History of nitroxide mediated polymerization in Canada

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Abstract

Nitroxide mediated polymerization (NMP), sometimes known as stable free radical polymerization (SFRP), is considered one of the main types of reversible deactivation radical polymerization (RDRP) that have emerged as a major advance in polymer synthesis during the past 30 years. This review examines NMP's development from a uniquely Canadian perspective. Inspired by reports of a reversible equilibrium between the TEMPO persistent radical and a growing polymeric radical chain, researchers at the Xerox Research Centre of Canada (XRCC) reported radical polymerizations of styrene with the hallmarks typically associated of living polymerizations: linear degree of polymerization of with conversion, narrow molecular weight distributions, and ability to re-initiate the chain end with additional monomer. This effort expanded to polymerizations in dispersed aqueous media (eg, miniemulsion) and to polymerizations directed for various architectures (block, graft, star), but NMP was ultimately limited generally to styrenic monomers. Consequently, NMP trailed other RDRP methods, such as atom transfer radical polymerization (ATRP) and reversible addition fragmentation transfer polymerization (RAFT), due to its limited monomer choice. With the advent of second-generation alkoxyamine initiators, however, the range of monomers polymerizable in a controlled manner greatly expanded to include acrylates, acrylamides, and eventually methacrylates (under certain conditions), providing renewed impetus towards using NMP. Consequently, Canadian researchers applied these new alkoxyamines for more versatile polymers, resulting in products such as stimuli-responsive polymers, CO_2-switchable latexes, bio-hybrid composites, organic photovoltaic materials, and photolithographic materials. The chronological progression of the developments in NMP from various Canadian laboratories highlights these achievements in new polymeric materials.

KEYWORDS

Nitroxide mediated polymerization, stable free radical polymerization, dispersity, alkoxyamines, copolymers

1 INTRODUCTION

Reversible deactivation radical polymerization (RDRP), commonly known as controlled radical polymerization (CRP), has emerged as one of the most prominent methods to make polymers with controlled microstructure.[1–5] Previously, to obtain polymers with such high structural control was largely restricted to living polymerization processes such as anionic, cationic, or group transfer polymerization techniques. In all those cases, strict control of the reaction conditions, such as low temperature, copiously purified reagents, and air-free transfers, was absolutely vital.[6] The beauty of RDRP techniques lies in the ability to approach the control of polymerization (defined herein as predictable degree of polymerization with conversion, low dispersity, and retention of active centres to re-initiate polymerization of additional monomer) but using less restrictive conditions[6] and even doing the polymerization in aqueous media (homogeneous and dispersed).[7,8] The rise of RDRP has been well documented academically; the commercial adoption has not matched this explosiveness—potential reasons are discussed in reviews by Destarac.[9,10] Regardless, RAFT (reversible addition fragmentation transfer radical polymerization),[11–18] ATRP (atom transfer radical polymerization),[19–23] and nitroxide mediated polymerization (NMP)[1,4,5] have now become common synthetic routes to make controlled microstructure polymers. The merits of each method have been debated and each have been the subject of extensive reviews. Interestingly, the report of these methods followed quickly one after the other—with the Commonwealth Scientific and Industrial Research Organisation (CSIRO) group in Australia reporting NMP in the mid-1980s,[24,25] followed by the Xerox Research Center of Canada (XRCC) in the early 1990s (using stable free radical polymerization [SFRP] as their terminology instead of NMP),[26,27] Matyjaszewski and co-workers,[21] and

Sawamoto and co-workers reporting ATRP first in 1995,[28] and then the CSIRO group describing RAFT initially in 1998.[29]

The focus of this review is centred on Canadian involvement in the development specifically of NMP. We will trace the innovation sprouting from XRCC's progress from simple bulk polymerization processes to polymerizations in dispersed aqueous media to the adoption by Canadian researchers using first-generation nitroxides, and then report on the further developments in NMP unimolecular initiators to revitalize NMP in the mid-2000s. The list of alkoxyamine initiators that are the focus of this review are listed in Figure 1 below.

The productivity and impact of Canadian researchers is suggested in Figure 2, where the number of publications from 1995 to 2019 accounts for about 12% (188/1 577 publications) of the global total using a Scopus keyword search of "nitroxide mediated polymerization," with Canada (188 publications) trailing only France (339) and the United States (293) The papers were also impactful and globally competitive, with the number of citations per publication (excluding self-citations) being 18.5 for Canada and 17.0 for the rest of the world. These metrics, although not comprehensive, do offer useful information, suggesting Canadian researchers were prolific and impactful in NMP.

The initial point of our review is a *Macromolecules* piece published by Michael Georges and co-workers in 1993 titled "Narrow molecular weight resins by a free-radical polymerization process."[26] Here, several hallmarks associated with NMP were described: reversible termination of a growing polymer chain, low dispersity (Đ ~ 1.3), and a predictable growth of monomodal chains with time. The initial recipe consisted essentially of two steps (Figure 3). First, 2,2,6,6-tetramethyl-l-piperidinyloxy (TEMPO) as the nitroxide (the persistent radical), benzoyl peroxide (BPO), and styrene were added together to form an adduct at 95ºC. The resulting adduct was then heated to 123ºC for 69 hours to produce a poly(styrene) capped with TEMPO units with the dispersity remaining low, and relatively high molecular weights (in some cases reaching 1.5×10^5 g mol^{-1} with Đ = 1.27). Suspension copolymerization of styrene and butadiene (86 mol% styrene in the initial monomer mixture) with BPO and TEMPO was also noted with a Đ = 1.36.[26] The same group then pursued the elucidation of the mechanism, using electron spin resonance (ESR) to confirm that reversible termination with TEMPO of the growing chains was actually occurring.[30,31]

The genesis of this review is rooted at XRCC, which was initiated as a materials research centre in Mississauga, Ontario, for Xerox Corp., in 1974, with a diverse research mandate, although resins for electrophotographic toners and photoreceptor materials were predominant. How were these researchers able to examine NMP while obstinately working on materials vital for Xerox's business at the time? It was desirable to have next-generations toners with better rheological properties to use less energy in the fuser rolls and to improve printability. Lower viscosity is generally correlated with narrower molecular weight distribution. Consequently, there was a strong impetus to develop resins analogous to styrene-butadiene copolymers that were common toner resins. Georges and co-workers were familiar with the reports from the CSIRO group regarding the use of TEMPO as a trapping agent, and ultimately pursued the use of TEMPO to regulate the polymerization of styrenic monomers initially. From here, we will chronologically trace the advances in NMP made by Canadian researchers, with appropriate juxtaposition to international progress in the area.

