Applicability of a Polymerized Ionic Liquid /Carbon Nanoparticle Composite Electrolyte to Reductive Cyclization and Dimerization Reactions

Sebastian Herold,^{†,‡} Siegfried R. Waldvogel,^{†,‡,1} R. Daniel Little,^{††,1} Seung Joon Yoo^{*,††,1}

[†] Institute of Organic Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55128 Mainz, Germany

[‡] Graduate School Material Science in Mainz, Johannes Gutenberg University Mainz, Staudingerweg 9, 55128 Mainz, Germany

^{††} Department of Chemistry and Biochemistry, University of California, Santa Barbara, California 93106-9510

* Corresponding author

E-mail address: sjyoo@chem.ucsb.edu

Abstract: Recently, a reusable polymerized ionic liquid/carbon nanoparticle composite electrolyte was developed and effectively applied to a variety of oxidative transformations. The efficient recovery of the composite material and its application in subsequent electroorganic conversions without sacrificing yield adds to the sustainability of the protocol. Herein, we describe our efforts to expand the operational window of the composite electrolyte to include cathodically initiated processes occurring at potentials up to -2.6 V. The results indicate that the composite electrolyte is applicable to reductive processes, but the scope of transformations appears to be limited.

Keywords: sustainable/green chemistry, electrochemical reductive cyclization, recyclable composite electrolyte, polymerized ionic liquid (PIL)

¹ ISE member

1. Introduction

With the importance of “green and sustainable chemistry” continuing to be appreciated, electroorganic chemistry has gained greater attention as one of the most environmentally friendly approaches to organic synthesis [1-7]. Because it is based upon the use of electrons as reagents, electroorganic synthesis can often replace the need for conventional toxic chemical reagents. However, electrochemical transformations may require the use of large amounts of supporting electrolyte in order to ensure the movement of charge [8]. This creates a problem as one must separate it from the product(s) following an electrolysis. Unless it can be recovered and reused, unconscionable amounts of waste are generated. Such practices are no longer tolerable.

To address these issues, researchers have developed a variety of substitutes for conventional supporting electrolytes, systems intended to minimize the formation of waste. Examples include, but are not limited to the development and use of solid polymer electrolytes (SPE) [9] and solid-supported bases [10], the development of thermomorphic multiphase solutions [11], as well as a dispersion consisting of aqueous silica gel [12], and a polymeric reagent that serves as the electron carrier [13]. In addition, electrochemical microreactors and thin-layer flow cells have been developed in order to conduct electroorganic synthesis in the absence of a supporting electrolyte [14-23]. Each approach has been developed to facilitate the separation of the supporting electrolyte and isolation of the product, while minimizing the generation and disposal of waste.

In an effort to devise a general approach that bypasses the need for a traditional supporting electrolyte, we have developed and described the use of a recyclable “*polymeric ionic liquid (PIL) and Super P[®] carbon black composite*” as a surrogate for conventional supporting electrolytes [24]. It is formed via a three step sequence calling for (1) dissolving a known amount of the solid poly(diallyldimethylammonium triflimide), **1** (PDDA/Tf₂N), in a solvent such as acetonitrile (concentration based on repeating unit) [25], (2) adding the desired weight percent of Super P[®] carbon black (weight percent based upon the mass of the PIL), and (3) sonicating the resulting suspension using a low cost laboratory sonicator to afford a dispersion that has thus far remained stable and in that state for more than 2 years (Figure 1). We attribute the stability to the existence of cation- π interactions between the Super P[®] carbon black and the positively charged pyrrolidinium subunits of the PIL [26].

Figure 1. Polymerized ionic liquid **1** (left) and the composite dispersion following sonication (right).

