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## Controlled/living polymerization towards functional poly(*p*-phenylene vinylene) materials†

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Poly(*p*-phenylene vinylene)s (PPVs) are an important class of highly fluorescent polymeric semiconductor materials. Despite their somewhat declining use in optoelectronic applications, PPV synthesis routes were in recent years significantly improved towards controlled/living polymerization. In this way, nowadays well-defined PPV structures that can be implemented in advanced polymer structures have become accessible, finding a potential application in new fields of research. This review summarizes the advances made and the types of polymers that have recently become available. Most notably, two polymerization approaches are compared, living polymerization towards well-defined PPVs *via* ring-opening metathesis polymerization (ROMP) and chain-transfer radical and anionic polymerization in the so-called sulfinyl precursor polymerization route.

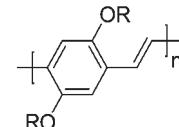


Fig. 1 General structure of poly(*p*-phenylene vinylene)s (PPVs).

## 1. Introduction

Since the discovery of polyacetylene as the first type of pi-conjugated polymer material in the 1970s,<sup>1</sup> a broad variety of (semi)conducting polymer materials were developed.<sup>2–5</sup> With plastic electronic applications such as organic light emitting diodes (OLEDs)<sup>6</sup> and organic photovoltaics (OPVs),<sup>7–12</sup> these materials found a secure position in innovative electronic applications and devices. Among the most common types of conjugated polymer materials, the class of poly(*p*-phenylene vinylene) (PPV) polymers play a special role.<sup>13,14</sup> PPVs are robust polymers that are comparatively simple in their synthesis and well-reproducible in their physical characteristics (depending on the substituents on the 2 and 5 positions at the phenyl core). While initially interesting for their electroluminescent properties (the first OLED was made from PPV material),<sup>15,16</sup> their use in optoelectronics has strongly declined over the past years due to their somewhat lower performance in photovoltaic devices, compared to the use of *e.g.* pyrrole-based structures (Fig. 1).<sup>17</sup>

However, the synthesis of PPVs has been well studied and a broad variety of synthesis techniques have been developed to date, making PPVs very valuable as work-horse materials.<sup>18</sup>

Next to step-growth procedures, which mostly provide oligo(*p*-phenylene vinylenes),<sup>19–22</sup> most predominantly chain-growth polymerizations are used to obtain PPVs with moderate to high molecular weight, ranging between 4000 g mol<sup>−1</sup> to 100 000 g mol<sup>−1</sup>.<sup>23</sup> Since the direct synthesis of PPV is often tedious, in many cases so-called precursor polymerization routes are employed,<sup>24,25</sup> in which a precursor polymer is obtained from an initial polymerization, then converted into the conjugated polymer in a post-polymerization step. As mentioned above, all these synthesis methods are comparatively popular and straightforward in use; however, with only one notable exception (metathesis polymerization),<sup>26</sup> reactions are fully uncontrolled. Uncontrolled means in this respect that no or only insufficient control over molecular weight is achieved, that end-groups of the polymers are not well defined and that dispersity is often high. As long as the main application of PPV was in optoelectronics, this was not an issue. For these applications, mechanical and optical properties (specifically the band gap) are of importance, thus ideally requiring good control over chain defects and microstructure but less over molecular weight and end-group functionalities.<sup>27</sup> Functionality – when required – was usually introduced *via* attachment of side-chains at the 2 and 5 positions of the phenyl ring, which is also required to keep PPVs soluble and hence

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processable.<sup>28,29</sup> Although controlled synthesis of PPVs for optoelectronic applications could be of interest from a fundamental point of view,<sup>30</sup> the major focus in this review is placed on biomedical application-driven controlled synthesis of PPVs.

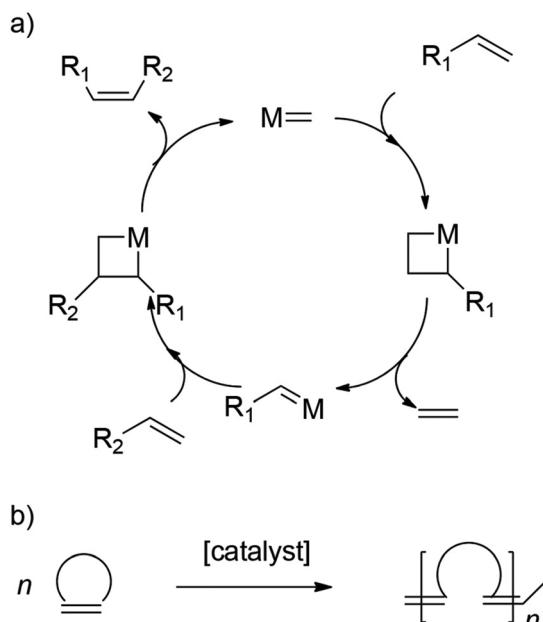
As PPVs and their derivatives have been mostly replaced in electronic applications, the question arises whether they can be used in other fields of application as well. An outstanding feature of PPVs is their inherent fluorescent properties,<sup>31–33</sup> hence PPVs are excellent candidates for biomedical applications, where fluorescent properties are used broadly for imaging and in fact, a steep rise in the usage of conjugated polymers in bioimaging and theranostic applications has been seen in recent years.<sup>34–40</sup> PPVs play a prominent role here due to their good performance with respect to fluorescence but also due to their high reliability in properties (good reproducibility of polymerizations, especially when using micro-reactor technology)<sup>41</sup> and the relative purity in which they are obtained, in the absence of toxic catalysts and heavy metals. However, in order to employ these materials in biomedical research, their complexity and functionality must be inherently increased. To interact in – or to mimic – biological processes and environments, the ability to self-assemble is required, as is the potential to efficiently couple bioreceptors or other materials to the conjugated materials. In other words, controlled/living polymerization strategies have become a necessity for the further evolution of conjugated polymers. For various types of conjugated polymers, living polymerization strategies such as, for example, the Grignard metathesis polymerization (GRIM), were introduced,<sup>42</sup> which gives access to complex block copolymer structures and which allows chain-end functionalization of polymer chains.