2 The 1990s

The initial publications largely dealt with styrenic monomers and to explain how a free radical polymerization process could provide characteristics superficially resembling the characteristics of living polymerizations. The initial reports were exciting, about radical polymerizations that exhibited traits that were associated with living polymerizations, and fuelled a flurry of subsequent activity. The effect of added nitroxide, and how the equilibrium between dormant and active chains controls the radical concentration and, hence, the molecular weight distribution, were all studied in detail.[31] Industrial adoption was a key concern as the initial polymerizations required several days at elevated temperatures > 125°C to achieve reasonable conversions. Thus, rate accelerants such as camphorsulfonic acid (CSA) were tested to reduce the polymerization times to a reasonable level,[32] and later were found to be essentially radical scavengers to reduce the accumulation of excess free radical due to the persistent radical effect.[33,34] The important role of thermal autoinitiation of styrene, especially at the relatively high polymerization temperatures used, was also recognized.[35] The control of the free radical concentration during SFRP of styrene also brought into question polymerization properties such as the Trommsdorf or gel effect, which could lead to runaway reactions and higher-than-expected molecular weights.[36] It was concluded that such an effect was muted due to the control of the radical concentration derived from the effect of the persistent radical.

From styrenic monomers, incorporating functionality was obviously important to alter solubility or to broaden applicability, for example, in compatibilization with other resins. For example, poly(styrene sulfonic acid, sodium salt) was polymerized with TEMPO in homogeneous aqueous media,[37] which was later explored with second-generation alkoxyamines such as 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxy (TIPNO) in its water-soluble carboxylic acid form[38] and the SG1-based nitroxide.[39,40] In another example, 4-acetoxystyrene was polymerized for application in 256-nm photoresist materials.[41] In addition to functional styrenics, copolymerization with other monomers was also explored to alter thermal and physical properties, even though homopolymerization of many of these monomers failed. Fukuda et al used a poly(styrene)-TEMPO macroinitiator to initiate the copolymerization of styrene with acrylonitrile (AN), methyl acrylate (MA), ethyl acrylate (EA), and vinylcarbazole (VCz).[42] The XRCC group also investigated statistical polymerization of styrenics with a wide variety of monomers, initially in suspension with butadiene,[26] and later over a wide composition range with isoprene (initial mole fraction of isoprene $f_{I,0}$ = 0.1-0.9, although somewhat broad with Đ = 1.56-1.77).[43] Styrene/isoprene copolymerization with TEMPO/BPO initiating system at 130°C was performed up to 6 hours with a conversion of 35% and M_n = 32 100 g mol^{-1}, with linear increase of M_n, with conversion and monomodal molecular weight distributions (dispersities were not reported). Isoprene and acrylate homopolymerizations continued to be explored, noting that excess free radicals were being produced and trapped readily by the monomer, and thus scavengers like glucose and hydroxyacetone were applied with some success.[44] In the case of isoprene, conversions ~ 50% were achieved (M_n = 10 000 g mol^{-1}, Đ = 1.36) after 7 hours polymerization at 145°C with hydroxyacetone as a scavenger. However, no chain extensions were reported to test for the ability of the poly(isoprene) chains to re-initiate a second batch of monomer.

Besides statistical copolymerization and incorporation of functional styrenics, block copolymerization, where an active TEMPO-terminated polymer was used as a macroinitiator to re-initiate a second block, was also reported. Specifically, the XRCC group reported diblock and triblock copolymers containing alkyl acrylates (eg, poly(*n*-butyl acrylate)-*b*-poly(styrene), poly(*n*-butyl acrylate)-*b*-poly(*tert*-butyl acrylate)-*b*-poly(*n*-butyl acrylate).[45] In this case, *n*-BA was polymerized at 155°C, and it was inferred from a linear M_n versus conversion in which the chains were exclusively capped with TEMPO. Subsequent chain extensions with styrene verified the activity of the chain end, with monomodal molecular weight distributions. The authors further reported re-activating the chains twice to make an all-acrylic triblock copolymer by first chain extending a poly(*n*-BA) macroinitiator with *tert*-butyl acrylate, and subsequently using the poly(*n*-BA)-*b*-poly(*t*-BA) diblock with another batch of *n*-BA to make the ABA triblock copolymer. However, no compositions were provided, and just a GPC chromatogram showing the macroinitiator and chain-extended product were shown. Further proof of the chain-end activity was reported later with a poly(styrene)-TEMPO macroinitiator (M_n = 1550 g mol^{-1}, Đ = 1.43), with benzoic acid and an ethyl acetate/dimethylsulfoxide solvent, to which 1,3 butadiene was added in a Parr bomb reactor at 125°C for 10 hours, resulting cleanly in a diblock product (M_n = 4070 g mol^{-1}, Đ = 1.34) with composition and end-groups verified by ^{1}H NMR (the degree of polymerization was kept deliberately low to enable quantification of the end group). Higher molecular weight blocks were also demonstrated using isoprene as the second block from a poly(styrene)-TEMPO terminated macroinitiator (M_n = 21 700 g mol^{-1}, Đ = 1.36), which was then subsequently chain-extended with isoprene to form a diblock (M_n = 38 100 g mol^{-1}, Đ = 1.30), which was subsequently used to form a triblock after addition of styrene (M_n = 43 600 g mol^{-1}, Đ = 1.24).[46] Interestingly, the molecular weight distributions narrowed progressively after each block addition. A further advance, particularly for RDRP in general, was the ability to make block copolymers in dispersed aqueous media, which was demonstrated for TEMPO-mediated systems.[47] In miniemulsion, poly(styrene)-b-poly(butyl acrylate) diblock copolymers were derived from a TEMPO-terminated poly(styrene) oligomer at 135°C in a high-pressure reactor. Best results in terms of chain-end activity involved the PS oligomer made in bulk to a low degree of polymerization (M_n = 1500 g mol^{-1}), which was then emulsified and used as a macroinitiator for n-BA with conversions > 99.5% and M_n = 34 600 g mol^{-1} and Đ = 1.18. It was noted here that partitioning of the TEMPO between the aqueous and oily phases was an important issue, which was further elucidated by the Cunningham group and others.

Other architectures besides linear statistical and block copolymers with TEMPO were also explored by the XRCC group to make arborescent or graft-like polymers.[48–50] The earliest reported polymerized chloromethylstyrene (CMS) in the presence of TEMPO/BPO to form a poly(CMS) with chloromethyl side branches in addition to styrene/CMS statistical copolymers.[48] Additionally, poly(CMS) was used as a macroinitiator for styrene polymerization, yielding an AB diblock where the arborescent groups could be grown from the chloride terminated groups. In contrast to this approach, in collaboration with the Buncel group at Queen's, star copolymers were derived from various unimers.[50] During the same time, Hawker demonstrated that a similar star or graft topology can be accessed (Figure 4).[51] Another similar approach was to make star and arborescent polymers with TEMPO, often combined with orthogonal polymerization strategies (using TEMPO-mediated NMP for one polymerization and using another polymerization, such as ring-opening polymerization, for another segment).[52]

Other examples of TEMPO-mediated polymerization being applied towards highly sophisticated microstructures were made by the Holdcroft group at Simon Fraser, where the derived materials were applied towards bulk heterojunction organophotovoltaics. One approach involved brominating a poly(3-hexylthiophene) and then grafting a TEMPO unit functionalized with a boronic ester, thereby producing a poly(3-hexylthiophene-*graft*-TEMPO) macroinitiator. The TEMPO was then used to copolymerize statistically a mixture of styrene and 4-chloromethylstyrene to produce the desired branches.[53] Finally, the chloromethylstyrene units were coupled to C_{60}-fullerenes to provide the electron-accepting units. A similar approach was later applied to incorporate triazole moieties for photovoltaic materials (Figure 5).[54] In a different application, Holdcroft and co-workers used TEMPO to precisely polymerize SSNa with divinylbenzene to add vinyl groups independently as a graft from a backbone of water-soluble SSNa. Here, divinylbenzene (DVB), which is usually used as a cross-linker, was copolymerized with the poly(SSNa)-TEMPO to form a block copolymer. Because of the nitroxide being in the dormant state most of the time, incorporation of DVB without excessive cross-linking was possible. The DVB units remaining were then used as initiating sites with styrene to form poly(styrene-*graft*-SSNa) for proton exchange membranes (Figure 6).[55]

