophisticated microstructures in dispersed aqueous media, something that could not have been done with classical living polymerizations. The initial TEMPO mediated systems involved the formation of seed latex with styrene, water, surfactant, water-soluble initiator and other additives followed by addition of more styrene, unimolecular alkoxyamine initiator BST and TEMPO to form the

emulsion with polymerization at 125 ºC. The resulting latex was stable, although particle size distributions were not given, the molecular weight distributions were somewhat broad (Đ = 1.39-1.54) and no evidence of chain end fidelity was provided (linear increase of monomer conversion with temperature) [119]. The authors stressed lower temperatures would be advantageous to minimize irreversible termination. Later studies focused on miniemulsion systems, with a water-soluble initiator such as potassium persulfate and TEMPO/BST as controller resulted in poly(styrene) latexes that were colloidally stable, possessed narrower molecular weight distributions (Đ = 1.15-1.25 up to conversions of 85%) and a linear increase in molecular weight with conversion [120-122]. In some of these cases, a hydrophobe to stabilize the monomer droplets was added (usually hexadecane but it can also be a hydrophobic macroalkoxyamine initiator/controller). The reasons why a miniemulsion system was more successful were not clear at that time but this was ascribed to compartmentalization effects, although not completely elucidated until later [123-126]. Figure 4 illustrates the particle size evolution for miniemulsion polymerization. In a miniemulsion system, the droplets are finely dispersed as sub-50 nm particles in water with intense agitation. The loci for polymerization are thus the monomer droplets. This is contrast to conventional emulsion polymerization, where droplets are much bigger and act as reservoirs to the polymerization loci, which are micelles of monomer stabilized with surfactant.   With miniemulsion polymerization, surfactants were also reported to form *in situ* at the interface between the particles and surrounding aqueous phase, resulting in particles as small as 20 nm, using much less surfactant than required for typical microemulsions [127].
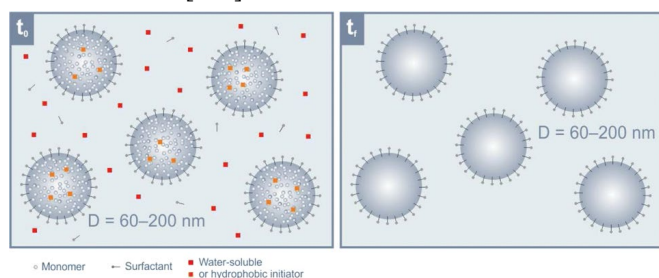
Figure 4: Miniemulsion protocol that is often used with NMP. The loci are formed by intense agitation initially to form very small droplets of monomer (D < 200 nm). The polymerization then is initiated inside each of the monomer droplets with the particle size remaining virtually unchanged throughout the polymerization. Reprinted with permission from Ref. [118], Royal Society of Chemistry.

Successive emulsion/miniemulsion systems with TIPNO and SG1 systems followed, using similar formulations to that of the TEMPO systems with varying conditions. With BlocBuilder-MA, however, the alkoxyamine can be readily solubilized by neutralization of the carboxylic acid group with base. Thus, surfactants were bypassed by making a water-soluble macroinitiator based on species such as SSNa, methacrylic acid and oligo(ethylene glycol) methacrylates [128-131]. Various systems have been developed along this

principle. Emulsion styrene-rich systems have come back to the forefront as the extra equipment required for miniemulsions has served as somewhat of a deterrent [132]. Further variants to the aqueous dispersed systems have been reported such as dispersion polymerization [133-135], and suspension polymerization [136-138].
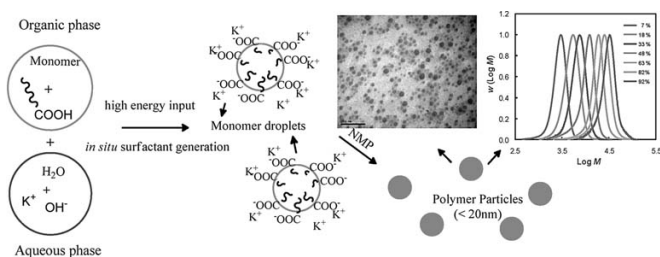
Figure 5: Mini-emulsion protocol described by Guo and Zetterlund using *in situ* surfactant produced at the interface by reaction with organic acid/base and ultrasonication to produce polymer nanoparticles < 20 nm in size. Reprinted with permission from Ref. [127], Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

3.   ACRYLATE POLYMERIZATIONS
3.1. Bulk acrylate polymerizations

Acrylate homopolymerizations via TEMPO suffered expectedly from the comparatively high equilibrium constant K and propagation rate constant k_p and build-up of the excess nitroxide at the temperatures required to activate TEMPO, resulting in ill-defined polymers. Reducing agents were used to mitigate this issue but the best results for acrylate homopolymerizations arrived with the advent of the second-generation nitroxides such as TIPNO and SG1, which permitted lower temperatures and thus lower k_p and in turn better polymerization control. The first polymerizations reported using these latter two alkoxyamines employed n-butyl acrylate (n-BA) as the model acrylate in bulk conditions [10,11]. With the proliferation of these new alkoxyamines, many acrylates were homopolymerized. Bulk acrylate homopolymerizations using TIPNO initiators include n-BA [12, 139-144], *tert*-butyl acrylate [145-148], methyl acrylate [149], and succinimidyl acrylate [12]. In bulk with SG1-type initiators, acrylates polymerized included n-BA [150-152], hydroxyethyl acrylate [153, 154], 2-dimethylaminoethyl acrylate [155, 156], oligoethylene glycol acrylate [157], *tert*-butyl acrylate [158-160], hydroxypropyl acrylate [161, 162], 3-hydroxypropyltriethoxysilane [108], 2-(N-carbazolyl) ethyl acrylate [163, 164], (4´-ethylbiphenyl-4-(4-propenoyloxybutyloxy)benzoate) [165], 2,2-tetrahydroperfluorodecyl acrylate [166], 2-(acryloyloxy)ethylbenzyldimethylammonium chloride [93], trimethylsilyl propargyl acrylate [109], and N-acryloxysuccinimide [167]. Sulfinyl nitroxides were also used to polymerize ethyl and butyl acrylate below 90 ºC [168] while PROXYL radicals were used to polymerize n-BA at low temperature [169].

3.2. Solution acrylate polymerizations

Acrylate polymerizations in solution were often adopted to control viscosity (and hence increase potentially the final conversion/yield) or state of monomer (eg. solid) or to control an exotherm. For example, acrylic acid (AA) was polymerized in 30 wt% dioxane solution to control the exotherm as bulk polymerizations became rapidly viscous, accelerating loss of control [170-172]. Other NMPs using TIPNO in homogeneous organic solution were done due to the solid nature of the bulky monomers that are typically targeted for organic electron materials [107, 109, 110, 173-184].

An aspect of acrylate radical polymerizations is the possibility of branching via chain transfer to polymer with reactions such as back-biting [185]. Ahmad et al reported that chain transfer to polymer for n-butyl acrylate was reduced in RDRP versus conventional radical polymerization due to the lower concentration of short-chain radicals in RDRP, which is a source for branching [186]. Konkolewicz et al. later modeled the effect of branching in ATRP versus conventional radical polymerization and found that only in certain acrylate systems will branching be lower than in conventional radical polymerization [187]. This was attributed to competing equilibria between deactivation/activation and exchange and only when tertiary radicals are de-activated rapidly will there be a significant decrease in branching.

3.3. Acrylate polymerizations in dispersed aqueous media

Acrylate polymerizations in emulsion/miniemulsion became more significant with the development of TIPNO and SG1 in the late 1990s, although TEMPO-based miniemulsion polymerizations were reported for n-BA [188, 189]. Most of the NMP of acrylates in dispersed aqueous media involved the use of n-BA. The details about the mechanisms for the different types of polymerization (eg. miniemulsion, emulsion and microemulsion) are left to other excellent reviews [114-118, 190-191]. The simplicity of using the miniemulsion polymerization, in terms of the particle nucleation step, led to its wider adoption by many groups working on NMP in dispersed media in the early 2000s. With the SG1-type of initiators, initial efforts focused on using hydrophobic MONAMS and thus the nitroxide and monomer would be in the oil-phase initially, stabilized by the addition of a surfactant [151]. Linear increases in molecular weight and Đ remained < 1.4 up to 80% conversion at 115 °C. The latex was colloidally stable but the particle size distribution varied considerably. Later, MONAMS was replaced with BlocBuilder-MA, which can be converted to a water-soluble form with addition of base, followed by a two-step process consisting of a poly(n-BA) seed latex and then followed by surfactant to prevent large droplets from forming. The poly(n-BA) seed was polymerized and then styrene was added to form a diblock with high conversion, (80%) with M_n = 61 kg mol^{-1}, M_w/M_n = 1.4 and solids content with 26 wt% and 330 nm sized latex particles [151]. Progress from this point involved derivatives of BlocBuilder-MA, such as DIAMA-Na, a difunctional sodium salt formed by reaction of BlocBuilder-

MA with tri(ethylene glycol) diacrylate [129]. The increased charge density led to smaller particles with narrower particle size distributions [129] (Figure 6).
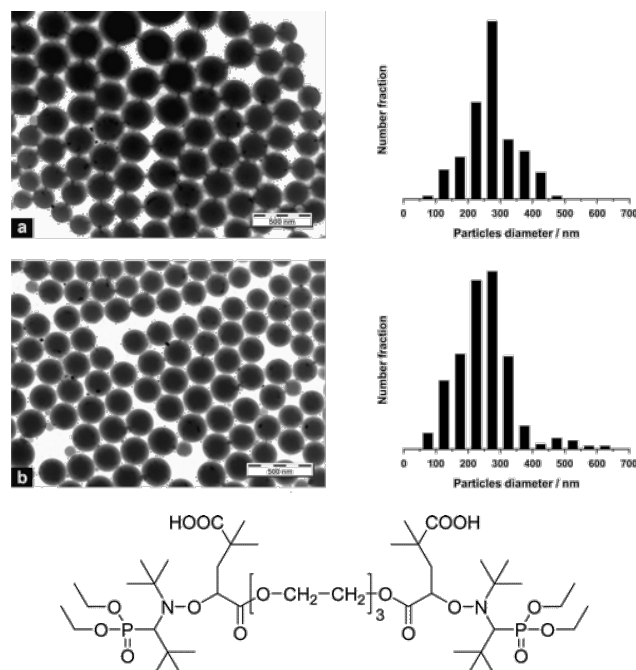
Figure 6: Schematic showing the effect of DIAMA-Na (DIAMA shown below the micrographs a) and b). The particle sizes were much smaller and the distribution narrower when DIAMA-Na was used, which was attributed to its increased charge density. Reprinted from Ref. [129] Nicolas, J.; Charleux, B.; Guerret, O.; Magnet, S. Nitroxide-mediated controlled free-radical emulsion polymerization using a difunctional water-soluble alkoxyamine initiator. Toward the control of particle size, particle size distribution, and the synthesis of triblock copolymers. *Macromolecules* **2005**, *38*, 9963–9973. Copyright 2005 American Chemical Society.

Later studies focused on making macroalkoxyamines that would serve as both initiator and surfactant. Delaittre et al used SG1-capped poly(sodium acrylate) as such macroinitiators for styrene *ab initio* polymerization [130, 131]. The same researchers continued this theme, using a neutralized poly(AA)-SG1 macroinitiator, to initiate the polymerization of diethylacrylamide (DEAAm) in water at 112-120 °C in a pressurized reactor, resulting in a pseudo-polymerization induced self-assembly (PISA) as the LCST of the poly(DEAAm) in water is much lower (~ 32 °C) than the polymerization temperature [192].

After cooling below the LCST, free diblock copolymer chains resulted in a homogeneous solution. Additional tailoring to make thermosensitive nanogels with multiple functionality was done by adding styrene during the dispersion polymerization and applying N,N-methylene bisacrylamide cross-linkers [193, 194] (Figure 7 and 8). A suspension-like polymerization using neutralized SG1-terminated poly(AA) was also used to polymerize a carbazole functional acrylate dispersed in toluene [160].
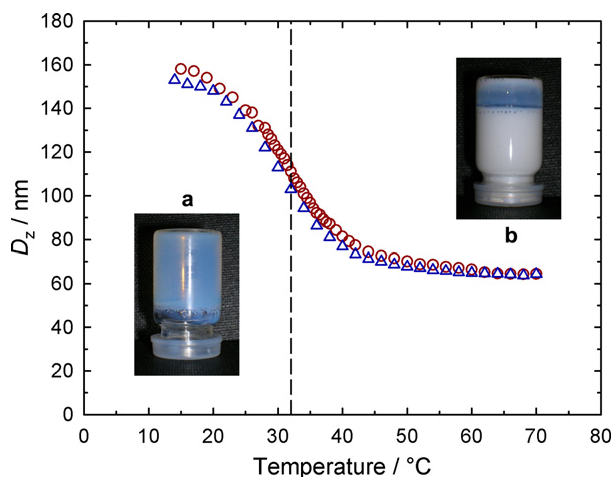
Figure 7: Polymerization-induced self-assembly (PISA) for for thermosensitive poly(NaA)-b-poly(DEAAm) nanogels. Reprinted with permission from Ref. [193], Copyright © 2007, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.
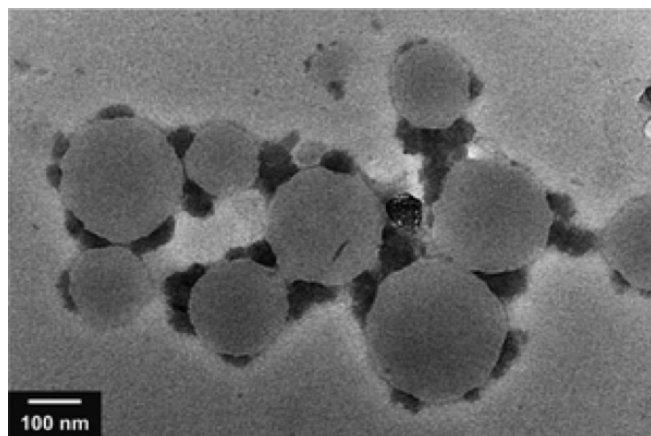
Figure 8: Cross-linked poly(NaA)-b-poly(DEAAm) nanogels from dried solutions at pH = 11 and 80 ºC. Reproduced from Ref. [194] with permission from The Royal Society of Chemistry.

A variation on the approaches described above was applied to a poly(2-ethylhexyl acrylate)-SG1 macroinitiator in toluene to initiate polymerizations of AA, 4VP and MAA [195]. Further, poly(dodecyl acrylate)-SG1 was used to initiate polymerizations of AA, MAA, 4-vinylbenzoic acid, MMA, 4VP, 2-aminostyrene and tert-butyl acrylate. These attempts were done to produce ionizable cores with AA or MAA by delayed addition of MMA. Another example using acrylate polymerizations with SG1-type initiators involved dispersion polymerization in super-critical CO_2 [196].

4. METHACRYLATE POLYMERIZATIONS
4.1. Bulk methacrylate polymerizations
Methacrylic ester polymerizations by NMP were reviewed comprehensively recently [197, 198]. Obviously, the most

common methacrylic ester, MMA, has considerable importance for resins used in a wide range of products, and thus the ability to make a wider variety of products by control of microstructure and molecular weight distribution is highly appealing. The earliest attempts at using TEMPO for MMA polymerizations resulted in failure, with the inability to control the polymerization. Efforts were directed as to why the polymerization failed; with the mechanism elucidated that β-hydrogen abstraction was occurring, resulting in terminal alkene groups [197, 198]. However, copolymerizations with styrenics up to limited compositions were successful. Even with the introduction of TIPNO and SG1 initiators, methacrylate homopolymerizations were not controlled and many kinetic studies followed to identify the reasons for their failure. This eventually led to the controlling co-monomer approach derived by Charleux and co-workers [13]. This approach examined the copolymerization kinetics as a function of the two key parameters controlling NMP: the average propagation rate $\langle k_p \rangle$ and average equilibrium constant between the dormant and active chains $\langle K \rangle$. Essentially, adding a small fraction of co-monomer (2.2-8.8 mol% of styrene in the initial composition) with a low K, such as styrene, dramatically reduced the $\langle k_p \rangle \langle K \rangle$, and led to controlled polymerizations (Figure 9).
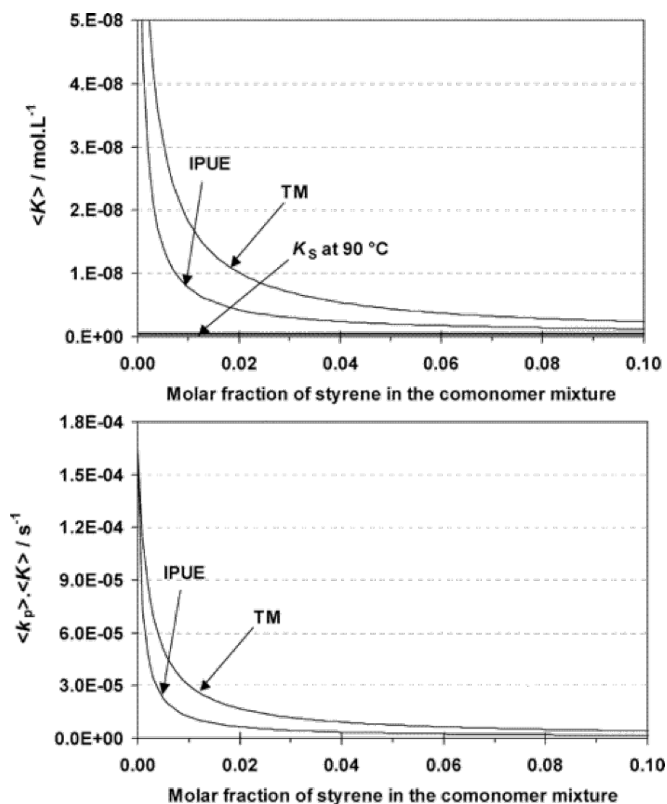
Figure 9: The product of the propagation rate constant and equilibrium constant for the MMA/S copolymerization (Reprinted from Charleux, B.; Nicolas, J.; Guerret, O. Theoretical expression of the average activation−deactivation equilibrium constant in controlled/living free-radical copolymerization operating via reversible termination. Application to a strongly improved control in nitroxide-mediated polymerization of methyl methacrylate. *Macromolecules* **2005**, *38*, 5485-5492 [13]. Copyright 2005 American Chemical Society.