Thus far, studies have focused upon *oxidative* processes including the oxidation of benzylic alcohols [24], the Friedel-Crafts heteroarylation of chalcone epoxides [27], and the Friedel-Crafts α -arylation of *N*-vinylamides [28]. In each instance, excellent yields were obtained, and the composite dispersion could be efficiently recovered and reused without the need for additional supporting electrolyte. In addition, the ability of the composite to modify the electrode surface in-situ leads to improved electron transfer kinetics between the modified electrode and the substrate [24].

The range of potentials that is accessible to the composite dispersion extends from ca., -2.6 V to $+2.6$ V (in acetonitrile vs Ag/0.1 N AgNO_3), a range that is sufficiently large to imagine using the composite dispersion as a medium in which to conduct a host of both oxidative and reductive processes. Herein, we describe our efforts to extend the scope to include reductive transformations, turning initially to an electrohydrocyclization (EHC) that served as the key step in a total synthesis of a natural product.

2. Experimental

All reagents used were of analytical grade. The molecular weight of poly(diallyldimethylammonium) chloride was 200 000-350 000 g/mol. All solvents were distilled prior to use. Acetonitrile that was used as the solvent for electrolyses was freshly distilled from CaH_2 . ^1H NMR and ^{13}C NMR spectra were recorded at the ambient probe temperature by using a Varian Unity Inova 500 MHz spectrometer (Agilent Technologies, Santa Clara, CA). Controlled potential electrolysis was carried out using a 600C Potentiostat (CH Instruments, Austin, TX). A Ag/AgNO₃ reference electrode (silver wire in 0.1 M *n*-Bu₄BF₄/CH₃CN solution; $c(\text{AgNO}_3) =$

0.01 M; $E_0 = -87$ mV vs ferrocene redox couple) was used and housed in a compartment that was separated from the rest of the cell using a Vycor frit [29].

2.1 Formation of the composite dispersion

The composite dispersion was prepared as reported previously [24]. Thus, a 0.5 M solution of PDDA(Tf₂N) (concentration based on repeating unit) was dissolved in dry acetonitrile (15 mL per compartment) and the desired amount (usually 1.2-10 wt % based on PIL) of Super P[®] carbon black (CB) was added. This suspension was then sonicated for 1.5 h to afford a stable dispersion of the composite electrolyte. The composite dispersion was directly prepared in an H-cell under an argon atmosphere. A Pt mesh anode was used as the anode. The RVC cathode had a porosity of 30 PPI. Otherwise all cathode materials used are listed in the corresponding tables.

2.2 Workup

The preferred workup calls for the dropwise addition of the catholyte into a solution of excess dichloromethane [30]. Upon addition, the composite material immediately precipitates. Filtration through a Buchner funnel separates the composite allowing it to be collected on filter paper, while the liquid contains the product. The recovered composite material was washed with dichloromethane and dried in a vacuum oven at 80 °C overnight after which it could be reused.

2.3 Dimethyl (2*E*,7*E*)-5,5-dimethylnona-2,7-dienedioate (2)

The known bis-unsaturated diester **2** was synthesized as described in the literature, by reduction of the corresponding glutaric acid derivative with LiAlH₄ followed by a Swern oxidation and subsequent Wittig olefination [31-32].

2.4 Dimethyl 2,2'-((1*S*,2*S*)-4,4-dimethylcyclopentane-1,2-diyl)diacetate (3)

For the synthesis of **3**, 0.122 g (0.5 mmol) of **2** and 0.134 g (1.0 mmol) of dimethyl malonate were added to the freshly prepared composite dispersion in the cathodic compartment. The resulting solution was degassed by sparging argon through the solution for 15 min. A controlled potential electrolysis was then initiated at a potential of -2.4 V (Ag/AgNO₃), and the progress of the reaction was monitored using TLC. After passing 74 C of charge, the current approached zero and TLC analysis showed the absence of starting material. Consequently, the electrolysis was terminated and the reaction mixture was worked up as described above. Further

purification of the product was accomplished via column chromatography over silica gel (9:1 hexanes/ethyl acetate) to obtain 0.089 g (0.368 mmol, 74%) of a colorless liquid whose spectroscopic data matched those reported in literature [31].