Here, we now focus on the strategies that can be used to control polymerizations leading to PPVs, namely on the ring-opening metathesis polymerization (ROMP) and the so-called anionic and radical precursor polymerization routes. This review is hence an update on a summary of (uncontrolled) PPV polymerization techniques that our group published a few years ago.<sup>18</sup>

## 2. Controlled synthesis of PPVs

### 2.1 Ring-opening metathesis polymerization

Ring-opening metathesis polymerization (ROMP) is a chain-growth polymerization process where unsaturated cyclic olefins are converted into polymeric materials. The reaction is based on olefin metathesis, a process that found its origin in the 1950s.<sup>43–48</sup> Here, a metal–carbene (alkylidene) complex undergoes reversible [2 + 2] cycloadditions with olefins, thereby completing metathesis *via* metallacyclobutane intermediates, as shown in Scheme 1.<sup>49,50</sup> When employing ring-strained cyclic alkenes, olefin metathesis leads to a polymerization in which the cyclic monomers are converted into linear polymers with unsaturated C=C bonds being built into the main chain. ROMP is a widely used polymerization technique for the controlled synthesis of (complex) polymer



**Scheme 1** (a) Simplified olefin metathesis mechanism and (b) conversion of cyclic alkenes to polymers in ROMP.

architectures, giving access to a broad variety of interesting materials. A variety of catalysts as well as monomers are employed, with the Grubbs and Schrock catalyst as well as the norbornene monomer (NBE) and its derivatives being the most prominent ones.<sup>51,52</sup>

**ROMP mechanism applied to the synthesis of PPVs.** With respect to conjugated polymers, ROMP features a significant advantage: *via* the olefin metathesis reaction, a vinylic bond is directly obtained in the main chain of the polymer. Hence, the pi-conjugated main-chain structure of PPV can in principle be directly made available *via* ROMP. In fact, polyacetylene can be accessed *via* ROMP of cyclooctatetraene.<sup>53</sup> Over the last few decades, PPVs have mainly been synthesized by the polymerization of a bis(halomethyl) benzene *via* the addition of a strong base (e.g. *N*atBuO or LiHMDS; see section 2.2).<sup>18</sup> Still, several attempts have been made to use ROMP for the synthesis of PPVs. In principle, a relatively high synthetic effort is required to reach this goal as monomer synthesis is tedious. Yet, ROMP is inherently a living polymerization process (if transfer reactions are absent) and not only is the conjugated polymer system directly accessed by ROMP, but also block copolymers and high-end-group functionality can be directly achieved. The first research in this field was performed by Kumar *et al.*,<sup>54</sup> in which 1,4-divinylbenzene was treated under vacuum using a tungsten alkylidene Schrock catalyst,<sup>55</sup> yielding an insoluble PPV oligomer in good yields and with low molecular weight (degree of polymerization, DP<sub>n</sub>, of 6). A follow-up of this work by Fox *et al.*<sup>56</sup> confirmed the insoluble character of PPV oligomers with DP<sub>n</sub> > 4. These solubility issues can mainly be overcome by using diene-like monomers – see Table 1, entry 1 – as shown by Conticello *et al.*<sup>57</sup> They managed to synthesize PPVs *via* an indirect precursor approach, yielding molecular weights



Table 1 Overview of monomers used for PPV synthesis via ROMP<sup>a</sup>

No.	Monomer structure	Catalyst	$M_n^{\text{APP}}/\text{g mol}^{-1}$	$D$	Isomerism	Ref.
1		2 <sup>nd</sup> generation Schrock catalyst	46 000	1.23	Alternating <i>cis</i> and <i>trans</i>	56
4		2 <sup>nd</sup> generation Schrock catalyst	63 000	1.34	<i>cis</i>	57
5		2 <sup>nd</sup> generation ruthenium catalyst	5000	1.22	Alternating <i>cis</i> and <i>trans</i>	58
6		3 <sup>rd</sup> generation ruthenium catalyst	25 000 10 550 26 210	1.21 1.30 1.32	Alternating <i>cis</i> and <i>trans</i>	59

<sup>a</sup> All data given in here are associated with a certain error with respect to  $M_n$ ,  $M_w$  and  $D$  values, as no precise Mark–Kuhn–Houwink–Sakurada (MKHS) parameters are available.

of 46 000 g mol<sup>-1</sup> and a dispersity ( $D$ ) of 1.23. Synthesis of this bicyclo[2.2.2]octadiene monomer (**1**) starts with a Diels–Alder reaction between the acetonide adduct of 3,5-cyclohexadiene-*cis*-1,2-diol and ethynyl *p*-tolyl sulfone. Reductive desulfonation of the anti cycloadduct, followed by acid-catalyzed hydrolysis yields a bicyclic diol, which can be converted into the desired biscarboxylate derivatives using Friedel Crafts acylation. Controlled polymerization of monomer **1** at room temperature using an olefin metathesis catalyst – [Mo(=NAr)–(=C(H)CMe<sub>2</sub>Ph)–(OCMe<sub>2</sub> (CF<sub>3</sub>))<sub>2</sub>] (Ar = 2,6-diisopropylphenyl) – is possible, yielding an intermediate with alternating *cis* and *trans* vinylene units (Fig. 2, structure **2**). In the next step, thermolytic conversion enables a facile way to synthesize PPVs (**3**).

<sup>1</sup>H and <sup>13</sup>C NMR spectra of the microstructure indicated that the polymer consists of the expected equal distribution of *cis*- and *trans*-vinylene units. The configuration of the metal complex inverts with each insertion of monomer, leading to an almost equal distribution of *cis* and *trans* vinylene units, with a small preference towards the *trans* distribution due to the preferred geometry of the methoxycarboxyl groups. Over the years, a variety of catalysts and monomers have been developed, by which control over microstructure became available. One example used similar reaction conditions and initiators as described above but a different type of monomer (see Table 1, structure **4**), leading to a rare case of an almost pure *cis* adduct (98%). Under a flow of HCl(g) and a temperature of 190 °C, the

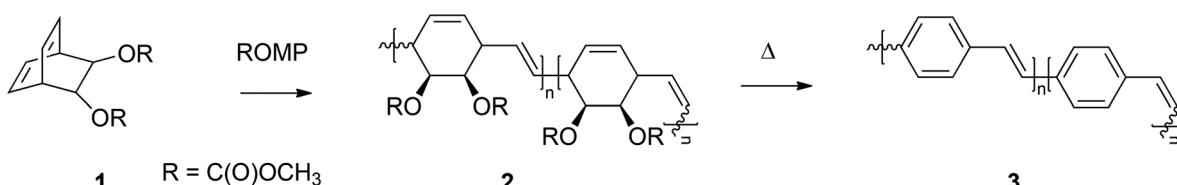


Fig. 2 Precursor route using ROMP towards the synthesis of conjugated PPVs.



*cis*-ROMP product is, however, conveniently converted into the preferred *trans*-PPV, as confirmed by UV spectroscopy ( $\lambda_{\text{max}} = 424$  nm) and the appearance of a strong absorption in the IR spectrum at  $963\text{ cm}^{-1}$ .<sup>58</sup>

Generally it could be observed that the optical properties of PPVs strongly depend on the microstructure of the material. An alternating pattern in microstructures – similar built-in *cis* and *trans* adducts – will lead to higher electroluminescence efficiencies, as the folded *cis*-vinylene linkages reduce the interchain fluorescence-quenching reactions.<sup>59</sup> As a result, the use of a 2<sup>nd</sup> generation Grubbs catalyst in combination with [2.2]paracyclophanedienes (5) leads to soluble PPV homopolymers of well-defined molecular weight and alternating microstructure. The living character was tested by the addition of a second batch of monomer, thereby increasing the molecular weight but maintaining similar low  $D$  values. Similar microstructures were obtained using microwave-assisted ROMP in combination with a 3<sup>rd</sup> generation Grubbs catalyst. The monomer, 4,12-di-2'-ethylhexyloxy-7,15-dimethoxy-[2.2]paracyclophane-1,9-diene (6), was synthesized using a two-step mechanism with a Wittig rearrangement, followed by a Hofmann elimination. Polymerization of monomer 6 for 1 h at 80 °C using microwave irradiation – compared to the 36 h needed to reach full conversion using conventional heating – indicated the benefits of microwave assisted polymerization. Molecular weights of up to 26 000 g mol<sup>-1</sup> in combination with a  $D$  of 1.32 underpinned the livingness of the polymerization. In the next step, pure *trans*-PPV could be obtained by prolonged irradiation of the product at 365 nm in THF, leading to maximum conversions of 95% *trans* product for reaction times of up to 36 h.<sup>60</sup>