This approach using styrene as a controller was thus adopted for other methacrylates besides MMA, such as methacrylic acid (MAA) [199], ethyl methacrylate (EMA) [200], n-butyl methacrylate (BMA) [200], *tert*-butyl methacrylate (t-BMA) [201], benzyl methacrylate (BzMA) [202], glycidyl methacrylate (GMA) [203], dimethylaminoethyl methacrylate (DMAEMA) [204], diethylaminoethyl methacrylate (DEAEMA) [205], 5-methacryloyloxy-2,6-norboranecarbolactone (NLAM) [206], glucose-functionalized methacryloyl galactose (AcGalEMA) [207], and 2-hydroxyethyl methacrylate (HEMA) [208].

Although styrene is often used as the controlling comonomer, many others have been used such as 2-vinylpyridine (2VP) for DMAEMA [209], SSNa for MAA [210], and pentafluorostyrene (PFS) for GMA [211], DMAEMA [212], oligo(ethylene glycol) methacrylate (OEGMA) [212], NLAM [206], (3-hydroxyadamantyl methacrylate (HAMA) [213, 214], 3-methyladamantyl methacrylate (MAMA) [213, 214] and γ-butyrolactone methacrylate (GBMLA) [213, 214]. Other controllers have imparted extra properties such as fluorescent VBK for MMA [94, 215], MAA [160], DMAEMA [216], BzMA [217], OEGMA and diethylene glycol methacrylate (DEGMA) [218], morpholinoethyl methacrylate (MEMA) [219] and methacryloyl ethyl pyrrolidone (MAEPR) [220]. 4-vinylphenyl boronic acid (VPBA), which has a glucose sensitive group, has been used to control MEMA [221]. An organic protected SSNa, trioctylammonium p-styrene sulfonate (SSTOA), has controlled GMA-rich copolymerizations [222]. Non-styrenics have also been reported as controllers for methacrylates such as acrylonitrile (AN) [206, 209, 223-225], *N, N* dimethylacrylamide (DMAm) [226] and even isoprene (I) was effective at 20 mol% in the initial composition for MMA mixtures [12]. There is no clear way to predict *a priori* how effective a given controller will be for a particular methacrylate but some experimental and theoretical considerations suggest the reactivity ratio and stability of the end group are important, as well as the individual k_p and K for each of the co-monomers [13, 94, 215]. Table 2 lists methacrylates polymerized using the controlling co-monomer approach.
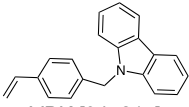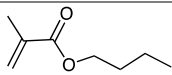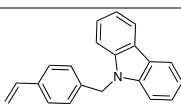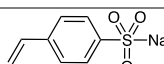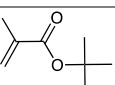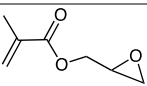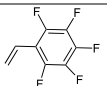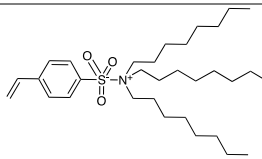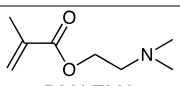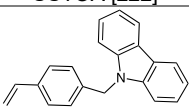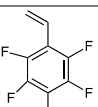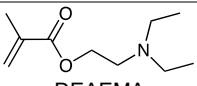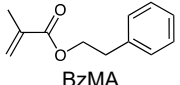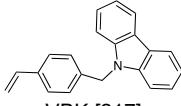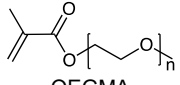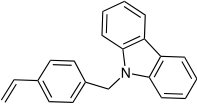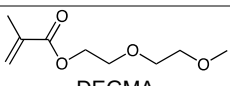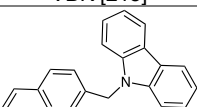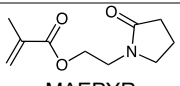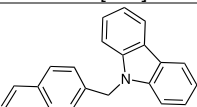
The controlling co-monomer approach is attractive for its simplicity, but the inclusion of the co-monomer can be viewed negatively (its effect on mechanical or physical performance, for example) although in other cases it can be viewed as imparting an additional desirable functionality (polarity, fluorescence). More completely, a nitroxide that could homopolymerize a methacrylate cleanly and then can chain extend with a structurally different monomer would be ideal. Guillaneuf et al. produced DPAIO as a candidate alkoxyamine [17, also see Figure 1]. It was very effective in controlling MMA with low Đ, but upon addition of a second batch of monomer, the polymerization ceased to be controlled after only a few cycles. Grubbs and co-workers developed N-phenyl alkoxyamines with the intention of polymerizing MMA and other methacrylate and then being able to cross-over to a second monomer like styrene to obtain the block copolymer [19, 20]. More recently, a nitroxide was synthesized by a very robust synthetic scheme
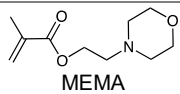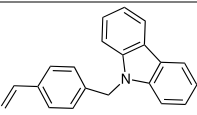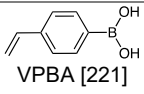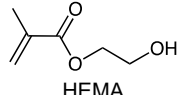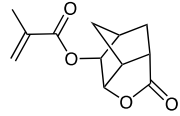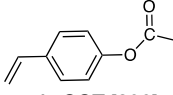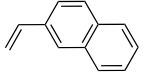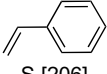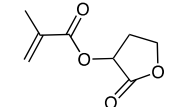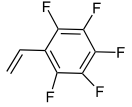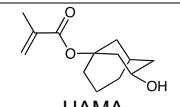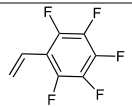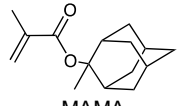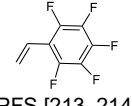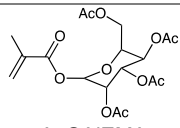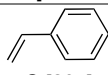
and was able to homopolymerize MMA, which was then used as a macroinitiator for chain extension with styrene [21, 22]. The clean cross-over from a methacrylate to a styrenic is particularly exciting as microphase-separated block copolymers could now be cleanly done with the respective homopolymer segments by NMP. Although distributions were broader at comparable temperatures to those used by the co-monomer approach, slight increases in temperature up to 100 ºC were effective in reducing Đ ~ 1.3-1.4 [22]. Further optimization with this alkoxyamine should be interesting to follow in forthcoming studies. Besides being used in bulk for MMA [21, 22], the alkoxyamine (3-(((2-cyanopropan-2-yl)oxy)(cyclohexyl)amino)-2,2-dimethyl-3-phenylpropanenitrile, see Figure 1 for structure) has been extended to suspension and emulsion polymerization conditions [227, 228].

4.2. Solution methacrylate polymerizations

Initially with TEMPO systems however, MMA/styrene copolymerizations were done in solution as it was thought to reduce the effect of radical build-up and exotherms [229-230]; a similar strategy was adopted Johnson et al with 1-alkylvinazene/styrene copolymerizations in DMF [231]. Polymerizations of methacrylate-rich compositions in ionic liquids for making ion gels were not very successful with TEMPO as the polymerizations had to be done at high temperatures, resulting in low chain end fidelity and broad molecular weight distributions [232, 233]. However, with a BlocBuilder-MA initiator, methacrylate-rich compositions using styrene as a co-monomer were controlled effectively in 1-butyl-3-methyl imidazolium bis (trifluoromethylsulfonyl) imide ($[C_1C_4Im][NTf_2]$) [234]. Most methacrylate polymerizations in organic solvent were done using BlocBuilder-MA initiators, to reduce the effect of exotherms or to solubilize solid monomers, with many of the examples using the co-monomer approach. For those using styrene as the controlling co-monomer in low concentrations, the following polymerizations were done in dioxane solution: MAA [199], EMA [200], BMA [200], GMA [203], t-BMA [201], NLAM [206] and AcGAlEMA [207]. When VBK, a solid, was used as the controlling co-monomer, the following methacrylate-rich copolymerizations were effectively obtained in DMF: OEGMA [218], DMAEMA [216], MEMA [219], MAEPYR [220] while another solid controlling co-monomer, trioctylammonium p-styrene sulfonate (SSTOA) was effective in controlling GMA using NHS-BlocBuilder-MA in toluene at 90 ºC [222].

Table 2: Methacrylates polymerized by nitroxide mediated polymerization using the copolymerization approach.

Methacrylate	Controlling co-monomer [ref]			
MMA	S [13, 200]	AN [223]	VBK [94, 215]	Am [226]
EMA	S [200]			
BMA	S [200]			
MAA	S [199]	VBK [260]	SSNa [210]	
t-BMA	S [201]			
GMA	S [203]	PFS [211]	SSTOA [222]	
DMAEMA	S [204]	2VP [209]	VBK [216]	PFS [212]
DEAEMA	S [205]	AN [225]		
BzMA	S [202]	VBK [217]		
OEGMA	VBK [218]	AN [224]		
DEGMA	VBK [218]			
MAEPYR	VBK [220]			

MEMA	VBK [219] VPBA [221]
HEMA	S [208] AN [208]
NLAM	pAcOST [206] 2-VN [206] S [206] AN [206] PFS [206]
GBLMA	PFS [213, 214]
HAMA	PFS [213, 214]
MAMA	PFS [213, 214]
AcGAlEMA	S [207]

4.3. Methacrylate polymerizations in dispersed aqueous media

Much of the innovation with methacrylates in dispersed aqueous media by NMP has occurred during the past decade, especially with the BlocBuilder-MA type of initiators, particularly using water-soluble macroalkoxyamines as surfactants/initiators. We will focus on this particular mode in this section and forward the reader to more comprehensive reviews of emulsion/miniemulsion polymerizations [115-118, 235, 236]. Various water-soluble macroalkoxyamine initiators, such as MMA/SSNa, MAA/S, were used to initiate polymerizations [237-239]. From such macroinitiators, nano-objects were formed via the PISA process [240-242]. PISA has drawn considerable attention, as it is a convenient method to apply a one-pot synthesis to produce nano-shaped objects in water with shapes such as rods, spheres and cylinders. Examples of the PISA process are shown in Figure 10. Here, pH was used to modulate the shape from sphere to vesicles and to more elongated structures, and interestingly, despite the use of a non-ionic poly(OEGMA-*ran*-S) macroinitiator that possessed only a single terminal acidic group, it was significant enough to cause a salting out effect due to the increase in ionic strength. This change affected the lower critical solution temperature (LCST) and thus the particle morphology [242].

5. ACRYLAMIDE POLYMERIZATIONS

Secondary acrylamides such as *N, N* dimethyl acrylamide (DMAm) [243], *N, N* diethyl acrylamide (DEEAm) [244], N-acryloyl morpholine (4AM) [245-246], acryloyl piperidine (4AP) [247] and N-(isobutoxylmethyl)acrylamide [248] have been polymerized easily by NMP with TIPNO and SG1 type of initiators. Acrylamide has been polymerized in water by NMP, with a linear relationship of molecular weight versus conversion [249, 250]. However, chain extensions were not conducted. More challenging has been primary acrylamides such as n-isopropyl acrylamide (NIPAM) [251-255] and methoxy propylacrylamide (MAPAM) [256]. Both monomers and related alkoxyalkyl acrylamides are of interest as the polymers exhibit LCST behavior in water. TIPNO mediated polymerization of NIPAM was reported by Binder and co-workers [255], yet by BlocBuilder-MA or with NHS-BlocBuilder-MA, poor control was exhibited [256]. Some have postulated chain transfer to solvent was prevalent in such systems, but it is not conclusive at this point [257-261].

A related family of monomers that have not been widely explored by NMP are methacrylamides. Zwitterionic carboxybetaine methacrylamide monomers were polymerized from surfaces using immobilized SG1-based initiators [262]. Good control of the molecular weight distribution was observed. Another methacrylamide with a protected amino group, N-(t-BOC-aminopropyl) methacrylamide (tBOC-MAm), was

terpolymerized with MMA and S or simply copolymerized with S and indicated poor incorporation of tBOC-MAm into the copolymer relative to the initial composition and loss of chain end fidelity [263]. Maleimides have been however copolymerized via BlocBuilder-MA in a sequence controlled radical polymerization that placed primary amino groups at selective locations along the chain via the appropriate choice of donor/acceptor monomers [264].
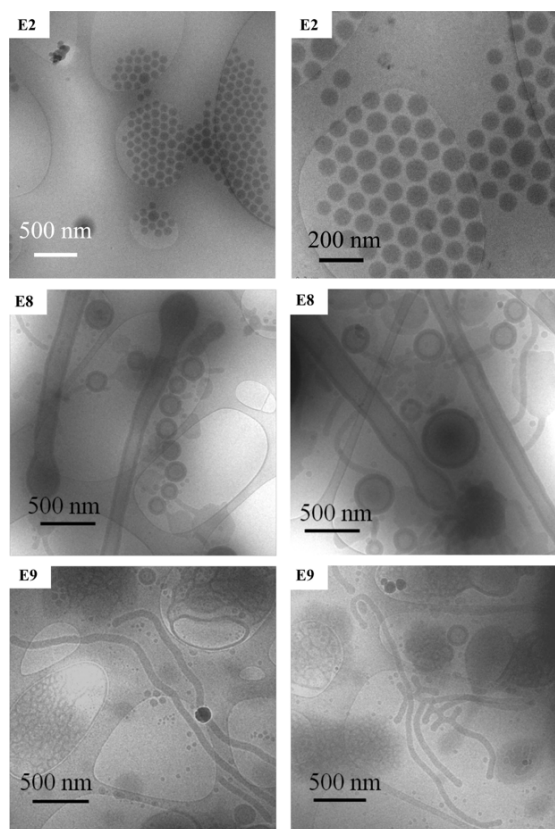
Figure 10: Polymerization-induced self-assembly (PISA) process using nitroxide-mediated polymerization as observed with cryo-TEM. The water soluble macroinitiator initiated the hydrophobic segment at different pHs: 4.0 (micrograph E2), 6.0 (micrograph E8) and 6.7 (micrograph E9). Reprinted from Qiao, X.G.; Lansalot, M.; Bourgeat-Lami, E.; Charleux, B. Nitroxide-mediated polymerization-induced self-assembly of poly (poly (ethylene oxide) methyl ether methacrylate-co-styrene)-b-poly (n-butyl methacrylate-co-styrene) amphiphilic block copolymers. *Macromolecules* **2013**, *46*, 4285-4295 [242]. Copyright 2013 American Chemical Society.

6. DIENE POLYMERIZATIONS

Dienes such as isoprene and butadiene could be polymerized by NMP with TEMPO [265-268] and then TIPNO [12, 269-278] type of initiators and later with SG1 type of initiators [279-287]. In comparison to other RDRP techniques, isoprene polymerizations were hampered by complexation with the metallic ligand used in ATRP [288] but there have been many recent reports of isoprene polymerizations by RAFT [289-293]. TEMPO controlled diene polymerizations were characterized by relatively

broad molecular weight distributions (Đ = 1.36-1.53) [266, 267]. TIPNO polymerizations had greatly reduced Đs [12] and TIPNO related initiators such as 2,2-dimethyl-3-(1-(4-(methoxycarbonyl)phenyl)ethoxy)-4-(4(methoxycarbonyl) phenyl)-3-azapentane indicated that isoprene could be controlled up to 60% conversion with linear $\overline{M_n}$ versus conversion and Đ ~ 1.2 at 125 °C for 72 h [269]. Furthermore, poly(styrene) macroinitiator ($\overline{M_n}$ = 4.2 kg mol^{-1}, Đ = 1.14, made to only 8% conversion) with good chain end fidelity was used to cleanly initiate isoprene, resulting in diblock copolymers ($\overline{M_n}$ = 10.1 kg mol^{-1}, Đ = 1.14) after 46.5 h at 125 °C. The same group also used a TIPNO functionalized PEO ($\overline{M_n}$ = 5.2 kg mol^{-1}, Đ = 1.1 to initiate isoprene polymerization in xylene solution in a pressurized vessel at 125 °C [270]. Conversions were kept modest (< 40%) to avoid side reactions and most PEO-PI block copolymers were monomodal with retention of low Đ ~ 1.1 and $\overline{M_n}$= 10-17 kg mol^{-1}, although reaction times were relatively long (16-34 h). A similar strategy was employed by the same group to study self-assembly of PEO-poly(ethylene oxide-*ran*-butylene oxide)-PI (PEO-b-P(EO-*ran*-BO)-PI) where the PEO-b-P(EO-*ran*-BO) contained the TIPNO terminal group [271]. A 2.3 kg mol^{-1} PEO-b-P(EO-*ran*-BO)-TIPNO initiated a series of triblock copolymers with controlled molecular weights (1.4 ≤ $\overline{M_n}$ ≤ 5.1 kg mol^{-1}) and low Đ (1.05 ≤ Đ ≤ 1.20). From these TIPNO-based initiators, iterations on the structure of the initiator permitted the design of more complex microstructures and resulting properties. For example, a TIPNO group was placed at the end of a rod-like segment, and subsequently initiated a batch of isoprene to make rod-coil block copolymers [272]. Grubbs et al. elegantly synthesized one-step alkoxyamines from commercially available precursors and subsequently initiated isoprene with modest degrees of polymerization. The low conversion polymerizations (16-25%) resulted in PIs with $\overline{M_n}$ = 5.0-9.4 kg mol^{-1} and Đ = 1.26-1.28 [273]. Braslau and co-workers employed a bis-nitroxide in order to form ABA triblock copolymers [274]. PIs with $\overline{M_n}$ = 1.5 kg mol^{-1} and Đ = 1.10 and 10.1 kg mol^{-1} and Đ = 1.18, respectively, initiated DMAm outer blocks, resulting in triblocks with total $\overline{M_n}$ = 7.0 kg mol^{-1} and Đ = 1.23 and 40.0 kg mol^{-1} and Đ = 1.26, respectively. Related to bifunctional initiation, α, ω telechelic poly(butadiene) (PB) was made from ROMP with TIPNO chain ends to initiate styrene and isoprene end-segments [275]. The resulting tri and pentablocks exhibited a disperse PB center block with much more monodisperse end-blocks. Subsequent hydrogenation of the dienes led to poly(ethylene) containing segments and microphase separated structures, despite the broad molecular weight distribution of the center block. Star polymers emanating from 6 and 12-arm TIPNO initiators did not however result in controlled polymerizations with isoprene with broad molecular weight distributions (Đ = 2.96) although the same dendritic initiators worked well with styrene and methyl acrylate [276]. Other dienes besides isoprene and butadiene can be polymerized via TIPNO NMP. For example, Rzayev and co-workers polymerized bicyclic dienes (Figure 11), which

would be further functionalized for thermally cross-linkable block copolymers and soluble poly(acetylene) derivatives [277, 278]. They noticed more rapid polymerizations with the bicyclic monomers compared to isoprene due to the rigid *s-cis* coplanar conformation of the diene.