At the beginning of the 1990s, excitement engendered from the initial reports of SFRP and later ATRP and RAFT prompted a flurry of activity. By the close of the decade, there was a maturation in the research, with much learned about the nature of the process and how to make it industrially amenable. At XRCC, this was embodied in the creation of the spinoff Vivamer, which ultimately was not proven successful, however. Still, from the late 1990s, there was a recognition that emulsion or miniemulsion processes using RDRP processes was going to be prominent. For example, the concept of multi-functional structured latex particles is desirable for biomedical applications, sensors, and xerographic materials where specific features can be imparted at particular parts of the chain. Consequently, the stability of emulsions and rate enhancements were central themes studied, first with the TEMPO-mediated systems, with miniemulsions favoured. Reports of TEMPO-mediated NMP in emulsion began to be reported first by the El-Aasser group,[56,57] with styrenic polymerizations .For example, Prodpan et al used BPO and TEMPO in conjunction with hexadecane costabilizer at 125°C.[56] The latexes were colloidally stable and conversions reached 90% within 12 hours and $M_n \sim 40\ 000\ \mathrm{g\ mol^{-1}}$ and Đ = 1.15-1.60. The XRCC approaches focused on a similar miniemulsion process, where TEMPO was reacted with styrene and benzoyl peroxide (BPO) to form a TEMPO-terminated poly(styrene) oligomer as the initiator. The resulting oligomer was mixed with sodium dodecylbenzenesulfonate (SDBS) as the surfactant in water to form the miniemulsion and then heated to 135°C for 6 hours, resulting in a stable latex with average particle size ~ 200 nm, $M_n = 18\ 800\ \mathrm{g\ mol^{-1}}$, Đ = 1.15 and a conversion of 99.7 wt%.[47] The latex was then used to initiate a second monomer (n-butyl acrylate), with a clean shift to higher $\mathrm{M_n} = 34\ 600\ \mathrm{g\ mol^{-1}}$ and a narrow molecular weight distribution maintained (Đ = 1.18) while the n-BA conversion was high (99.4%). The key issue with TEMPO-mediated NMP in dispersed aqueous media was the high temperature required, typically about 130°C, necessitating high-pressure reactors, which was feasible.

At the close of the decade, NMP using TEMPO was well established and the reports of aqueous dispersed phase polymerizations (ie, miniemulsion) were promising. However, the fundamental shortcomings were becoming increasingly noticeable, as RAFT and ATRP were rapidly being adopted for (meth)acrylic monomers, for example, and reports of emulsion and miniemulsion polymerization using those methods were being rapidly disseminated. Despite the progress made, NMP with TEMPO resulted in lengthy processes and was largely restricted to styrenic monomers, despite the reports of some success using acrylic monomers.[58,59] As the 1990s closed, it seemed that NMP was not viewed as a method of choice for making polymers with controlled microstructures via RDRP. There would have to be a drastic change to the design of nitroxides for NMP to be competitive with ATRP and RAFT processes.

3 The 2000s

By the early 2000s, it was widely acknowledged that RAFT and ATRP were at the forefront of RDRP technologies, with their ability to readily polymerize a wide range of methacrylates, acrylates, and in the case of RAFT especially, vinyl esters. Further, dispersed aqueous systems were also maturing rapidly as both ATRP[60–62] and RAFT[63–65] were adapted, particularly aided by the lower temperatures required for these latter methods. NMP was seeming to lag behind but two key papers revived NMP with the intention to lift the general restriction of TEMPO to polymerize only styrenic monomers. In one study, Hawker and co-workers reported a new alkoxyamine, termed TIPNO (2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxy), which was effective in controlling acrylic and acrylamide monomers with relatively short polymerization times and generally lower temperatures.[66,67] The open structure of the alkoxyamine led to a higher deactivation rate constant, enabling control of monomers with higher propagation rate constants like acrylates. A number of acrylic monomers such as methyl acrylate, n-butyl acrylate and octyl acrylate were polymerized readily with TIPNO in bulk and solution.[66] The other key publication was from Benoit et al in 2000, which described the synthesis of SG1 (*N*-*tert*-butyl-*N*-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide) that was developed in collaboration with Elf Atochem (then becoming Arkema), another alkoxyamine that used a similar design principle.[68,69] Like TIPNO, the SG1 nitroxide was able to control acrylates (like n-butyl acrylate)[68,69] and acrylamides[70,71] readily. Methacrylate homopolymerization was elusive, but in the case of TIPNO- and SG1-derived unimolecular initiators, methacrylic esters could be controlled with the addition of a low concentration of a controlling co-monomer such as styrene. This was more completely elucidated by Charleux and co-workers in a *Macromolecules* paper published in 2005.[72] A derivation was presented for the equilibrium constant between dormant and active chains for both penultimate and terminal copolymerization models of methacrylate-rich copolymerizations as a function of monomer composition and reactivity ratios. The equilibrium constant dramatically decreased with a low concentration ~ 4.4-8.8 mol% controlling co-monomer in the initial mixture (in this initial case, styrene) and, later, end-group determination found that the chains were predominantly capped by the controlling co-monomer, substantially repressing the formation of β-hydrogen elimination reactions that dominate when the methacrylic monomer is at the chain terminus.[73]

In Canada at this time, the TEMPO-mediated systems were maturing, with dramatic jumps in understanding of the process, in particular by the Cunningham group at Queen's

University in the area of dispersed aqueous systems.[7,8,74] They made major contributions in *ab initio* miniemulsion polymerizations,[75–78] such as rate enhancements,[79] partitioning of the nitroxide,[80,81] and the effect of nitroxide/initiator ratio.[82,83] Miniemulsions were easier to study as the particle nucleation step is less complicated, and technically of more interest, as it is much easier to incorporate additives like pigments, dyes, and waxes to make a composite particle (hence XRCC adopted this direction). The key drawback of using miniemulsion is the inclusion of a hydrophobe, which could possibly have a deleterious effect on some properties.

Partitioning of TEMPO between the aqueous and dispersed phase was viewed as critical towards understanding the mechanism of the polymerization and the colloidal stability. The more polar was the TEMPO, the less likely it was to enter the oily phase, and to control the molecular weight distribution. This was summarized by a study which found hydroxyl and 4-amino terminated TEMPO had partition coefficients about an order of magnitude less than TEMPO at 120°C-135°C. This resulted in broader molecular weight distributions and differing molecular weights for a given conversion. These results are summarized in Figure 7, where the rate and M_n versus conversion for KPS-initiated miniemulsion polymerizations with TEMPO and TEMPO-OH were dramatically different with effectively less initiator to monomer, resulting in higher molecular weights than expected.

