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Discovery of an Anionic Polymerization Mechanism for High Molecular Weight PPV Derivatives via the Sulfinyl Precursor Route

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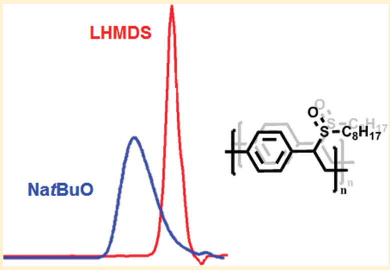

ABSTRACT: The polymerization of PPV via the sulfinyl precursor route has been investigated with respect to its mechanism. When polymerized in *sec*-butanol, a purely radical polymerization mechanism is observed as in most precursor polymerization routes. Accordingly, an increase in the reaction temperature induced an increase in the overall yield alongside with a reduction of the average molecular weight of the polymer. Upon changing the monomer concentration in solution before addition of the base NatBuO, an increase in molecular weight is observed, signifying that the polymerization is faster than the mixing of the two reaction components. When changing the solvent to NMP, a competition of anionic and radical polymerization has been established while in THF an anionic polymerization mechanism occurs exclusively. To prevent termination reactions, LDA and LHMDS were introduced as base whereby LHMDS shows less propensity to initiate anionic chain growth due to higher steric hindrance. With polymerizations in presence of the radical quencher TEMPO, the anionic polymerization mechanism could unambiguously be proven.

INTRODUCTION

During the past decades, conjugated polymers have gained a lot of interest because of their excellent characteristics for applications in electronic devices such as organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and generally organic photovoltaics (OPVs).[1] Poly(*p*-phenylenevinylene) (PPV) and its derivatives in particular are conjugated polymers with interesting electrical and optoelectronic properties. To introduce these materials in all kinds of devices, it is of utmost importance that the solubility and processability of these polymers are guaranteed.[2] PPVs with suitable physical properties are accessible via so-called precursor approaches based on *in situ* formation of the active monomer that yields nonconjugated polymers that can, however, easily be transformed into the final PPV via elimination reactions. There are many known precursor routes toward PPV materials, notably the Gilch,[3] Wessling,[4,5] xanthate,[6] sulfinyl,[7] and the dithiocarbamate[8,9] route. All these routes have in common that they proceed via the *in situ* formation of a *p*-quinodimethane system, which is formed through a base-induced elimination reaction (Scheme 1). For all these routes, except for the xanthate route, a self-initiating radical mechanism has been proposed.[10−16] The sulfinyl route should be distinguished from all other precursor routes since it starts from a nonsymmetrical monomer, which allows for highly efficient formation of the *p*-quinodimethane system which was confirmed by *in situ* UV−vis experiments and theoretical calculations.[17] At the same time the sulfinyl functional group prevents the formation of head-to-head and tail-to-tail additions. In this way, polymers with a low intrinsic chemical defect level can hence be synthesized.[18] Some years ago the sulfinyl precursor route was studied in our group in *N*-methylpyrrolidone (NMP) as the solvent and sodium *tert*-butoxide (NatBuO) was applied as the required base. Thereby bimodal polymer product distributions were observed, and indication was given that a competition between a radical (resulting in high molecular weight polymer) and an anionic (resulting in low molecular weight material) polymerization mechanism was responsible for the bimodality.[19−22]

In this paper, we now report on a polymerization of a monosubstituted *p*-quinodimethane system that purely proceeds via an anionic polymerization mechanism, which is achieved via careful selection of reaction conditions and type of base employed to form the monomer.

EXPERIMENTAL SECTION

Materials. All solvents and reagents were purchased from Acros or Aldrich and were used without further purification. Tetrahydrofuran (THF) was dried by distillation from Na/benzophenone. Analytical size exclusion chromatography (SEC) was performed using a Spectra Series P100 (Spectra Physics) pump equipped with two mixed-B columns (10 μm, 2 cm × 30 cm, Polymer Laboratories) and a refractive index detector (Shodex) at 70 °C. THF was used as the eluent at a flow rate of 1.0 mL/min. Molecular weight distributions were determined relative to polystyrene standards.

Synthesis of Monomer 4 (1-(Chloromethyl)-4[(octylsulfinyl)methyl]benzene). Monomer **4** was synthesized according to a known procedure.[23−25] In the final step a few drops of concentrated