1   **2**   **3**
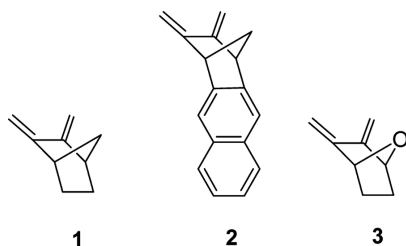
Figure 11: Bicyclic dienes polymerized by NMP with TIPNO type of initiators. Reprinted from Ref. [277] Luo, K.; Rzayev, J. Living radical polymerization of bicyclic dienes: Synthesis of thermally cross-linkable block copolymers. *Macromolecules* **2009**, *42*, 9268-9274. Copyright 2009 American Chemical Society.

BlocBuilder-MA-mediated polymerization of dienes was first reported by Matsuoka et al. who polymerized tBA with SG1 and then used the resulting PtBA-SG1 as a macroinitiator for isoprene polymerization [279]. After deprotection, an amphiphilic PAA-PI diblock copolymer resulted and the resulting material was examined for its brush properties at water surfaces. No detailed kinetic investigations were undertaken however. Hadziiaonnou and co-workers synthesized a poly(3-hexylthiophene)-based (P3HT) macroinitiator with a terminal alkene that was coupled to BlocBuilder-MA via intermolecular radical addition [280]. The resulting initiator was used to polymerize isoprene in toluene at 115 °C and was very slow compared to the same polymerization with styrene, methyl acrylate and 4-vinylpyridine. The narrow molecular weight distribution was retained but conversion of isoprene only reached 17% after 24 h (P3HT-b-PI where $M_{n\ P3HT}$ = 6.0 kg mol^{-1} and $M_{n\ PI}$ = 7.7 kg mol^{-1}, Đ = 1.3). Following these initial studies, detailed kinetic investigations were pursued by Harrisson *et al* [281, 282] and Bagryanskaya *et al* [283]. In the former case, NMP of isoprene with several SG1-type of initiators revealed controlled polymerizations at 115 °C. Further, post-functionalize of the α and ω ends could lead to different functionalities on each end. The polymerizations tended to be slower compared to styrenic or acrylic monomers at similar temperatures. Interestingly, alkoxyamines with acidic initiating groups were consumed more slowly compared to ester or cyanomethyl-functionalized SG1; this was suggested to be due to intramolecular hydrogen bonding that was supported later by the findings of Bagryanskaya *et al* [283]. More diene polymerizations have followed, based on the success of the BlocBuilder-MA mediated polymerizations. Anionic exchange membranes were made from crosslinkable isoprene containing precursors initiated by SG1 [284] and phase inversion membranes [285] based on amphiphilic diblock terpolymers were synthesized using the nitroxide developed by Studer and coworkers [286]. Recently, an

interesting extension to the diene family by NMP was reported for myrcene [287], which is obtained from renewable resources [293]. Myrcene (Myr) is convenient compared to other dienes since it is not as volatile and thus non-pressurized vessels can be used; this makes it particularly amenable to emulsion polymerizations, as has been recently described for conventional radical polymerizations [294]. Myr was homopolymerized in bulk at 120 °C with low Đ (1.1-1.4) with a succinimidyl ester-functional BlocBuider (NHS-BlocBuilder-MA). The resulting poly(Myr) cleanly initiated styrene and styrene/Myr mixtures to afford the requisite block copolymers [287]. Further, myrcene was statistically copolymerized with styrene, with reactivity ratios of r_S = 0.25-0.34 ± 0.19 for styrene and r_{Myr} = 1.88-2.19 for Myr and the statistical P(Myr-*stat*-S) copolymers exhibited a range of T_gs from -77 to 30 °C, depending on Myr molar fraction [287].

Another terpene related monomer to Myr that has been (co)polymerized by RDRP is D-limonene [295-297]. Ren and Dubé described the copolymerization of n-butyl acrylate with D-limonene by BlocBuilder-MA with mixed results [298]. Incorporation of D-limonene was poor, polymerization rates were decreased with higher initial composition of D-limonene and although the molecular weight distributions remained relatively narrow with Đ = 1.2-2.3, sharp increases in $\overline{M_n}$ at higher conversions, indicating a loss of control. The failure of NMP to control the copolymerizations was found to be due to a competition between the activation-deactivation equilibrium of the alkoxyamine and the degradative chain transfer due to the allylic hydrogen in D-limonene [298, 299].

7. VINYL ESTER POLYMERIZATIONS

Monomers for radical polymerization processes are generally grouped as being more activated monomers (MAMs) (eg. styrenics, (meth)acrylates, (meth)acrylamides) or less activated monomers (LAMs) (eg. vinyl esters such as vinyl acetate (VAc), vinyl amides such as n-vinylpyrrolidone (NVP) and vinyl carbazole [29]. This difference in these classifications is due to the stability of the radical. Most of the successful vinyl ester polymerizations by RDRP processes have been due to RAFT and the combination of unlike monomers in block copolymers has been accomplished by a change in mechanism by appropriate end group modification [300-303] or by switchable RAFT agents [304-307]. With respect to NMP, some reports suggested vinyl chloride (VC) with TEMPO was homopolymerized at 70 °C and block copolymers formed but no details about the activity of the chain ends was provided [308]. Other early attempts using TEMPO involved typically copolymerizations of styrene with VAc and VPyr [309]. Interestingly, Yoshida reported a photo radical polymerization using a TEMPO based initiator for VAc that exhibited controlled behavior (linear M_n versus conversion) although the molecular weight distributions broadened with time with Đ

approaching 2 [310]. Later, more detailed investigations into VC polymerization by NMP with BlocBuilder-MA type of initiators was done, indicating that such polymerizations were feasible at low temperatures (30-42 °C) in dichloromethane (DCM) or dimethyl sulfoxide (DMSO) with sufficient chain end fidelity (91% SG1 functionality on the chain ends) to produce block copolymers with MMA, and MMA/S mixtures [311]. Some interesting developments have occurred recently via NMP with alternating copolymerizations involving LAMs. Studer's group copolymerized, in an alternating fashion, hexafluoroisopropyl acrylate (MAM) with 7-octenyl vinyl ether (LAM) relatively low LAM compositions [312]. Relatively high molecular weights (15.0-34.9 kg mol^{-1}) and narrow molecular weight distributions (Đ = 1.2-1.5) were observed as well as evidence of alternating monomer sequences. More recently with SG1-based initiating systems, using the cue from the VC polymerizations with BlocBuilder-MA, Ameduri and coworkers showed that VAc could be copolymerized in an alternating fashion with tert-butyl trifluoromethacrylate (MAF-TBE), even though neither monomer was homopolymerizable (MAF-esters cannot be polymerized by radical polymerization; they are most often polymerized anionically) with NMP at the given conditions (40 °C in DMSO) [313]. Linear evolution of molecular weight with conversion was observed up to $\overline{M_n}$ = 17 100 g mol^{-1} and low Đ = 1.33) (Figure 12).
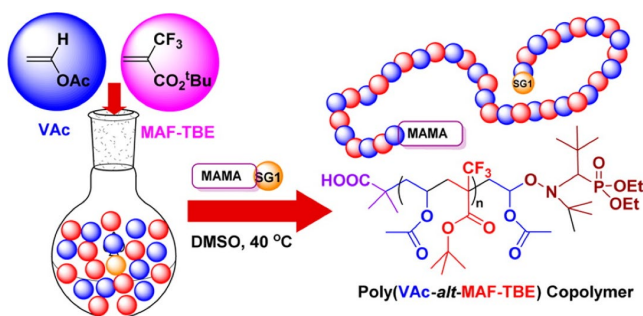
Figure 12: Alternating copolymerization of vinyl acetate (VAc) with *tert*-butyl trifluoromethacrylate (MAF-TBE) using BlocBuilder-MA.   Reprinted from Ref. [313] Banerjee, S.; Domenichelli, I.; Ameduri, B. Nitroxide-mediated alternating copolymerization of vinyl acetate with tert-butyl-2-trifluoromethacrylate using an SG1-based alkoxyamine. *ACS Macro. Lett.* **2016**, *5*, 1232-1236. Copyright 2016, American Chemical Society.

The control of sequence by this donor/acceptor complex with 1:1 monomer sequences was confirmed; however, attempts to chain-extend the poly(VAc-*alt*-MAF-TBE)-SG1 with either VAc (at 40 and 65 °C) or S (at 120 °C) failed to form block copolymers. The authors suggested the C-ON bond was not sufficiently labile to permit addition of another new monomer (however addition of an alternating pair was not attempted). Still, the resulting amorphous copolymers could be further functionalized or grafted from the ester sites along the backbone. As is, the copolymers have potential as coatings (particularly due to the low viscosity inherent with narrow molecular weight distribution polymers dissolved in solvents) and as membrane materials.

8. CYCLIC KETENE ACETALS

The polymerization of cyclic ketene acetals (CKAs) generated much interest in the 1980s as it used radical ring-opening polymerization to make polyesters [314-316]. This feature allows degradability of vinyl-based polymers, which is attractive for biomedical materials where controlled degradation is desirable. Thus, incorporation of monomers with cyclic ketene functionality has enabled polymers with ester linkages along the backbone produced by conventional and reversible deactivation radical polymerization processes. This methodology was not common via NMP until very recently with the use of SG1-based initiators. Initial reports focused on using CKAs such as 2-methylene-1,3-dioxepane (MDO) [317] and 5,6-benzo-2-methylene-1,3-dioxepane (BMDO) [318, 319] as co-monomers for methacrylic esters with controlling comonomers such as acrylonitrile [319] (Figure 13).

Adding MDO and BMDO into formulations resulted in almost complete inhibition of the polymerization. Further studies about the nature of the CKA led to the development of the more effective 2-methylene-4-phenyl-1,3-dioxolane (MPDL, also abbreviated as MPDO), which was shown to be an effective controlling co-monomer for methacrylates [320-322]. It was postulated that the styrenic structure of the MPDL facilitated cleavage of the MPDL-SG1 macroalkoxyamine, thereby permitting cross-propagation. Improvements of the synthetic yield of MPDL were recently reported and this should lead to further studies, particularly with the non-cytotoxicity reported on various cell lines from the various MPDL-containing copolymers [322]. The combination of controlled vinyl polymerization with a controller that is degradable suggests exciting future applications in biomedical materials developed from SG1-based initiators.
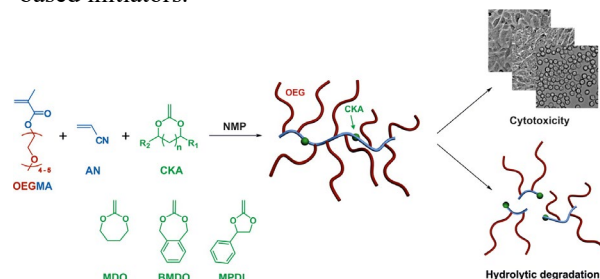
Figure 13: Cylic ketene acetals (CKAs) commonly used in NMP.   Reprinted from Ref. [322], copyright © 2007, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

9. AZLACTONES

Various monomer systems that have been shown to be capable of being polymerized by NMP have not been utilized to their advantage. Azlactones are particularly interesting for biological applications, as their ring structure permits reactions with many different nucleophiles (eg. primary amines, thiols and hydroxyl groups) and the related possibility of click chemistry [323]. Grubbs and co-workers have shown its promise with TIPNO-type of initiators for the one of the most common

azlactones such as 2-vinyl-4,4-dimethyl-5-oxazolone (VDMO) as well as the styrenic azlactone 2-(4'-vinyl)phenyl-4,4-dimethyl-5-oxazolone (VPDMO), and 2-isopropenyl-4,4-dimethyl-5-oxazolone (IDMO) [324] (Figure 14). VDMO was readily homopolymerized and was statistically copolymerized with a number of monomers such as S, MA, nBA, 2-methyl-methoxy acrylate, t-BA, MMA (over a wide composition range from 10-75% MMA), DMAm, VPyr and acrylonitrile, resulting in copolymers with low Đ = 1.04-1.39 at polymerization temperatures = 123 °C [324].

VDMO   VPDMO   IDMO
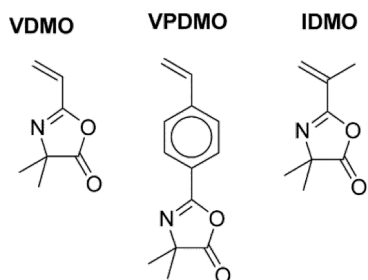
Figure 14: Various azlactone monomers – VDMO has been polymerized by NMP and copolymerized with several co-monomers. Reprinted from Tully, D. C.; Roberts, M. J.; Geierstanger, B. H.; Grubbs, R. B. Synthesis of reactive poly(vinyl oxazolones) via nitroxide-mediated "living" free radical polymerization. *Macromolecules* **2003**, *36*, 4302-4308 [324]. Copyright 2003 American Chemical Society.

VPDMO polymerized much like a styrenic monomer by NMP while IDMO could not be homopolymerized and resembled an MMA homopolymerization with TIPNO (uncontrolled and high Đ > 1.5), which is not surprising. However, when just a relatively small concentration ~ 30 mol% of co-monomer such as styrene was added, the control of molecular weight was enhanced dramatically. Block copolymers with styrene from VDMO macroinitiator were attaininable while poly(VDMO-*b*-nBA) could only be accessed using a poly(BA) macronitiator, suggesting that VDMO in a terminal alkoxyamine was not an efficient initiator for acrylates. It should be noted however that recently azlactone functional SG1-basedalkoxyamines have been prepared and used as initiators for NMP of other monomers such as styrene, nBA and MMA/AN [325].

10. 1-ALKENES

1-alkenes such as 1-hexene and 1-octene and norbornenes were shown to be copolymerizable with acrylates using TIPNO [326, 327]. Rates were sluggish as the initial concentration of the alkene was increased. For 1-hexene copolymerizations with methyl acrylate ([1-hexene]:[MA] = 1:2 to 3:4 mol:mol) to over 20 mol% in the initial monomer mixture, yields ranged from 30 to 15%, respectively, after 15 h polymerization at 120 °C. The maximum incorporation of the 1-hexene was 6.8-9.7 mol% but the molecular weight distributions remained narrow

(1.08-1.13) [326]. The authors suggested that termination reactions with the alkenes were more prominent. In the same study, the authors copolymerized various norbornene derivatives as these were suggested to have effective etch resistance in photolithographic applications. 50/50 molar compositions of methyl acrylate with the norbornene provided copolymers with up to 30 mol% norbornene incorporation and modest molecular weights (4800-7500 g mol^{-1}; which is generally good for photolithographic applications) but still relatively narrow, unimodal molecular weight distributions (1.17-1.51). Again, yields of copolymers were typically low ~ 30 wt% after long polymerization times of 15 h at 120 °C. Table 3 shows the various 1-alkenes copolymerized with acrylates using TIPNO along with their relevant characteristics.

Table 3: 1-Alkenes copolymerized with methyl acrylate using TIPNO type of alkoxyamine initiators.

Monomer	Norbornene incorp. (mol %)	M_n^b	M_w/M_n^b	Yield (g)
(0.04 mol, 3.77 g)	18.0	7,000	1.17	1.9
(0.04 mol, 4.32 g)	16.1	7,300	1.51	2.1
OCOCH₃ (0.04 mol, 6.08 g)	25.5	4,800	1.43	2.3
n-hexyl (0.04 mol, 6.10 g)	24.9	6,900	1.26	2.2
COOtBu (0.04 mol, 7.76 g)	28.1	7,500	1.33	3.0

Reprinted from Ref. [326] Gu, B.; Liu, S.; Leber, J. D.; Sen. A. Nitroxide-mediated copolymerization of methyl acrylate with 1-alkenes and norbornenes. *Macromolecules* **2004**, *37*, 5142-5144. Copyright 2004 American Chemical Society.

CONCLUSION

The various families of monomers that NMP can be used to attain functional polymers have occurred in step with developments in the alkoxyamine initiators. The earliest TEMPO systems were dominated by control of styrenic monomers and many commercially relevant monomers such as (meth)acrylates and (meth)acrylamides were only polymerizable when copolymerized with styrenics with high content of the latter. As the TIPNO and SG1-based initiators were developed in the late 1990s-early 2000s, the monomers that could be polymerized by NMP were expanded to

acrylates and acrylamides and methacrylates, with some modification (eg. the co-monomer approach). In situ NMP has controlled homopolymerization of methacrylates and newer alkoxyamines such as DPAIO, TITNO, phenyl alkoxamines and others have indicated some control over methacrylates, with newer initiators being very promising. Vinyl esters such as VC have been homopolymerized effectively recently, and some like VAc can be copolymerized in an alternating fashion with the appropriate choice of co-monomer. Vinyl esters remain somewhat elusive by NMP. Further, other monomer families such as vinyl azlactones and cyclic ketene acetals represent an interesting potential area for NMP that has not been fully explored: biological materials, particularly since they contain no metallic residues.

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REFERENCES

[1] Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. Narrow molecular weight resins by a free-radical polymerization process. *Macromolecules* **1993**, *26*, 2987-2988.

