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Controlling molecular weight and polymer architecture during the Passerini three component step-growth polymerization†

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A new approach to control the molecular weight and polymer architecture using the Passerini three-component step-growth polymerization is described. Starting from an AB-type monomer, linear homopolymers, diblock copolymers, as well as star-shaped polymers were synthesized in an efficient manner. By varying the ratio of the AB-type monomer and a suitable irreversible chain transfer agent (ICTA), different polymer architectures with specific molecular weights and high end-group fidelity were obtained.

In order to obtain better control over the material properties of polymers, it is essential to synthesize polymers with well-defined structures.¹ Usually, living/controlled polymerization techniques, such as RAFT (reversible addition-fragmentation chain transfer) or ATRP (atom transfer radical polymerization), which are the most extensively studied controlled radical polymerization techniques, or anionic polymerization are used to prepare well-defined macromolecular architectures.² However, well-defined polymers were also synthesized *via* polycondensation reactions by using monomers that selectively react with the polymer chain ends.^{3–5} For instance, our group synthesized defined macromolecular architectures using head-to-tail ADMET (acyclic diene metathesis) polymerization.^{6,7} This synthesis procedure was accomplished by taking advantage of the different reactivities of terminal double bonds and acrylates in olefin metathesis reactions.⁸

Recently, multicomponent reactions (MCRs) have been introduced to the field of polymer science as straightforward polymerization technique with a step-growth character.⁹ This type of reaction is performed with more than two starting materials in one-pot and leads to functional materials in a straightforward fashion. In polymer chemistry, isocyanide-based multicomponent reactions (IMCRs), such as the Passerini three-component reaction (Passerini-3CR), are often used.^{10,11} For instance, by using bifunctional components, a

polymerization process is induced and substituted polyesters, polyamides, or poly(ester amide)s are obtained.^{12–14} Furthermore, with AB-type bifunctional monomers, it is possible to perform the reaction with only two components, which leads to an easier and more efficient polymerization process.^{15,16} It is also possible to synthesize multi-block copolymers with sequence-ordered sidegroups.¹⁷ Moreover, several applications of metal-catalyzed MCRs are described in polymer chemistry.^{18,19}

This work focusses on the synthesis of well-defined polymer architectures employing the Passerini-3CR as polymerization technique. The approach relies on the use of a monocarboxylic acid as an irreversible chain transfer agent (ICTA) in combination with bifunctional monomer **3** and an isocyanide to achieve control over the molecular weight (Scheme 1).

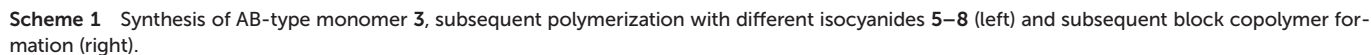
The thus resulting carboxylic acid end-group subsequently allows the synthesis of block copolymers. Moreover, the use of a tricarboxylic acid as core unit should result in the formation of star-shaped homo- and copolymers. Thus, an AB-type monomer, containing a carboxylic acid and an aldehyde unit, was prepared (**3**, Scheme 1) by a thiol–ene reaction of 10-undecenal **1** and 3-mercaptopropionic acid **2**.¹⁵ This type of AB-monomer was chosen for practical reasons discussed previously.¹⁵

The Passerini polymerization of monomer **3** was then performed in dichloromethane (DCM) at room temperature using four different isocyanides (**5–8**, Scheme 1) with a ratio of monomer **3**:isocyanide **5–8**:10-undecenoic acid **4** of 20:100:1. 10-Undecenoic acid **4** served as ICTA. Molecular weights of the obtained polymers were measured by SEC and additionally calculated from ¹H NMR data. If this process proceeds as anticipated, monomer **3** as well as the formed oligomers of **3** and the respective isocyanide would add irreversibly to **4** (and later on growing polymer chains) until all monomer is consumed and the molecular weight would be predetermined by the ratio of **3**:**4**, comparable to the monomer: initiator ratio in controlled/living polymerizations. Indeed, for all investigated isocyanides **5–8**, the expected molecular

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To further demonstrate the control over the molecular weight using this method, different ratios of AB-type monomer **3** and ICTA **4** (10 : 1 to 40 : 1) were investigated (Fig. S1†). It was shown that the molecular weights of the resulting polymers

To extend this study, ICTA **4** was replaced by a trifunctional core unit **9**, which should result in the formation of a star-shaped homopolymer and subsequently a star-shaped copolymer (Scheme 2). The Passerini polymerization was performed with *tert*-butyl isocyanide **5** and AB-type monomer **3** with a ratio of monomer **3**:isocyanide **5**:trimesic acid **9** of 60:300:1.

