Polymer Synthesis

Radical/Anionic S_{RN}1-Type Polymerization for Preparation of Oligoarenes**

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Synthetic polymers have strongly influenced and changed modern life. Their worldwide annual production rose to 230 million tons in the year 2009.^[1] Polymers have been prepared either by chain-growth or by step-growth polymerization.^[2] These two classes can be divided into subclasses by further specifying the chemical nature of the polymerization process (Figure 1).



Figure 1. Classification of polymerization processes.

Chain-growth polymerization^[3] has been achieved by radical, coordination, or ionic chemistry. Herein, we introduce a novel chain-growth polymerization technique that occurs by an unprecedented strongly alternating radical/ anionic cross-over process. The new method does not use any transition metal and allows preparation of oligoarenes, which have found applications in materials science.^[4,5] As metal impurities alter physical properties of a synthetic polymer, materials prepared by transition-metal-based catalysis have to be rigorously purified. Most transition metals used in such polymerizations are expensive, and the necessity of using sophisticated purification procedures leads to a further increase of costs.

It is known that a radical polymerization can be transformed into an anionic polymerization by a cross-over process (Scheme 1). Such a transformation is best achieved by termination of the radical process by a reagent that installs a functional group that is able to initiate an anionic polymerization.^[6] The reverse process is also well-established. However, alternating in situ radical/anionic cross-over polymerizations are unknown. Our design principle is based on

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- [**] We thank the Westfälische Wilhelms-University for supporting our work. Dr. Heinrich Luftmann and Dr. Matthias Letzel (WWU Münster) are acknowledged for conducting the MS studies.
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201206096.

radical to anion cross-over (known)



anion to radical cross-over (known)

alternating radical/anionic S_{RN}1-type polymerization (present work)



 $\textit{Scheme 1.}\ Radical/anionic cross-over polymerization processes (I = initiator).$

the knowledge that an arene radical anion bearing an anionic leaving group X (for example, Br, I) readily fragments X⁻, generating an aryl radical (Ar[•]).^[7] Such radicals react with various nucleophiles (Nu⁻) to radical anions (Ar-Nu⁻), which upon oxidation (electron transfer to the starting arvl halide) provide the arylation products Ar-Nu in a chain process. These established transformations are classified as $S_{RN}1$ reactions^[8,9] (nucleophilic radical substitutions), and aryl Grignard reagents (Ar-MgX) can act as nucleophiles in such processes.^[10] We assumed that aryl Grignard reagents bearing an anionic leaving group at the arene moiety are suitable monomers in unprecedented radical/anionic S_{RN}1type polymerizations for preparation of oligoarenes. Reaction of an initiator radical with such a monomer should generate a radical anion, which will fragment X^- to give an aryl radical.^[11] This reactive radical will then add to the anionic monomer to give the corresponding radical anion by C-C bond formation. Subsequent X⁻ elimination generating the chain-extended aryl radical completes the chain propagation step. The mechanism of the novel polymerization process is depicted in Scheme 1, exemplified for the preparation of poly(*m*-phenylene).^[4,5]

Aryl Grignard (Ar-MgX) reagents undergo highly efficient homocoupling to biaryls (Ar-Ar) by oxidation with the 2,2,6,6-tetramethylpiperidine-*N*-oxyl radical (TEMPO).^[12,13] This homocoupling, which most likely proceeds via a biaryl radical anion intermediate, was applied as initiation step. As monomer for initial studies, we chose aryl magnesium compound **1a**, which is readily generated from the symmetrical bisiodide by I–Mg exchange, with commercially available *i*PrMgCl (Table 1).^[14] Oxidative homocoupling of **1a** should lead to a biaryl radical anion bearing two iodide substituents. Elimination of an iodide will generate the corresponding biaryl radical, which in turn should be able to initiate polymerization (Scheme 2).