[2] Veregin, R. P. N.; Georges, M. K.; Kazmaier, P. M.; Hamer, G. K. Free radical polymerizations for narrow polydispersity resins: electron spin resonance studies of the kinetics and mechanism. *Macromolecules* **1993,** *26*, 5316-5320.

[3] Hawker, C. J. Molecular weight control by a "living" free-radical polymerization process. *J. Am. Chem. Soc.* **1994**, *116*, 11185-11186.

[4] Hawker C. J.; Hedrick, J. L. Accurate control of chain ends by a novel "living" free-radical polymerization process. *Macromolecules* **1995**, *28*, 2993-2995.

[5] Fukuda, T.; Terauchi, T.; Goto, A. Ohno, K.; Tsujii, Y.; Miyamoto, T.; Yamada, B. Mechanisms and kinetics of nitroxide-controlled free radical polymerization. *Macromolecules* **1996**, *29*, 6393-6398.

[6] Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. Polymerization of methyl methacrylate with the carbon tetrachloride/dichlorotris-(triphenylphosphine)ruthenium(II)/methyl aluminum bis(2,6-di-tert-butylphenoxide) initiating system: possibility of living radical polymerization. *Macromolecules* **1995**, *28*, 1721-1723.

[7] Wang, J. S.; Matyjaszewski, K. Controlled living radical polymerization–atom-transfer radical polymerization in the presence of transition-metal complexes. *J. Am. Chem. Soc.* **1995**, *117*, 5614-5615.

[8] Chiefari, J.; Chong, Y, K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. Living free-radical polymerization by reversible addition-fragmentation chain transfer: the RAFT process. *Macromolecules* **1998,** *31*, 5559-5561.

[9] Destarac, M.; Charmot, D.; Franck, X.; Zard, S. Z. Dithiocarbamates as universal reversible addition-fragmentation chain transfer agents. *Macromol. Rapid. Comm.* **2000**, *21*, 1035-1039.

[10] Benoit, D.; Grimaldi, S.; Robin, S.; Finet, J.-P.; Tordo, P.; Gnanou. Y. Kinetics and mechanism of controlled free-radical polymerization of styrene and n-butyl acrylate in the presence of an acyclic β-phosphonylated nitroxide. *J. Am Chem. Soc.* **2000**, *122*, 5929-5939.

[11] Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. Development of a universal alkoxyamine for "living" free radical polymerizations. *J. Am. Chem. Soc.* **1999**, *121*, 3904-3920.

[12] Benoit, D.; Harth, E.; Fox, P.; Waymouth, R. M.; Hawker, C. J. Accurate structural control and block formation in the living polymerization of 1,3-dienes by nitroxide-mediated procedures. *Macromolecules* **2000**, *33*, 363-370.

[13] Charleux, B.; Nicolas, J.; Guerret, O. Theoretical expression of the average activation−deactivation equilibrium constant in controlled/living free-radical copolymerization operating via reversible termination. Application to a strongly improved control in nitroxide-mediated polymerization of methyl methacrylate. *Macromolecules* **2005**, *38*, 5485-5492.

[14] Sciannamea, V.; Jérôme, R.; Detrembleur, C. In-situ nitroxide-mediated radical polymerization (NMP) processes: their understanding and optimization. *Chem. Rev.*, **2008**, 108, 1104-1126.

[15] Detrembleur, C.; Claes, M.; Jérôme, R. Controlled radical polymerization of alkyl methacrylates in the presence of NO/NO₂ mixtures. *Advances in controlled/living radical polymerization.* **2003**, 496-518.

[16] Detrembleur, C.; Jérôme, C.; De Winter, J.; Gerbaux, P.; Clément, J.L.; Guillaneuf, Y.; Gigmes, D. Nitroxide mediated polymerization of methacrylates at moderate temperature. *Polym. Chem.* **2014**, *5*, 335-340.

[17] Guillaneuf, Y.; Gigmes, D.; Marque, S. R. A.; Astolfi, P.; Greci, L.; Tordo, P.; Bertin, D. First effective nitroxide-mediated polymerization of methyl methacrylate. *Macromolecules* **2007**, *40*, 3108-3114.

[18] Payne, K. A.; Nesvadba, P; Debling, J.; Cunningham, M. F.; Hutchinson, R. A. Nitroxide-mediated polymerization at elevated temperatures. *ACS Macro Lett.* **2015**, *4*, 280-283.

[19] Greene, A. C.; Grubbs, R. B. Synthesis and evaluation of N-phenylalkoxyamines for nitroxide-mediated polymerization. *Macromolecules* **2009**, *42*, 4388-4390.

[20] Greene, A. C.; Grubbs, R. B. Nitroxide-mediated polymerization of methyl methacrylate and styrene with new alkoxyamines from 4-nitrophenyl 2-methylpropionat-2-yl radicals. *Macromolecules* **2010**, *43*, 10320-10325.

[21] Ballard, N.; Aguirre, M.; Simula, A.; Aguirre, A.; Leiza, J. R.; Asua, J. M.; van Es, S. A new class of alkoxyamines for efficient controlled homopolymerization of methacrylates. *ACS Macro. Lett.* **2016**, *5*, 1019-1022.

[22] Ballard, N; Simula, A.; Aguirre, M.; Leiza, J. R.; van Es, S.; Asua, J. M. Synthesis of poly(methyl methacrylate) and block copolymers by semi-batch nitroxide mediated polymerization. *Polym. Chem.* **2016**, *7*, 6964-6972.

[23] Hawker, C. J. "Living" free radical polymerization: a unique technique for the preparation of controlled macromolecular architectures. *Acc. Chem. Res.,* **1997**, *30*, 373-382.

[24] Hawker, C. J.; Bosman, A. W; Harth, E. New polymer synthesis by nitroxide mediated living radical polymerizations. *Chem. Rev.* **2001**, 101, 3661-3688.

[25] Studer, A.; Schulte, T. Nitroxide-mediated radical processes. *Chem. Rec.* **2005**, 5, 27-35.

[26] Bertin, D.; Gigmes, Marque, S. R.; Tordo, P. Kinetic subtleties of nitroxide mediated polymerization. *Chem. Soc. Rev.,* **2011**, *40*, 2189-2198.

[27] Solomon, D. H. Genesis of the CSIRO polymer group and the discovery and significance of nitroxide-mediated living radical polymerization *J. Polym. Sci. A Polym. Chem.,* **2005**, *43,* 5748-5764.

[28] Grubbs, R. B. Nitroxide-mediated radical polymerizations: limitations and versatility. *Polym. Rev.* **2011**, *51*, 104-137.

[29] Nicolas, J.; Guillaneuf, Y.; Lefay, C.; Bertin, D.; Gigmes, D.; Charleux, B. Nitroxide-mediated polymerization. *Prog. Poly. Sci.* **2013**, *38*, 63-235.

[30] Gigmes, D. (ed.) *Nitroxide-Mediated Polymerization: From Fundamentals to Applications in Materials Science.* Royal Society of Chemistry: Polymer Chemistry Series. RSC, London, **2016**.

[31] D'hooge D. R.; Van Steenberge, P. H. M.; Reyniers, M. F.; Marin, G. B. *Prog. Polym. Sci.* **2016**, *58*, 59-89.

[32] Barclay, G. G.; Hawker, C. J.; H. Ito, H.; Orellana, A.; Malenfant, P. R. L.; Sinta, R. F. The "Living" Free Radical Synthesis of Poly (4-hydroxystyrene): Physical Properties and Dissolution Behavior. *Macromolecules* **1998**, *31*, 1024-1031.

[33] Devonport, W.; Michalak, L.; Malmstrom, E.; Mate, M.; Kurdi, B. Hawker, C. J.; Barclay, G. G.; Sinta. R. Living" free-radical polymerizations in the absence of initiators: controlled autopolymerization. *Macromolecules* **1997**, *30*, 1929-1934.

[34]   Keoshkerian, B.; Georges, M. K.; Boils-Boissier, D. Living free radical in aqueous systems. *Macromolecules* **1995**, *28*, 6381-6382.

[35]   Bouix, M.; Gouzi, J.; Charleux, B.; Vairon, J.-P.; Guinot, P. Synthesis of amphiphilic polyelectrolyte block copolymers using "living" radical polymerization. Application as stabilizers in emulsion polymerization. *Macromol. Rapid Commun.* **1998**, *19*, 209-213.

[36]   Nowakowska, M.; Zapotoczny, S.; Karewicz, A. Synthesis of poly(sodium styrenesulfonate-block-vinylnaphthalene) by nitroxide-mediated free radical polymerization. *Macromolecules* **2000**, *33*, 7345–7348.

[37]   Phan, T. N. T.; Ferrand, A.; Ho, M. T.; Liénafa, L.; Rollet, M.; Maria, S.; Bouchet, R.; Gigmes, D. *Polym. Chem.* **2016**, *7,* 6901-6910.

[38]   Gao, L.-C.; Fan, X. H.; Shen, Z.-H.; Chen, X.; Zhou, Q.-F. Jacketed polymers: controlled synthesis of mesogen-jacketed polymers and block copolymers. *J. Polym. Sci. A: Polym. Chem.* **2009**, 47, 319-330.

[39]   Moroni, M.; Hilberer, A.; Hadziionannou, G. Synthesis of a functional polymer with pendent luminescent pheylvinylene units through nitroxide-mediated free radical polymerization. *Macromol. Rapid. Comm.* **1996**, 17, 693-702.

[40]   Knoop, C. A.; Studer, A. Hydroxy- and silyloxy-substituted TEMPO derivatives for the living free-radical polymerization of styrene and n-butyl acrylate: synthesis, kinetics, and mechanistic studies. *J. Am. Chem. Soc.* **2003**, 125, 16327-16333.

[41]   Studer, A.; Harms, K.; Knoop, C.; Müller, C.; Schulte, T. New sterically hindered nitroxides for the living free radical polymerization: X-ray structure of an α-H-bearing nitroxide. *Macromolecules* **2004**, 37, 27-34.Jing, Y.; Mardyukov, A.; Bergander, K.; Damiliuc, C. G.; Studer, A. Synthesis of bulky nitroxides, characterization, and their application in controlled radical polymerization. *Macromolecules* **2014**, 47, 3595-3602.

[42]   Maric, M. Chapter 4: NMP under homogeneous conditions in bulk, organic solvents and aqueous systems. In *Nitroxide-Mediated Polymerization: From Fundamentals to Applications in Materials Science.* Gigmes, D. (ed.) Royal Society of Chemistry: Polymer Chemistry Series. RSC, London, **2016**, Chapter 4, 153-198.

[43]   Lokaj, J.; Holler, P. Nitroxide-mediated homopolymerization and copolymerization of 2-vinylpyridine with styrene. *J. Appl. Polym. Sci.* **2001**, *80*, 2024-2030.

[44]   Chalari, I.; Pispas, S.; Hadjichristidis, N. Controlled free-radical polymerization of 2-vinylpyridine in the presence of nitroxides. *J. Polym. Sci. A: Polym. Chem.* **2001**, *39*, 2889-2895.

[45]   Wohlrab, S.; Kuckling, D. Multisensitive polymers based on 2-vinylpyridine and N-isopropylacrylamide. *J. Polym. Sci. A: Polym. Chem.* **2001**, *39*, 3797-3804.

[46]   Ding, X. Z.; Fischer, A.; Brembilla, A.; Lochon, P. Behavior of 3-vinylpyridine in nitroxide-mediated radical polymerization: The influence of nitroxide concentration, solvent, and temperature. *J. Polym. Sci. A: Polym. Chem.* **2000**, *38*, 3067-3073.

[47]   Bohrisch, J.; Wendler, U.; Jaeger, W. Controlled radical polymerization of 4-vinylpyridine. *Macromol. Rapid Commun.* **1997**, *18*, 975-982.

[48]   Fischer, A.; Brembilla, A.; P. Lochon, P. Nitroxide-mediated radical polymerization of 4-vinylpyridine: study of the pseudo-living character of the reaction and influence of temperature and nitroxide concentration. *Macromolecules* **1999**, *32*, 6069-6072.

[49]   Baumann, M.; Schmidt-Naake, G. Controlled radical copolymerization of styrene and 4-vinylpyridine. *Macromol. Chem. Phys.* **2000**, *201*, 2751-2755.

[50]   Lacroix-Desmazes, P.; Delair, T.; Pichot, C.; Boutevin B. Synthesis of poly(chloromethylstyrene-b-styrene) block copolymers by controlled free-radical polymerization. *J. Polym. Sci. A: Polym. Chem.* **2000**, *38*, 3845-3854.

[51]   Ohno, K.; Ejaz, M.; Fukuda, T.; Miyamoto, T.; Shimizu, T. Nitroxide-controlled free radical polymerization of p-tert-butoxystyrene. Kinetics and applications. *Macromol. Chem. Phys.* **1998**, *199*, 291-297.

[52]   Yoshida, E.; Tchiguchi, Y. Synthesis of a random block copolymer comprising poly (styrene-ran-p-methoxystyrene) and poly (styrene-ran-t-butoxystyrene) by 2, 2, 6, 6-tetramethylpiperidine-1-oxyl-mediated living radical polymerization. *Polym. J.* **1999**, *31*, 429-434.

[53]   Dang, J. D.; Virdo, J. D.; Lessard, B. H.; Bultz, E.; Paton, A. S.; Bender T. P. A Boron Subphthalocyanine Polymer: Poly(4-methylstyrene)-co-poly(phenoxy boron subphthalocyanine). *Macromolecules* **2012**, *45*, 7791-7798.

[54]   Otsuka, H.; Sato, T.; Endo, T. Synthesis and controlled polymerization of p-(1-methylcyclohexyloxy) styrene and quick-response deblocking ability of the obtained polymer. *Macromol. Rapid Commun.* **2000**, *21*, 48-52.

[55]   Gray, M. K.; Zhou, H.; Nguyen, S. T.; Torkelson, J. M. Synthesis and glass transition behavior of high molecular weight styrene/4-acetoxystyene and styrene/4-hydroxystyrene gradient copolymers made via nitroxide-mediated controlled radical polymerization. *Macromolecules* **2004**, *37*, 5586-5595.

[56]   Pragliola, S.; Ober, C. K.; Mather, P. T.; Jeon, H. G. Mesogen-jacketed liquid crystalline polymers via stable free radical polymerization. *Macromol. Chem. Phys.* **1999**, *200*, 2338-2344.

[57]   Gray, M. K.; Kinsinger, M. I.; Torkelson, J. M. Diffusion-controlled polymer-polymer reactions in bulk: Novel strategy for model experiments and reactive compatibilization using polymers synthesized via controlled radical polymerization. *Macromolecules* **2002**, *35*, 8261-8264.

[58]   Yoshida, E. Synthesis of a well-defined polybromostyrene by living radical polymerization with a nitroxyl radical. *J. Polym. Sci. A: Polym. Chem.* **1996**, *34*, 2937-2943.

[59]   Sessions, L. B.; Cohen, B. R.; Grubbs, R. B. Alkyne-functional polymers through Sonogashira coupling to poly (4-bromostyrene). *Macromolecules* **2007**, *40*, 1926-1933.

[60]   Daimon, K. Kazmaier, P. M.; Georges, M. K.; Hamer, G. K.; Veregin, R. P. N. Substituent effect on styrene polymerization in the nitroxide mediated stable free radical polymerization. *ACS Polymer Preprints* **1997**, *38*, 653-654.

[61]   Sessions, L. B.; Milnea, L. A.; Ericson, K. D.; Glueck, D. S.; Grubbs, R. B. Alkyne-functional homopolymers and block copolymers through nitroxide-mediated free radical polymerization of 4-(phenylethynyl)styrene. *Macromolecules* **2003**, *38*, 2116-2121.

[62]   Boutevin, B.; Hervaud, Y.; Boulahna, A.; El. Asri, M. Free-radical polymerization of dimethyl vinylbenzylphosphonate controlled by tempo. *Macromolecules* **2002**, *35*, 6511-6516.

[63]   Coote, M. L. Davis, T. P. Propagation kinetics of para-substituted styrenes: A test of the applicability of the Hammett relationship to free-radical polymerization. *Macromolecules* **1999**, *32*, 4290-4298.

[64]   Roa-Luna, M.; Diaz-Barber, M. P.; Vivaldo-Lima, E.; Lona, L. M. F.; McManus, N. T.; Penlidis, A. *J. Macromol. Sci. A: Pure Appl. Chem.* **2007**, *44*, 193-203.

[65]   D'hooge, D.; Reyniers, M.-F..; Marin, G. B. *Macromol. React. Eng.* **2013**, *7*, 362-379.

[66]   Gonçalves, M. A. D.; Pinto, V. D.; Dias, R. C. S. Rui P. Fn. N. Costa, M.; Aguiar, L. G.; Giudici, R. *Macromol. React. Eng.* **2013**, *7*, 155-175.

[67]   Aguiar, L. G.; Gonçalves, M. A. D.; Pinto, V. D.; Dias, R. C. S.; Costa, M. R. P. F. N.; Guidici, R. *Macromol. React. Eng.* **2014**, *8*, 295-313.

[68]   Fierens, S. K.; D'hooge, D. R.; Van Steenberge, P. H. M.; Reyniers, M.-F.; Marin, G. B. *Chem. Eng. J.* **2015**, *278*, 407-420.

[69]   Masan, E.; Li, X.; Zhu, S. *Prog. Polym. Sci.* **2016**, *45*, 71-101.

[70]   Lessard, B. H.; Maric, M. One-step poly(styrene-alt-maleic anhydride)-block-poly(styrene) copolymers with highly alternating styrene/maleic anhydride sequences are possible by nitroxide-mediated polymerization. *Macromolecules* **2010**, *43*, 879-885.

[71]   Benoit, D.; Hawker, C. J.; Huang, E. E.; Lin, Z.; Russell, T. P. One-step formation of functionalized block copolymers. *Macromolecules* **2000**, *33*, 1505-1507.

[72]   Zamfir, M.; Lutz, J.-F. Ultra-precise insertion of functional monomers in chain-growth polymerizations. *Nature Comm.* **2012**, *3*, 1138.