Until now, all PPV homopolymers that were synthesized by ROMP predominantly led to solubility issues with regard to analysis or processing of the materials. Tackling these solubility issues was mainly done by adjusting monomer structures and by the introduction of solubilizing side chains (Table 1, entry 4). However, another approach is to synthesize PPV-containing block copolymers as was first shown by Miao *et al.*<sup>58</sup> Herein, PPVs were chain-extended with norbornadienes (NBE), leading to macromolecular structures containing 16% of PPV built into the chain, typical molecular weights of 26 000 g mol<sup>-1</sup> and dispersity values of 1.1 for the resulting copolymer. Lower molecular weight, soluble PPV-materials with negligible interference in the light absorption properties and mechanical flexibility of the material – due to the built-in NBE – were obtained. Similar research was performed by Bazan *et al.*<sup>61</sup> where PPVs were chain-extended with 2,3-bis(trifluoromethyl) norbornadienes, leading to PPV-*b*-PNBE block copolymers (Fig. 3, left structure). In this way, soluble PPV<sub>20</sub>-*b*-PNBE<sub>200</sub> was synthesized, for which unfortunately no information about the photophysical properties of the block copolymer was reported. Lately, Porz *et al.*<sup>62</sup> also increased the solubility of PPV chains by block copolymerization with NBE (Fig. 3, right structure). Employment of a double ROMP approach led first to the polymerization of NBE monomer, after which chain extension with PPVs led to the desired PPV-*b*-PNBE block copolymers. GPC results for the block copolymer indicated molecular

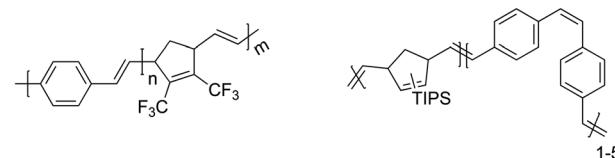


Fig. 3 Chemical structures of PPV block copolymers with NBE-type monomers.

weights of 28 500 g mol<sup>-1</sup> with a  $D$  of 1.8. Incorporation of roughly 1–5 PPV units was achieved in this work, which corresponds to a maximum of 2000 g mol<sup>-1</sup> for the PPV unit. A comparatively higher polydispersity of 1.8 was associated with undesired cyclization reactions. UV-Vis and fluorescence analysis showed a redshift in the absorption as well as emission spectrum after copolymerization of the PPV with NBE. Furthermore, analysis of the quantum yield revealed a significant decrease (0.12 instead of 0.68), clearly showing the negative effect of copolymerization on the photophysical properties of PPVs. Although significant changes in the photo-optical properties with respect to the PPV materials was obtained, chain extension of PPV on NBE did lead to the desired solubility for the PPV materials. Turner *et al.*<sup>63</sup> demonstrated that it is possible to synthesize PPV homopolymers containing an  $\alpha$ -bromo-ester *via* ROMP. Reactivation of the bromine end-group using atom transfer radical polymerization (ATRP) reaction conditions in combination with methyl methacrylate (MMA) as monomer, led to the well-defined synthesis of PPV-*b*-PMMA copolymers.<sup>64</sup> A variety of PPV homopolymers with a  $M_n$  of 22 800 g mol<sup>-1</sup> and a  $D$  of 1.44 was successfully chain-extended with MMA, to yield apparent  $M_n$  values of 54 500 g mol<sup>-1</sup> and a somewhat lower  $D$  of 1.32. In addition, results for absorbance, emission and quantum yield indicate no significant change in the PPV characteristics upon di block copolymer formation. Hence, the PPV-conjugated backbone is not affected by the ATRP reaction conditions.

Thus, as shown, ROMP can be efficiently used to access PPVs with all the features of a living polymerization. Block copolymerizations are, at least to date, limited to block extensions *via* ROMP – hence limiting the choice of available materials. At the same time, accessibility of the cyclic monomers is relatively low, which probably explains why the ROMP route is – compared to other synthesis pathways – not studied in high detail. Despite these disadvantages, the technique has high potential.

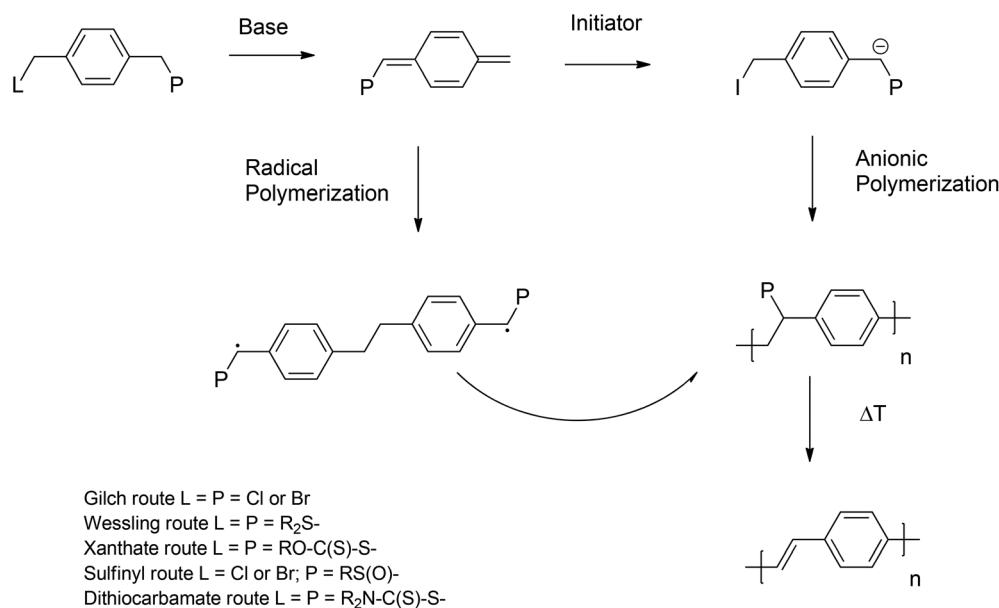
## 2.2 Radical and anionic polymerization

As already mentioned above, PPV materials are accessible *via* step growth (direct routes) or chain growth (indirect or precursor route) mechanisms. Extensive work on the so-called 'direct' routes – all step growth and hence inherently non-living – has been performed over the last decades, employing Wittig,<sup>65–67</sup> Horner,<sup>64,68</sup> McMurry,<sup>69,70</sup> Knoevenagel<sup>71,72</sup> and Siegrist<sup>73</sup> polycondensation reactions or the palladium-catalyzed Heck,<sup>74,75</sup> Stille<sup>76</sup> and Suzuki<sup>77</sup> coupling reactions.

