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Toward Controlled Gilch Synthesis of Poly(*p*-phenylene vinylenes): Anionic vs Radical Chain Propagation, a Mechanistic Reinvestigation

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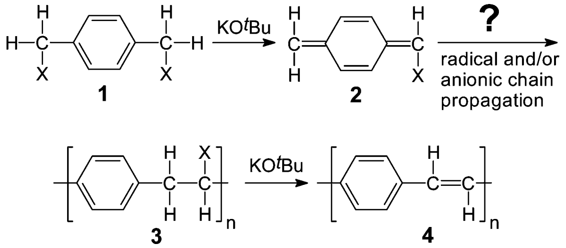
ABSTRACT: It is a broad consensus that the first step in the Gilch synthesis of poly(*p*-phenylene vinylenes) (PPVs) is 1,6-dehydrohalogenation of the 1,4-bis(halomethylene)benzene starting materials. The mechanism of the subsequent chain growth of the resulting α-halo-*p*-quinodimethane monomers, however, is still a matter of discussion. We re-evaluated the arguments presented for anionic chain propagation and set them against the evidence obtained for a radical mechanism. We conclude that (i) the initial dehydrohalogenation of the starting material represents an E_2 type 1,6-elimination without anionic intermediates, (ii) anionic chain propagation does not play a role in standard Gilch syntheses, but instead, (iii) the PPVs grow predominantly via radical chain polymerization. However, since the growing species are α,*ω*-macro-diradicals, recombination does not cause chain termination as in conventional radical polymerizations. This is one reason for the formation of very high-molecular weight PPVs. The monofunctional benzylhalogenides, sometimes assumed to act as initiators of anionic chain growth and to suppress gelation of the reaction mixtures by lowering the PPVs' molar masses, clearly do not play this role: while we could verify that these additives lower the risk of gelation, they are neither incorporated as end groups into the PPVs nor do they lower the molar masses. Instead, gelation is most probably due to physical crosslinking, induced by the very high entanglement density of the PPV chains immediately after their formation. Additives such as monofunctional benzylhalogenides seem to accelerate de-entanglement, possibly either by retarding the conversion of the still quite flexible poly(*p*-xylylene) (PPX) precursors into the semirigid PPVs, thereby giving the chains a better chance to de-entangle, or by preferential solvation and successful competition with segment−segment interactions. In agreement with the proposed mechanism is the reproducible observation that additives which antagonize gelation efficiently, simultaneously increase the magnitude of the only relevant side reaction of Gilch reactions, i.e., formation of [2.2]paracyclophanes.

1. Introduction

Poly(*p*-phenylene vinylenes) (PPVs) are promising functional polymers for organic electronics,[1−4] and the Gilch synthesis is classed among the most powerful routes for their preparation.[5−13] Consequently, literature is abounding in papers describing tailored Gilch-PPVs together with their properties when applied in devices such as light-emitting diodes (LEDs). These studies, however, also make evident that ultimate device performance requires polymers which are not only perfect in design but also free of constitutional defects and impurities.[14−19] In order to produce such materials, profound knowledge is needed about all details of the polymer formation processes. Mechanistic knowledge is moreover the key to tailored chain lengths, narrow polydispersities, inert chain end groups, and strategies making accessible PPV-based (block) copolymers. Unfortunately, this comprehensive knowledge is not available so far for the Gilch reaction: while it is generally accepted that α-halo-*p*-quinodimethane **2** represents the real monomer, formed via single 1,6-dehydrohalogenation of starting material **1**, and that the halogenated poly(*p*-xylylene) (PPX) intermediate **3** is converted into PPV **4** via a second dehydrohalogenation event, there is still controversial discussion about the mechanism of the chain propagation reaction itself (Scheme 1).

Scheme 1. Key Steps of the PPV Synthesis via the Gilch Reaction (X = a, Cl; b, Br)[a]



[a] In this scheme, as well as in most of the subsequent schemes, lateral substituents such as flexible side chains, bulky groups, and electron-donating or electron-withdrawing functionalities, which are usually attached to the PPVs for tailoring their properties, are omitted for clarity reasons.