[73]   Fierens, S. K.; Telitel, S.; Van Steenberge, P. H. M.; Reyniers, M.-F.; Marin, G. B.; Lutz, J.-F.; D'hooge, D. R. Model-based design to push the boundaries of sequence control. *Macromolecules* **2016**, *49*, 9336-9344.

[74]   Matyjaszewski, K. Architecturally complex polymers with controlled heterogeneity. *Science* **2011***, 333*(6046), 1104-1105.

[75]   Farcet, C.; Lansalot, M.; Charleux, B.; Pirri, R.; Vairon, J. P. Mechanistic aspects of nitroxide-mediated controlled radical polymerization of styrene in miniemulsion, using a water-soluble radical initiator. *Macromolecules* **2000**, *33*, 8559-8570.

[76] Simms, R. W.; Hoidas, M. D.; Cunningham, M. F. Nitroxide-mediated styrene surfactant-free emulsion polymerization. *Macromolecules* **2008**, *41*, 1076-1079.

[77] Fukuda, T.; Terauchi, T.; Goto, A.; Ohno, K.; Tsujii, Y.; Miyamoto, T.; Kobatake, S.; Yamada, B. Mechanisms and kinetics of nitroxide-controlled free radical polymerization. *Macromolecules* **1996**, *29*, 6393-6398.

[78] Baumann, M.; Schmidt-Naake, G. Acetic anhydride–accelerating agent for nitroxide-controlled free-radical copolymerization of styrene and acrylonitrile. *Macromol. Chem. Phys.* **2001**, *202*, 2727-2731.

[79] Baumann, M.; Roland, A. I.; Schmidt-Naake, G.; Fischer, H. Synthesis of polystyrene-block-poly (styrene-co-acrylonitrile) block copolymers and thermoanalytical studies of nitroxide-terminated poly (styrene-co-acrylonitrile) copolymers. *Macromol. Mater. Eng.* **2000**, *280/281*, 1-6.

[80] Baumert, M.; R. Mulhaupt, R. Carboxy-terminated homo-and copolymers of styrene using dicarboxylic acid-functional azo initiator and 2, 2, 6, 6-tetramethyl-1-piperidyloxyl (TEMPO). *Macromol. Rapid Commun.* **1997**, *18*, 787-794.

[81] Lokaj, J.; Brozova, L.; Holler, P.; Pientka, Z. Synthesis and gas permeability of block copolymers composed of poly (styrene-co-acrylonitrile) and polystyrene blocks. *Collect. Czech. Chem. Commun.* **2002**, *67*, 267-278.

[82] Appelt, M.; Schmidt-Naake, G. Stable free-radical copolymerization of styrene with acrylates using OH-TEMPO. *Macromol. Chem. Phys.* **2004**, *205*, 637-644.

[83] Jianying, H.; Jiayan, C.; Jiaming, Z.; Yihong, C.; D. Lizong, D.; Yousi, Z. Some monomer reactivity ratios of styrene and (meth) acrylates in the presence of TEMPO. *J. Appl. Polym. Sci.* **2006**, *100*, 3531-3535.

[84] Cuervo-Rodriguez, R.; Fernandez-Monreal, C.; Madruga, E. L. Kinetic study of the stable free-radical copolymerization of styrene with butyl methacrylate. *J. Polym. Sci. A: Polym. Chem.* **2002**, *40*, 2750-2758.

[85] Baumert, M.; Fröhlich, J.; Stieger, M.; Frey, H.; Mülhaupt, R.; Plenio, H. Styrene-vinylferrocene random and block copolymers by TEMPO-mediated radical polymerization *Macromol. Rapid Commun.* **1999**, *20*, 203-209.

[86] Baethge, H.; Butz, S.; Schmidt-Naake, G. "Living" free radical copolymerization of styrene and N-vinylcarbazole. *Macromol. Rapid Comm.* **1997**, *18*, 911-916.

[87] Baethge, H.; S. Butz, S.; Han, C.-H.; Schmidt-Naake, G. Rate enhancement of the N-oxyl-controlled free radical copolymerization of styrene with N-vinylcarbazole. *Angew. Makromol. Chem.* **1999**, *267*, 52-56.

[88] Schmidt-Naake, G.; Butz, S. Living free radical donor-acceptor copolymerization of styrene and N-cyclohexylmaleimide and the synthesis of poly [styrene-co-(N-cyclohexylmaleimide)]/ polystyrene block copolymers. *Macromol. Rapid Comm.* **1996**, *17*, 661-665.

[89] Butz, S.; Hillermann, J.; Schmidt-Naake, G.; Kressler, J.; R. Thomann, R.; Heck, B.; Stühn, B. Synthesis and microphase separation of diblock copolymers of styrene and p-chlorostyrene prepared by using N-oxyl capped macroinitiators. *Acta Polym.* **1998**, *49*, 693-699.

[90] Arsalani, N.; Fattahi, H.; Entezami, A. A. Synthesis of amphiphilic diblock and random copolymers of styrene and N-vinylpyrrolidone using nitroxide-mediated living free radical polymerization. *Iranian Polym. J.* **2006**, *15*, 997.

[91] Mannan, M. A.; Fukuda, K.; Miura, Y. Living radical polymerization of sodium 4-styrenesulfonate mediated by new water-soluble nitroxides. *Polym. J.* **2007**, *39*, 500-501.

[92] Nicolay, R.; Marx, L.; He, P. Synthesis and evaluation of a functional, water-and organo-soluble nitroxide for "living" free radical polymerization. *Macromolecules*, **2007**, *40*, 6067-6075.

[93] Phan, T. N. T.; Bertin, D. Synthesis of water-soluble homopolymers and block copolymers in homogeneous aqueous solution via nitroxide-mediated polymerization. *Macromolecules* **2008**, *41*, 1886-1895.

[94] Lessard, B.; Ling, E. J. Y.; Morin, M. S. T.; Maric, M. Nitroxide-mediated radical copolymerization of methyl methacrylate controlled with a minimal amount of 9-(4-vinylbenzyl)-9H-carbazole. *J. Polym. Sci. A: Polym. Chem.* **2011**, *49*, 1033-1045.

[95] Zhang, W.; Yan, Y.; Zhou, N.; Cheng, Z.; Zhu, J.; Xia, C.; Zhu, X. Controlled synthesis and fluorescent properties of poly(9-(4-vinylbenzyl)-9H-carbazole) via nitroxide-mediated living free-radical polymerization. *Eur. Polym. J.* **2008**, *44*, 3300-3305.

[96] Lindner, S. M.; Thelakkat, M. Nanostructures of n-type organic semiconductor in a p-type matrix via self-assembly of block copolymers. *Macromolecules* **2004**, *37*, 8832-8835.

[97] Li, C. Y.; Tenneti, K. K.; Zhang, D.; Zhang, H.; Wan, X.; Chen, E.-Q.; Zhou, Q.-F.; Carlos, A.-O.; Igos, S.; Hsiao, B. S. Hierarchical assembly of a series of rod-coil block copolymers: supramolecular LC phase in nanoenviroment. *Macromolecules* **2004**, *37*, 2854-2860.

[98] Gopalan, P.; Y. Zhang, Y.; Li, X.; U. Wiesner, U.; Ober, C. K. Liquid crystalline rod-coil block copolymers by stable free radical polymerization: Synthesis, morphology, and rheology. *Macromolecules* **2003**, *36*, 3357-3364.

[99] Pragliola, S.; Ober, C. K.; Mather, P. T.; Jeon, H. G. Mesogen-jacketed liquid crystalline polymers via stable free radical polymerization. *Macromol. Chem. Phys.* **1999**, *200*, 2338-2344.

[100] Li, C.-F.; Zhang, Q.-K.; Tian, H.-J.; Chai, C.-P.; Gao, L.-C.; Shen, Z.; Fan, X.-H.; Luo, Y.-J. Hierarchically ordered ABA triblock copolymer with large difference in glass transition temperatures of the two blocks. *J. Polym. Sci. A: Polym. Chem.* **2014**, *52*, 1737-1744.

[101] Wan, X.-H.; Tu, H.-L.; Tu, Y.-F.; Zhange, D.; Sun, L.; Zhou, Q.-F.; Dong, Y.-P.; Tang, M. Nitroxide-mediated free radical synthesis of mesogen-jacketed liquid crystal polymers. *Chinese J. Polym. Sci.* **1999**, *17*, 189-192.

[102] Wan, X.-H.; Tu, Y.-F.; Zhang, D.; Zhou, Q.-F. Nitroxide-mediated 'living' free radical synthesis of novel rod–coil diblock copolymers with polystyrene and mesogen-jacketed liquid-crystal polymer segments. *Polym Int.* **2000**, *49*, 243-247.

[103] Tu, Y.-F.; Wan, X.-F.; Zhang, D.; Zhou, Q.-F.; Wu, C. Self-assembled nanostructure of a novel coil-rod diblock copolymer in dilute solution *J. Am. Chem. Soc.* **2000**, *122*, 10201-10205.

[104] Tu, Y. F.; Wan, X.; Zhang, H.; Fan, X.; Chen, X.; Q.-F. Zhou, Q.-F.; Chau, K. Self-assembled nanostructures of rod-coil diblock copolymers with different rod lengths..*Macromolecules* **2003**, *36*, 6565-6569.

[105] Messerschmidt, M.; Millaruelo, M.; Komber, H.; Häussler, L.; Voit, B.; Krause, T.; Yin, M.; W.D. Habicher, W. D. Synthesis of partially protected block copolymers based on 4-hydroxystyrene using NMRP and a sequence of polymer analogous reactions. *Macromolecules* **2008**, *41*, 2821-2831.

[106] Gao, L.-C.; Pan, Q.-W.; Wang, C.; Yi, Y.; Chen, X.-F.; Fan, X.-H.; Zhou, Q.-F. ABA-type liquid crystalline triblock copolymers via nitroxide-mediated radical polymerization: Design, synthesis, and morphologies. *J. Polym. Sci. A: Polym. Chem.* **2007**, *45*, 5949–5956.

[107] Shipman, P. O.; Cui, C.; Lupinska, P.; Lalancette, R. A.; Sheridan, J. B.; Jäkle, F. Nitroxide-mediated controlled free radical polymerization of the chelate monomer 4-styryl-tris (2-pyridyl) borate (StTpyb) and supramolecular assembly via metal complexation. *ACS Macro Lett.* **2013**, *2*, 1056-1060.

[108] Gamys, C.G.; Beyou, E.; Bourgeat-Lami, E.; David, L.; Alcouffe P. Tunable morphologies from bulk self-assemblies of poly(acryloxypropyl triethoxysilane)-b-poly(styrene)-b-poly(acryloxypropyl triethoxysilane) triblock copolymers. *Macromol. Chem. Phys.* **2012**, *213*, 10–18.

[109] Lang, A.S.; Neubig, A.; Sommer, M.; Thelakkat, M. NMRP versus click chemistry for the synthesis of semiconductor polymers carrying pendant perylene bisimides. *Macromolecules* **2010**, *43*, 7001–7010.

[110] Muth, M.-A.; Carrasco-Orozco, M.; Thelakkat, M. Liquid-crystalline perylene diester polymers with tunable charge-carrier mobility. *Adv. Funct. Mater.* **2011**, *21*, 4510–4518.

[111] Zhao, B.; Li, D.; Hua, F.; Green, D. R. Synthesis of thermosensitive water-soluble polystyrenics with pendant methoxyoligo(ethylene glycol) groups by nitroxide-mediated radical polymerization. *Macromolecules* **2005**, *38*, 9509-9517.

[112] Hua, F.; Jiang, X.; Zhao, B. Thermosensitive diblock copolymers with pendant methoxytris(oxyethylene) groups in dilute aqueous solutions. *Macromolecules* **2006**, *39*, 3476-3479.

[113] Jiang, X.; Zhao, B. End group effect on the thermo-sensitive properties of well-defined water-soluble polystyrenics with short pendant oligo (ethylene glycol) groups synthesized by nitroxide-mediated radical polymerization. *J. Polym. Sci. A: Polym. Chem.* **2007**, *45*, 3707-3721.

[114] Cunningham, M.; Lin, M.; Smith, J.-A.; McAuley, K.; Keoshkerian, B.; Georges, M. Nitroxide-mediated living radical polymerization in dispersed systems. *Prog. Colloid Polym. Sci.* **2004**, *124*, 88-93.

[115]   Cunningham, M. F. Controlled/living radical polymerization in aqueous dispersed systems. *Prog. Polym. Sci.* **2008**, *33*, 365-398.

[116]   Cunningham, M. F. Living/controlled radical polymerizaitons in dispersed phase systems. *Prog. Polym. Sci.* **2002**, *27*, 1039-1067.

[117]   Monteiro, M. J.; Cunningham, M. F. Polymer nanoparticles via living radical polymerization in aqueous dispersions: design and applications. *Macromolecules* **2012**, *45*, 4939-4957.

[118]   Delaittre, G. Chapter 5: Nitroxide-mediated polymerization in dispersed media in Nitroxide mediated polymerization: from fundamentals to applications in materials science. Gigmes, D. (ed.) RSC Polymer Chemistry Series, RSC, London. **2016**.

[119]   Bon, S. A. F.; Bosveld, M.; Klumperman, B.; German, A. L. Controlled radical polymerization in emulsion. *Macromolecules* **1997**, *30*, 324-326.

[120]   Keoshkerian, B.; MacLeod, P. J.; Georges, M. K. Block copolymer synthesis by a miniemulsion stable free radical polymerization process. *Macromolecules* **2001**, *34*, 3594-3599.

[121]   MacLeod, P.; Barber, R.; Odell, P. G.; Keoshkerian, B.; Georges, M. K. Stable free radical miniemulsion polymerization. *Macromol. Symp.* **2000**, *155*, 31-38.

[122]   Farcet, C.; Lansalot, M.; Charleux, B.; Pirri, R.; Vairon, J. P. Mechanistic aspects of nitroxide-mediated controlled radical polymerization of styrene in miniemulsion, using a water-soluble radical initiator. *Macromolecules* **2001**, *33*, 8559-8570.

[123]   Maehata, H.; Buragina, C.; Cunningham, M.; Keoshkerian, B. Compartmentalization in TEMPO-mediated styrene miniemulsion polymerization. *Macromolecules* **2007**, *40*, 7126-7131.

[124]   Monteiro, M. Nanoreactors for polymerizations and organic reactions. *Macromolecules* **2010**, *43*, 1159-1168.

[125]   Bentein, L.; D'hooge, D.R.; Reyniers, M.F.; Marin, G.B. Kinetic modeling of miniemulsion nitroxide mediated polymerization of styrene: effect of particle diameter and nitroxide partitioning up to high conversion. *Polymer* **2012**, *53*, 681-693.

[126]   Zetterlund, P. B. Controlled/living radical polymerization in nanoreactors: compartmentalization effects. *Polym. Chem.* **2011**, *2*, 534-549.

[127]   Guo, Y.; Zetterlund, P. B. Synthesis of nanosized (<20 nm) polymer particles by radical polymerization in miniemulsion employing in situ surfactant formation. *Macromol. Rapid Commun.* **2011**, *32*, 1669–1675.

[128]   Charleux, B.; Nicolas, J. Water-soluble SG1-based alkoxyamines: a breakthrough in controlled/living free-radical polymerization in aqueous dispersed media. *Polymer* **2007**, *48*, 5813–5833.

[129]   Nicolas, J.; Charleux, B.; Guerret, O.; Magnet, S. Nitroxide-mediated controlled free-radical emulsion polymerization using a difunctional water-soluble alkoxyamine initiator. Toward the control of particle size, particle size distribution, and the synthesis of triblock copolymers. *Macromolecules* **2005**, *38*, 9963–9973.

[130]   Delaittre, G.; Nicolas, J.; Lefay, C.; Save, M.; Charleux, B. Surfactant free synthesis of amphiphilic diblock copolymer nanoparticles via nitroxide-mediated emulsion polymerization. *Chem. Comm.* **2005**, 614–616.

[131]   Delaittre, G.; Nicolas, J.; Lefay, C.; Save, M.; Charleux, B. Aqueous suspension of amphiphilic diblock copolymer nanoparticles prepared *in situ* from a water-soluble poly(sodium acrylate) alkoxyamine macroinitiator. *Soft Matter* **2006**, *2*, 223–231.

[132]   Nicolas, J.; Charleux, B.; Guerret, O.; Magnet, S. Nitroxide-Mediated Controlled free-radical emulsion polymerization of styrene and n-butyl acrylate with a water-soluble alkoxyamine as initiator. *Angew. Chem. Int. Ed.* **2004**, *43*, 6186-6189.

[133]   Holderle, M.; Baumert, M.; Mulhaupt, R. Comparison of controlled radical styrene polymerizations in bulk and nonaqueous dispersion. *Macromolecules* **1997**, *30,* 3420-3422.

[134]   Gabaston, L. I.; Jackson, R. A.; Armes, S. P. Living free-radical dispersion polymerization of styrene. *Macromolecules* **1998**, *31*, 2883-2888.

[135]   Oh, S.; Kim, K.; Lee, B. H.; Shim, S. E.; Choe, S. TEMPO-mediated dispersion polymerization of styrene in the presence of camphorsulfonic acid. *J. Polym. Sci. A: Polym. Chem.* **2006**, *44*, 62-68.

[136]   Schmidt-Naake, G.; Drache, M.; Taube, C. TEMPO-controlled free radical suspension polymerization. *Angew. Makromol. Chem.* **1999**, *265*, 62-68.

[137]   Taube, C.; Schmidt-Naake, G. TEMPO-controlled radical suspension polymerization of poly (styrene)-block-poly (styrene-co-acrylonitrile) and poly (styrene)-block-poly (styrene-co-butyl methacrylate) *Macromol. Mater. Eng.* **2000**, *279*, 26-33.

[138]   Taube, C.; Schmidt-Naake, G. TEMPO-Controlled Radical Suspension Polymerization in an Oil/Water System in an Autoclave. *Chem. Eng. Technol.* **2001**, *24*, 1013-1017.