Related to the partitioning of the nitroxide, the Cunningham group extensively studied the TEMPO/KPS ratio and KPS concentration in the miniemulsion polymerization of styrene.[82,83] The behaviour was complex, at TEMPO/KPS = 1.7, initiator efficiencies = 0.63-0.78, but low dispersities were maintained when the initiator concentration was lower. At higher initiator concentrations, during the early phase of the polymerization, Đ were higher ~ 1.7 until levelling eventually to < 1.3, with a higher-than-expected increase in M_n. It was suggested that polymerization was uncontrolled in the earlier stages of polymerization as the high concentration of KPS entered into the aqueous phase and may have initiated some uncontrolled polymerization due to the limited solubility of TEMPO in the aqueous phase. Increasing the TEMPO/KPS = 4 resulted in completely initiated chains (efficiencies ~ 1) with low Đ during all stages of the polymerizations. Eventually, these variables were systematically studied, and control of polymerization was largely distilled into the choice of initiator and the partitioning properties of the initiator. For example, using TEMPO-OH generally resulted in more of the nitroxide partitioning into the aqueous phase and controlling the Đ during the early stages of polymerization. However, the water-solubility of the oligomers likely made their entry into particles slower, resulting in differences in the molecular weight observed.[82]

Besides the critical role of partitioning, the role of the surfactant was also studied, with two of the most common being sodium dodecyl benzene sulfonate (SDBS) and DOWFAX 8390 (a mixture of mono and di-hexadecyl disulfonated diphenyloxide sodium salts with noted differences in polymerization rates).[84] It was noted that SDBS produced radicals when ascorbic acid was used (as a rate accelerator and a reducing agent), resulting in faster polymerization rates. In studies focusing on the use of DOWFAX 8390, little effect on polymerization in terms of M_n and dispersity was observed, even though very small particles 50 nm-160 nm could be achieved, as was the possibility of homogeneous nucleation. The small particle size was probed further by Maeheta et al as the chain-end fidelity and polymerization rate were affected by the particle size with slower polymerization rate seen in smaller particles.[85] Various factors were suggested, such as geminate recombination of thermally initiated radicals and improved deactivation in smaller particles, which lead to lower termination rates and higher chain-end fidelity.

Instead of employing surfactants and using hydrophobes to make a miniemulsion, Cunningham's group explored emulsion polymerization conditions with SG1-type initiators, without any surfactant or hydrophobe.[86] This was an attempt to probe conditions where surfactants or hydrophobes may prove to have negative effects on the properties of the final latex. Their approach, in contrast to the method adopted by Charleux and co-workers (ie, making a water-soluble SG1-terminated macroinitiator separately and then initiating styrene or acrylic polymerizations),[87,88] was a two-stage process. To avoid the macroinitiator approach, Simms and Cunningham used the water-soluble KPS initiator to stabilize the latex with a mixture of SG1 and styrene. After effectively seeding the sulfate stabilized latex with the SG1/styrene mixture (SG1:KPS = 1.5, careful buffering with K_2CO_3 to maintain pH = 6 as excessively low pH resulted in poor control and high pH resulted in no polymerization), more styrene was added to complete the polymerization. After an induction period of about 4 hours, the polymerization continued with noticeable growth after another 3-5 hours at 90°C. After recovery and drying of the SG1-terminated poly(styrene) from the latex, the resulting macroinitiator (M_n = 16 200 g mol^{-1}, Đ = 1.77) was added to n-butyl acrylate for bulk chain extension at 90°C, resulting in a monomodal product with slight low M_n tailing. Another attempt to avoid using surfactant was described by Szkurhan and Georges.[89] They attempted to employ emulsion conditions, where a TEMPO-terminated macroinitiator was dissolved in an aqueous poly(vinyl alcohol) solution, swollen with monomer and then subsequently polymerized at 135°C for 6 hours to give colloidally stable particles ~ 450 nm with conversions up to 67% with M_n = 22 900 g mol^{-1} and low Đ = 1.11.

As noted previously, one of the negative features associated with TEMPO is long polymerization times, even at elevated temperatures. Various rate accelerants discovered by the XRCC group were applied in TEMPO-mediated miniemulsion, although with limited success, likely due to the issue of dissolving the solid accelerant camphorsulfonic acid (CSA) at the beginning of the polymerization. Since most of these rate accelerants were thought to act as nitroxide scavengers, they were added in a semi-batch approach to control the excess nitroxide that was built-up due to the persistent radical effect, as was done with ascorbic acid, resulting in extremely rapid polymerizations (2-3 hours with conversions > 98% and *Đ* < 1.3) with high chain-end fidelity as measured via fluorescence probes.[90–92]

Since joining McGill in 2003, my group quickly began adopting NMP with TEMPO, based on my exposure to this process while employed at XRCC, targeting macromolecular surfactants and functional latex particles. We found it limiting, in terms of monomer choice and process time, with polymerizations occurring for excessively long times ~ 1 day at elevated temperatures. We consequently discovered the advances to NMP via SG1-based initiators from Arkema[68–71,93,94] and began applying the BlocBuilder initiator to the design of our materials. The initial commercial offerings from Arkema were the MONAMS type of unimolecular initiator, which was highlighted in several early works from Arkema and CPE Lyon[93,94] and from Cunningham's group.[95–97] Later, Arkema began offering the BlocBuilder initiator to research groups, which we proceeded to use. Initially, we examined the incorporation of polar acrylates, namely acrylic acid[98] and its protected form, *tert*-butyl acrylate,[99] in statistical copolymers with styrene in addition to poly(oligo(ethylene glycol) acrylate homo and block copolymers with styrene.[100] We discovered these monomers could be rapidly polymerized and controlled readily (with acrylic acid being more problematic due to the organic acid's propensity to attack the nitroxide, rendering it to the inactive hydroxylamine). We further noted that chain transfer with acrylates is occurring in NMP just as it is in conventional radical polymerization,[101] and we thus turned towards methacrylic esters, which was timed with the report by Charleux et al regarding the ability to produce essentially pure poly(methacrylate) resins by NMP using a low concentration of styrene as a controlling co-monomer.[72] Some of our first forays into applying this approach was published in early 2009 by producing various poly(methacrylate-*ran*-styrene) macroinitiators (methacrylates = methyl, ethyl, and butyl), followed by subsequent chain extensions with epoxy functional glycidyl methacrylate (GMA)/styrene mixtures, to produce nearly all methacrylic block copolymers with epoxy functionality by NMP.[102] We closed out the decade by demonstrating the versatility of the BlocBuilder initiator. We polymerized benzyl methacrylate with a low concentration of styrene,[103] made organo and water-soluble block copolymers with methacrylates,[104] and synthesized one-shot block copolymers of poly(styrene-*alt*-maleic anhydride)-block-poly(styrene) (in non-stoichiometric feeds, at low temperature, which enabled >90% alternating sequences in the first block by NMP).[105]