Table 1: Polymerization of Mg compound 1 a under different conditions.



| Entry | TEMPO [mol%] | Conc [mol L ⁻¹] | t [h] | Yield [%] | <i>M</i> _n [g mol ⁻¹] ^[a] | PDI |
|-------------------|-----------------|-----------------------------|----------|--------------|--|------|
| 1 | 5 | 0.5 | 1 | 40 | 3400 | 2.04 |
| 2 | 5 | 0.5 | 2 | 46 | 5700 | 2.20 |
| 3 | 5 | 0.5 | 3 | 42 | 6600 | 1.87 |
| 4 | 5 | 0.5 | 5 | 66 | 8800 | 2.16 |
| 5 | 5 | 0.5 | 15 | 66 | 11 700 | 1.83 |
| 6 | 5 | 0.5 | 24 | 66 | 12000 | 1.95 |
| 7 ^[b] | 5 | 0.5 | 24 | - | - | - |
| 8 | 5 | 1.0 | 24 | 68 | 5500 | 1.89 |
| 9 | 5 | 0.25 | 24 | 50 | 9300 | 2.04 |
| 10 | _ | 0.5 | 24 | 81 | 19600 | 1.74 |
| 11 | 7.5 | 0.5 | 24 | 60 | 11 300 | 1.97 |
| 12 | 10 | 0.5 | 24 | 70 | 13 700 | 1.80 |
| 12 | 20 | 0.5 | 24 | 59 | 13300 | 1.68 |
| 14 | 30 | 0.5 | 24 | 54 | 10400 | 1.61 |
| 15 | 40 | 0.5 | 24 | 50 | 10300 | 1.60 |
| 16 | 50 | 0.5 | 24 | 26 | 6500 | 1.60 |
| 17 ^[c] | 10 | 0.5 | 24 | 59 | 9400 | 2.23 |

[[]a] Polystyrene standard was used for GPC analysis. [b] Reaction at 0°C. [c] Conducted with 1b (X=Br) to give 2b (X=Br, R=H, Br, iPr).



Scheme 2. Initiation by oxidative homocoupling of 1a.

Polymerizations were conducted in tetrahydrofuran (THF), and TEMPO was used as oxidant in most experiments and was added at -40 °C. We noted that initiation occurred upon warming the reaction mixture to room temperature. Initial polymerizations were performed with 5 mol% TEMPO (0.5 M), and polymer **2a** was isolated by repeated precipitation. Analysis was conducted by NMR spectroscopy, mass spectrometry, and gel permeation chromatography (GPC).

Polymerization for 1 h provided **2a** with a M_n of 3400 gmol⁻¹ and a PDI of 2.04 in 40% yield (Table 1, entry 1). Yield and M_n were increased upon increasing polymerization time to 24 h (entries 2–6). Polymerization did not occur at 0°C (entry 7), and reactions were best conducted at a concentration of 0.5 M (entries 8 and 9). Interestingly, the highest M_n (19600 gmol⁻¹) and yield (81%) resulted in the absence of TEMPO (entry 10). We assume that traces of dioxygen acted as oxidant to initiate the polymerization in this case, which further reduces the cost of the process.

However, the TEMPO initiation method has also benefits, as varying the initiator amount allowed for a rough adjustment of the molecular weight of 2a. The largest polymers were obtained with 10 mol% of TEMPO, and at higher initiator loading, M_n decreased (entries 11–16). The nonlinearity of the amount of added initiator with respect to M_n indicates that the S_{RN}1 polymerization is not a living process. Most likely, the reaction of the polymeric aryl radical with the anionic monomer 1a is faster than initiation. The anionic leaving group influences reaction outcome, as the Br derivative **1b** as monomer delivered a moderate result (entry 17), and also the countercation influences polymerization. The Li (Li-1a) and Zn derivatives (Zn-1a) afforded worse results (see the Supporting Information). In contrast to anionic polymerizations, where moisture has to be carefully excluded from the reaction mixture, the radical/anionic S_{RN}1 polymerization is not sensitive in that regard, as hydrolysis of the monomer leads to an inactive aryliodide that does not influence the reaction outcome.

The high regioregularity of the poly(*m*-phenylene) synthesis was confirmed by ¹³C NMR analysis (Figure 2), which clearly shows the *meta* connectivity of the arene moieties (only four resonances for the arene C atoms), and therefore a mechanism where polymerization occurs by an anionic process through aryne intermediates^[15] can be unambiguously excluded.



180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 $\delta\,(^{13}{\rm C})\,/\,{\rm ppm}$

Figure 2. ¹³C NMR spectrum of **2a** (75 MHz, CDCl₃, RT; $M_n = 19600 \text{ g mol}^{-1}$, PDI = 1.74).