This unsatisfying situation is due to the fact that Gilch polymerizations comprise a sequence of fast partial steps, and sophisticated techniques are required to reliably identify relevant intermediates. This is also the reason why knowledge developed for related PPV syntheses, such as the Wessling, sulfonyl and sulfinyl routes, is adduced as support of the mechanistic concepts proposed for the Gilch reaction. Clearly, this procedure will not basically solve the mechanistic puzzle, but since there is indeed some mechanistic affinity between the various PPV syntheses, one might gain some urgently required insight by drawing those parallels. Because we decided to profoundly elucidate the chain-growth mechanism of the Gilch synthesis,[20−23] collection of all accessible mechanistic information for the related PPV syntheses, as well, was the first step. On the basis

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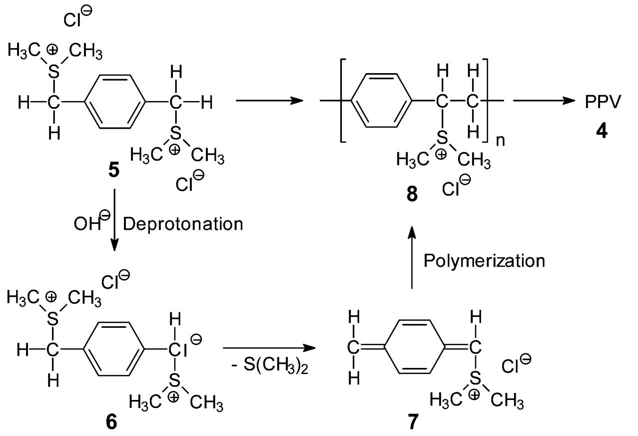
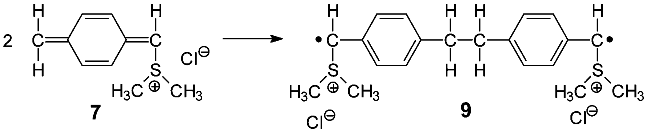
Scheme 2. The Key Steps of the Wessling Synthesis of PPV



Scheme 3. Assumed Spontaneous Diradical Formation Process in the Wessling Route, Which Is the Initiation Event for the Subsequent Radical Chain Propagation



of this groundwork, and guided by implications derived therefrom, an appropriate standard Gilch procedure was defined and the products obtained under these conditions were carefully analyzed. Subsequently, the effect of various reagents and additives was addressed. Moreover, simulation studies were carried out. On the basis of the collected information, the current mechanistic understanding of the chain propagation has been critically re-evaluated and consolidated explanations have been derived for effects observed in the presence of additives. In particular, we address the question why there is such a mysterious reversible gelation during that reaction under the usually applied reaction conditions.

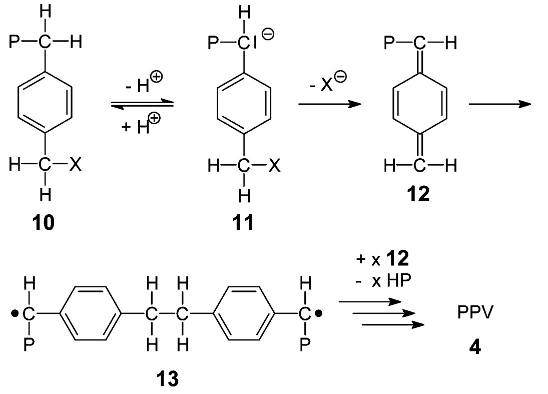
2. Gilch and Gilch-Related PPV Syntheses, Milestones of Mechanistic Perception

2.1. The Wessling Route. In this type of PPV synthesis, biscationic starting materials **5** are treated with sodium hydroxide.[24,25] Hörhold could show that activation of **5** proceeds stepwise via deprotonation leading to ylide **6**, followed by elimination of dimethyl sulfide in a second step (Scheme 2). The formed *p*-quinodimethane intermediate **7** represents the active monomer and is polymerized in the subsequent chain growth process.[26] It was also Hörhold who provided good arguments for 1,6-type chain polymerization of **7**, but no decision was possible whether this process proceeds via radicals or anions.