To overcome the inherent drawbacks of step-growth polymerization (limited molecular weight, necessity for high functional conversions), the so called ‘indirect’ or ‘precursor’ quinodimethane routes were introduced (see Scheme 2), resulting in high-molecular-weight polymers, which were relatively easy and cost effective to synthesize.<sup>23</sup> Precursor routes follow a chain growth mechanism, which in principle could be employed to ultimately achieve living polymerization reaction conditions. Polymerization proceeds starting from a premonomer, which upon the addition of a base forms an actively polymerizing *p*-quinodimethane monomer species.<sup>78</sup> The *in situ*-formed monomer spontaneously polymerizes *via* biradical formation, which then follows for most parts a classical free-radical polymerization (FRP) pathway, leading to precursor polymers (see Scheme 2). In a second step, thermal elimination of the precursor polymer yields the formation of the desired conjugated polymer.<sup>79,80</sup> Different ‘precursor’ routes were established, depending on the choice of leaving group (L) and polarizer (P) attached to the premonomer (Scheme 2). The L group is eliminated from the premonomer and the P group from the prepolymer. Symmetric monomers were employed in the Gilch,<sup>81</sup> Wessling,<sup>82–84</sup> Xanthate<sup>28,85</sup> and dithiocarbamate<sup>86</sup> (DTC) routes, whereas the sulfinyl<sup>87–90</sup> route starts from an asymmetric premonomer. In this way, the polymerization and elimination processes are completely decoupled, allowing full analysis and improved control over the reaction. However, care has to be taken, as complete decoupling of these processes does require carefully selected reaction conditions. In addition, low defect levels as a result of good microstructural control – mainly head-to-tail attachment during the polymerization – were obtained when employing the sulfinyl route, leading to polymers with superior performances with regard to optoelectronic properties.<sup>91,92</sup>

**Discovery of the anionic mechanism.** The sulfinyl precursor route is one of the best studied mechanisms towards the synthesis of soluble and high-molecular-weight PPVs as it allows decoupling of monomer formation from polarizer elimination. The route was developed by Louwet *et al.*<sup>25,86</sup> and ever since, optimization of the route has continued. Polymerization of the premonomer starts with the addition of a base – usually sodium *tert*-butoxide ( $\text{Na}^+\text{BuO}^-$ ) – to the aprotic *N*-methyl-2-pyrrolidone (NMP) as solvent. Polymer analysis often reveals bimodal product distributions, indicating strong competition between a radical (high-molecular-weight part) and an anionic (low-molecular-weight part) polymerization mechanism (see Fig. 4 and 5).<sup>86,93,94</sup> Both pathways enable the formation of a *p*-quinodimethane system after the addition of a base. In the anionic route, the base acts not only as a supplement to form the active monomer species but also as an anionic chain initiator, whereby chains will grow until all the monomer has been consumed. The anionic pathway is thus of a living nature. The radical pathway is inherently uncontrolled due to the absence of any control agent (*e.g.* halocarbon chain transfer agents).

Initially, the low molecular weight material was considered simply as a side product and was removed from the desired high-molecular-weight material by selective precipitation. Only later, investigations into the polymerization mechanism of the sulfinyl route led to the discovery that the type of solvent and base used during the polymerization can suppress either the radical or anionic pathway, leading to monomodal distributions in the product mixtures.<sup>95</sup> Polymerizations in *sec*-butanol, using  $\text{Na}^+\text{BuO}^-$  as base, led to a purely radical polymerization mechanism with high-molecular-weight polymers ( $M_n > 50\,000 \text{ g mol}^{-1}$ ). Under these conditions, anionic polymerizations cannot proceed due to the protic solvent. The polymer-

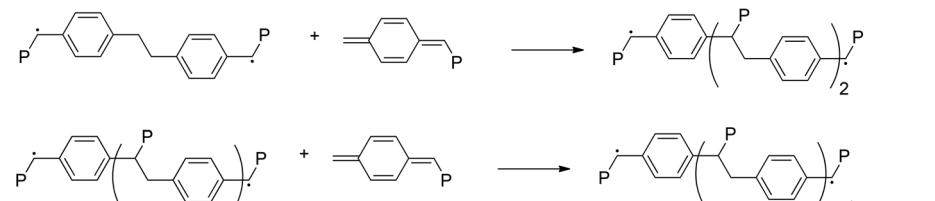


**Scheme 2** General scheme for the synthesis of PPVs using quinodimethane ‘precursor’ routes.

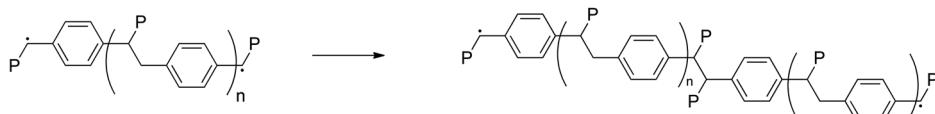


## Radical Pathway

## Chain Initiation and Propagation



## Recombination



## Anionic Pathway

## Propagation

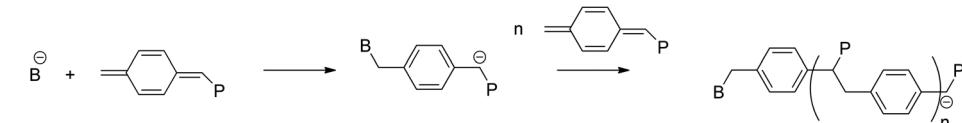
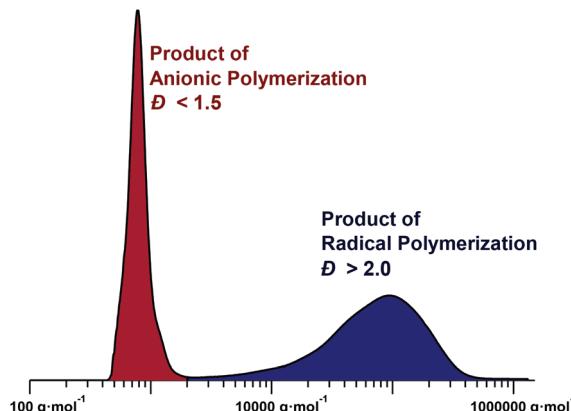
Fig. 4 The most important reactions in the mechanisms of *p*-quinodimethane polymerization in the radical or anionic pathway.<sup>40</sup>

Fig. 5 Typical GPC chromatogram for the polymerization of a sulfinyl premonomer in NMP (right peak product of radical polymerization, left peak product of anionic polymerization). See ESI† for experimental details.

ization showed an increase in yield with increasing temperature, which can be interpreted as a direct result of an increasing initiation and propagation rate, compared to the termination rate.<sup>18</sup> At the same time, a decrease in molecular weight was also observed, which can again be linked to higher initiation rates. In addition, the effect of the monomer concentration on the polymerization was investigated. The results clearly indicated no significant difference in molecular weight upon increasing the monomer concentration, verifying the self-initiation character of the reaction. Addition of a second batch of monomer during the polymerization revealed no

increase in molecular weight, confirming that the reaction is effectively non-living. The radical nature of the polymerization was ultimately proven by the addition of a radical scavenger, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO). In the presence of TEMPO, no polymerization occurred at all when aprotic solvents were used.<sup>94–97</sup>