2.5 Dimethyl (2*E*,8*E*)-deca-2,8-dienedioate (5)

The bis-unsaturated diester **5** was obtained by oxidative cleavage of *trans*-cyclohexane 1,2-diol with $\text{PhI}(\text{OAc})_2$ followed by a Wittig olefination, as described in the literature [33-34].

2.6 Dimethyl 2,2'-((1*S*)-cyclohexane-1,2-diyl)diacetate (6)

For the synthesis of **6**, 0.150 mg (0.66 mmol) of **5** and 0.261 mg (1.98 mmol) of dimethyl malonate were added to the freshly prepared composite dispersion in the cathodic compartment. The resulting solution was degassed as described above. Thereafter, a controlled potential electrolysis was performed at a potential of -2.45 V (Ag/AgNO_3) and the progress of the reaction was monitored by TLC. Once the starting material had disappeared, the reaction was worked up by following the usual protocol. Purification of the product using column chromatography over silica gel did not successfully purify the product, so the yield was determined using ^1H NMR and naphthalene as an internal standard. The spectroscopic data matched those previously reported in literature [35].

2.7 Methyl (1*R*,2*S*,3*R*)-5-oxo-2,3-diphenylcyclopentane-1-carboxylate (8)

For the synthesis of the β -keto ester **8**, 0.162 mg (1 mmol) of methyl cinnamate was added to the freshly prepared composite dispersion in the cathodic compartment. Subsequently the cathodic compartment was degassed using argon for 15 min, as described above. A controlled potential electrolysis was initiated at a potential of -2.08 V (Ag/AgNO_3) and the progress of the reaction was monitored by TLC. The current dropped to zero after passing 74 C of charge. Consequently, the reaction mixture was worked up by following the usual protocol. Column chromatography (silica gel) of the crude product (9:1 hexanes/ethyl acetate) afforded 0.044 g (0.149 mmol, 30%) of a white solid whose analytical data was in accord with those reported in literature [36].

2.8 Control experiment leading to methyl (1*R*,2*S*,3*R*)-5-oxo-2,3-diphenylcyclopentane-1-carboxylate (8)

For the synthesis of the β -keto ester **8** in a traditional electrolyte system, 0.162 mg (1 mmol) of methyl cinnamate was added to 15 mL of a 0.8 M Et₄NOTs/CH₃CN solution in the cathodic compartment. The anolyte consisted of 15 mL of a 0.8 M Et₄NOTs/CH₃CN solution. A porous glass frit was used as a separator between the catholyte and anolyte containing compartments of an H-cell. Pt mesh was used as the anode and a copper sheet as the cathode. The temperature was maintained at 10 °C throughout the electrolysis. Prior to electrolysis the cathodic compartment was degassed with argon as described above. Subsequently a controlled potential electrolysis was initiated at a potential of -2.08 V (Ag/AgNO₃) and the progress of the reaction was monitored by TLC. The current dropped to zero after passing 60 C of charge; the electrolysis was terminated and the catholyte was poured into 50 mL of H₂O and extracted three times with 30 mL of ether. The combined organic phases were dried over MgSO₄ and the solvent was evaporated. Column chromatography (silica gel) of the crude product (9:1 hexanes/ethyl acetate) afforded 0.050 g (0.170 mmol, 35%) of a white solid whose analytical data was in accord with those reported in literature [36].

3. Results and Discussion

As illustrated below, electrohydrocyclization (EHC) of the bis-unsaturated diester **2** proceeded in high yield to afford structure **3**, a substance that was subsequently converted to the sesquiterpene called sterpurene (**4**) [31]. Superficially, all appears well viz., the desired transformation occurred efficiently and the adduct served admirably en route to completion of the first total synthesis of a natural product. As is often the case however, “the devil is in the details”. In particular, we note that 54 g of the supporting electrolyte (Et₄NOTs) was used in the electrohydrocyclization of 4.6 g of bisenoate **2**. While the yield was excellent, the isolation of **3** required its separation from large quantities of the supporting electrolyte. Furthermore, for the process to be truly efficient, the supporting electrolyte had to be recovered and purified before it could be reused. These tedious and wasteful operations appeared to provide us with an ideal test case for which we could explore the applicability of the composite dispersion as a suitable reaction medium for reductive processes.