Absorption and emission spectra of 2a showing the typical curves for this substance class can be found in the Supporting Information. As analyzed by mass spectrometry (MALDI, matrix-assisted laser desorption), synthetic 2a contains three



series of poly(*m*-phenylenes) that differ in the termination moiety. iPr (2a-iPr), H (2a-H), and I (2a-I) were identified as terminating substituents, and all polymers contain at least one iodine atom (see the structure of 2a in Table 1). Assuming that the three different polymer types are ionized to the same extent, integration of the peaks of the individual series in the MALDI spectra allows for estimation of the relative ratio of the three series (see the Supporting Information, MALDI analysis was conducted for $M_{\rm n} < 10000 \,{\rm g \, mol^{-1}}$). We found that for the lower molecular weight polymers (region 1500 to 3000 gmol^{-1}), the ratio of **2a**-*i*Pr to **2a**-H to **2a**-I-termination is 21:27:52. For medium-sized poly(m-phenylene) (5000 to 6800 gmol^{-1}) we noted a change in the relative abundance with a lowering of the "iPr-fraction" (2a-iPr/2a-H/2a-I)11:29:60) and the largest series (7500 to 10000 gmol^{-1}) showed an even lower fraction of the *i*Pr-terminated polymers, while the relative amount of H-terminated macromolecules remained nearly constant throughout all mass regions (2a - iPr/2a - H/2a - I = 7:27:66). The source of H-terminated polymers is not quite clear to us at this moment, as mass-spectrometric analysis shows no deuterium incorporation either by performing the polymerization process in deuterated THF or/and by quenching the reaction with D₂O. Other solvents, such as Et₂O and C₆H₅CF₃, provided worse results. The I-terminated series were either formed by oxidation of the polymeric radical anion, by dimerization of two polymeric aryl radicals, or by I-abstraction of the polymeric aryl radical from isopropyl iodide (isopropyl iodide was formed as byproduct in the initial I-Mg exchange reaction). *i*Pr-terminated poly(*m*-phenylenes) most likely derived from reaction of the polymeric aryl radical with unreacted iPrMgX.

As all of the polymers contain at least one iodine substituent, the molecular weight of **2a** $(M_n = 13400 \text{ gmol}^{-1})$, PDI = 1.70) could be further increased by transforming the polymer to the corresponding magnesiated 2a-MgCl followed by oxidative homocoupling with TEMPO^[12,18] to give Hterminated poly(m-phenylene) in a quantitative yield with $M_{\rm p} = 21300 \,\mathrm{g}\,\mathrm{mol}^{-1}$ and PDI = 1.50 (see the Supporting Information). Moreover, end-group modification can be achieved by transforming the polymer 2a ($M_n =$ 5700 gmol^{-1} , PDI = 2.20) into the corresponding magnesiated 2a-MgCl, followed by oxidative cross-coupling^[19] with 3 in the presence of TEMPO to give 4 ($M_n = 6500 \text{ gmol}^{-1}$, PDI = 1.90).^[20] Alkoxyamine 4 was then successfully used as a macroinitiator for the nitroxide-mediated polymerization (NMP)^[21,22] of styrene to give poly(*m*-phenylene)-*block*-poly-(styrene) copolymer 5, which was isolated as a white solid $(30\%, 80700 \text{ gmol}^{-1}, \text{PDI} = 1.23, \text{Scheme 3}).^{[23]}$

Along with the possibility to chemically postmodify the iodinated oligoarene, we found that end-group tailoring can also be achieved by polymerizing the anionic monomer in the presence of an additional aryl Grignard derivative lacking the anionic leaving group. This was shown by polymerizing monomer **1a** in the presence of varying amounts (5 to 50 mol%) of alkoxyamine **3** using the air initiation procedure (Table 2). End-group analysis was performed with MALDI-MS as discussed above. We looked at a M_n range between 2500 and 4500 g mol⁻¹ for these MS investigations (see the



Scheme 3. Synthesis of block copolymer **5** by end-group modification of **2a** and subsequent NMP of styrene.

Table 2: End-capping during polymerization.