In contrast, a purely anionic polymerization pathway is followed if the reaction conditions are adjusted carefully. In principle, in order to achieve anionic polymerization conditions, radical formation must be suppressed and a base or anionic initiator must be used that is able to effectively start chain growth at a balanced rate (too-fast initiation will favour oligomer formation rather than polymerization as the base is necessarily present in molar excess to facilitate premonomer elimination). A variety of bases –  $\text{Na}^+\text{Bu}_3\text{O}^-$ , lithium diisopropyl amide (LDA) and lithium bis(trimethylsilyl) amide (LiHMDS) – were tested in aprotic solvents, leading to the sterically hindered LiHMDS as the most suitable base. The latter showed a reduction in the rate of initiation – due to steric hindrance – leading to PPVs of significant molecular weight. THF was chosen as the optimal solvent as it is able to stabilize the anionic chain ends sufficiently and under these conditions, THF in combination with LiHMDS, an exclusively anionic pathway for the synthesis of PPVs *via* the sulfinyl route could be achieved. Verification of the anionic character was tested by adding TEMPO, which in this case did not quench the polymerization; see Table 2 for a collation of quench tests for the various polymerization pathways. Why no radical polymerization occurs in THF with LiHMDS is not fully clear; it can, however, be speculated that the anionic polymerization is



**Table 2** Verification of the anionic character of the polymerization of PPVs with LiHMDS as base and THF as solvent<sup>a,b</sup><sup>94</sup>

Base	Solvent	Additive	$M_w^{\text{APP}}$ /g mol <sup>-1</sup>	$D$	Yield %
NatBuO	sec-BuOH	None	208 400	4.0	52
NatBuO	sec-BuOH	TEMPO	9800	1.4	<1
NatBuO	THF	None	1 324 100	6.9	79
NatBuO	THF	TEMPO	111 800	2.7	21
LiHMDS	THF	None	43 300	2.5	84
LiHMDS	THF	TEMPO	49 400	3.5	82

<sup>a</sup> Reactions are performed at room temperature with  $[M]_1 = 0.05$  M.

<sup>b</sup> Molecular weights shown are for non-eliminated prepolymers.

simply faster than biradical formation from monomer self-initiation. While the radical route proceeds typically within several minutes, anionic polymerizations reach full monomer conversion on a timescale of seconds, often during mixing of the components.

Via the above described methodology, the general mechanisms of precursor polymerizations were elucidated. Moreover, for the sulfinyl route, a choice can be made on the reaction mode based on the solvent and base employed, giving access to much better control over the polymerizations.

**Chain transfer polymerization route.** First, advances towards controlled polymerization for the radical pathway are discussed. Commonly, radical polymerizations are controlled by adding specific control agents to the polymerization that capture the radical species, either in reversible termination reactions or *via* degenerative transfer mechanisms.<sup>99</sup> PPV polymerizations are comparatively fast due to the extremely high initiation and propagation rate, which result from the high driving force required to restore aromaticity from the quinodimethane premonomer. This high driving force complicates any effort to interfere with the polymerization in either control strategy. Furthermore, the biradical character of the initiating species complicates any control scheme. Since self-initiation is incompatible with a reversible termination mechanism, transfer agents need to be employed to reach any control over molecular weight. Only chain transfer agents (CTA) with a similarly high reactivity compared to propagation can be employed, which severely limits the choice of available agents. RAFT and MADIX agents were tested without any success.<sup>100</sup> From the list of conventional CTAs, carbon tetrabromide ( $\text{CBr}_4$ ) is the most promising as it typically shows extremely high transfer rates in classical FRP. In fact,  $\text{CBr}_4$  is able to exert some control over polymerizations following the dithiocarbamate (DTC) and sulfinyl routes. Molecular weight can be adjusted between a few hundred to several tens of thousands of Da without, however, producing a living character in the polymerization. Polymers synthesized *via* the DTC route displayed a decrease in number-average molecular weight ( $M_n$ ) from 98 000 g mol<sup>-1</sup> to 500 g mol<sup>-1</sup> when going from 0 to 8 equiv. of control agent relative to the monomer, respectively. The accompanying chain transfer constant (ratio of kinetic rate coefficient of chain transfer over the propagation rate coefficient) was determined as 0.46, a value lower than typical for

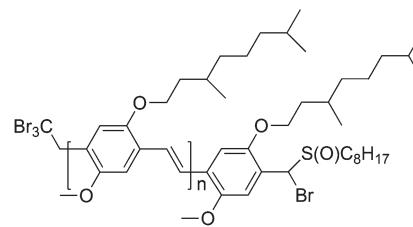
$\text{CBr}_4$  in vinyl polymerizations but still in the range of other CTAs.<sup>97</sup> Controlling the molecular weight of the sulfinyl route, however, appears to be much more difficult, which is reflected in a 100-times lower value for the chain transfer constant; see Table 3. As a result, the molecular weight is not easily controlled, as  $M_n$  values showed a decrease from 89 000 g mol<sup>-1</sup> to roughly only 10 000 g mol<sup>-1</sup> upon the addition of 0 to 12 equiv. of control agent, respectively. Differences in value indicate that the use of  $\text{CBr}_4$  is less favoured in the sulfinyl route or that the rate of propagation of the sulfinyl route is much higher compared to the DTC route. Still, good control over the molecular weight for both routes was established, creating a controlled – yet non-living – radical pathway for the synthesis of PPVs *via* the sulfinyl and DTC routes.

Interestingly, polymers produced *via* the  $\text{CBr}_4$  chain-transfer route feature bromine end-groups in the omega-position; see Fig. 6.<sup>97,101</sup> At the other chain end, a  $\text{CBr}_3$  should be found; to date, however, this could not be confirmed. Nevertheless, the omega end-group bromine is of high interest as this functionality can serve as a macroinitiator in an ATRP chain extension. Based on  $\text{CBr}_4$ -derived PPV with a molecular weight of roughly 10 000 g mol<sup>-1</sup>, several block copolymers were derived *via* reactivation of the chains in the presence of *tert*-butyl acrylate (*t*-BuA) or styrene. In addition, copper-catalyzed azide–alkyne conjugation (CuAAC) (aka click reactions)<sup>102–106</sup> were also tested, since a terminal bromine is easily converted into an azide.<sup>97,100</sup>

First, chain extension of the PPVs with either *t*-BuA or styrene was employed, leading to a PPV-*b*-PtBuA or PPV-*b*-PS block copolymer, respectively. A PPV homopolymer with  $M_n = 6200$  g mol<sup>-1</sup> led after chain extension with 100 equiv. of styrene up to  $M_n$  values of 10 200 g mol<sup>-1</sup> and a dispersity of 1.9 for reaction times of up to 2 h. A similar increase in molecular weight after chain extension was obtained when *t*-BuA was used as monomer.  $M_n$  values of up to 10 900 g mol<sup>-1</sup> and  $D = 1.8$  were achieved for reaction times of up to 2 h when

**Table 3** Chain transfer constants for conjugated PPVs synthesized *via* the sulfinyl ( $T = 30$  °C) and DTC ( $T = 35$  °C) precursor routes<sup>98</sup>