Bisenoate **2** was dissolved in a composite reaction medium consisting of 0.5 M of the PIL, PDDA(Tf₂N), in acetonitrile containing 1.2 weight percent (wt %) of Super P[®] carbon black. A controlled potential electrolysis, carried out at –2.4 V (Ag/AgNO₃) using an RVC cathode and a Pt mesh anode, afforded the desired adduct, **3**, in essentially the same yield as that obtained when the reaction was carried out using 0.9 M Et₄NOTs as the supporting electrolyte [31]. Thus, the composite dispersion served admirably for the reductive cyclization. The workup was straightforward. The catholyte was simply added dropwise to dichloromethane, thereby precipitating the composite and allowing it to be recovered and reused (Figure 2). In this manner a 93% recovery of the composite was achieved and a tedious isolation procedure was bypassed [37]. Additional electrolysis of **2** using the recovered composite electrolyte generated the product in a 65 % yield, confirming the reusability of composite for consecutive reductions without a significant decrease in the product yield.

Figure 2. Recovery of the composite for reuse.

Inspired by these results, we sought to expand the scope of reductive processes by exploring the electrohydrocyclization of the six-membered ring precursor, bisenoate **5**. Its synthesis was achieved via oxidative cleavage of *trans*-cyclohexane-1,2-diol with $\text{PhI}(\text{OAc})_2$ followed by a Wittig olefination [32]. We were surprised and disappointed to discover that unlike the smooth and efficient electrohydrocyclization of **3** leading to the formation of a five-membered ring, the controlled potential electrolysis of **5** failed when conducted in the presence of 1.2 wt % of Super P[®] carbon black (Table 1, entries 1 and 2). The first indication that things were awry was witnessed by a rapid decay of the current (to zero) after the consumption of only 8 C of charge. We reasoned that an increase in the weight percent of conductive carbon nanoparticles might prove beneficial. This is based upon our previous discovery that the increase will be accompanied by an increase in the surface area of the electrode [24], thereby improving access to the in-situ modified electrode. Fortunately, the approach proved modestly successful. When we increased the amount of carbon nanoparticles to 8 wt %, the current did not shut down rapidly. Instead, 130 C of charge was consumed during the course of electrolysis before the current dropped (Figure 3). Nevertheless, the product was obtained in only trace amounts (entry 3). In another experiment, the amount of carbon nanoparticles was increased to 10 wt % while at the same time the concentration of $\text{PDDA}(\text{Tf}_2\text{N})$ was reduced from 0.5 M to 0.3 M (concentration based on repeating unit), the latter in order to decrease the viscosity of the medium and facilitate the diffusion of **5**. Once again, the current remained steady for a longer time, and a 30% yield of the desired cyclization product **5** was obtained (entry 4). Thus, by simply increasing the weight percentage of conducting carbon nanoparticles, we were able to increase the product yield from zero to 30%. While the yield is low from a synthetic standpoint, it is consistent with literature results where a 34% yield of the EHC product has been reported using a conventional supporting electrolyte in dry solvent [38]. That value is also comparable to the 44% we obtained from a controlled potential electrolysis of **5** in dry acetonitrile using 0.2 M *n*-Bu₄NBr as a supporting electrolyte and dimethyl malonate as a proton donor.

Figure 3. Current/time graphs for the attempted six-membered ring formation; effect of different amounts of conducting carbon black nanoparticles; blue line: 1.2 wt % carbon black nanoparticles (Table 1, entry 1); red line: 8 wt % carbon black nanoparticles (Table 1, entry 3).