[139]   Hill, N. L.; Braslau, R. Synthesis and characterization of a novel bisnitroxide initiator for effecting "outside-in" polymerization. *Macromolecules* **2005**, *38*, 9066-9074.

[140]   Ruehl, J.; Nilsen, A.; Born, S.; P. Thoniyot, P.; L.-P. Xu, L.-P.; Chen, S.; Braslau, R. Nitroxide-mediated polymerization to form symmetrical ABA triblock copolymers from a bidirectional alkoxyamine initiator. *Polymer* **2007**, *48*, 2564-2571.

[141]   Stalmach, U.; de Boer, B.; Post, A. D.; P. F. van Hutten, P. F.; Hadziioannou, G. Synthesis of a Conjugated Macromolecular Initiator for Nitroxide-Mediated Free Radical Polymerization. *Angew. Chem. Int. Ed.* **2001**, *40*, 428-430.

[142]   Lohmeijer, B. G. G.; U. S. Schubert, U. S. The LEGO toolbox: Supramolecular building blocks by nitroxide-mediated controlled radical polymerization. *J. Polym. Sci. A: Polym. Chem.* **2005**, *43*, 6331-6344.

[143]   Marx, L.; Hemery, P. Synthesis and evaluation of a new polar, TIPNO type nitroxide for "living" free radical polymerization. *Polymer* **2009**, *50*, 2752-2761.

[144]   Marx, L.; Eskandani, Z.; P. Hemery, P. Synthesis of versatile TIPNO-based alkoxyamines. *React. Funct. Polym.* **2009**, *69*, 306-318.

[145]   Rodlert, M.; Harth, E.; Rees, I.; Hawker, C. J. End-group fidelity in nitroxide-mediated living free-radical polymerizations. *J. Polym. Sci. A Polym. Chem.* **2000**, *38*, 4749-4763.

[146]   O'Reilly, R. K.; Joralemon, M. J.; Hawker, C. J.; Wooley, K. L. Fluorogenic 1, 3-Dipolar Cycloaddition within the Hydrophobic Core of a Shell Cross-Linked Nanoparticle. *Chem. - A Euro. J.* **2006**, *12*, 6776-6786.

[147]   Cheng, C.; Qi, K.; Khoshdel, E.; Wooley, K. L. Tandem synthesis of core-shell brush copolymers and their transformation to peripherally cross-linked and hollowed nanostructures. *J. Am. Chem. Soc.* **2006**, *128*, 6808-6809.

[148]   Tsimelzon, A.; Deamer, D.; Braslau, R. Synthesis and Self-Assembly of Amphiphilic Diblock Copolymers using a Fluorescently Labeled N-Alkoxyamine Initiator. *Macromol. Rapid. Comm.* **2005**, *26*, 1872-1877.

[149]   Miura, Y.; Miyake, K. Synthesis of poly(dimethylsiloxane)-containing diblock and triblock copolymers by the combination of anionic ring-opening polymerization of hexamethylenecyclotrisiloxane and nitroxide-mediated polymerization of methyl acrylate, isoprene and styrene. *J. Polym. Sci. A.: Polym. Chem.* **2005**, *43*, 6153-6165.

[150]   Farcet, C.; Belleney, J.; Charleux, B.; Pirri, R. Structural characterization of nitroxide-terminated poly (n-butyl acrylate) prepared in bulk and miniemulsion polymerizations. *Macromolecules* **2002,** *35*, 4912-4918.

[151]   Farcet, C.; Charleux, B.; Pirri, R. Poly (n-butyl acrylate) homopolymer and poly [n-butyl acrylate-b-(n-butyl acrylate-co-styrene)] block copolymer prepared via nitroxide-mediated living/controlled radical polymerization in miniemulsion. *Macromolecules* **2001**, *34*, 3823-3826.

[152]   Karaky, K.; Péré, E.; Pouchan, C.; Garay, H.; Khoukh, A.; François, J.; Desbrières, J.; Billon, L. Gradient or statistical copolymers by batch nitroxide mediated polymerization: effect of styrene/methyl acrylate feed. *New J. Chem.* **2006**, *30*, 698-705.

[153]   Bian, K. Cunningham M. F. Nitroxide-mediated living radical polymerization of 2-hydroxyethyl acrylate and the synthesis of amphiphilic block copolymers. *Macromolecules* **2005**, *38*, 695–701.

[154]   Clement, B.; Trimaille, T.; Alluin, O.; Gigmes, D.; Mabrouk, K.; Feron, F.; Decherchi, P.; Marqueste, T.; Bertin, D. Convenient access to biocompatible block copolymers from SG1-based aliphatic polyester macro-alkoxyamines. *Biomacromolecules* **2009**, *10*, 1436–1445.

[155]   Bian, K.J.; Cunningham, M. F. Nitroxide-mediated radical polymerization of 2-(dimethylamino)ethyl acrylate and its sequential block copolymerization with styrene and n-butyl acrylate. *J. Polym. Sci. A: Polym. Chem.* **2006**, *44*, 414–426.

[156]   Bian, K.; Cunningham, M. F. Surface-initiated nitroxide-mediated radical polymerization of 2-(dimethylamino)ethyl acrylate on polymeric microspheres. *Polymer* **2006**, *47*, 5744–5753.

[157]   Lessard, B.; Maric, M. Nitroxide-mediated synthesis of poly(poly(ethylene glycol) acrylate) (PPEGA) comb-like homopolymers and block copolymers. *Macromolecules* **2008**, *41*, 7870–7880.

[158]   Lessard, B.; Graffe, A.; Marić, M. Styrene/tert-butyl acrylate random copolymers by nitroxide mediated polymerization: effect of free nitroxide on copolymer composition and kinetics. *Macromolecules* **2007**, *40*, 9284-9292.

[159]   Lessard, B.; Tervo, C.; Maric, M. High molecular weight poly(tert-butyl acrylate) by nitroxide mediated polymerization: effect of chain transfer to solvent. *Macromol. React. Eng.* **2009**, *3*, 245-256.

[160]   Lessard, B.; Marić, M. Water-soluble/dispersible carbazole-containing random and block copolymers by nitroxide mediated radical polymerization *Can. J. Chem. Eng.* **2013**, *91*, 618-629.

[161]   Hoogenboom, R; Popescu, D; Steinhauer, W.; Keul, H.; Möller, M. Nitroxide-mediated copolymerization of 2-hydroxyethyl acrylate and 2-hydroxypropyl acrylate: copolymerization kinetics and thermoresponsive properties. *Macromol. Rapid Commun.* **2009**, *30*, 2042–2048.

[162]   Eggenhuisen, T. M.; Becer C. R.; Fijten, M.W.M.; Eckardt, R.; Hoogenboom, R.; Schubert, U. S. Libraries of statistical hydroxypropyl acrylate containing copolymers with LCST properties prepared by NMP. *Macromolecules* **2008**, *41*, 5132–5140.

[163]   Savelyeva, X.; Lessard, B.; Marić, M. Amphiphilic poly(4-acryloylmorpholine)/poly(2-(N-carbazolyl) ethyl acrylate) random and block copolymers synthesized by nitroxide mediated polymerization. *Macromol. React. Eng.* **2012**, *6*, 200-212.

[164]   Lessard, B. H.; Beouch, L.; Goubard, F.; Wantz, G.; Marić, M.; Gigmes, D.; Dumur, F. Poly (2-(N-carbazolyl) ethyl acrylate) as a host for high efficiency polymer light-emitting devices. *Organic Electronics* **2015**, *17*, 377-385.

[165]   Barbosa, C. A.; Gomes, A. S. Living tandem free radical polymerization of a liquid crystalline monomer. *Polym. Bull.* **1998**, *41*, 15–20.

[166]   Lacroix-Desmazes, P.; Andre, P.; Desimone J. M.; Ruzette, A. V.; Boutevin, B. Macromolecular surfactants for supercritical carbon dioxide applications: synthesis and characterization of fluorinated block copolymers prepared by nitroxide-mediated radical polymerization. *J. Polym. Sci. A: Polym. Chem.* **2004**, *42*, 3537–3552.

[167]   Handké, N.; Trimaille, T.; Luciani, E.; Rollet, M.; Delair, T.; Verrier, B.; Bertin, D.; Gigmes, D. Elaboration of densely functionalized polylactide nanoparticles from n-acryloxysuccinimide-based block copolymers. *J. Polym. Sci. A: Polym. Chem.* **2011**, *49*, 1341–1350.

[168]   Drockenmuller, E.; Lamps, J. P.; Catala, J.M. Living/controlled radical polymerization of ethyl and n-butyl acrylates at 90° C mediated by β-sulfinyl nitroxides: Influence of the persistent radical stereochemistry. *Macromolecules* **2004**, *37*, 2076-2083.

[169]   Cameron, N. R.; Reid, A. J. n-Butyl acrylate polymerization mediated by a PROXYL nitroxide. *Macromolecules* **2002**, *35*, 9890-9895.

[170]   Couvreur, L.; Lefay, C.; Belleney, J.; Charleux, B.; Guerret, O.; Magnet, S. First nitroxide-mediated controlled free-radical polymerization of acrylic acid. *Macromolecules* **2003**, *36*, 8260-8267.

[171]   Couvreur, L.; Lefay, C.; Charleux, B. Direct synthesis of controlled poly(styrene-co-acrylic acid)s of various compositions by nitroxide-mediated random copolymerization. *Macromol. Chem. Phys.* **2003**, *204*, 2055-2063.

[172]   C. Lefay, C.; Belleney, J.; Charleux, B.; Guerret, O.; Magnet, S. End-group characterization of poly (acrylic acid) prepared by nitroxide-mediated controlled free-radical polymerization. *Macromol. Rapid Commun.* **2004**, *25*, 1215-1220.

[173]   Kaul, E.; Senkovskyy, V.; Tkachov, R.; Bocharova, V.; Komber, H.; Stamm, M.; A. Kiriy, A. Synthesis of a bifunctional initiator for controlled Kumada catalyst-transfer polycondensation/nitroxide-mediated polymerization and preparation of poly(3-hexylthiophene)−polystyrene block copolymer therefrom. *Macromolecules* **2010**, *43*, 77–81.

[174]   Maria, S. B.; Susha, A. S.; Sommer, M.; Talapin, D. V.; Rogach, A. L.; Thelakkat, M. Semiconductor block copolymer nanocomposites with lamellar morphology via self-organization. *Macromolecules* **2008**, *41*, 6081-6088.

[175]   Sommer, M.; Lindner, S.; Thelakkat, M. Microphase-separated donor–acceptor diblock copolymers: influence of HOMO energy levels and morphology on polymer solar cells. *Adv. Funct. Mater.* **2007**, *17*, 1493-1500.

[176]   Lindner, S. M.; Kaufmann, N.; Thelakkat, M. Nanostructured semiconductor block copolymers: π–π Stacking, optical and electrochemical properties. *Org. Electron.* **2007**, *8*, 69-75.

[177]   Deng, L.; Furuta, P.T.; Garon, S.; Li, J.; Kavulak, D.; Thompson, M.E.; Fréchet, J.M., Living radical polymerization of bipolar transport materials for highly efficient light emitting diodes. *Chem. Mat.*, **2006**, 18, 386-395.

[178]   Boiteau, L.; Moroni, M.; Hilberer, A.; Werts, M.; de Boer, B.; G. Hadziioannou, G. Synthesis of a diblock copolymer with pendent luminescent and charge transport units through nitroxide-mediated free radical polymerization. *Macromolecules* **2002**, *35*, 1543-1548.

[179]   Tsuchiya, K.; Kasuga, H.; Kawakami, A.; Taka, H.; Kita, H.; Ogino, K. Synthesis of bipolar charge transporting block copolymers and characterization for organic light-emitting diode. *J. Polym. Sci. A: Polym. Chem.* **2010**, *48*, 1461-1468.

[180]   Maeda, R.; Hayakawa, T.; Tokita, M.; Kijuchi, R.; J. Kouki, J.; Kakimoto, M.-A.; Urushibata H. Double liquid crystalline side-chain type block copolymers for hierarchically ordered nanostructures: Synthesis and morphologies in the bulk and thin film. *React. Funct. Polym.* **2009**, *69*, 519-529.

[181]   Lohwasser, R. H.; Gupta, G.; Kohn, P.; Sommer, M.; Lang, A. S.; Thurm-Albrecht, T.; Thelakkat, M. Phase Separation in the Melt and Confined Crystallization as the Key to Well-Ordered Microphase Separated Donor–Acceptor Block Copolymers. *Macromolecules* **2013**, *46*, 4403-4410.

[182]   Babiuch, K. Wyrwa, R.; Wagner, K.; Seemann, T.; Hoeppener, S.; Becer, C. R.; Linke, R.; Gottschaldt, M.; Weisser, J.; Schnabelrauch, M.; Schubert, U. S. Functionalized, biocompatible coating for superparamagnetic nanoparticles by controlled polymerization of a thioglycosidic monomer. *Biomacromolecules* **2011**, *12*, 681-691.

[183]   Ott, C.; Hoogenboom, R.; Schubert, U. S. Post-modification of poly (pentafluorostyrene): a versatile "click" method to create well-defined multifunctional graft copolymers. *Chem. Comm.* **2008**, 3516-3518.

[184]   Becer, C. R.; Babiuch, K.; Pilz, D.; Hornig, S.; Heinze, T.; Gottschaldt, M.; Schubert, U. S. Clicking pentafluorostyrene copolymers: synthesis, nanoprecipitation, and glycosylation. *Macromolecules* **2009**, *42*, 2387-2394.

[185]   Ahmad, N. M.; Britton, D.; Heatley, F. Lovell, P. A. Chain transfer to polymer in emulsion polymerization. *Macromol. Symp.* **1999**, *143*, 231-241.

[186]   Ahmad, N.M.; Charleux, B.; Farcet, C.; Ferguson, C.J.; Gaynor, S.G.; Hawkett, B.S.; Heatley, F.; Klumperman, B.; Konkolewicz, D.; Lovell, P.A.; Matyjaszewski, K. Chain transfer to polymer and branching in controlled radical polymerizations of n-butyl acrylate. *Macromol. Rapid Comm.* **2009**, 30, 2002-2021.

[187]   Konkolewicz, D.; Sosnowski, S.; D'hooge, D.R.; Szymanski, R.; Reyniers, M.F.; Marin, G.B.; Matyjaszewski, K. Origin of the difference between branching in acrylates polymerization under controlled and free radical conditions: a computational study of competitive processes. *Macromolecules* **2011**, *44*, 8361-8373.

[188]   Keoshkerian, B.; Szkurhan, A. R. Georges, M. K. Nitroxide miniemulsion acrylate polymerization. *Macromolecules* **2001**, *34*, 6531-6532.

[189]   Georges, M. K.; Lukkarila, J. L.; Szkurhan, A. R. TEMPO-mediated n-butyl acrylate polymerizations. *Macromolecules* **2004**, *37*, 1297-1303.

[190]   Zetterlund, P. B.; Kagawa, Y.; Okubo, M. Controlled/living radical polymerization in dispersed systems. *Chem. Rev.* **2008**, *108*, 3747-3794.

[191]   Van Steenberge, P. H. M.; D'hooge, D. R.; Reyniers, M.-F.; Marin, G. B.; Cunningham, M. F. 4-dimensional modeling strategy for an improved understanding of miniemulsion NMP of acrylates initiated by SG1-macroinitiator.. *Macromolecules* **2014**, *47*, 7732-7741.

[192]   Maeda, Y.; Nakamura, T.; Ikeda, I. Change in solvation of poly((N,N-diethylacrylamide) during phase transition in aqueous solutions as observed by IR spectroscopy *Macromolecules* **2002**, *35*, 10172-10177.

[193]   Delaittre, G.; Save, M.; Charleux, B. Nitroxide-Mediated Aqueous Dispersion Polymerization: From Water-Soluble Macroalkoxyamine to Thermosensitive Nanogels. *Macromol. Rapid. Comm.* **2007**, *28*, 1528-1533.

[194] Delaittre, G.; Save, M.; Gaborieau, M.; Castignolles, P.; Rieger, J.; Charleux, B. Synthesis by nitroxide-mediated aqueous dispersion polymerization, characterization, and physical core-crosslinking of pH-and thermoresponsive dynamic diblock copolymer micelles. *Polym. Chem.* **2012,** *3,* 1526-1538.

[195] Charbonnier, A.; Brochon, C.; Cloutet, E.; Navarro, C.; Hadziioannou, G. Synthesis of functional polymer particles by dispersion polymerization in organic media: A tool toward stable electrophoretic inks. *J. Polym. Sci. A: Polym. Chem.* **2013,** *51,* 4608-4617.

[196] Grignard, B.; Phan, T.; Bertin, D.; Gigmes, D.; Jérôme, C. Detrembleur, C. Dispersion nitroxide mediated polymerization of methyl methacrylate in supercritical carbon dioxide using in situ formed stabilizers. *Polym. Chem.* **2010,** *1,* 837-840.

[197] Guegain, E.; Guillaneuf, Y.; Nicolas, J. Methacrylic esters: insights and solutions to a long-standing problem. *Macromol. Rapid Comm.* **2015,** *36,* 1227-1247.

[198] Nicolas, J.; Guégain, E.; Guillaneuf, Y. Chpater 7: NMP of methacrylic esters: how to circumvent a long-time obstacle in Nitroxide mediated polymerization: form fundamentals to applications in materials science. Gigmes, D. (ed) RSC Polymer Chemistry Series, RSC, London UK **2016.**

[199] Dire, C.; Charleux, B.; Magnet, S.; Couvreur, L. Nitroxide-mediated copolymerization of methacrylic acid and styrene to form amphiphilic diblock copolymers. *Macromolecules* **2007**, *40,* 1897-1903.

[200] Lessard, B.; Marić, M. Incorporating glycidyl methacrylate into block copolymers using poly(methacrylate-*ran*-styrene) macroinitiators synthesized by nitroxide-mediated polymerization. *J. Polym. Sci. A: Polym. Chem.* **2009,** *47,* 2574-2588.