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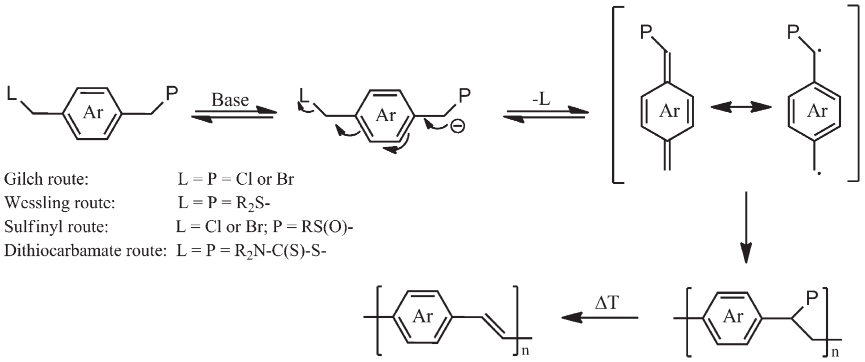
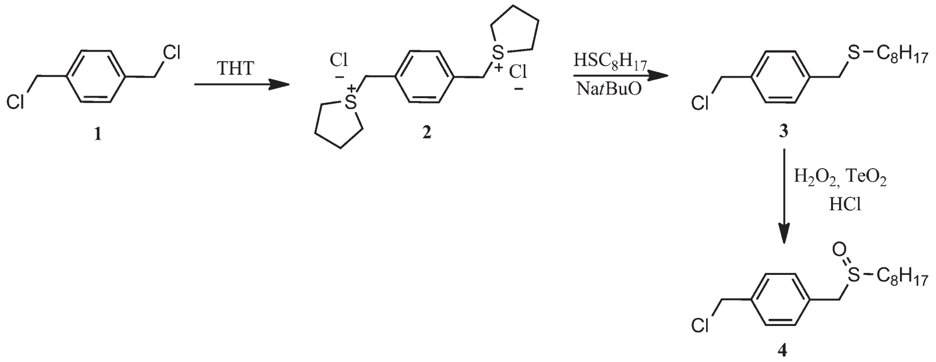
Scheme 1. General Reaction Scheme for the Formation of *p*-Quinodimethane Systems and Subsequent Conversion to PPVs



Gilch route: L = P = Cl or Br
Wessling route: L = P = R_2S-
Sulfinyl route: L = Cl or Br; P = RS(O)-
Dithiocarbamate route: L = P = R_2N-C(S)-S-

Scheme 2. Synthesis of Monomer 4



HCl (37%) were added to catalyze the reaction. Premonomer purity is of utmost importance for the polymerization outcome, so special attention was devoted to the purification of the monomer **4**. Monomer **4** was purified using column chromatography (silica, eluent $CHCl_3$) and subsequently recrystallized twice from a hexane/chloroform mixture.

Polymerization Procedure. Standard radical polymerization procedure with sudden base addition: All glassware was dried overnight in a drying oven at 110 °C and flamed under vacuum prior to use. A solution of premonomer **4** (0.6 g, 2 mmol) in *sec*-butanol (10 mL) and a solution of Na*t*BuO (0.5 g, 5 mmol) in *sec*-butanol (25 mL) were flushed with N_2. The base solution was then added in one go to the monomer solution at a given temperature and was stirred for 1 h. The reaction mixture was poured in water (50 mL), neutralized with 1.0 M HCl, and extracted with CH_2Cl_2. The solvent of the combined organic layers was removed under reduced pressure, and the prepolymer was analyzed without further purification. The prepolymer was then dissolved in toluene (10 mL) and heated at 110 °C for 3 h. After cooling down, the polymer was precipitated in ice cold methanol (100 mL) and filtered on a Teflon filter. The polymer was obtained as a red powder. For the test using reversed addition the premonomer solution was added as fast as possible to the base solution.

Influence of Temperature. The general procedure for fast addition of the base to monomer was followed. The different polymerization temperatures were obtained as follows: 0 °C with an ice/water mixture; −64 °C with a $CHCl_3$/liquid nitrogen mixture. The polymerizations at 30, 50, and 75 °C were performed in a thermostatic flask.

Anionic Polymerization. The general procedure for fast base addition was followed. In this case 1.2 equiv of base (LDA (2 M in THF/*n*-heptane) or LHMDS (1 M in THF)) was used during polymerization.