Hörhold's results were confirmed by Hatch[27] and Lahti[28] who verified stepwise monomer activation via hydrogen−deuterium exchange using $CD_3OD/NaOCD_3$. Moreover, they could directly observe the *p*-quinodimethane **7** using low-temperature in situ UV−vis and NMR spectroscopies. Later on, Wessling postulated radical polymerization of **7**, initiated by dimeric diradicals **9** (Scheme 3).[29]

In contrast to this, Lahti et al.,[28] Garay and Lenz,[30] and Hsieh[31] reported results pointing toward anionic chain propagation, while Hall et al.[32] and, later, Lahti et al.[33,34] realized that polymerization also proceeds in acidic media but is suppressed when 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) is added as a scavenger. Also Cho et al., who first favored anionic chain growth,[35] revised his earlier interpretation of kinetic studies and has favored radical chain growth since then.[36−38] To summarize, the majority of available information supports 1,6-type radical polymerization of *p*-quinodimethane **7** for the Wessling synthesis.

Scheme 4. The Key Steps in the Sulfinyl and Sulfonyl Routes Leading to PPV



X („leaving group") = Cl, Br

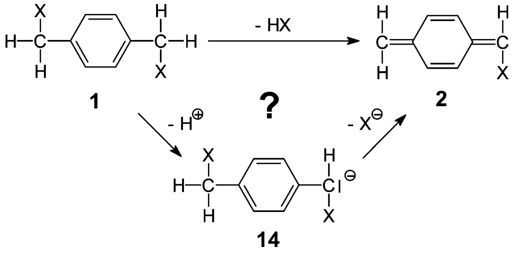
P („polarizable group") = SO-Bu or SO_2-Bu

2.2. The Sulfinyl and Sulfonyl Routes. In contrast to the Wessling route, uncharged starting materials **10** are used in the sulfinyl and sulfonyl routes. Moreover, these starting materials **10** are asymmetrically substituted in their α and α′ positions: the halogen substituent X acts as leaving group while the sulfinyl or sulfonyl group P is introduced to polarize the benzylic C−H bond (Scheme 4).

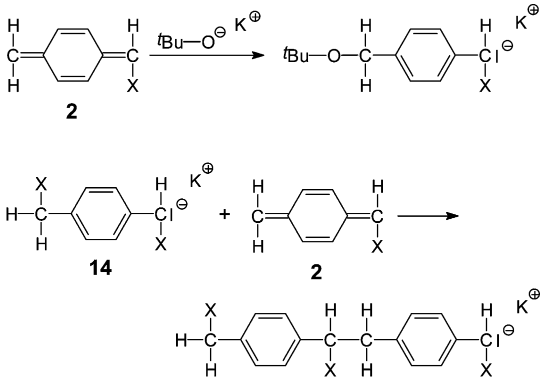
Initially, Vanderzande et al. assumed that monomer activation proceeds analogously to what is known for the Wessling route, i.e., via deprotonation of starting material **10** first, followed by elimination of leaving group X as a discrete second step. Also, he could provide experimental evidence of radical chain propagation of the *p*-quinodimethane intermediate **12**.[39,40] As the initiating event, dimerization of a small number of species **12** was anticipated, leading to dimeric diradicals **13**. This overall picture of the mechanism is still valid today. The only minor correction that was indicated concerned monomer activation:[41] deprotonation of starting material **10** and elimination of the halogen leaving group X seem to proceed simultaneously here, maybe due to the absence of cationic sulfur which stabilizes the anion in the Wessling route. Nevertheless, in 1999, Vanderzande came up with a surprise:[42] he showed that high-molecular weight polymers are formed in the polar, protic solvent *N*-methylformamide whereas a bimodal molar mass distribution is obtained in the polar, aprotic solvent *N*-methylpyrrolidone (NMP). This observation led to the assumption that anionic and radical chain growth occur in parallel in NMP. This interpretation was supported by further experiments where either water or TEMPO was added to the entries in NMP: in the case of water, the low-molecular weight part of the bimodal distribution curve was missing while it was the high-molecular weight part with TEMPO. To conclude, the sulfonyl and sulfinyl routes proceed as radical chain growth processes under most synthetic conditions, but specific media seem to exist where radical and anionic chain growth proceed simultaneously.