[201] Lessard, B.; Tervo, C.; De Wahl, S.; Clerveaux, F. Jr.; Tang, K. K.; Yasmine, S.; Andjelić, S.; D'Alessandro, A.; Marić, M. Poly(tert-butyl methacrylate/styrene) macroinitiators as precursors for organo and water-soluble functional copolymers using nitroxide mediated controlled radical polymerization. *Macromolecules* **2010,** *43,* 868-878.

[202] Zhang, C.; Lessard, B.; Marić, M. Synthesis and characterization of benzyl methacrylate/styrene random copolymers made by nitroxide-mediated controlled radical polymerization. *Macromol. React. Eng.* **2010,** *4,* 415-423.

[203] Moayeri, A.; Lessard, B.; Marić, M. Nitroxide mediated controlled synthesis of glycidyl methacrylate-rich copolymers enabled by SG1-based alkoxyamines bearing succinimidyl ester groups. *Polym. Chem.* **2011,** *2,* 2084-2092.

[204] Zhang, C.; Marić, M. Synthesis of stimuli-responsive, water-soluble poly[(dimethylamino)ethyl methacrylate/styrene] statistical copolymers by nitroxide mediated polymerization. *Polymers* **2011,** *3,* 1398-1422.

[205] Darabi, A.; Jessop, P.G.; Cunningham, M.F. One-pot synthesis of poly ((diethylamino) ethyl methacrylate-co-styrene)-b-poly (methyl methacrylate-co-styrene) nanoparticles via nitroxide-mediated polymerization. *Macromolecules* **2015,** *48,* 1952-1958.

[206] Wang, Z.-J.; Maric, M. Synthesis of narrow molecular weight distribution norbornene-lactone functionalized polymers by nitroxide-mediated polymerization: candidates for 193 nm photoresist materials. *Polymers* **2014,** *6,* 565-582.

[207] Ting, S. R. S.; Min, E. H.; Escale, P.; Save, M.; Billon, L.; Stenzel, M. H. Lectin recognizable biomaterials synthesized via nitroxide-mediated polymerization of a methacryloyl galactose monomer. *Macromolecules* **2009,** *42,* 9422-9434.

[208] Mei, W.; Maric, M. "Nitroxide-mediated polymerization of 2-hydroxyethyl methacrylate (HEMA) controlled with low concentrations of acrylonitrile and styrene" in press, *Macromol. React. Eng.* **2017,** DOI:10.1002/ mren.201600067.

[209] Zhang, C.; Marić, M. pH and temperature-sensitive statistical copolymers of poly[2-(dimethylamino)ethyl methacrylate-stat-2-vinylpyridine] with functional succinimidyl-ester chain ends synthesized by nitroxide mediated polymerization. *J. Polym. Sci. A: Polym. Chem.* **2012,** *50,* 4341-4357.

[210] Brusseau, S.; Belleney, J.; Magnet, S.; Couvreur, L.; Charleux, B. Nitroxide-mediated copolymerization of methacrylic acid with sodium 4-styrene sulfonate: towards new water-soluble macroalkoxyamines for the synthesis of amphiphilic block copolymers and nanoparticles. *Polym. Chem.* **2010,** *1,* 720-729.

[211] Wang, Z. J.; Marić, M. Nitroxide mediated synthesis of low dispersity random copolymers for low-loss optical waveguides. *J. Polym. Sci. Part A: Polym. Chem.* **2013,** *51,* 2970–2978.

[212] Becer, C. R.; Kokado, K.; Weber, C.; Can, A.; Chujo, Y. Schubert, U. S. Metal-free synthesis of responsive polymers: Cloud point tuning by controlled "click" reaction. *J. Polym. Sci., Part A: Polym. Chem.* **2010,** *48,* 1278.

[213] Wang, Z.-J.; Wylie, K. and Marić, M., Synthesis of Narrow Molecular Weight Distribution Copolymers for ArF Photoresist Materials by Nitroxide Mediated Polymerization. *Macromol. React. Eng.* **2017,** in press. DOI: 10.1002/mren.201600029.

[214] Marić, M., Seok, J., Métafiot, A. and Wylie, K., Nitroxide-mediated polymerization of adamantyl-functional methacrylates for 193 nm photoresists. *Can. J. Chem. Eng.* **2017,** 95, 708-716.

[215] Lessard, B.; Guillaneuf, Y.; Mathew, M.; Liang, K.; Clément, J.-L.; Gigmes, D.; Hutchinson, R.; Marić, M. Understanding the controlled polymerization of methyl methacrylate with low concentrations of 9-(4-vinylbenzyl)-9H-carbazole comonomer by nitroxide mediated polymerization: the pivotal role of reactivity ratios. *Macromolecules* **2013,** *46,* 805-813.

[216] Lessard, B.; Marić, M. "Smart" poly(dimethylaminoethyl methacrylate-ran-9-(4-vinylbenzyl)-9H-carbazole) copolymers synthesized by nitroxide mediated radical polymerization. *J. Polym. Sci. A: Polym. Chem.* **2011,** *49,* 5270-5283.

[217] Zhang, C.; Marić, M. Statistical terpolymers with thermo-responsive fluorescence response in an ionic liquid: effects of solvatophilicity on LCST phase separation and reversibility. *Polym. Chem.* **2014,** *5,* 4926-4938.

[218] Lessard, B.; Ling, E. J. Y.; Marić, M. Fluorescent, thermoresponsive oligo(ethylene glycol) methacrylate/9-(4-vinylbenzyl)-9H-carbazole copolymers designed with multiple LCSTs via nitroxide mediated controlled radical polymerization. *Macromolecules* **2012,** *45,* 1879-1891.

[219] Lessard, B.; Savelyeva, X.; Marić, M. Smart morpholine-functional statistical copolymers synthesized by nitroxide mediated polymerization. *Polymer* **2012,** *53,* 5649-5656.

[220] Savelyeva, X.; Maric, M. Pyrrolidone-functional smart polymers via nitroxide-mediated polymerization. *J. Polym. Sci. A: Polym. Chem.* **2014,** *52,* 2011-2024.

[221] Savelyeva, X.; Chondon, D.; Maric, M. Vinyl phenylboronic acid controlling co-monomer for nitroxide mediated synthesis of thermoresponsive poly(2-N morpholinoethyl methacrylate). *J. Polym. Sci. A: Polym. Chem.* **2016,** *54,* 1560-1572.

[222] Consolante, V.; Marić, M. Nitroxide-mediated polymerization of an organo-soluble protected styrene sulfonate: development of homo and random copolymers. *Macromol. React. Eng.* **2011,** *5,* 575-586.

[223] Nicolas, J.; Brusseau, S.; Charleux, B. A minimal amount of acrylonitrile turns the nitroxide-mediated polymerization of methyl methacrylate into an almost ideal controlled/living system. *J. Polym. Sci. A: Polym. Chem.* **2010,** *48,* 34-47.

[224] Chenal, M.; Mura, S.; Marchal, C.; Gigmes, D.; Charleux, B.; Fattal, E.; Couvreur, P.; Nicolas, J. Facile synthesis of innocuous comb-shaped polymethacrylates with PEG side chains by nitroxide-mediated radical polymerization in hydroalcoholic solutions. *Macromolecules* **2010,** *43,* 9291-9303.

[225] Darabi, A.; Shirin-Abadi, A.R.; Jessop, P.G.; Cunningham, M.F. Nitroxide-mediated polymerization of 2-(diethylamino) ethyl methacrylate (DEAEMA) in water. *Macromolecules* **2014,** *48,* 72-80.

[226] Phan, T. N. T.; Maiez-Tribut, S.; Pascault, J.-P.; Bonnet, A.; Gerard, P.; Guerret, O.; Bertin, D. Synthesis and characterizations of block copolymer of poly(n-butyl acrylate) and gradient poly (methyl methacrylate-co-N, N-dimethyl acrylamide) made via nitroxide-mediated controlled radical polymerization. *Macromolecules* **2007,** *40,* 4516-4523.

[227] Ballard, N., Aguirre, M., Simula, A., Leiza, J.R., van Es, S. and Asua, J.M., 2017. High solids content nitroxide mediated miniemulsion polymerization of n-butyl methacrylate. *Polym. Chem.* **2017,** *8,* 1628-1635.

[228] Ballard, N., Aguirre, M., Simula, A., Leiza, J.R., van Es, S. and Asua, J.M., 2017. Nitroxide mediated suspension polymerization of methacrylic monomers. *Chem. Eng. J.* **2017,** *316,* 655-662.

[229] Nicolas, J.; Mueller, L.; Dire, C.; Matyjaszewski, K.; Charleux, B. Comprehensive modeling study of nitroxide-mediated controlled/living radical copolymerization of methyl methacrylate with a small amount of styrene. *Macromolecules* **2009,** *42,* 4470-4478.

[230] Burguière, C.; Dourges, M.; Charleux, B.; Vairon, J. P. Synthesis and characterization of ω-unsaturated poly (styrene-b-n-butyl methacrylate) Block Copolymers using TEMPO-mediated

Controlled Radical Polymerization. *Macromolecules* **1999**, *32*, 3883-3890.

[231]   Johnson, D. M.; Clarke, N. A.; Rasmussen, P. G. The copolymerization of 1-alkylvinzenes with styrene. *J. Macromol. Sci. A: Pure Appl. Chem.* **2001**, *38*, 773-783.

[232]   Zhang, H.; Hong, K.; Mays, J. W. First report of nitroxide mediated polymerization in an ionic liquid. *Polym. Bull.* **2004**, *52*, 9-16.

[233]   Ryan, J.; Aldabbagh, F.; Zetterlund, P. B.; Yamada, B. First nitroxide-mediated controlled/living free radical polymerization in an ionic liquid. *Macromol. Rapid Commun.* **2004**, *25*, 930-934.

[234]   Brusseau, S.; Boyron, O.; Schikaneder, C.; Santini, C. C.; Charleux, B. Nitroxide-mediated controlled/living radical copolymerization of methyl methacrylate with a low amount of styrene in ionic liquid. *Macromolecules* **2011**, *44*, 215-220.

[235]   Zetterlund, P.B.; Thickett, S.C.; Perrier, S.; Bourgeat-Lami, E.; Lansalot, M. Controlled/living radical polymerization in dispersed systems: an update. *Chem. Rev.* **2015**, 115, 9745-9800.

[236]   Jennings, J.; He, G.; Howdle, S.M.; Zetterlund, P.B. Block copolymer synthesis by controlled/living radical polymerisation in heterogeneous systems. *Chem. Soc. Rev.* **2016**, *45*, 5055-5084.

[237]   Dire, C.; Magnet, S.; Couvreur, L.; Charleux, B. Nitroxide-mediated controlled/living free-radical surfactant-free emulsion polymerization of methyl methacrylate using a poly (methacrylic acid)-based macroalkoxyamine initiator. *Macromolecules* **2008**, *42*, 95-103.

[238]   Thomson, M.E.; Manley, A.M.; Ness, J.S.; Schmidt, S.C.; Cunningham, M.F. Nitroxide-mediated surfactant-free emulsion polymerization of n-butyl methacrylate with a small amount of styrene. *Macromolecules* **2010**, *43*, 7958-7963.

[239]   Thomson, M.E.; Ness, J.S.; Schmidt, S.C.; Cunningham, M.F. High solids nitroxide-mediated microemulsion polymerization of MMA with a small amount of styrene and synthesis of (MMA-co-St)-block-(BMA-co-St) polymers. *Macromolecules* **2011**, 44, 1460-1470.

[240]   Groison, E.; Brusseau, S.; D'Agosto, F.; Magnet, S.; Inoubli, R.; Couvreur, L.; Charleux, B. Well-defined amphiphilic block copolymer nanoobjects via nitroxide-mediated emulsion polymerization. *ACS Macro Lett.* **2011**, *1*, 47-51.

[241]   Qiao, X.G.; Lansalot, M.; Bourgeat-Lami, E.; Charleux, B. Nitroxide-mediated polymerization-induced self-assembly of poly (poly (ethylene oxide) methyl ether methacrylate-co-styrene)-b-poly (n-butyl methacrylate-co-styrene) amphiphilic block copolymers. *Macromolecules* **2013**, 46, 4285-4295.

[242]   Lansalot, M.; Rieger, J.; D'Agosto, F. Polymerization-Induced Self-Assembly: The Contribution of Controlled Radical Polymerization to The Formation of Self-Stabilized Polymer Particles of Various Morphologies. *Macromolecular Self-Assembly* **2016**, 33-82.

[243]   Diaz, T.; Fischer, A.; Jonquieres, A.; Brembilla, A.; Lochon, P. Controlled polymerization of functional monomers and synthesis of block copolymers using a β-phosphonylated nitroxide. *Macromolecules* **2003**, *36*, 2235-2241.

[244]   Schierholz, K.; Gavehchi, M.; Fabre, P.; Nallet, F.; Papon, E.; Guerret, O.; Gnanou, Y. Acrylamide-based amphiphilic block copolymers via nitroxide mediated polymerization. *Macromolecules* **2003**, *36*, 5995-5999.

[245]   Eggenhuisen, T. M.; Becer, C. R.; Fijten M. W. M. Eckhardt, R.; Hoogenboom, R.; Schubert, U. S. Libraries of statistical hydroxypropyl acrylate containing copolymers with LCST properties prepared by NMP. *Macromolecules* **2008**, *41*, 5132-5140.

[246]   Delaittre, G.; Rieger, J.; Charleux, B. Nitroxide-mediated living/controlled radical polymerization of N,N-diethylacrylamide. *Macromolecules* **2011**, *44*, 462-470.

[247]   Savelyeva, X.; Li, L.; Bennett, I.; Metafiot, A.; Maric, M. Stimuli-responsive 4-acryloylmorpholine (4AM)/4-acryloylpiperidine (4AP) copolymers via nitroxide mediated polymerization. Submitted to *J. Polym. Sci. A.: Polym. Chem.* **2017, 55, 2160-2170.**.

[248]   King, B.;. Lessard, B. H. Controlled synthesis and degradation of poly(N-(isobutoxymethyl) acrylamide) homopolymers and block copolymers. *Macromol. React. Eng.* **2017**, *11*, 1600073.

[249]   Grassl, B.; Clisson, G.; Khoukh, A.; Billon, L. Nitroxide-mediated radical polymerization of acrylamide in water solution. *Eur. Polym. J.* **2008**, *44*, 50-58.

[250]   Rigolini, J.; Grassl, B.; Billon, L.; Reynaud, S.; Donard, O. F. X. Microwave-assisted nitroxide-mediated radical polymerization of acrylamide in aqueous solution. *J. Polym. Sci. A: Polym. Chem.* **2009**, *47*, 6919-6931.

[251]   Li, D.; Brittain, W.J. Synthesis of poly(N,N-dimethylacrylamide) via nitroxide-mediated radical polymerization. *Macromolecules* **1998**, *31*, 3852–3855.

[252]   Ganachaud, F.; Monteiro, M.J.; Gilbert, R.G.; Dourges, M.A.; Thang, S.H.; Rizzardo, E. Molecular weight characterization of poly(n-isopropylacrylamide) prepared by living free-radical polymerization. *Macromolecules* **2000,** *33*, 6738–6745.

[253]   Schulte, T.; Siegenthaler, K.O.; Luftmann, H.; Letzel, M.; Studer, A. Nitroxide-mediated polymerization of n-isopropylacrylamide: electrospray ionization mass spectrometry, matrix-assisted laser desorption ionization mass spectrometry, and multipleangle laser light scattering studies on nitroxide-terminated poly-n-isopropylacrylamides. *Macromolecules* **2005**, *38*, 6833–6840.

[254]   Gibbons, O.; Carroll, W.M.; Aldabbagh, F.; Yamada, B. Nitroxide mediated controlled statistical copolymerizations of n-isopropylacrylamide with n-tert-butylacrylamide. *J. Polym. Sci. A: Polym. Chem.* **2006**, *44*, 6410–6418.

[255]   Binder, W.H.; Gloger, D.; Weinstabl, H.; Allmaier, G.; Pittenauer, E. Telechelic poly(n-isopropylacrylamides) via nitroxide mediated controlled polymerization and click chemistry: livingness and grafting-from methodology. *Macromolecules* **2007**, *40*, 3097–4107.

[256]   Savelyeva, X.; Li, L.; Maric, M. Using controlled radical polymerization to confirm the lower critical solution temperature of an N-(alkoxyalkyl) acrylamide polymer in aqueous solution. *J. Polym. Sci. A: Polym. Chem.* **2014**, *53*, 59-67.

[257]   Gibbons, O.; Carroll, W.M.; Aldabbagh, F.; Zetterlund, P.B.; Yamada, B. Nitroxide-mediated radical polymerization of n-tert-butylacrylamide. *Macromol. Chem. Phys.* **2008**, *209*, 2434–2444.

[258]   Moller, M.; Hentschel, C.; Chi, L.; Studer, A. Aggregation behaviour of peptide-polymer conjugates containing linear peptide backbones and multiple polymer side chains prepared by nitroxide mediated radical polymerization. *Org. & Biomol. Chem.* **2011**, *9*, 2403–2412.

[259]   O'Connor, P.; Zetterlund, P.B.; Aldabbagh, F. Nitroxide-mediated stabilizer-free inverse suspension polymerization of n-isopropylacrylamide in supercritical carbon dioxide. *J. Polym. Sci. A: Polym. Chem.* **2011**, *49*, 1719–1723.

[260]   Sugihara, Y.S.Y.; O'Connor, P.; Zetterlund, P.B.; Aldabbagh, F. Chain transfer to solvent in the radical polymerization of n-isopropylacrylamide. *J. Polym. Sci. A: Polym. Chem.* **2011**, *49*, 1856–1864.

[261]   Magee, C.; Sugihara, Y.; Zetterlund, P. B.; Aldabbagh, F. Chain transfer to solvent in the radical polymerization of structurally diverse acrylamide monomers using straight-chain and branched alcohols as solvents. *Polym. Chem.* **2014**, *5*, 2259-2265.

[262]   Abraham, S.; Unsworth, L.D. Multi-functional initiator and poly (carboxybetaine methacrylamides) for building biocompatible surfaces using "nitroxide mediated free radical polymerization strategies. *J. Polym. Sci. A: Polym. Chem.* **2011**, *49*, 1051-1060.