Meanwhile, as we were adopting SG1-type nitroxides, the Cunningham group began moving away from the TEMPO-mediated systems to SG1-type nitroxides in aqueous dispersed media. Initially starting with formulations using SG1, they made enormous strides in understanding the partitioning of initiator into the aqueous and oily phase, and conducting polymerizations without surfactant.[86] Given this initial success with styrene, the versatility of the SG1-type of alkoxyamine was highlighted by the polymerization of a methacrylic ester, n-butyl methacrylate (BMA), with and without a surfactant.[106] The surfactant-free process generally involved using BlocBuilder/Na_2CO_3 aqueous solutions to form the ionized alkoxyamine initiator with a low concentration of hydrophilic monomer methyl acrylate, which was then subsequently mixed with a BMA/styrene dispersion in water to form a seed latex. Additional monomer was pumped into the mixture, resulting in stable latexes.[106] Later work developed methods to increase the solids loading up to 40 wt%.[107]

Other notable progress in Canada involved translating NMP from batch to continuous processes.[108–115] Initial reports during the decade dealt with semi-batch processes for water-borne coatings targeting $M_n < 6000$ g mol^{-1}.[108] In this initial case, 4-hydroxy TEMPO was mixed with initiator and a low concentration of styrene to make an oligomeric initiator in xylenes at 138ºC (stage 1) followed by gradual addition of more styrene in semi-batch mode over a period of 6 hours, followed by a holding step to high conversion. The results presented high conversion with 70% resin in solution, with comparatively low Đ (as low as ~ 1.5), while having batch times similar to that of conventional radical polymerization (Figure 8). Start-up was identified as a challenging step due to the high concentrations of initiating species present, which consume the nitroxide and primary radical consumption rates.

Semi-batch studies further confirmed the results from the earlier study.[109] Later studies reported styrene miniemulsion polymerization in a continuous tubular reactor, exhibiting linear M_n with conversion, like a batch reactor, with low Đ and high chain fidelity exhibited during chain-extension experiments.[109] Conversions approached 90% with $M_n \sim 25\,000$ g mol^{-1} and Đ ~ 1.3 using a TEMPO-terminated poly(styrene) oligomer that was then fed to a tubular reactor after adding water and SDBS surfactant and homogenization to make the pre-feed miniemulsion.[110] The latex was remarkably free of coagulum (< 0.5 wt%), comparable to the batch reactor case, with comparable particle sizes (170 nm for the tubular reactor versus 164 nm for the batch case). Later work from this group, in collaboration with researchers from Mexico, focused on tailoring molecular weight distributions using continuous reactors by varying feed rates, among other variables.[111,112] Later studies further extended the work in tubular reactors by demonstrating the well-controlled synthesis of block copolymers (di and triblock copolymers with n-BA),[113] as well as elucidating the residence time distribution used by the initial report.[114]

Progress in NMP was not restricted in the 2000s to Xerox and its alumni. The Adronov group at McMaster University creatively employed NMP to functionalize carbon nanotubes[115] and to dendronize carborane functionalized styrene precursors for cancer therapy agents.[116–117] In the first case, poly(styrene) (PS) and poly(styrene-*block*-acrylic acid) (PS-*b*-PAA; derived from the PS-*b*-poly(*tert*-butyl acrylate)) were prepared using a TIPNO-derived unimolecular initiator. The TIPNO-terminated PS or PS-*b*-PtBA were heated to 125°C with the cleaved polymer radical attaching to single walled carbon nanotubes (SWNT) through radical coupling. In the case of the PS-*b*-P*t*BA, the cleavage of the *t*BA to reveal acrylic acid units resulted in SWNT composites with varying solubility. The resulting SWNT composites could then be dispersed readily in various media. Figure 9 describes the above-mentioned process.

Using the same TIPNO unimolecular alkoxyamine as above, a carborane-functionalized styrene was polymerized to produce a well-defined polymer with high boron content, which is critical for certain chemotherapy treatments. Further, conjugation of carboranes has been demonstrated with biological molecules, and in particular dendronized forms are attractive as carriers for drugs. Thus, even when starting from styrenic precursors, very sophisticated functional polymers can be designed with NMP (Figure 10).

Additionally, Penlidis and co-workers at the University of Waterloo extensively studied polymerization optimization and network formation, using styrene/divinylbenzene copolymerization with TEMPO-based NMP. As mentioned earlier, opportunities for ideal network formation are possible due to the control of the concentration of radical species, allowing styrene and divinylbenzene to be copolymerized. Consequently, this was studied in detail, first by analyzing the copolymerization behaviour[118–120] and using this background to simulate network development in such systems,[121] and to increase the rate of copolymerization.[122] Following this initial work, various aspects of the polymerization process itself were examined.[123–135] The role of diffusion controlled effects on the various steps during the polymerization, such as chain propagation, termination, and the activation/deactivation cycles, were modelled and then tested, which was found to not have a strong effect on the NMP of styrene with TEMPO.[123,124] Further, the type and manner of initiation[125,126] were studied to provide the framework for designing experiments to extract reliable parameters for polymerization modelling.[128,132–135]

4 The 2010s

The BlocBuilder and TIPNO initiators greatly enhanced the versatility of NMP, which was highlighted in several publications by Canadian researchers during the past decade. For example, we started to consider incorporating functional methacrylates like the epoxy functional GMA. However, we noted GMA in high concentrations interacted with the carboxyl functional BlocBuilder, leading us to adopt a protected BlocBuilder, the N-hydroxysuccinimide–capped form termed NHS-BlocBuilder described by Bertin and co-workers,[136] which led to controlled GMA-rich copolymerization (~ 90 mol% GMA in the initial monomer mixture).[137] This was a particularly interesting result as the succinimidyl ester permits subsequent conjugation to amines, but NHS-BlocBuilder also decomposes about 15 times faster than BlocBuilder at similar temperatures.[136] As a consequence, the higher decomposition rate mimics superficially the effect of added free nitroxide, which was used previously to help control the polymerization with the BlocBuilder unimolecular initiator (usually about 5 mol%-10 mol% free nitroxide relative to the unimolecular initiator). This greatly simplifies the formulation process by eliminating the need of additional free nitroxide. We employed this simplified protocol [138] and conjugation to amine functional materials was also applied.[139]

Another aspect that we delved in particularly was the nature of the controlling co-monomer for the BlocBuilder family of alkoxyamines. Just merely using styrene could be very limiting. For example, a low concentration of styrene in the copolymer may sufficiently reduce the polarity of the molecule or alter properties like T_g greatly, which prompted the search for alternatives like acrylonitrile.[140] In that case, acrylonitrile made the polymer more polar while not affecting the cytotoxicity in cell-viability studies.[141] We also sought to incorporate a functionality into the controlling co-monomer for a specific purpose. For example, we used electron-donating 9-(4-vinylbenzyl)-9H-carbazole (VBK) to impart fluorescence and combine it with a stimuli-responsive chain. For example, we used dimethylamino ethyl methacrylate (DMAEMA),[142] a mixture of oligoethylene glycol methacrylate (OEGMA)/diethylene glycol methacrylate (DEGMA),[143] (to tune lower critical glass transition temperatures (LCSTs) in aqueous media) and methacryloyl ethyl morpholine (MEMA),[144] as monomers to give stimuli-responsive polymers. We also used 4-vinylphenylboronic acid (VPBA), which can be applied towards glucose sensing in combination with a thermoresponsive DMAEMA co-monomer.[145] One particular interesting aspect concerning VBK was the very low concentration required for it to be an effective controlling co-monomer ~ 1 mol%,[146] compared to ~ 8 mol% for styrene, and using a combination of kinetic studies and ESR studies revealed the subtle role of the reactivity ratios in increasing the probability of a terminal VBK monomer unit attached to the nitroxide.[147] Other controlling co-monomers like 2-vinylpyridine were successfully implemented to provide added pH-responsiveness and tuning to the resulting copolymer LCST.[148]