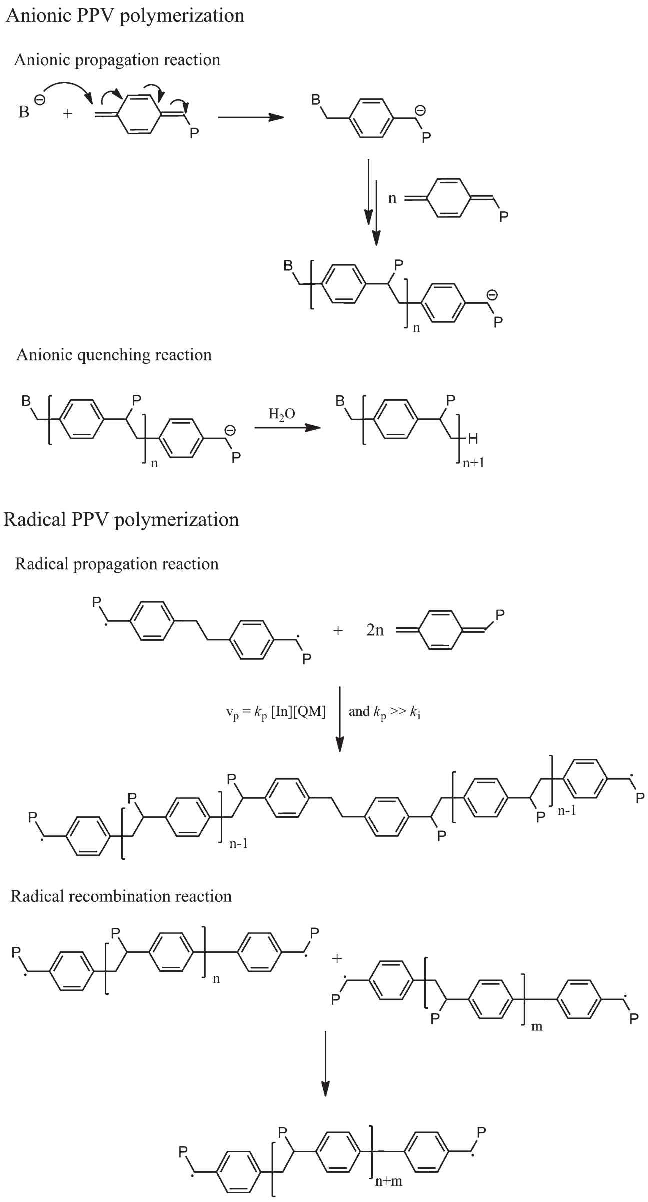
Test the Anionic Nature of the Polymerization with TEMPO. The procedure was similar to the standard polymerization procedure, but 0.5 equiv of TEMPO was added to the premonomer solution.

RESULTS AND DISCUSSION

In order to find pathways toward a purely anionic PPV polymerization, detailed studies into the exact reaction mechanism also for the radical pathway are important. Only if the latter process is understood, then a differentiation between the both reaction modes can be made on the basis of the resulting polymer distributions. Scheme 3 summarizes the reactions that can take place in each case. In the anionic pathway, the base that is added to form the quinodimethane from the premonomer also can act as an anionic chain initiator as in classical anionic polymerization. Subsequently, the chains are growing until either all monomer is consumed or until the reaction is quenched dedicatedly with an end-capper molecule. In the radical polymerization mode, a biradical species is formed from the monomer (see also Scheme 3), whereby a dimerization of the monomer was proposed to self-initiate the reaction. The so-obtained biradicals can subsequently undergo chain propagation, growing on both sides of the chain. Upon termination of the reaction, again a biradical is formed (alongside a chain defect in the final polymer due to head-to-head coupling), thus reducing the overall radical concentration but not terminating chain growth. It is for this reason that the reaction can also be referred to as a "pseudo" termination.

From the fact that high molecular weight material is typically obtained with a low defect level in the product (stemming from head-to-head couplings) the propagation rate constant (k_p) has to be much larger than the rate constant for initiation (k_i).[26] Self-termination reactions that would indeed lead to a stop in chain growth, like cyclization, are unlikely to occur once the formation of high molecular weight material is reached. For smaller (bi)radical species, such reaction was however observed.[27] Also, termination by disproportionation, which would eliminate one of the radical centers per chain is not possible due to the absence of β-hydrogen atoms, so recombination is the only mode of termination.

Scheme 3. Anionic Polymerization Compared to the Radical Polymerization Reactions in *p*-Quinodimethane Polymerization



For most quinodimethane polymerizations, the radical polymerization pathway is postulated.[28] Thus, in the next section the radical polymerization is described with respect to the outcome of the polymerization upon variation of certain reaction conditions.

Radical Polymerization. To assess if there was a possibility to achieve a purely anionic PPV polymerization, more information on the radical mechanism and particularly on the influence of certain reaction parameters on the outcome of the polymerization is required. It was demonstrated earlier that if *sec*-butanol was used as the solvent, polymerization proceeds exclusively along a radical pathway.[29] So far, however, it was not yet systematically studied how the outcome of these polymerizations is changed when the reaction conditions are varied. In order to identify conditions for anionic polymerizations, it is of high importance to understand these influences as only then a truly anionic PPV polymerization can be characterized and discerned from a "conventional" radical polymerization.

As a proof-of-concept we studied the polymerization of 1-chloromethyl-4-[(*n*-octylsulfinyl)methyl]benzene (**4**) as the premonomer in *sec*-butanol as the solvent employing Na*t*BuO as the base, affording plain-PPV which is insoluble when eliminated (Scheme 4). The full three-step synthesis and characterization of the sulfinyl premonomer **4** are described elsewhere.[23−25]

To start, the effect of temperature on the radical polymerization was investigated. Results from polymerizations performed at temperatures between 0 and 75 °C are collated in Table 1. All reactions have been carried out twice to ensure reproducibility. All polymerizations, except stated otherwise, were started by sudden addition of the entire base solution to the monomer solution. All reported molecular weights (based on polystyrene calibration of the SEC) are given for the noneliminated PPV material **5** because of the insolubility of the conjugated plain-PPV **6**.