[263]   Marić, M.; Lessard, B. H.; Consolante, V.; Ling, E. J. Y. Incorporating primary amine pendant groups into copolymers via nitroxide mediated polymerization. *React. Funct. Polym.* **2011**, *71*, 1137-1147.

[264]   Srichan, S.; Mutlu, H.; Lutz, J.F. On the synthesis of sequence-controlled poly (vinyl benzyl amine-co-N-substituted maleimides) copolymers. *Eur. Polym. J.* **2015**, *62*, 338-346.

[265]   Keoshkerian, B.; Georges, M.; Quinlan, M.; Veregin, R.; Goodbrand, B. Polyacrylates and polydienes to high conversion by a stable free radical polymerization process: Use of reducing agents. *Macromolecules* **1998**, *31*, 7559-7561.

[266]   Georges, M. K.; Hamer, G. K.; Listigovers, N. A. Block copolymer synthesis by a nitroxide-mediated living free radical polymerization process. *Macromolecules* **1998**, *31*, 9087-9089.

[267]   Li, I.Q.; Howell, B.A.; Dineen, M.T.; Kastl, P.E.; Lyons, J.W.; Meunier, D.M.; Smith, P.B.; Priddy, D.B. Block copolymer preparation using sequential normal/living radical polymerization techniques. *Macromolecules* **1997**, *30*, 5195-5199.

[268]   García-Valdez, O.; Ledezma-Rodríguez, R.; Saldívar-Guerra, E.; Yate, L.; Moya, S.; Ziolo, R. F. Graphene oxide modification with graft polymers via nitroxide mediated radical polymerization. *Polymer* **2014**, *55,* 2347-2355.

[269]   Greene, A. C.; Grubbs, R. B. Synthesis and evaluation of an ester-functional alkoxyamine for nitroxide-mediated polymerization. *J. Polym. Sci. A.: Polym. Chem.* **2009**, *47*, 6342-6352.

[270] Wegrzyn, J. K.; Stephan, T.; Lau, R.; Grubbs, R. B. Preparation of poly(ethylene oxide)-block-poly(isoprene) by nitroxide-mediated free radical polymerization from PEO macroinitiators. *J. Polym. Sci. A: Polym. Chem.* **2005,** *43,* 2977-2984.

[271] Cai, Y.; Aubrecht, K. B.; Grubbs, R. B. Thermally induced changes in amphiphilicity drive reversible restructuring of assemblies of ABC triblock copolymers with statistical polyether blocks. *J. Am. Chem. Soc.* **2011,** *133,* 1058-1065.

[272] Gopalan, P.; Li, X.; Li, M.; Ober, C. K.; Gonzalez, C. P.; Hawker, C. J. Rod-coil block copolymers: an iterative synthetic approach via living free-radical procedures. *J. Polym. Sci. A.: Polym. Chem.* **2003,** *41,* 3640-3656.

[273] Grubbs, R. B.; Wegrzyn, J.K.; Xia, Q. One-step synthesis of alkoxyamines for nitroxide-mediated free radical polymerization. *Chem. Comm.* **2005,** *1,* 80-82.

[274] Ruehl, J.; Nilsen, A.; Born, S.; Chen, S.; Braslau, R. Nitroxide-mediated polymerization to form symmetrical ABA triblock copolymers from a bidirectional alkoxyamine initiator. *Polymer* **2007,** *48,* 2564-2571.

[275] Banik. S. M.; Monnot, B. L.; Weber, R. L.; Mahanthappa, M. K. ROMP-CT/NMP synthesis of multiblock copolymers containing linear poly(ethylene) segments. *Macromolecules* **2011,** *44,* 7141-7148.

[276] Miura, Y.; Dairoku, M. Synthesis and characterization of 6- and 12-arm star polymers by nitroxide-mediated radical polymerization of St and MA from dendritic TIPNO-based hexafunctional and dodecafunctional macroinitiators. *J. Polym. Sci. A: Polym. Chem.* **2007,** *45,* 4364-4376.

[277] Luo, K.; Rzayev, J. Living radical polymerization of bicyclic dienes: Synthesis of thermally cross-linkable block copolymers. *Macromolecules* **2009,** *42,* 9268-9274.

[278] Luo, K.; Kim, S. J.; Cartwright, A. N.; Rzayev, J. Soluble polyacetylene derivatives by chain-growth polymerization of dienes. *Macromolecules* **2011,** *44,* 4665-4671.

[279] Matsuoka, H.; Suetomi, Y.; Kaewsaiha, P.; Matsumoto, K. Nanostructure of a poly (acrylic acid) brush and its transition in the amphiphilic diblock copolymer monolayer on the water surface. *Langmuir* **2009,** *25,* 13752-13762.

[280] Mougnier, S. J.; Brochon, C.; Cloutet, E.; Magnet, S.; Navarro, C.; Hadziioannou, G. Facile and versatile synthesis of rod-coil poly(3-hexylthiophene)-based block copolymers by nitroxide-mediated radical polymerization. *J. Polym. Sci. A: Polym. Chem.* **2012,** *50,* 2463-2470.

[281] Harrison, S.; Couvreur, P.; Nicolas, J. SG1 nitroxide-mediated polymerization of isoprene: Alkoxyamine structure/control relationship and α,ω chain-end functionalization. *Macromolecules* **2011,** *44,* 9230-9238.

[282] Harrison, S.; Couvreur, P.; Nicolas, J. Use of solvent effects to improve control over nitroxide-mediated polymerization of isoprene. *Macromol. Rapid Comm.* **2012,** *33,* 805-810.

[283] Bagryanskaya, E. G.; Brémond, P.; Butscher, T.; Marque, S. R. A.; Parkhomenko, D.; Roubaud, V.; Viel, S. Hydrogen-bonding effects for the C-ON bond homolysis and reformation reactions of alkoxyamines. *Macromol. Chem. Phys.* **2015,** *216,* 475-488.

[284] Tsai, T.-H.; Ertem, S. P.; Maes, A. M.; Seifert, S.; Herring, A. M.; Coughlin, E. B. Thermally cross-linked anion exchange membranes from solvent processable isoprene containing ionomers. *Macromolecules* **2015,** *48,* 655-662.

[285] Hörenz, C.; Pietsch, C.; Goldmann, A. S.; Barner-Kowollik, C.; Schacher, F. H. Phase inversion membranes from amphiphilic diblock terpolymers. *Adv. Mater. Interfaces* **2015,** *2,* 1500042.

[286] Miele, S.; Nesvadba, P.; Studer, A. 1-tert-Butyl-3,3,5,5-tetraalkyl-2-piperazinon-4-oxyls: highly efficient nitroxides for controlled radical polymerization. *Macromolecules* **2009,** *42,* 2419-2427.

[287] Métafiot, A.; Kanawati, Y.; Gerard, J.-F.; Defoort, B.; Marić, M. Synthesis of β-myrcene-based polymers and styrene block and statistical copolymers by SG1 nitroxide-mediated controlled radical polymerization. *Macromolecules* **2017,** 50, 3101-3120.

[288] Germack, D. S.; Wooley, K. L. Isoprene polymerization via reversible addition fragmentation chain transfer polymerization. *J. Polym. Sci. A: Polym. Chem.* **2007,** *45,* 4100-4108.

[289] Bartels, J. W.; Cauët, S. L.; Billings, P. L.; Lin, L. Y.; Zhu, J. H.; Fidge, C.; Pochan, D. J.; Wooley, K. L. Evaluation of isoprene chain extension from PEO macromolecular chain transfer agents for the preparation of dual, invertible block copolymer nanoassemblies. *Macromolecules* **2010,** 43, 7128-7138.

[290] Germack, D. S.; Harrisson, S.; Brown, G. O.; Wooley, K. L. Influence of the structure of nanoscopic building blocks on the assembly of micropatterned surfaces. *J. Polym. Sci. A: Polym. Chem.* **2006,** *44,* 5218-5228.

[291] Jitchum, V.; Perrier, S. Living radical polymerization of isoprene via the RAFT process. *Macromolecules* **2007,** *40,* 1408-1412.

[292] Cheng, C.; Qi, K.; Khoshdel, E.; Wooley, K. L. Tandem synthesis of core-shell brush copolymers and their transformation to peripherally cross-linked and hollowed nanostructures. *J. Am. Chem. Soc.* **2006,** *128,* 6808-6809.

[293] Sylvestre, A. J. D.; Gandini, A. Rosin: Major Sources, Properties and Applications. In Monomers, Polymers and Composites from Renewable Resources, 1st ed.; Belgacem, M. N., Gandini, A., Eds.; Elsevier: Oxford, 2008; 67-88.

[294] Sarkar, P.; Bhowmick, A. K. Green approach toward sustainable polymer: synthesis and characterization of poly(myrcene-co-dibutyl itaconate). *ACS Sustain. Chem. Eng.* **2016,** *4,* 2129-2141.

[295] Satoh, K.; Matsuda, M.; Nagai, K.; Kamigaito, M. AAB-sequence living radical chain copolymerization of naturally occurring limonene with maleimide: an end-to-end sequence-regulated copolymer. *J. Am. Chem. Soc.* **2010,** *132,* 10003-10005.

[296] Nonoyama, Y.; Satoh, K.; Kamigaito, M. Renewable β-methylstyrenes for bio-based heat-resistant styrenic copolymers: radical copolymerization enhanced by fluoroalcohol and controlled/living copolymerization by RAFT. *Polym. Chem.* **2014,** *5,* 3182-3189.

[297] Matsuda, M.; Satoh, K.; Kamigaito, M. 1:2-sequence-regulated radical copolymerization of naturally occurring terpenes with maleimide derivatives in fluorinated alcohol. *J. Polym. Sci. A: Polym. Chem.* **2013,** *51,* 1774-1785.

[298] Ren, S.; Dubé, M. A. Nitroxide-mediated polymerization of n-butyl acrylate and D-limonene. *Macromol. Symp.* **2016,** *360,* 152-159.

[299] Zhang, Y.; Dubé, M.A.; Vivaldo-Lima, E. Modeling degradative chain transfer in D-Limonene/n-butyl methacrylate free-radical copolymerization. J. Renew. Mater. **2015,** *3,* 318-326.

[300] Favier, A.; Luneau, B.; Vinas, J.; Lassaoui, N.; Gigmes, D.; Bertin, D. Exchange of substituents between (macro) alkoxyamines and (macro) RAFT agents (ESARA): a bridge between nitroxide-mediated and RAFT controlled radical polymerization techniques. *Macromolecules* **2009,** *42,* 5953–5964.

[301] Detrembleur, C.; Debuigne, A.; Jerôme, C.; Phan, T. N. T.; Bertin, D.; Gigmes, D. Joining efforts of nitroxide-mediated polymerization (NMP) and cobalt-mediated radical polymerization (CMRP) for the preparation of novel ABC triblock copolymers. *Macromolecules* **2009,** *42,* 8604–8607.

[302] Guillaneuf, Y.; Dufils, P.-E.; Autissier, L.; Rollet, M.; Gigmes, D.; Bertin, D. Radical chain end chemical transformation of SG1-based polystyrenes. *Macromolecules* **2010,** *43,* 91-100.

[303] Petton, L.; Ciolino, A.E.; Stamenović, M.M.; Espeel, P.; Du Prez, F.E. From NMP to RAFT and Thiol-Ene Chemistry by In Situ Functionalization of Nitroxide Chain Ends. *Macromol. Rapid. Comm.* **2012,** *33,* 1310-1315.

[304] Benaglia, M.; Chiefari, J.; Chong, Y.K.; Moad, G.; Rizzardo, E; Thang, S.H. Universal (switchable) RAFT agents. *J. Am. Chem. Soc.* **2009,** *131,* 6914-6915.

[305] Benaglia, M.; Chen, M.; Chong, Y.K.; Moad, G.; Rizzardo, E.; Thang, S.H. 2009. Polystyrene-block-poly (vinyl acetate) through the use of a switchable RAFT agent. *Macromolecules* **2009,** *42,* 9384-9386.

[306] Keddie, D.J. A guide to the synthesis of block copolymers using reversible-addition fragmentation chain transfer (RAFT) polymerization. C*hem. Soc. Rev.* **2014,** *43,* 496-505.

[307] Moad, G.; Keddie, D.; Guerrero-Sanchez, C.; Rizzardo, E.; Thang, S.H. Advances in switchable RAFT polymerization. *Macromol. Symp.* **2015,** *350,* 34-42.

[308] Wannemacher, T.; Braun, D.; Pfaendner, R. Novel copolymers via nitroxide mediated controlled free radical polymerization of vinyl chloride. *Macromol. Symp.* **2003,** *202,* 11-23.

[309] Zaremski, M. Y.; Plutalova, A. V.; Lachinov, M. B.; Golubev, V. B. Concept for quasiliving nitroxide-mediated radical copolymerization. *Macromolecules* **2000,** *33,* 4365-4372.

[310] Yoshida, E. Nitroxide-mediated photo-living radical polymerization of vinyl acetate. *Coll. Polym. Sci.* **2010,** *288,* 73-78.

[311] Abreu, C. M. R.; Mendoça, P. V.; Serra, A. C.; Noble, B. B.; Guliashvili, T.; Nicolas, J.; Coote, M. L.; Coelho, J. F. J.

Nitroxide-mediated polymerization of vinyl chloride at low temperature: kinetic and computational studies. *Macromolecules* **2016**, *42*, 490-498.

[312] Tesch, M.; Hepperle, J. A. M.; Klaasen, H.; Letzel, M.; Studer, A. Alternating copolymerization by nitroxide-mediated polymerization and subsequent orthogonal functionalization. *Angewandte Chemie – Int. Ed.* **2015**, *54*, 5054-5059.

[313] Banerjee, S.; Domenichelli, I.; Ameduri, B. Nitroxide-mediated alternating copolymerization of vinyl acetate with tert-butyl-2-trifluoromethacrylate using an SG1-based alkoxyamine. *ACS Macro. Lett.* **2016**, *5*, 1232-1236.

[314] Bailey, W. J.; Ni, Z.; Wu, S. R. Free radical ring-opening polymerization of 4, 7-dimethyl-2-methylene-1, 3-dioxepane and 5, 6-benzo-2-methylene-1, 3-dioxepane. *Macromolecules* **1982**, *15,* 711–714.

[315] Bailey, W. J.; Wu, S. R.; Ni, Z. Free radical ring-opening polymerization of 4-n-Hexyl-and 4-n-Decyl-2-methylene-1, 3-dioxolanes. *J. Macromol. Sci., Chem.* **1982**, *A18*, 973–986.

[316] Bailey, W. J.; Wu, S. R.; Ni, Z. Synthesis and free radical ring-opening polymerization of 2-methylene-4-phenyl-1, 3-dioxolane. *Makromol. Chem.* **1982**, 183, 1913–1920.

[317] Delplace, V.; Tardy, A.; Harrisson, S.; Mura, S.; Gigmes, D.; Guillaneuf, Y.; Nicolas, J. Degradable and comb-like PEG-based copolymers by nitroxide-mediated radical ring-opening polymerization. *Biomacromolecules* **2013**, *14*, 3769-3779.

[318] Tardy, A.; Delplace, V.; Siri, D.; Lefay, C.; Harrisson, S.; De Fatima Albergaria Pereira, B.; Charles, L.; Gigmes, D.; Nicolas, J.; Guillaneuf, Y. Scope and limitations of the nitroxide-mediated radical ring-opening polymerization of cyclic ketene acetals. *Polym. Chem.* **2013,** *4*, 4776-4787.

[319] Delplace, V.; Harrisson, S.; Tardy, A.; Gigmes, D.; Guillaneuf, Y.; Nicolas, J. Nitroxide-mediated radical ring-opening copolymerization: Chain-end investigation and block copolymer synthesis. *Macromol. Rapid Commun.* **2014**, *35*, 484-491.

[320] Albergaria Pereira, B.D.F.; Tardy, A.; Monnier, V.; Guillaneuf, Y.; Gigmes, D.; Charles, L. Elucidation of a side reaction occurring during nitroxide-mediated polymerization of cyclic ketene acetals by tandem mass spectrometric end-group analysis of aliphatic polyesters. *Rapid Commun Mass Spectrom.* **2015**, *29*, 2302-2308.

[321] Delplace, V.; Guégain, E.; Harrisson, S.; Gigmes, D.; Guillaneuf, Y.; Nicolas, J. A ring to rule them all: A cyclic ketene acetal comonomer controls the nitroxide-mediated polymerization of methacrylates and confers tunable degradability. *Chem Commun.* **2015**, 51, 12847-12850.

[322] Tran, J.; Guégain, E.; Ibrahim, N.; Harrisson, S.; Nicolas, J. Efficient synthesis of 2-methylene-4-phenyl-1,3-dioxolane, a cyclic ketene acetal for controlling the NMP of methyl methacrylate and conferring tunable degradability. *Polym. Chem.* **2016**, *7*, 4427-4435.

[323] Buck, M. E.; Lynn, D. M. Azlactone-functionalized polymers as reactive platforms for the design of advanced materials: progress in the last ten years. *Polym. Chem.* **2012**, *3*, 66-80.

[324] Tully, D. C.; Roberts, M. J.; Geierstanger, B. H.; Grubbs, R. B. Synthesis of reactive poly(vinyl oxazolones) via nitroxide-mediated "living" free radical polymerization. *Macromolecules* **2003**, *36*, 4302-4308.

[325] Delplace, V.; Harrisson, S.; Ho, H.T.; Tardy, A.; Guillaneuf, Y.; Pascual, S.; Fontaine, L.; Nicolas, J., One-step synthesis of azlactone-functionalized SG1-based alkoxyamine for nitroxide-mediated polymerization and bioconjugation. *Macromolecules* **2015**, *48,* 2087-2097.

[326] Gu, B.; Liu, S.; Leber, J. D.; Sen. A. Nitroxide-mediated copolymerization of methyl acrylate with 1-alkenes and norbornenes. *Macromolecules* **2004**, *37*, 5142-5144.

[327] Liu. S.; Sen. A. Living/controlled copolymerization of acrylates with nonactivated alkenes. *J. Polym. Sci. A: Polym. Chem.* **2004**, *42*, 6175-6192.