Besides the nature of the controlling co-monomer, we also took advantage, like many others, of the presence of the initiator fragment on the chain end for use in conjugation. For example, using NHS-BlocBuilder, the succinimidyl ester was reacted with an excess of ethylene diamine to place a primary group at the chain end, which could be used for subsequent application in reactive blending.[149] The resulting amine/anhydride coupling was used to create stable morphologies with elongated styrene-acrylonitrile copolymers with terminal primary amines (SAN-NH_2) that were compatibilized with commercial anhydride functionalized poly(ethylene). Such morphologies would be applicable to barrier materials.

We continued towards adapting NMP where it would be most useful, biomedical and photoresist applications, since NMP avoids discolouration issues from catalysts, ligands, and chain transfer agents that are commonly inherent in ATRP and RAFT. For example, we applied SG1-based NMP to make gradient copolymers for directed self-assembly,[150] and we also employed controlling co-monomers that would result in methacrylic-rich copolymers that do not absorb light in the relevant wavelength for 193-nm UV photoresists.[151] In the former case, using PMMA-*grad*-PS, using styrene as the controlling co-monomer with BlocBuilder, was able to approach the well-defined structures previously attained via ionic polymerization methods, but with slightly larger domain sizes due to the mixing of the two component monomers of the fuzzy interface between the PMMA-rich and PS-rich segments of the chain.

In terms of bio-applications, an interesting approach using NMP was employed by Unsworth and co-workers.[152–154] NMP was chosen since it does not use potentially cytotoxic metals that could be present in ATRP ligands. These studies were unique for several reasons: the modification of the surface was desired to modify the cell adhesion and protein fouling of the biomaterial, and the alkoxyamine was designed to provide silane groups for adhesion while also giving a phosphate residue from the SG1-derived initiator that aids in promoting cell adhesion. Furthermore, methacrylamide-functional zwitterionic monomers N-[3(dimethylamino)propyl]-methacrylamide (DAPMAm) to provide carboxybetaine groups were polymerized with the surface-initiated NMP. A later study by the same group examined changes in spacer length on the adsorption characteristics of the surface (eg, how adsorbed protein conformation is altered, effect on film hydration, and clot formation).[153] The polymers grown from the surface were relatively short but had narrow molecular weight distributions (M_n ~ 5 000 g mol^{-1}, and Đ ~ 1.1-1.3), and the spacer groups on the monomer were found to play a role in inducing structural changes of proteins adsorbed onto the surface (*Figure 11*).=

As recalled earlier, NMP was particularly effective for polymerization of 1,3 dienes with TIPNO[66,155] and this was further demonstrated by the controlled polymerization of bio-based dienes such as myrcene (Myr)[156–158] and farnesene (Far).[159] Myrcene was polymerized with living ionic polymerizations previously,[160–162] and by RAFT in 2015,[163] yet not by NMP, despite the facility of NMP with other dienes such as isoprene and butadiene. We showed that Myr could be polymerized in a controlled manner with BlocBuilder and statistically copolymerized with styrene,[155] GMA,[157] and IBOMA.[158] However, high molecular weights were relatively difficult to attain, due to the propensity of chain transfer reactions.[164] Similar observations were made in our attempts to polymerize Far by NMP in bulk and in solution.[159] Higher molecular weights are desirable since poly(Myr) and poly(Far) have much higher entanglement molecular weights M_e compared to poly(isoprene), which is directly related to mechanical properties. We thus tried to employ rubbery macroinitiators,[164] and are currently applying polymerizations in dispersed aqueous media to take potential advantage of compartmentalization effects to push to higher molecular weights.

A particular interesting application of NMP involves the creation of bio-hybrids, where bio-based materials like cellulose, chitosan, and starch are modified with synthetic polymers to provide properties that are not possible from the base material. Lefay et al described modification of chitosan by grafting of the SG1-type initiator followed by growth of poly(MMA-*ran*-AN) and poly(styrene sulfonate) chains.[165] We grafted stimuli-responsive poly(dimethylamino ethyl methacrylate)-rich compositions onto chitosan in order to make bio-hybrids with synthetic polymers.[166] Cellulose was also modified with SG1-based initiators in a similar manner.[167] The Cunningham group has recently made extensive contributions towards using NMP to make hybrid materials with chitosan, cellulose, and starch, using both *grafting from* (where the initiator is grafted onto the carbohydrate backbone and used to polymerize from the site on the backbone) and grafting to (where a pre-made polymer is linked to a complementary functionality on the backbone) approaches.[168,169] The first reports produced from this group involved the use of chitosan,[170–174] where it was functionalized with the BlocBuilder initiator by first linking a methacrylic acid to the amine groups present on the chitosan backbone and then using intermolecular radical addition (IRA) to attach the initiator. Subsequently, various polymers were grown from the sites to impart different solubility or add some functionality such as thermoresponsiveness or complexing behaviour. For example, poly(oligo(ethylene glycol) methacrylate) was grafted on chitosan for dye removal in aqueous solutions[173] while amino-functional polymers were grafted onto chitosan to apply CO_2-switchable surfaces for metal recovery.[174] Similar approaches were used when another poly(saccharide), nanocrystalline cellulose (NCC), was applied, as indicated below, for the grafting of MMA and MA onto the backbone (Figure 12).[175–179]

Starch has been also touted as a bio-based alternative to make hybrid materials with thermoplastics, for example, in pressure-sensitive adhesives (PSAs).[180–181] Modifying PSAs with starch is attractive as starch is relatively cheap and bio-based but requires synthetic polymers to provide the properties needed for the desired functionality. To modify the properties of the starch, a similar grafting-from approach was applied, where the hydroxyl groups from the starch were reacted with chloromethylstyrene (CMS) followed by IRA with BlocBuilder to form the starch with surface-initiating groups. Following this, polymerization using MMA/S, MA, and AA ensued. High conversions for MMA/S and MA > 90% were attained after 2 hours polymerization, while AA was much lower (~ 26%).[181]