The obtained data show good reproducibility. The obtained yields increase with the reaction temperature. This can be interpreted as a result of an increased propagation rate compared to the initiation or termination rate with increasing temperature. At the same time, the average degree of polymerization increases with decreasing temperature which may as well be attributed to a lower initiation rate toward lower temperatures. Analysis of the filtrate confirms that all monomer is consumed and that only paracyclophanes are present as a side product from the initiating biradical.[27] This species effectively limits the achievable yield and hence an increase in initiation (as expected with increasing temperature) must not necessary be followed by a higher yield. In addition to the change in temperature, also the effect of varying the initial base concentration $[B]_i$ and premonomer $[M]_i$ (resulting however in constant total concentrations in the mixture) upon the outcome of the reaction was investigated at 30 and 0 °C. Also here, a good reproducibility is given. It should be noted that both sets of experiments represent solutions that

Scheme 4. Synthesis of Plain-PPV via the Sulfinyl Precursor Route

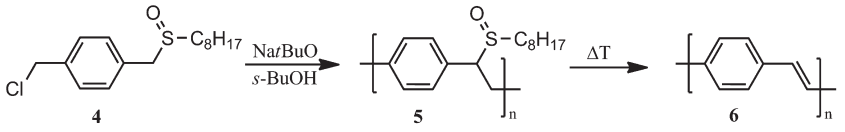


Table 1. Effect of Temperature on the Polymerization of Premonomer[a] in *sec*-Butanol

	procedure 1[b]			procedure 2[c]		
T (°C)	yield (%)	$10^{-3}M_w$/g mol^{-1}	PDI	yield (%)	$10^{-3}M_w$/g mol^{-1}	PDI
75	90	150	1.80			
	89	145	1.95			
50	88	370	2.27			
	83	450	2.85			
30	78	535	2.98	83	620	2.80
	80	560	2.66	78	590	2.95
0	73	685	2.45	63	780	2.49
	65	680	2.96	65	810	2.47

[a] Polymerizations with 1-chloromethyl-4-[(*n*-butylsulfinyl)methyl]benzene as premonomer. [b] Premonomer dissolved in *sec*-butanol (14 mL), initial premonomer concentration $[M]_i = 143$ mM; base (Na*t*BuO) dissolved in *sec*-butanol (6 mL), initial base concentration $[B]_i = 434$ mM; $[B]_i/[M]_i = 3.03$. [c] Premonomer dissolved in *sec*-butanol (10 mL), initial premonomer concentration $[M]_i = 200$ mM; base (Na*t*BuO) dissolved in *sec*-butanol (10 mL), initial base concentration $[B]_i = 260$ mM; $[B]_i/[M]_i = 1.30$.

Table 2. Effect of Premonomer Concentration on the Polymerization of Premonomer **4** in *sec*-Butanol

conc premonomer/mmol L^{-1} [a]	initial solvent volume (mL)[b]	yield (%)	$10^{-3}M_w$/g mol^{-1}	PDI
80	15	56	399	3.44
66.7	20	66	328	3.82
50	30	73	265	3.26
40	40	68	213	3.23
25	70	57	145	2.89
18.2	100	61	119	2.93

[a] Concentration premonomer **4** after addition of base solution. [b] 2 mmol of premonomer **4** dissolved in *sec*-butanol; base dissolved in *sec*-butanol (10 mL), initial base concentration $[B]_i = 210$ mM; $T = 30$ °C; all experiments were performed *in duplo*, and results are given as averages.

Table 3. Effect of Sequentail Polymerizations of Premonomer **4** in *sec*-Butanol

polymerization step	conc premonomer/mmol L^{-1} [a]	initial solvent volume/mL[b]	$10^{-3}M_w$/g mol^{-1}	PDI
1	80	15	394	3.69
2	44.4	35	319	3.40
3	30.8	55	270	3.37
4	23.5	75	242	3.04
5	19.1	95	209	3.13

[a] Concentration premonomer **4** of the complete reaction mixture after addition of base solution. [b] Total solvent volume of given reaction step, initial base concentration $[B]_i = 210$ mM; $T = 30$ °C; all experiments were performed *in duplo*, and results are given as averages.

result in identical base and monomer concentrations after mixing. Still, a moderate increase of ∼15% in molecular weight can be observed when $[B]_i/[M]_i$ is decreased. Thus, it may be concluded that the polymerization must proceed with a very high overall rate of polymerization; otherwise, the initial concentrations of both components could not have an influence on the outcome of the polymerization. It should be noted that such effect complicates the kinetic analysis tremendously since mixing effects must be considered as a rate-limiting step, a task that is not easily done.

To clarify unambiguously the effect of concentration of base and premonomer on the molecular weight, further experiments were performed whereby the same amount of premonomer **4** (2 mmol) was systematically dissolved in an increasing amount of solvent. The Na*t*BuO base (2.1 mmol in 10 mL of solvent) was added without delay. The results from these polymerizations are collated in Table 2.