Table 1. Reaction conditions for the electrohydrocyclization of **5** leading to the six-membered ring **6**.

Entry ^[a]	Cathode	Dimethyl malonate/equiv.	Super P [®] /wt %	Conc. PIL/M	E/V vs Ag/AgNO ₃	Yield/%
1	RVC	2	1.2	0.5	-2.45	-
2	RVC	2	1.2	0.5	-2.6	-
3	glassy carbon	3	8	0.5	-2.45	traces ^[b]
4	glassy carbon	3	10	0.3	-2.45	30 ^[b]

^[a] Pt mesh anode, divided cell (porous glass frit); ^[b] ¹H NMR yield.

Remaining hopeful, we turned our attention to an intermolecular reductive coupling of methyl cinnamate **7**, a process that is known to deliver the β -keto ester **8** via electrohydrodimerization and a subsequent Dieckmann cyclization [36]. Indeed, using a copper cathode, a Pt mesh anode, and 0.5 M PDDA(Tf₂N)/CH₃CN/1.2 wt % Super P[®] carbon black at a potential of -2.08 V (vs Ag/0.1 M AgNO₃) afforded **8** in a 30% yield. For comparison, a control experiment carried out using 0.8 M Et₄NOTs dissolved in CH₃CN, delivered the product in nearly the same yield (35%) illustrating that in our hands, the composite dispersion worked as well as the customary protocol. Literature yields for the transformation, using traditional quaternary ammonium supporting electrolytes, vary from 9-74%, depending upon the reaction conditions [38].

Table 2. Reaction conditions for the reductive coupling of methyl cinnamate in the composite dispersion.

Entry	Cathode	Temperature/°C	Super P [®] /wt %	Conc. PIL/M	E/V vs Ag/AgNO ₃	Yield/% ^[b]
1 ^[a]	Cu	room temperature	1.2	0.5	-2.08	30 (35)
2 ^[a]	Cu	10 °C	1.2	0.5	-2.08	30
3 ^[c]	graphite	room temperature	1.2	0.5	-	32 (50)

^[a] Pt mesh anode, divided cell (porous glass frit); ^[b] isolated yield; in parentheses: yield based on recovered starting material; ^[c] constant current electrolysis, Pt mesh anode, undivided cell, $j = 3.7 \text{ mA cm}^{-2}$, 113 C.

Given the results described above, the scope of *reductive* processes to which the composite dispersion can be applied appears to be limited. Nevertheless, the successful electrohydrocyclization of structure **2** leads us to wonder why that transformation works

satisfactorily while the other substrates do not. We suggest that two factors are responsible, each of kinetic origin. Thus we note first that the rate of electrohydrocyclization of **2** should exceed that of **5** since the cyclization rate leading to a 5-membered ring surpasses that leading to a six; the presence of the gem-methyl unit in **2** accentuates the rate difference and once again favors formation of the 5-membered ring [39]. The second factor arises as a consequence of the comparatively slow rate of cyclization of **5**, and is witnessed experimentally by the rapid drop in current to zero (*vide supra*). We suggest that the slower cyclization rate allows time for the polymeric cation portion of the PIL to compete with the substrate for access to the cathode, eventually blocking its access and shutting down the cyclization pathway (Figure 4).

Figure 4. Blocking access to the cathode.

Coverage of the cathode by oligomeric ammonium salts (up to four repeating units) has previously been reported by Waldvogel and co-workers. However, in their approach, coverage of the cathode was *desired* in order to minimize the evolution of hydrogen, a process that serves to drain electrical energy during cathodic reduction processes carried out in protic media [40-43]. Use of a polycation with a lower molecular weight might solve the problem since electron tunneling should be still possible, leading to radical anions of the organic substrates. However, in the present instance, a high molecular weight of the polymer was needed to ensure efficient precipitation and recovery of the composite material. Thus, the high molecular weight polymerized ionic liquid *and*, as described earlier, the presence of conducting carbon nanoparticles play critical roles in ensuring success.