Switchable latexes made by NMP have received considerable attention, in particular the development of amine-functional polymers that can be converted by reaction with CO_2 to form amidine salts (Figure 13).[182,183] This has enormous implications in transport and storage of latexes, among many other applications. For example, the latex can be aggregated, dried, and shipped as a wet cake and then re-dispersed with CO_2 and agitation upon arrival at the destination point. Such re-dispersion may not be possible with conventional surfactant technology, while also being a safer process and reducing transportation costs. Additionally, CO_2-switching can lead to interesting self-assembly behaviour, where addition of carbonated water may render a block copolymer completely soluble, while removal of CO_2 may induce self-assembly of the block copolymer in the media. Consequently, notable applications have involved breathable vesicles, multi-compartment micelles, membranes, drawing agents for forward osmosis, and CO_2-switchable coatings and gels.[182] NMP as a method is comparable with ATRP and RAFT to design CO_2-switchable block and statistical copolymers.[184–187] The first report used diethylamino ethyl methacrylate (DEAEMA) as the CO_2-switchable monomer, but the latex was prepared using conventional radical polymerization for simplicity.[184] The later reports used NMP to prepare polymers and latexes.[185,187]

The utility of SG1-based initiators was passed onto the next-generation of researchers from my group, with Benoit Lessard's independent work at the University of Ottawa focused mostly on organic electronic materials, where NMP is attractive as the polymerization method. Prior to joining Ottawa, Lessard conducted a post-doctoral fellowship with Tim Bender at the University of Toronto, working on boron phthalocyanine (BPC) derivatives for photovoltaic applications.[188–192] The general protocol was to incorporate the BPC into polymers instead of small molecules, enabling convenient processing techniques. Generally, acrylic acid or methacrylic acid were added as a co-monomer to a styrenic or to BMA, where the acid was later used to couple with a bromo-functional BPC.[190] Lessard and co-workers have continued towards incorporating functionality via NMP for molecules applied towards photovoltaics.[193–196] For example, 1-(4-vinylbenzyl)-3-butylimidazolium bis(trifluoromethyl sulphonyl)-imide (VBBI) ionic liquid monomer was incorporated into statistical copolymers with MMA (with reactivity ratios r_{VBBI} = 11.57-12.12, r_{MMA} =1.18-1.23, depending on the method used to evaluate reactivity ratios) and monomodal molecular weight distributions (M_n up to 20 000 g mol^{-1} and $Đ$ ~ 1.4-1.5). Chain extensions with styrene revealed good chain-end fidelity with a clear monomodal shift observed in the GPC traces from the macroinitiator. Dielectrics based on poly(pentafluorostyrene-*ran*-MMA) for OFETs were also shown to be effective if the fluorine content was not too high.[197]

With the SG1 and TIPNO family of alkoxyamines, the issue of using a small amount of controlling co-monomer for the polymerization of methacrylate-rich compositions nevertheless remains a problem. Despite adding functionality through the controlling co-monomer, it might not always be necessary, and even when adding some desirable property, it may still detract potentially from another. Consequently, there has been a long-standing drive to develop alkoxyamines that can homopolymerize exclusively methacrylic esters.[198] Many attempts have been made, with some success, although for various reasons these approaches have not been adopted widely. In some cases, homopolymerization of the methacrylate was possible, but cross-over to a different monomer, like styrene, was not cleanly accomplished.[199] Other cases using *in situ* nitroxide formation for methacrylate homopolymer were reported, although the molecular weight distribution broadened and the nature of end-groups was not necessarily easily controlled in initial reports,[200] but later work showed promise with all-methacrylic systems.[201] Later, Greene and Grubbs described N-phenyl alkoxyamines that were capable of cross-over to different blocks (ie, methacrylic to styrenic) but the polymerizations suffered from disproportion reactions at higher conversions > 50%.[202] More recently, the Leiza and Asua groups demonstrated an alkoxyamine, termed Dispolreg 007 (3-(((2-cyanopropan-2-yl)oxy)cyclohexylamino)-2,2-dimethyl-3-phenylpropanenitrile), that readily polymerized methacrylates with effective cross-over to styrenics[203–211] and was amenable to polymerizations in bulk,[203] solution,[209] suspension,[207] and miniemulsion.[208,210,211] Further, the synthesis of alkoxyamine was simple and easily scalable. This report piqued our interest as we were uncertain about the future supply of BlocBuilder to our lab, particularly as we began scaling up formulations for various industrial projects, and it became relevant for us to have the capability of making our own initiator in-house. We thus started working on making our own initiator and have had some success in adopting the Dispolreg 007 initiator to our projects. We polymerized bio-derived methacrylates in miniemulsion,[212] which was also demonstrated with a different terpene-based methacrylate by the Basque group.[211] Our latexes consisted of stable particles ~ 400 nm with tunable glass transition temperatures when isobornyl methacrylate and long-chain vegetable-oil derived alkyl methacrylates were statistically polymerized.[212] We also attempted to polymerize bio-based dienes (farnesene) with Dispolreg 007, with homopolymerization being effective, but statistical polymerization with a methacrylate result in a surprisingly bimodal molecular weight distribution.[159] However, block copolymerization was possible with clean cross-over from a poly(farnesene) macroinitiator to a GMA-rich block with Dispolreg 007. Besides the starch composites from the Cunningham/Dube collaborations, other bio-based copolymerization using D-limonene with BlocBuilder were reported, with difficulty in incorporating the D-limonene.[213] We experienced similar challenges in polymerization of itaconic acid derivatives with BlocBuilder, due to the less reactive 1-alkene monomer.[214]

Other Canadian groups have continued applying and refining NMP over the last five years. Penlidis and co-workers have continued modelling and testing cross-linked networks and associated experimental design procedures.[215–218] Besides the advances in switchable latexes and bio-based composites, the Cunningham group has continued with incorporating functionality into miniemulsion particles[219] with designing macromolecular surfactants for use in emulsion polymerizations.[220,221]