The results indicate that the initial premonomer concentration has only a minor effect on the overall yield of the polymerization; however, a monotonous decrease of the molecular weight with decreasing the premonomer concentration can be clearly observed. Higher premonomer concentrations afford higher concentrations of the intermediate *p*-quinodimethane system, thus accelerating the propagation reaction and consequently allowing the chains to grow to higher molecular weights. All these results are indicative of a radical chain growth mechanism.

In the next step, it was tested if a termination reaction is operational. Whether termination occurs or not can be probed by sequential polymerization reactions. If no termination occurs, then addition of a new batch of premonomer to a already polymerized solution should afford for polymers of higher molecular weight due to chain extension reactions. Hence, premonomer **4** (2 mmol in 15 mL of *sec*-butanol) and base solutions (2.1 mmol of Na*t*BuO in 10 mL of *sec*-butanol) were added to fully polymerized reaction mixtures (after 40 min of the initial reaction). This process was repeated five times. Before adding the monomer and base solution, 5 mL of the reaction mixture was quenched to provide a sample for comparison. The results from the experiments are given in Table 3.

The obtained results reveal that the molecular weight drops after each sequential addition of monomer. Clearly no chain extension takes place, and thus it can be concluded that a termination process is active during polymerization. When the results of the molecular weights in function of the premonomer concentration of the last two sets of experiments are compared, it is evident that the slope for the sequential polymerization experiment is less steep than the slope for the premonomer concentration experiment (Figure 1). This difference can be explained by the fact that every time a sample is taken out of the reaction medium for GPC analysis the GPC sample will also contain polymeric material obtained in the previous polymerization step, and an accumulation of several individual polymerizations is seen. It should be noted that the above experiments demonstrate that a chain-terminating reaction takes clearly place; the nature of this reaction remains however unclear. Transfer reactions could in principle also be responsible, but also termination related to traces of oxygen in the reaction mixture. Anyhow, no living polymerization is observable under the chosen reaction conditions, and the polymerization behavior is in line with a radical chain growth mechanism.

Anionic Polymerization. To the best of our knowledge, there are no literature examples in which unambiguously an anionic polymerization mechanism was observed for *p*-quinodimethane systems, except for the procedure in which the sulfinyl route is performed in a solvent like dry NMP[19−22] (see Figure 2). In this case, bimodal behavior was observed and attributed to simultaneous occurrence of an anionic and a radical polymerization pathway.

To describe the extent of competition between the radical and the anionic polymerization mechanism, this reaction was subsequently further investigated in NMP as the solvent. The relative integrated surface in the GPC chromatogram of the polymeric versus the oligomeric fraction was calculated, and the sum of both surfaces was taken as 100%. This practical approach may not be fully correct since the distributions overlap with each other. Nevertheless, for a qualitative comparison such evaluation is sufficient. In Table 4 the results are illustrated for a series of experiments for which the dependence of the competition between anionic and radical polymerization on the initial premonomer and base concentration was investigated. All experiments were performed *in duplo*, and results are given as averages.

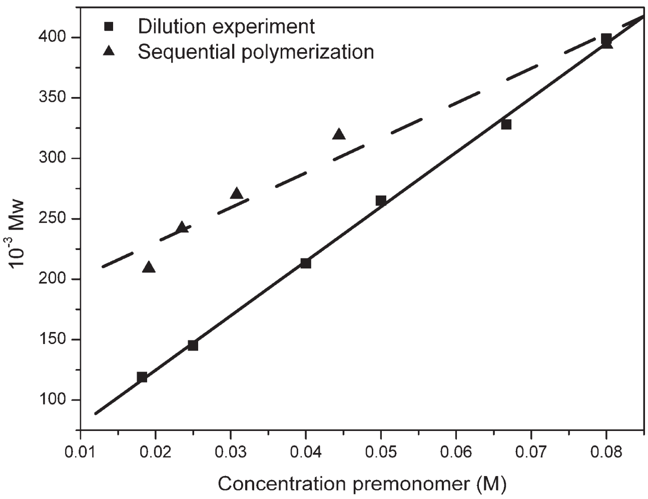


Figure 1. Radical propagation and termination reactions: (squares) dilution experiment (see Table 2) and (triangles) sequential polymerizations (see Table 3).

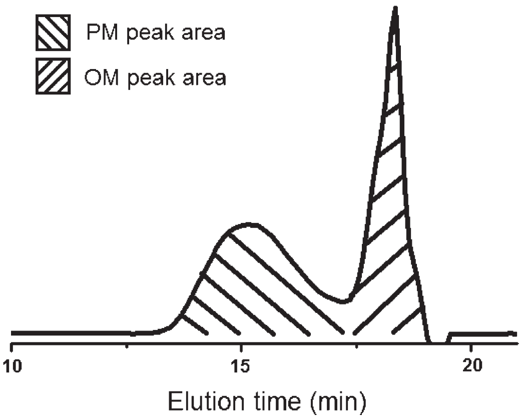


Figure 2. Typical GPC chromatogram for the polymerization in NMP (OM = oligomeric material, PM = polymeric material).