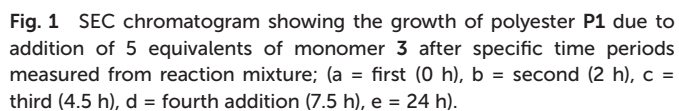


Table 1 Molecular weights of polyesters **P1** and **P5–P7** obtained by using different ratios of monomer **3** and ICTA **4** (determined by ^1H NMR and SEC)

Polymer	Ratio [3] : [4]	M_n calc. [g mol ⁻¹]	M_n NMR [g mol ⁻¹]	M_n SEC [g mol ⁻¹]	\bar{D} M_w/M_n
P5	10 : 1	3760	4146	9100	1.60
P1	20 : 1	7335	7377	12 000	1.51
P6	30 : 1	10 911	10 997	14 200	1.40
P7	40 : 1	14 486	14 515	15 700	1.37



Scheme 2 Synthesis of star-shaped homopolymer **P10**, subsequent copolymerization with benzyl isocyanide **8** (left) and activation of the end group with CDI **10** (right).

Subsequent SEC analysis revealed this time lower molecular weights than the theoretical calculation, which is typical for star-shaped polymers (Fig. S3†). ^1H NMR analysis of star-shaped homopolymer **P10** indicated complete conversion of the ICTA by a slight shift of the aromatic protons **a** of the core unit compared to the protons of trimesic acid **9** (Fig. 2, top). With a ratio of 60:1 (AB-type monomer **3**:core **9**), full monomer conversion was detected by ^1H NMR. The ratio of the protons **a** of the core, to the protons **b** and **c** of the arms, confirmed this assumption. This star-shaped polyester **P10** was chain-extended by a further Passerini reaction with benzyl isocyanide **8** under the same reaction conditions, leading to star-shaped block-copolymer **P11** (Fig. 2, middle). While the first block still exhibits 20 monomer units, the second block was synthesized with a ratio of 10:1 (AB-type monomer **3**:

homopolymer **P10**). This leads to an overall ratio of the two blocks of 20:10, which was confirmed by the integrated signal of protons **b-c** and **d-g**.

In order to investigate the reactivity and end-group fidelity of the carboxylic acid end groups, **P10** was activated with carbonyldiimidazole **10** (CDI). The reaction was carried out in DCM at room temperature for one day to obtain polyester **P12**. The modification of the end group with CDI was verified by ^1H NMR analysis (Fig. 2, bottom). The ratio of the protons **e**, **d** and **f** to protons **a** of the core unit indicate full conversion of the end groups. This proves that the carboxylic acid chain ends are still reactive and further modifications can be carried out.

In summary, a new approach for the synthesis of polymers with defined macromolecular architecture by a non-classic step-growth polymerization technique was demonstrated. An AB-type monomer containing an aldehyde and carboxylic acid moiety was synthesized and polymerized in a Passerini reaction with four different isocyanides and an ICTA. With this simple polyaddition process, α -amide substituted polyesters with controlled molecular weights were synthesized. Furthermore, diblock copolymers, star-shaped homo- and copolymers could be synthesized in this way. Analysis by NMR as well as GPC-ESI-MS clearly confirmed the structures of the investigated polymers and strongly indicated the absence of cyclizations or other side-reactions. By modifying the carboxylic acid end group, further reactions can be performed on the polymer to tune the properties of these materials. The described strategy offers a variety of straightforward new possibilities for the design of defined polymer architectures.

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Fig. 2 ^1H NMR spectra of star-shaped homopolymer **P10**, star shaped copolymer **P11** and esterified star-shaped homopolymer **P12**.



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