Conjugated PPVs	Chain transfer constant $C_{\text{tr}}$
MDMO-PPV (DTC route)	0.46
MDMO-PPV (sulfinyl route)	0.0038

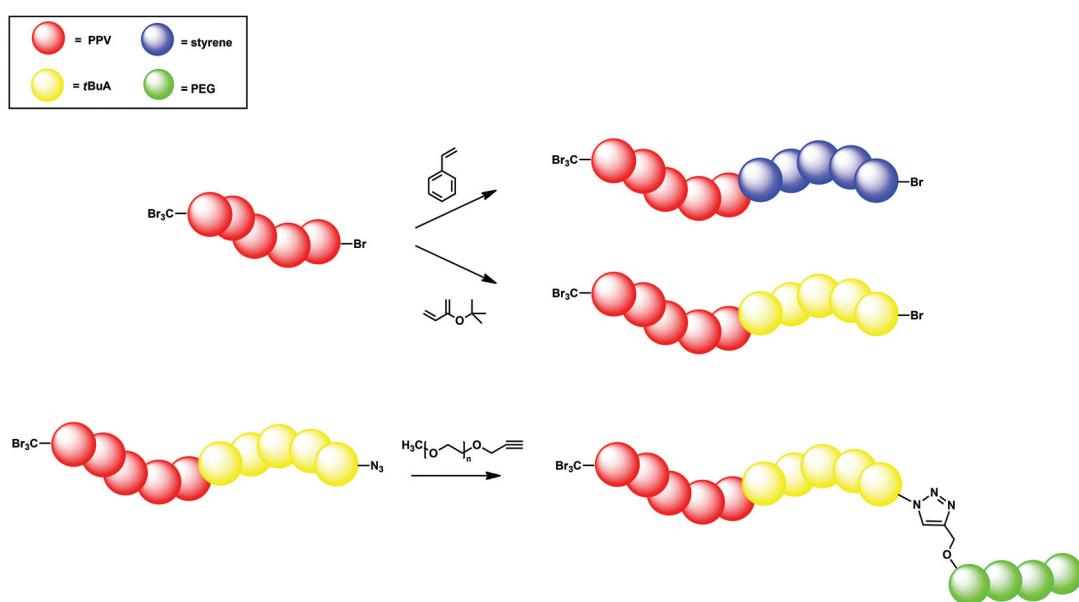
**Fig. 6** Suggested chemical structure of PPV synthesized *via* the radical precursor route using  $\text{CBr}_4$  as CTA.

starting from a PPV homopolymer with  $M_n = 5300 \text{ g mol}^{-1}$  and  $D = 1.9$ . In the next step, the bromine end of the PPV-*b*-*PtBuA* block copolymer ( $M_p = 10\,500 \text{ g mol}^{-1}$ ) was substituted by an azide. CuAAC conjugation with an alkyne-functionalized PEG ( $M_p = 6500 \text{ g mol}^{-1}$ ) led to successful PPV-*b*-*PtBuA*-*b*-PEG tri-block copolymer synthesis with a peak molecular weight ( $M_p$ ) of  $19\,200 \text{ g mol}^{-1}$ . The major drawback of this synthetic route towards PPV block copolymers is the use of preparative recycling methods to remove the excess  $\text{CBr}_4$  after polymerization, as  $\text{CBr}_4$  may act as a co-initiator during ATRP. Still, chain-length control and especially the ability to form more complex macromolecular structures in both sequential and modular design approaches allow PPV segments to be built into any polymer architecture based on this concept (Fig. 7).

**Anionic polymerization route.** While the radical route described above provides facile pathways towards complex PPV materials, the anionic route was also further investigated. With the anionic polymerizations described above, relatively broad molecular weight distributions were obtained, with the average molecular weight being poorly controllable, due to the lack of dedicated anionic initiators. To overcome the above described issue, Neef *et al.* proposed to employ 4-methoxyphenol as the initiator during the anionic polymerization of a Gilch approach.<sup>107</sup> Relatively good control over the polymerization was claimed, as molecular weights decreased from  $125\,700 \text{ g mol}^{-1}$  to  $51\,300 \text{ g mol}^{-1}$  when 2.0 mol% of initiator was used. However, it was demonstrated by others<sup>108</sup> that 4-methoxyphenol rather acts as a radical inhibitor for the Gilch polymerization route. The latter typically undergoes radical polymerization as indicated above. Recently the concept of anionic polymerization was further investigated for the sulfinyl route, using a different set of anionic initiators. For a variety of

monomers and specifically designed anionic initiators – see Fig. 8 for chemical structures – the improvement that can be obtained from using anionic initiators was tested, for which the results are given in Table 4. Polymerizations were carried out in THF as solvent, using LiHMDS as base and a monomer concentration of 0.05 M at  $0^\circ\text{C}$  for 5 minutes.

The anionic polymerization pathway for the sulfinyl route was explored using 1-chloromethyl-2,5-bis(2-ethylhexyloxy)-4-[(methylsulfinyl)methyl] benzene 7 (BEH-monomer),<sup>96</sup> 1-chloromethyl-2-methoxy-5-(3,7-dimethyloctyloxy)-4-[(octylsulfinyl)methyl] benzene 8 (MDMO-monomer),<sup>109</sup> 6-(2-chloromethoxy-5-[(octylsulfinyl)methyl]phenoxy) hexanoic acid methyl ester 9 (CPM-monomer)<sup>108</sup> as monomers and 1-(*tert*-butyl)-4-[(*n*-octylsulfinyl)methyl] benzene 11 as initiator. In addition, 1-bromo-methyl-2,5-dicyano-4-[(octylsulfinyl)methyl] benzene 10 (CN-monomer), in combination with initiator 14 was also tested.<sup>108</sup> Results for the precursor polymer clearly indicate that an anionic pathway is followed, as low molecular weights ( $M_n$  values of roughly  $4500 \text{ g mol}^{-1}$ ) were obtained for MDMO-, CPM- and CN-PPV without the addition of an initiator (Table 4).<sup>96</sup> BEH-PPV showed a somewhat higher molecular weight value ( $M_n = 20\,000 \text{ g mol}^{-1}$ ), which could be related to the chemical structure of the monomer (*e.g.* bulky side chains) or small monomer impurities still present. The use of 25 mmol L<sup>-1</sup> initiator indicated the profound effect of the initiator on the molecular weight and dispersity of all PPVs tested.  $M_n$  and  $D$  values of BEH-PPV decreased from  $20\,000 \text{ g mol}^{-1}$  to  $1400 \text{ g mol}^{-1}$  and 3.2 to 1.8, respectively. Results concerning MDMO- and CPM-PPV, on the other hand, showed a decrease from  $4100 \text{ g mol}^{-1}$  to  $1300 \text{ g mol}^{-1}$  and  $4700 \text{ g mol}^{-1}$  to  $1300 \text{ g mol}^{-1}$  in molecular weight, respectively. The latter effect was also shown for CN-PPV – however less pronounced for lower



**Fig. 7** Schematic of (tri)block copolymers synthesized via the controlled radical sulfinyl precursor route in combination with ATRP (top) and ATRP/click (bottom) reaction conditions.