It is clear that there is a high sensitivity for the competition between the two polymerization mechanisms and that already small changes in the reaction preparation have a profound influence on the transition in mechanism. In the analysis of the results, the relative peak areas for the oligomeric (OM) and polymeric (PM) material is used to assess the predominance of each mechanism. The OM material is assigned (as previously done) to material stemming from anionic polymerization, while PM is the result of the radical growth mode as described in the previous section. It should hereby be noted that the peak areas from SEC analysis do not represent true ratios of concentration of polymers due to the weighting of the molecular weight distributions. Transformation into the number distribution is required for that purpose, which however requires absolute molecular weight detection. Thus, with the numbers in Table 4, the amount of oligomers is underestimated. Also, the given molecular weights are only crude estimates since the selection of integration limits are only arbitrary. A full deconvolution of the distributions is not easily done, but the presented data are good enough to clearly show the underpinning trends. Small changes in initial concentrations of base and premonomer have pronounced effects on the molecular weight and the relative amount of the polymeric fraction. In comparison with Table 2 (radical polymerization only), changes of initial base or premonomer concentration do not give rise to strong variations in the outcome of the polymerization reaction. However, the more competitive the anionic mechanism becomes, the lower the molecular weight of the polymeric fraction is. A higher amount of the oligomeric material seems to go along with a high ratio of initial base concentration versus initial premonomer concentration. In an anionic polymerization, a sensitivity for the initial base versus premonomer concentration can be expected because the base concentration directly influences the rate of initiation (compared to the radical pathway where the rate of initiation is dependent on the *p*-quinodimethane concentration and hence only indirectly coupled with the amount of base). An experiment that demonstrates this hypothesis unambiguously is an experiment in which the effect of a reversed addition (addition of premonomer **4** solution to the base solution) is studied (Table 5).

Clearly, reversed addition has a tremendous effect on the molecular weight and on the relative contribution of the polymeric fraction. When mixed, the monomer faces a comparatively

Table 5. Addition of Base versus Reversed Addition[a]

addition	yield (%)	$10^{-3}M_w$ (PM)/ g mol^{-1}	% PM	$10^{-3}M_w$ (OM)/ g mol^{-1}
normal	61	170	87	3.5
reversed	41	10.4	36	2.9

[a] T = room temperature.

Table 4. Overview of Polymeric (PM) and Oligomeric (OM) Fractions for the Various Premonomer 4 and Base Concentrations[a]

ratio mL(M)[b]/mL(B)[c]	total yield (%)	$[B]_i$/mM	$[M]_i$/mM	$[B]_i/[M]_i$	$10^{-3}M_w$ (PM)/g mol^{-1}	% PM	$10^{-3}M_w$ (OM)/g mol^{-1}
14/6	33	0.37	0.14	2.6	73	67	3.1
14/8	44	0.28	0.14	2.0	117	80	3.1
10/10	65	0.22	0.20	1.1	176	89	3.3

[a] T = room temperature. [b] Amount of solvent (NMP) in which the premonomer is dissolved; $[M]_i$ = initial premonomer concentration. [c] Amount of solvent (NMP) in which the base is dissolved; $[B]_i$ = initial base concentration.

Table 6. Effect of Temperature on the Amount of the Oligomeric (OM) Fraction

T (°C)	yield (%)	$10^{-3}M_w$ (PM)/g mol^{-1}	% PM	$10^{-3}M_w$ (OM)/g mol^{-1}
RT	68	182	90	3.0
0	43	54	52	3.3

high base concentration, which apparently favors the anionic initiation over the radical pathway. An alternative experiment that demonstrates that the reaction can be directed toward one specific mechanism is to perform the polymerization at low temperature (see Table 6 for results). Anionic initiation typically is associated with a low activation energy; thus, decreasing the temperature should increase the amount of oligomeric material. As can be seen from the data in Table 6, this hypothesis can be confirmed.

To identify reaction conditions that allow for a purely anionic polymerization mechanism, all radical initiation events must be suppressed and termination reactions of an anionic polymerization eliminated. There are two possible (anionic) termination reactions that can potentially occur, i.e., quenching from deprotonation of the solvent or reaction with the protonated base, which is formed during the *p*-quinodimethane formation. This reasoning implies that strong bases (which will be less likely to terminate an anionic chain growth in its protonated form) and an aprotic solvent are essential conditions for a living anionic polymerization.

Consequently, lithium diisopropylamide (LDA) was tested as a base in dry THF. In such reaction, only low molecular weight oligomers were formed, indicating that anionic polymerization occurs exclusively. LDA has been reported in the literature as being an initiator for the anionic polymerization of methacrylate monomers.[30] For this reason LDA was exchanged for a more sterically hindered base, i.e., lithium hexamethyldisilazide (LHMDS), and used as the base during the polymerization. For the polymerization of premonomer **4**, plain-PPV polymers with 10 times higher molecular weight were obtained with LHMDS compared to LDA as a base in dry THF (Table 7). This increase in molecular weight is indicative of a largely reduced anionic initiation rate with the sterically more hindered base. In consequence, less chains are initiated, and thus each individual chain can grow to higher degree of polymerization due to the changed ratio of initiated species over the total monomer concentration.