5 OUTLOOK AND CONCLUSIONS

NMP was one of the first RDRP methods developed, and a Canadian-based group was very active in highlighting the capabilities of TEMPO as a persistent radical in the early 1990s. The use of TEMPO proliferated, with marked inroads made in adapting such systems for the controlled polymerization in dispersed aqueous media, for example. However, the limitations in TEMPO-mediated NMP quickly became apparent as the new millennium dawned, and NMP was seemingly eclipsed by ATRP and RAFT. Yet NMP witnessed a resurgence with the development of TIPNO and SG1-type initiators, and with the ability to polymerize acrylates, acrylamides, and methacrylates (with the use of a controlling co-monomer). Canadian groups participated in this resurgence, highlighting the versatility of the second-generation of alkoxyamines with notable contributions in stimuli-responsive materials, controlled miniemulsion polymerizations, hybrid materials with natural polymers, CO_2-switchable latexes, and copolymers for organic electronic applications. In all these cases, it should be noted that this research was not done in a vacuum; it was done in unison with other researchers around the globe, and these diverse interactions led to the advances made by local researchers. There has been a wide array of international collaborations, through visiting scientists, sabbatical stays, and post-doctoral fellows and students who contributed to this progress. For example, Eduardo Vivaldo Lima from the National Autonomous University of Mexico collaborated with the Penlidis group at Waterloo on modelling NMP, and also with other Canadian groups, such as Marc Dubé's at the University of Ottawa. Further, Vivaldo Lima did his PhD with Archie Hamielec and Phil Wood at McMaster, exemplifying the deep influence that Canadian pioneers in polymer science and engineering (eg, Hamielec, Ken O'Driscoll, and Alf Rudin) have had on trainees. Other connections forged include those with Enrique Saldivar Guerra's group at the Centro de Investigación en Química Aplicada, in Saltillo, Mexico, whose PhD student, Omar Garcia Valdez, did a post-doctoral fellowship with Mike Cunningham, working on NMP grafting from polysaccharides. Members of the polymer group at Queen's (Cunningham and Hutchinson) also collaborated with researchers in Brazil to model NMP in different reactor configurations (including J. C. Pinto from the Universidade Federal do Rio de Janeiro).[111,112] Numerous examples exist from other international collaborations, such as the Netherlands (eg, Niels Smeets studying catalytic chain transfer polymerization through the Cunningham group, which complemented the NMP miniemulsion work). Of course, other European groups have been prominent and gracious in their interactions, particularly with me, such as Bernadette Charleux (then at CPE-Lyon), Julien Nicolas (Universite Paris-Sud), Denis Bertin (Aix-en-Marseille), Didier Gigmes (Aix-en-Marseille), and more recently through joint PhD students (eg, Adrien Metafiot via Jean-Francois Gerard through INSA Lyon). They have served as hosts for my students (Benoit Lessard at Marseille to access EPS) and have visited us in Canada (such as at the first Canadian NMP conference, in Ottawa in 2016). BASF Corp. in Germany and the United States has been involved in several collaborations, too, ranging from unique amphiphilic block copolymer stabilizers for emulsion polymerization and high temperature alkoxyamine initiators. The Leiza and Asua groups at the Basque University in Spain have collaborated with Canadian researchers and, in my case, provided welcome advice to my students regarding the synthesis of their Dispolreg 007 alkoxyamines. Asia is also well represented, through industrial collaborations with Fuji Xerox in Japan (Hideo Maehata) and via academic interactions (Xin Su from Sichuan University, and recently with Mitsuo Sawamoto and Shigeru Yamago from Kyoto University). There are many more international interactions in NMP (literally dozens of researchers and professors, and many more students), but I hope this short vignette illustrates that positive scientific advances are done best when collaboration among scientists crosses all manner of borders (real and artificial).

Where do we go from here? I do not think that we could have anticipated the kinds of breakthroughs made 20 years ago in NMP, but industrial adoption still has not been as rapid as the initial excitement suggested, in line with other prognostications. It will be curious to reflect 20 years from now on whether industrial adoption of NMP-synthesized polymers has caught up with the research from the literature, and to see if Canadian polymer scientists have made as significant an impact on this new phase of research.

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FIGURE CAPTIONS

FIGURE 1 Nitroxides for NMP: (a) 2,2,6,6-tetramethyl-l-piperidinyloxy (TEMPO); (b) styryl-TEMPO ; (c) (2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxy) (TIPNO); (d) the unimolecular initiator styryl-TIPNO; (e) N-tert-butyl-N-[1-diethylphosphono-(2,2-dimethylpropyl)] nitroxide (SG1), (f) N-tert-butyl-N-1-diethylphosphono-2,2-dimethylpropyl-O- 1-methoxycarbonylethylhydroxylamine (MONAMS), and (g) 2-[N-tert- butyl-2,2-dimethylpropyl)aminoxy]propionic acid (BlocBuilder); (h) 2,2-diphenyl-3-phenylimino-2,3-dihydroindol-1-yloxyl nitroxide (DPAIO); (i) N-(1-methyl-(1-(4- the N-phenyl alkoxyamine nitrophenoxy)carbonyl)ethoxy)-N-(1-methyl-(1- (4-nitrophenoxy)carbonyl)ethyl); (j) 3-(((2-cyanopropan-2-yl)oxy)cyclohexylamino)-2,2-dimethyl-3-phenylpropanenitrile (Dispolreg 007).

FIGURE 2 Number of publications versus year for Canada against the global total for a Scopus keyword search “nitroxide mediated polymerization,” June 2020.

FIGURE 3 Steps in the nitroxide mediated polymerization (NMP) using 2,2,6,6-tetramethyl-l-piperidinyloxy (TEMPO): i) TEMPO-styryl adduct formation at 100ºC and ii) chain growth at 125ºC with a reversible chain-termination step.

FIGURE 4 Method to make a three-armed star using 2,2,6,6-tetramethyl-l-piperidinyloxy (TEMPO). Reproduced with permission from Hawker.[51] Copyright 1995, John Wiley and Sons.

FIGURE 5 Synthetic route for polythiophene-graft-(styrene-graft-C60): functionalization of TEMPO with boronylate and reaction with bromide-functionalized poly(3-hexylthiophene) form grafting sites for fullerenes. Reproduced with permission from Chen at al.[53] Copyright 2007, John Wiley and Sons.

FIGURE 6 Scheme to make poly(styrene-graft-poly(sodium styrene sulfonate)) using TEMPO starting initially with styrene sodium sulfonate and divinylbenzene. Reprinted with permission from Ding et al.[55] Copyright 2002, American Chemical Society.

FIGURE 7 (A) Comparison of conversion versus time for TEMPO-mediated (n) and OH-TEMPO-mediated (u) styrene miniemulsion polymerizations; temperature = 135ºC. (B)

Comparison of number average molecular weight versus conversion for TEMPO-mediated (n) and OH-TEMPO-mediated (u) styrene mini- emulsion polymerizations; temperature = 135°C. Reproduced with permission from Ma et al.[80] Copyright 2001, John Wiley and Sons.

FIGURE 8 Number average molecular weight (solid symbols) versus molecular weight and dispersity (open symbols) as a function of global conversion for a continuous miniemulsion polymerization. The conventional radical polymerization is given by circles, Luperox231/TEMPO-OH (triangles), TBPA/TEMPO-OH (diamonds), and unimer PE-T (square). Reprinted with permission from Yanxiang et al.[108] Copyright 2003, American Chemical Society.

FIGURE 9 Single walled carbon nanotubes (SWNT) are functionalized by reaction of TEMPO terminated poly(styrene-ran-chloromethyl styrene) via radical addition. Reprinted with permission from Liu et al.[115] Copyright 2005, American Chemical Society.

FIGURE 10 Carborane functionalized styrene is polymerized using a TIPNO-based initiator, which is further functionalized to produce various generations of dendronized polymers for application as boron neutron therapy agents. Reprinted with permission from Benhabbour et al.[117] Copyright 2008, American Chemical Society.

FIGURE 11 Application of nitroxide mediated polymerization (NMP) using a silane terminated SG1-based initiator to grow polymer with carboxybetaine groups from the surface, in order to modify the surface for cell adhesion. Reprinted with permission from Abraham and Unsworth.[152] Copyright 2011, John Wiley and Sons.

FIGURE 12 Grafting of nanocrystalline cellulose (NCC) with poly(methyl methacrylate) (PMMA) and poly(methyl acrylate) (PMA) after first coupling BlocBuilder onto the NCC modified with chloromethylstyrene (CMS). Reproduced with permission from Roeder et al.[175] Copyright 2016, Royal Society of Chemistry.

FIGURE 13 Example of switchable CO_2-latexes using either an amidine salt-functional initiator or monomer such as diethylaminoethyl methacrylate (DEAEMA). Reprinted with permission from Pinaud et al.[184] Copyright 2012, American Chemical Society.