[a] Polystyrene standard was used for GPC analysis. [b] 2a contains 2a-H, 2a-iPr, and 2a-I (ratios are given in the Supporting Information).
[c] For the 2a series, only 2a-I was detected by MALDI-MS.

Supporting Information).^[24] With 5 mol % **3**, a slight reduction of M_n was noted, and around 25% of the polymers contained the alkoxyamine moiety derived from **3** as the end group (Table 2, entry 1). By increasing the amount of the end-capping reagent **3**, a decrease of M_n was achieved (entries 2–8). Thus, this approach offers an alternative for rough adjustment of the molecular weight. Importantly, upon increasing the concentration of **3**, a gradual decrease of formation of polymers of type **2a** was observed and at higher loadings of **3**, **2a** was not identified. The only polymers formed under these conditions were **4**-I and **6**. Overall yield remained nearly constant in these polymerizations, and the PDI gradually decreased upon increasing the loading of **3**.

To study the scope of the novel polyarene synthesis, other monomers were then tested. Under optimized conditions, the more electron-rich poly(m-phenylene) 7 was successfully

prepared from the corresponding iodoaryl magnesium derivative (Scheme 4). The method also allowed the synthesis of the chiral poly(*m*-phenylene) $\mathbf{8}$,^[16,17,25] and random copoly-



Scheme 4. Poly(arenes) 7–11 prepared by S_{RN}1-type polymerization.

mers consisting of *m*-phenylene and *p*-phenylene moieties were successfully obtained (9). Interestingly, NMR analysis of polymer 9 (see the Supporting Information) revealed that the monomer composition (3:1) used is well-reflected in the polymer composition. Therefore, rate constants of the reaction of the two different growing aryl radicals with the two different aryl Grignard reagents are similar. For preparation of 7 and 8, the TEMPO method provided better results as compared to the air-initiated processes.

Poly(*p*-phenylene) synthesis turned out to be more challenging. To solubilize the polymer, we had to install an alkyl group, and to ensure regioselective metalation we chose an alkylated iodobromoarene as substrate. Iodine-magnesium exchange on 4-bromo-1-iodo-2-octylbenzene with *i*PrMgCl provided the corresponding aryl magnesium derivative, which compared to **1a** was far less reactive for steric reasons. Another problem is the generally less efficient halide elimination in bromoaryl radical anions as compared to iodide elimination in the corresponding iodoarylradical anions. Nevertheless, polymerization was achieved upon heating the reaction mixture to 70 °C and poly(*p*-phenylene) **10** was obtained in 41% yield with M_n of 4100 gmol⁻¹. Initiation with TEMPO was less efficient in that case.^[26] We were pleased to find that highly fluorescent poly(naphtha-lene)^[27] **11** was successfully prepared by this novel method.

In conclusion, we have introduced a novel method for preparation of polyarenes. The process, which occurs by an alternating radical/anionic chain growth polymerization, does not require any transition metal. Initiation can be achieved either by traces of air or upon adding the commercially available TEMPO radical. Polymerizations are experimentally easy to conduct. In contrast to known anionic chaingrowth polymerizations, strict exclusion of moisture is not necessary to run these reactions. The process has been successfully applied to the preparation of poly(m-phenylenes), poly(p-phenylenes), and a polynaphthalene, which are interesting compounds in materials science, documenting the potential of the novel approach. The polyarenes thus obtained contain an iododaryl moiety at one terminus of the polymer chain. This functional chain end is readily chemically further transformed, as documented by successful metalation of the polyarene with subsequent oxidative homo and cross-coupling. Furthermore, end-group tailoring can be achieved upon polymerizing the anionic monomer in the presence of an aryl Grignard reagent, which lacks the ionic leaving group (capping reagent). M_n and PDI of the resulting polyarenes decrease upon increasing the concentration of the capping reagent. At higher concentration of the capping reagent, complete capping was achieved. Future studies will be devoted to identify an improved initiation method and to further extending the anionic/radical S_{RN}1-type polymerization process towards the use of other anionic haloarenes as monomers.

Received: July 30, 2012 Revised: September 19, 2012 Published online: October 29, 2012

Keywords: chain-growth polymerization · Grignard reagents · oligoarenes · radical anions · TEMPO

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