To verify the anionic character of the polymerization procedure using LHMDS in THF, the effect of 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) on the molecular weight was investigated and compared to a classical radical polymerization of PPV (Na*t*BuO in *sec*-butanol) (Table 8 and Figure 3) since a stable nitroxide should inhibit polymerization if a radical mechanism is operational.

For the polymerizations conducted with LHMDS no major changes were observed, nor on the molecular weight, nor in the yields of the reactions. This nicely verifies that the polymers were indeed obtained through an anionic polymerization mechanism. To further illustrate that the base is responsible for the change to an anionic mechanism, the effect of TEMPO was also studied on the polymerization in THF using Na*t*BuO as a base. Again high molecular weight material was obtained in the absence of the radical inhibitor, and a drastic decrease of both yield and molecular weight was observed in the presence of TEMPO. It was shown earlier on that 1 equiv of TEMPO is needed to stop the radical polymerization completely.[31] This explains the observed reduced molecular weight but still the presence of oligomers when 0.5 equiv of TEMPO is used.

Table 7. Results for Polymerization of Premonomer 4 in THF with LDA and LHMDS[a]

base	T (°C)	$10^{-3}M_w$/g mol^{-1}	PDI
LDA	−64	1.8	1.3
LDA	0	3.6	1.9
LHMDS	−64	46.1	2.1
LHMDS	0	64.0	3.2

[a] T = room temperature; $[M]_i$ (initial monomer concentration) = 0.05 M.

Table 8. Results for the Verification of the Anionic Nature of the Polymerization of Premonomer 4 with LHMDS as a Base in THF[a]

base	solvent	additive	$10^{-3}M_w$/g mol^{-1}	PDI	yield (%)
Na*t*BuO	*sec*-butanol	none	208.4	4.0	52
Na*t*BuO	*sec*-butanol	TEMPO	9.8	1.4	<1
Na*t*BuO	THF	none	1324.1	6.9	79
Na*t*BuO	THF	TEMPO	111.8	2.7	21
LHMDS	THF	none	43.3	2.5	84
LHMDS	THF	TEMPO	49.4	3.5	82

[a] T = room temperature; $[M]_i$ (initial monomer concentration) = 0.05 M.

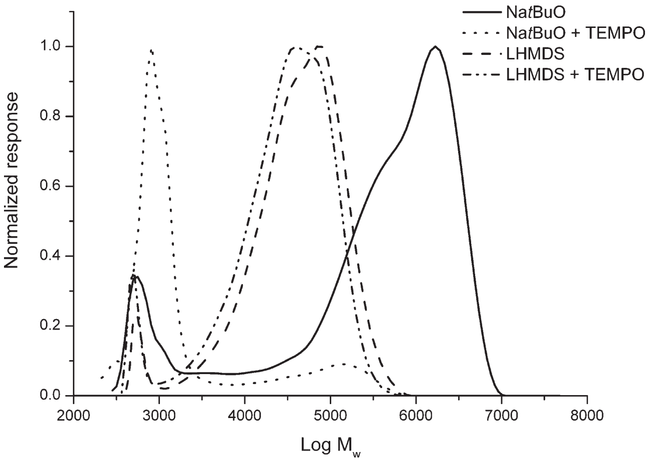


Figure 3. Verification of anionic nature of the polymerization of premonomer **4** with LHMDS as a base in THF.

It can hence be concluded that the polymerization of PPVs in THF proceeds entirely via an anionic polymerization mechanism if a strong base such as LDA or LHMDS is used for the formation of the active *p*-quinodimethane monomer. The base acts at the same time as reagent to form the monomer but also to some extent initiates the polymerization.

CONCLUSION

The polymerization mechanism and the change in the outcome of the polymerizations upon variation of the reaction conditions are demonstrated for the sulfinyl precursor route. When polymerized in *sec*-butanol with a base such as Na*t*BuO, a purely radical polymerization mechanism is observed. In this case, the polymer molecular weight can be systematically varied by changing the reaction temperature or via changing the initial monomer concentration in solution before mixing with the base. A purely anionic polymerization mechanism for PPVs can be obtained when the reaction conditions are chosen carefully to exclude radical initiation and quenching reactions of an anionic polymerization. This is achievable when the sulfinyl precursor route is performed in dry THF as the solvent and LHMDS is used as the base. LDA also leads to an exclusive anionic polymerization but does result in overall lower molecular weights due to an increased propensity to initiate the polymerization compared to the sterically more hindered LHMDS.

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REFERENCES

(1) Skotheim, T. A.; Reynolds, J. R. In *Handbook of Conducting Polymers: Conjugated Polymers Processing and Applications*, 3rd ed.; CRC Press: New York, 2007; pp 5-3, 7-1, 10-1.