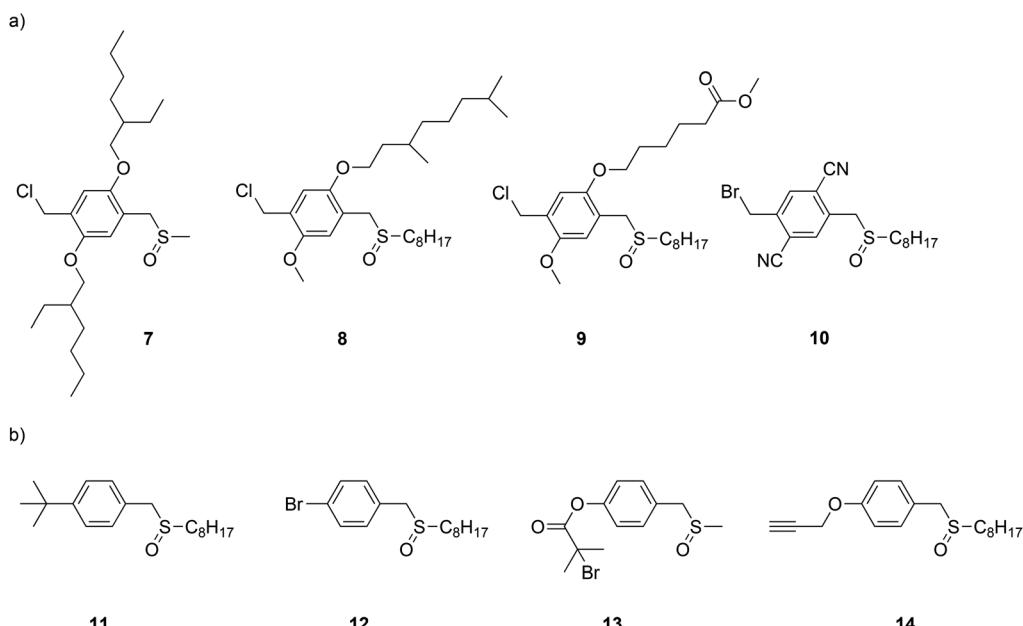


Fig. 8 Chemical structures of monomers (a) and initiators (b) used to date in anionic sulfinyl route polymerizations.

Table 4 Polymerization outcome of anionic polymerizations following the sulfinyl route for a variety of monomers (7–10) with LiHMDS in THF (5 min; 0 °C; [M] 0.05 M)<sup>96,108</sup>

Precursor polymer	[I]/mmol L <sup>-1</sup>	$M_n^{\text{app}}/\text{g mol}^{-1}$	$D$	Type of initiator <sup>a</sup>
BEH-PPV	0	20 000	3.2	11
	5	4100	2.2	
	25	1400	1.8	
MDMO-PPV	0	4100	2.4	11
	5	2600	1.8	
	25	1300	1.2	
CPM-PPV	0	4700	2.9	11
	5	3000	2.1	
	25	1300	1.7	
CN-PPV	0	4900	3.1	14
	5	4600	2.1	
	25	1300	2.0	

<sup>a</sup> Chemical structures are displayed in Fig. 8.

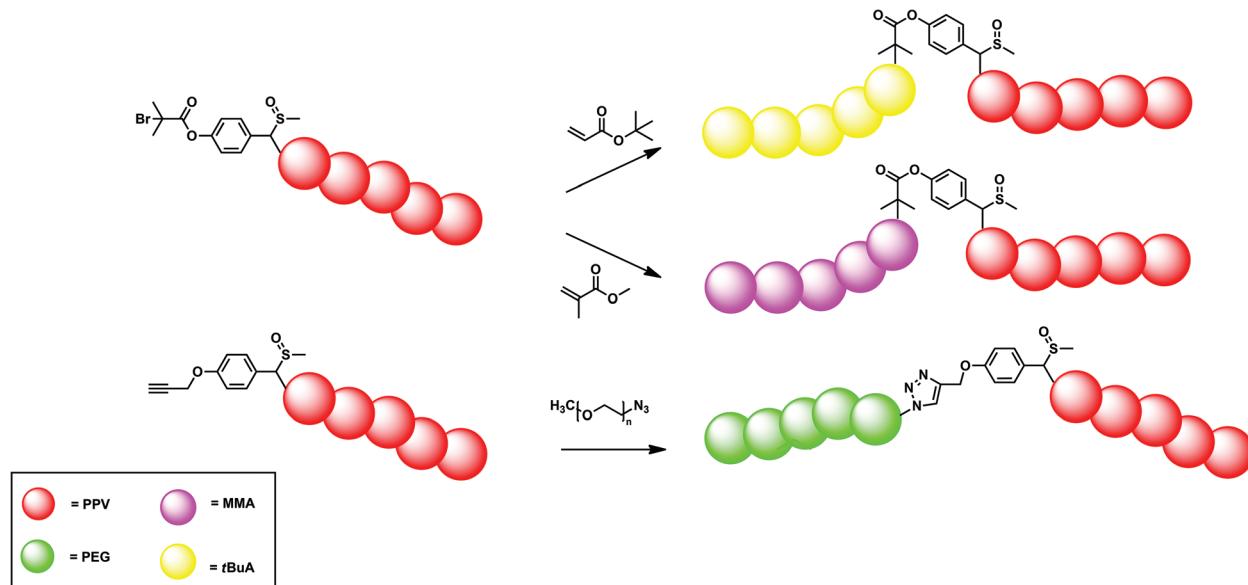
initiator concentrations – as molecular weights could be tuned between 4900 g mol<sup>-1</sup> and 1300 g mol<sup>-1</sup>. In addition, lower dispersity values (<2.0) were obtained when adding an initiator. Generally linear relationships between initiator concentration and  $M_n$  are found, again underpinning the living nature of the reactions.

Still, small deviations from the ideal anionic behaviour were found and the initiation efficiency of the anionic initiators was investigated by varying the type of initiator – *tert*-butyl functionalized initiator (11) and bromine-functionality (12) – and studying the polymer end-group by means of electrospray ionization mass spectrometry (ESI-MS).<sup>110,111</sup> BEH-PPV with molecular weights of 1200 g mol<sup>-1</sup> and

2800 g mol<sup>-1</sup> for the precursor and conjugated polymer, respectively, was investigated. The elimination could be directly followed, showing that the endgroup structure is not affected by establishing the conjugated chain system. All chains contained the initiator moiety, which could be confirmed by comparing spectra with the *tert*-butyl terminal group compared to the bromine. Bromine features a distinct isotopic pattern, which clearly indicated that all peaks did indeed contain the anionic initiator, confirming the high initiation efficiency. At the  $\omega$ -chain-end, mainly sulfinyl groups have been identified, showing that polymers could in principle be chain-extended in sequential monomer addition approaches.