4. Conclusions

Our previous investigations clearly demonstrate the applicability of the composite dispersion as an effective reaction medium in which to carry out *oxidative* processes. The present study has shown that the composite reaction medium can be applied to synthetic transformations that occur at very negative working potentials (ca. -2.4 to -2.6 V vs Ag/AgNO₃), but not without difficulty. Thus, one must exercise caution when attempting to use the composite dispersion for a transformation carried out reductively. We are presently exploring the development of an alternative reaction medium that can be recycled and will permit reductions to be carried out in a manner that eliminates the use and disposal of conventional supporting electrolytes.

Acknowledgements

We are grateful for the support from CARLOTTA (FKZ 01DM14005) that allowed SH to study and carry out portions of this research at UCSB, and partial support from the Center for the Sustainable Use of Renewable Feedstocks (CenSURF), an NSF Center for Chemical Innovation (CHE-1240194).

References

- [1] M. A. Matthews, Pure Appl. Chem. 73 (2001) 1305.
- [2] B. A. Frontana-Uribe, R. D. Little, J. G. Ibanez, A. Palma, R. Vasquez-Medrano, Green Chem. 12 (2010) 2099.
- [3] J. B. Sperry, D. L. Wright, Chem. Soc. Rev. 35 (2006) 605.
- [4] J.-I. Yoshida, K. Kataoka, R. Horcajada, A. Nagaki, Chem. Rev. 108 (2008) 2265.
- [5] E. Steckhan, T. Arns, W. R. Heineman, G. Hilt, D. Hoormann, J. Jörissen, L. Kröner, B. Lewall, H. Pütter, Chemosphere 43 (2001) 63.
- [6] B. R. Rosen, E. W. Werner, A. G. O'Brien, P. S. Baran, J. Am. Chem. Soc. 136 (2014) 5571.
- [7] S. R. Waldvogel, B. Janza, Angew. Chem. Int. Ed. 53 (2014) 7122.
- [8] C. G. Sowell, R. L. Wolin, R. D. Little, Tetrahedron Lett. 31 (1990) 485.
- [9] J. Jörissen, Electrochim. Acta 41 (1996) 553.
- [10] T. Tajima, T. Fuchigami, J. Am. Chem. Soc. 127 (2005) 2848.
- [11] K. Chiba, Y. Kono, S. Kim, Y. Kitano, M. Tada, Proc. Electrochem. Soc 2002-10 (2002) 9.