(2) Burroughes, J.; Bradley, D.; Brown, A.; Marks, R.; Mackay, K.; Friend, R.; Burns, P.; Holmes, A. *Nature* **1990**, *347*, 539–541.

(3) Gilch, H. G.; Wheelwright, W. L. *J. Polym. Chem. Ed.* **1966**, *4*, 1337–1349.

(4) Wessling, R. A.; Zimmerman, R. G. US Patent 3401152, 1968.

(5) Wessling, R. A.; Zimmerman, R. G. US Patent 3706677, 1972.

(6) Son, S.; Dodabalapur, A.; Lovinger, A. J.; Galvin, M. E. *Science* **1995**, *269*, 376–378.

(7) Louwet, F.; Vanderzande, D.; Gelan, J.; Mullens, J. *Macromolecules* **1995**, *28*, 1330–1331.

(8) Henckens, A.; Duyssens, I.; Lutsen, L.; Vanderzande, D.; Cleij, T. *Polymer* **2006**, *47*, 123–131.

(9) Henckens, A.; Lutsen, L.; Vanderzande, D.; Knipper, M.; Manca, J.; Arnouts, T.; Poortman, J. *Proc. SPIE Int. Soc. Opt. Eng.* **2004**, *5464*, 52–59.

(10) Hontis, L.; Vrindts, V.; Lutsen, L.; Vanderzande, D.; Gelan, J. *Polymer* **2001**, *42*, 5793–5796.

(11) Schwalm, T.; Wiesecke, J.; Immel, S.; Rehahn, M. *Macromolecules* **2007**, *40*, 8842–8854.

(12) Cho, B.; Kim, Y.; Han, M. *Macromolecules* **1998**, *31*, 2098–2106.

(13) Issaris, A.; Vanderzande, D.; Gelan, J. *Polymer* **1997**, *38*, 2571–2574.

(14) Issaris, A.; Vanderzande, D.; Adriaensens, P.; Gelan, J. *Macromolecules* **1998**, *31*, 4426–4431.

(15) Hontis, L.; Lutsen, L.; Vanderzande, D.; Gelan, J. *Synth. Met.* **2001**, *119*, 135–136.

(16) Vandenbergh, J.; Wouters, J.; Adriaensens, P.; Mens, R.; Cleij, T.; Lutsen, L.; Vanderzande, D. *Macromolecules* **2009**, *42*, 3661–3668.

(17) Hermosilla, L.; Catak, S.; Van Speybroeck, V.; Waroquier, M.; Vandenbergh, J.; Motmans, F.; Adriaensens, P.; Lutsen, L.; Cleij, T.; Vanderzande, D. *Macromolecules* **2010**, *43*, 7424–7433.

(18) Roux, H.; Adriaensens, P.; Vanderzande, D.; Gelan, J. *Macromolecules* **2003**, *36*, 5613–5622.

(19) Louwet, F.; Vanderzande, D.; Gelan, J. *Synth. Met.* **1995**, *69*, 509–510.

(20) Hontis, L.; Van Der Borght, M.; Vanderzande, D.; Gelan, J. *Polymer* **1999**, *40*, 6615–6617.

(21) Van Der Borght, M.; Adriaensens, P.; Vanderzande, D.; Gelan, J. *Polymer* **2000**, *41*, 2743–2753.

(22) Adriaensens, P.; Van Der Borght, M.; Hontis, L.; Issaris, A.; van Breemen, A.; de Kok, M.; Vanderzande, D.; Gelan, J. *Polymer* **2000**, *41*, 7003–7009.

(23) van Breemen, A.; Vanderzande, D.; Adriaensens, P.; Gelan, J. *J. Org. Chem.* **1999**, *64*, 3106–3112.

(24) Van Der Borght, M.; Vanderzande, D.; Adriaensens, P.; Gelan, J. *J. Org. Chem.* **2000**, *65*, 284–289.

(25) Lutsen, L.; van Breemen, A.; Kreuder, W.; Vanderzande, D.; Gelan, J. *Helv. Chim. Acta* **2000**, *83*, 3113–3121.

(26) Becker, H.; Spreitzer, H.; Ibrom, K.; Kreuder, W. *Macromolecules* **1999**, *32*, 4925–4932.

(27) Wiesecke, J.; Rehahn, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 567–570.

(28) Schwalm, T.; Wiesecke, J.; Immel, S.; Rehahn, M. *Macromol. Rapid Commun.* **2009**, *30*, 1295–1322.

(29) van Breemen, A.; Issaris, A.; de Kok, M.; Van Der Borght, M.; Adriaensens, P.; Gelan, J.; Vanderzande, D. *Macromolecules* **1999**, *32*, 5728–5735.

(30) Antoun, S.; Teyssié, P.; Jérôme, R. *J. Polym. Sci., Part A* **1997**, *35*, 3637–3644.

(31) Wiesecke, J.; Rehahn, M. *Macromol. Rapid Commun.* **2007**, *28*, 78–83.