This hypothesis was further tested, in order to see if direct block copolymer synthesis would be possible. Therefore, PPV was first synthesized using standard conditions as described above in combination with initiator 11. The mixture was allowed to react at 0 °C for 15 minutes, after which *tert*-butyl acrylate was added and allowed to react for an additional 15 minutes. In this way, partly successful PPV block copolymers were obtained, as indicated by the bimodality in the GPC chromatograms. Formation of PPV-*b*-PtBuA block copolymers did occur but PPV homopolymer ( $M_n = 5200$  g mol<sup>-1</sup> and  $D = 1.7$ ) was still present in the mixture, indicating a somewhat hindered reinitiation of chains. Isolation of the block copolymer using preparative recycling GPC did lead nevertheless to isolation of the block copolymer ( $M_n = 48\,300$  g mol<sup>-1</sup> and  $D = 1.2$ ). Still, this method is not suitable to efficiently produce PPV block copolymers on a large scale. As a result, alternative methods were further elucidated (Fig. 9).

As shown, the main advantage of the anionic polymerization approach is the ability to introduce specific functionalities into the polymer alpha chain end. Fig. 8 shows the



**Fig. 9** Schematic overview of the different block copolymers synthesized via the controlled anionic precursor route following the dual initiator approach in combination with either SET-LRP (top) or click (bottom) reaction conditions.

structures of three functional initiators, two introducing a bromine end-group (12 and 13),<sup>110</sup> of which only initiator 13 is suitable for ATRP re-initiation, and one for direct CuAAC conjugation (14).<sup>112</sup> *Via* the bromine-functional initiator, a dual initiator strategy could be followed, by employing single electron transfer living radical polymerization (SET-LRP).<sup>98,110,113–116</sup> It is important to note here that chain extensions were performed at the precursor polymer level, thus the polymer still carried the sulfinyl groups on the backbone. In the case of the conjugated polymer being used, the conjugation could interfere with the copper species, leading to undesired oxidation reactions. *t*-BuA monomer in combination with copper species (Cu0) as metal and tris[2-(dimethylamino)ethylamine] (Me<sub>6</sub>TREN) as ligand were mixed together in DMF as solvent and used to chain-extend BEH-PPV homopolymers. Successful block copolymerization was achieved in this way. Molecular weights of the block copolymer showed an increase from 5300 g mol<sup>-1</sup> for the homopolymer to 6800 g mol<sup>-1</sup>, 8900 g mol<sup>-1</sup> and 24 900 g mol<sup>-1</sup> when adding 50, 100 and 200 equiv. of *t*-BuA monomer, respectively. Distributions were monomodal but featured a *D* of 1.8, due to the relatively high dispersity of 1.9 of the pure PPV block. Next to GPC analysis, infrared results also confirmed PPV-*b*-PtBuA block copolymer formation. In addition, a blue shift in  $\lambda_{\text{max}}$  in the UV-Vis as well as the emission of the fluorescence spectrum was observed after block copolymerization, indicating the quenching effect of the acrylate block on the photophysical properties of the PPV block.

While the SET-LRP approach is very successful, it still limits the choice of the second block to vinyl-type monomers. As a result, development of a modular approach allowing any type of building block is likewise highly attractive. Therefore, CuAAC ligation was also approached, starting from an alkyne

functional initiator (14).<sup>111</sup> It is noteworthy to add that direct attachment of an alkyne to the phenyl ring does not lead to successful CuAAC reactions. With the introduction of a small spacer (see Fig. 8 for structure), however, click reactions were carried out with good success, even if preparative column chromatography was required to fully purify the residual block copolymers. Azide-functional poly(ethylene glycol) (PEG) was coupled using 5 equiv. of Cu(i)Br and *N,N,N',N',N''*-pentamethyldiethylene triamine (PMDETA) as metal and ligand system, respectively, in dry DMF as solvent. GPC traces of the block copolymers confirmed the successful coupling of either a short PEG block ( $M_n = 2700$  g mol<sup>-1</sup>) or a larger PEG block ( $M_n = 6200$  g mol<sup>-1</sup>). Molecular weight distributions showed a clear shift from the PPV homopolymer ( $M_n = 4700$  g mol<sup>-1</sup>) to higher molecular weights upon coupling with the large PEG-azide functionalized block ( $M_n = 14\,600$  g mol<sup>-1</sup>). UV-Vis results for the PPV-*b*-PtBuA block synthesized *via* the dual-initiator approach indicated a quenching effect of the PPV optical properties upon coupling. PPV-*b*-PEG block copolymers, however, still show comparable  $\lambda_{\text{max}}$  results compared to plain homopolymer PPVs. The nature and length of the PEG block seemingly did not influence the optical properties of the conjugated PPV block.

With the successful formation of both PPV block copolymers from materials stemming from the anionic precursor route, new application domains towards PPV materials with complex architectures were opened. Thus, first the acrylate block copolymers were converted to amphiphilic structures in order to test for self-assembly behavior. Consequently, PPV-*b*-PtBuA was treated with trifluorom acid, to yield PPV-*b*-PAA blocks. Both PPV-*b*-PtBuA and PPV-*b*-PEG blocks showed amphiphilic behavior and the ability to self-assemble in water. Preliminary dynamic light scattering (DLS) results indicated



particle formation and hence provide a proof-of-concept for further studies into this domain.

### 3. Conclusions and future perspectives

Over the last decades, extensive research towards PPV materials *via* a living polymerization mechanism has led to a variety of synthesis routes. ROMP resulted in well-controlled PPV homopolymers or – coupled with norbornenes or MMA – block copolymers. However, synthesis is still accompanied by tedious monomer synthesis. As a result, more attention was drawn by the so called 'precursor' routes and more specifically the sulfinyl precursor route. Research towards the mechanism behind the sulfinyl route led to the discovery of a purely radical or anionic route, depending on the type of base (LiHMDS anionic; Na<sub>7</sub>BuO radical) and solvent (THF anionic; *s*-BuOH radical) used during the polymerization. Although challenging, the radical polymerization route could be controlled with respect to molecular weight and dispersity when employing an excess amount of CBr<sub>4</sub> as CTA. In the next step, reactivation of the bromine-endcapped PPV using ATRP reaction conditions, led to the formation of PPV diblock copolymer structures of a different nature. Taking this one step further, triblock copolymer synthesis using click reaction conditions was achieved. The anionic route, on the other hand leads, to a truly living polymerization and excellent molecular weight control when employing specific initiators during the polymerization. Upon functionalization of the initiator, the PPV alpha endgroup is easily functionalized, giving access to block copolymer formation *via* SET-LRP chain extension or click chemistry polymer ligation.

The combination of both methods hence gives facile access to build PPVs into virtually any complex polymer architectures for the first time. PPVs of various structures can in this way be added, for example, to polymers dedicated to biomedical applications. In this case, PPV could, for example, serve as a fluorescence tag. Also, nanoparticles as inherently fluorescing nanocarriers for concomitant payload delivery and cell imaging could be foreseen. In any case, by implementing PPVs into other materials, pathways to yet unexplored applications are opened, giving access to new fields of application and hence a significant revival of PPV research. With the development of the techniques described herein, practically any polymer segment nowadays used in biologically relevant applications can be replaced by hydrophilic or hydrophobic PPVs, adding substantial functionality to materials. Without doubt, future applications will focus on the development of even more advanced structures as described herein.

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