- [12] M. Kuroboshi, K. Goto, H. Tanaka, *Synthesis* 6 (2009) 903.
- [13] J. Yoshida, K. Ogura, N. Kawabata, *J. Org. Chem.* 49 (1984) 3419.
- [14] C. A. Paddon, G. J. Pritchard, T. Thiemann, F. Marken, *Electrochem. Commun.* 4 (2002) 825.
- [15] D. Horii, M. Atobe, T. Fuchigami, F. Marken, *Electrochem. Commun.* 7 (2005) 35.
- [16] J.-I. Yoshida, H. Kim, A. Nagaki, *ChemSusChem* 4 (2011) 331.
- [17] R. Horcajada, M. Okajima, S. Suga, J.-I. Yoshida, *Chem. Commun.* (2005) 1303.
- [18] J. Kuleshova, J. T. Hill-Cousins, P. R. Birkin, R. C. D. Brown, D. Pletcher, T. J. Underwood, *Electrochim. Acta* 69 (2012) 197.
- [19] J. Kuleshova, J. T. Hill-Cousins, P. R. Birkin, R. C. D. Brown, D. Pletcher, T. J. Underwood, *Electrochim. Acta* 56 (2011) 4322.
- [20] R. A. Green, D. Pletcher, S. G. Leach, R. C. D. Brown, *Org. Lett.* 17 (2015) 3290.
- [21] T. Arai, H. Tateno, K. Nakabayashi, T. Kashiwagi, M. Atobe, *Chem. Commun.* 51 (2015) 4891.
- [22] R. Stalder, G. P. Roth, *ACS Med. Chem. Lett.* 4 (2013) 1119.
- [23] R. A. Green, R. C. D. Brown, D. Pletcher, *J. Flow. Chem.* 5 (2015) 31.
- [24] S. J. Yoo, L.-J. Li, C.-C. Zeng, R. D. Little, *Angew. Chem. Int. Ed.* 54 (2015) 3744.
- [25] The addition of acetonitrile ensures that the viscosity of the reaction medium is much less than that typically associated with ionic liquids.
- [26] T. Fukushima, A. Kosaka, Y. Ishimura, T. Yamamoto, T. Takigawa, N. Ishii, T. Aida, *Science* 300 (2003) 2072.
- [27] N.-N. Lu, N.-T. Zhang, C.-C. Zeng, L.-M. Hu, S. J. Yoo, R. D. Little, *J. Org. Chem.* 80 (2015) 781.
- [28] L.-J. Li, Y.-Y. Jiang, C. M. Lam, C.-C. Zeng, L.-M. Hu, R. D. Little, *J. Org. Chem.* 80 (2015) 11021.
- [29] V. V. Pavlishchuk, A. W. Addison, *Inorg. Chim. Acta* 298 (2000) 97.
- [30] We initially assumed that the low product yields could be attributed to difficulties associated with the separation of the product and composite. In an effort to ensure a complete separation, an excess of dichloromethane was added. For example, for a catholyte volume of 15 mL, 250 mL of dichloromethane was used. Clearly, this detracts from the sustainability of the protocol since it requires an additional energy-wasting step to recover and reuse the dichloromethane. As indicated in the text, however, separation was not the

problem. Thus, a smaller quantity of dichloromethane could have been used, recovered, and reused.

- [31] L. Moëns, M. M. Baizer, R. D. Little, *J. Org. Chem.* 51 (1986) 4497.
- [32] P. Eilbracht, M. Acker, W. Trotzauer, *Chem. Ber.* 116 (1983) 138.
- [33] K. C. Nicolaou, V. A. Adsool, C. R. H. Hale, *Org. Lett.* 12 (2010) 1552.
- [34] Y. S. Hon, K. P. Chu, P. C. Hong, L. Lu, *Synth. Commun.* 22 (1992) 429.
- [35] J. A. Miranda, C. J. Wade, R. D. Little, *J. Org. Chem.* 70 (2005) 8017.
- [36] I. Nishiguchi, T. Hirashima, *Angew. Chem. Suppl.* (1983) 70.
- [37] R. Marcilla, M. L. Curri, P. D. Cozzoli, M. T. Martínez, I. Loinaz, H. Grande, J. A. Pomposo, D. M. Mecerreyes, *Small* 2 (2006) 507.
- [38] J. H. P. Utley, R. D. Little, M. F. Nielsen, in: O. Hammerich, B. Speiser (Eds.), *Organic Electrochemistry*, CRC Press, Boca Raton, 2016, p. 621, and references therein.
- [39] K. D. Moeller, L. V. Tinao, *J. Am. Chem. Soc.* 114 (1992) 1033.
- [40] J. Kulisch, M. Nieger, F. Stecker, A. Fischer, S. R. Waldvogel, *Angew. Chem. Int. Ed.* 50 (2011) 5564.
- [41] C. Edinger, V. Grimaudo, P. Broekmann, S. R. Waldvogel, *ChemElectroChem* 1 (2014) 1018.
- [42] C. Edinger, J. Kulisch, S. R. Waldvogel, *Beilstein J. Org. Chem.* 11 (2015) 294.
- [43] C. Edinger, S. R. Waldvogel, *Eur. J. Org. Chem.* (2014) 5144.