2.3. The Gilch Route. In the Gilch synthesis of PPV, 1,4-bis-(halomethylene)benzenes **1** are used as starting materials. Despite its early discovery,[5] elucidation of the polymerization mechanism was not a matter of publications for quite a long time. Today, it is beyond question that *p*-quinodimethanes **2** represent the active monomers in the Gilch process,[20,23] but the

Scheme 5. Possible Reaction Pathways for Monomer Activation during the Gilch Synthesis of PPVs



Scheme 6. Assumed Initiation Events in the Case of Anionic Chain Propagation during Gilch Syntheses



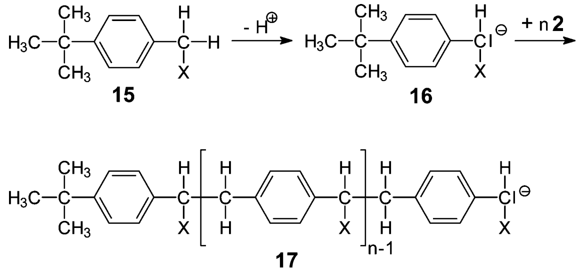
question whether initial dehydrohalogenation of starting material **1** proceeds stepwise via anions **14**, or synchronous via 1,6-elimination of HX, is still unsolved (Scheme 5).

An essentially more controversial discussion is still ongoing on the subsequent chain propagation process: some authors favor anionic polymer growth, others a radical mechanism. In the case of a hypothetical anionic polymerization, it is assumed that initiation proceeds via attack of a nucleophile such as KO^{t}Bu or anion **14** to the *p*-quinodimethane monomer **2** (Scheme 6).

The strongest argument supporting anionic chain propagation was born from a general problem of Gilch syntheses: this is the rapid (often reversible) gelation of the reaction mixture, correlated with partial insolubility of the formed polymers.[59] Hsieh and co-workers observed that when monofunctional benzyl halogenides **15** such as 4-*tert*-butylbenzylchloride are added, gelation is retarded or even completely prevented and the degrees of polymerization of the formed PPVs are lowered systematically.[43−45] These findings were interpreted as an indication of anionic chain growth: it was assumed that **15** is deprotonated, leading to carbanion **16**, analogously to what might be the first step in monomer activation (**1** → **14**, Scheme 5). However, since **16** cannot undergo elimination of a halogenide from its 6-position (as is the case with **14**, see Scheme 5), deprotonation of **15** should result in an increased carbanion concentration. If so, larger numbers of growing anionic chains **17** are the consequence, and these chains must have necessarily lower average molar masses compared to those formed without additives. Exactly this was assumed to be the reason for the reduced, or even completely prevented, formation of gel in the presence of species such as **15**.

Other research groups supported the mechanistic picture presented in Scheme 7: Ferraris et al. and Yin et al.[46,47] interpreted decreasing PPV molar masses and multimodal molar mass distributions in the presence of 4-ethoxyphenol and polyethylene glycol, respectively, as indication of anionic chain growth. Huang et al., on the other hand, concluded from their

Scheme 7. Assumed Initiation of Anionically Growing Chains in the Presence of Monofunctional Benzylhalogenide Additives 15



experiments that anionic and radical chain propagation occur parallel or complementary: he verified that increasing quantities of monofunctional benzyl compounds result in a systematic decrease in yields and molar masses of the PPVs, but they observed similar effects when scavengers such as 2,6-di-*tert*-butyl-4-methylphenol were present.[48,49] Finally, there is also strong experimental evidence of an exclusively radical chain growth: Vanderzande et al. published convincing studies which can only be understood based on radical chain growth,[50] and their results are in excellent agreement with what we reported recently (Scheme 8).[20−23] This is that some of the *p*-quinodimethane monomers **2** dimerize spontaneously, leading to diradicals **18**. These diradicals represent the initiators of subsequent bilateral radical chain growth of the α,*ω*-macro-diradicals **3*** via 1,6-type addition of further monomers **2**. Additionally, we have good reasons to assume that a significant number of recombination events are involved in the chain growth process: because α,*ω*-macro-diradicals **3*** are the growing species, radical recombination does not terminate chain growth, in contrast to conventional radical polymerizations, but leads back to another α,*ω*-macro-diradical **3***, which continues propagation further. Since there is also no way of chain termination via disproportionation, in fact, the chain growth should be essentially nonterminating in the absence of side reactions and impurities. This mechanistic picture could be corroborated by, for example, the tremendously high molar masses found for these PPVs, far beyond one million, and by studying quantitatively the effect of persistent 2,2,6,6-tetramethylpiperidine-*N*-oxyl radicals.[21] Moreover, [2.2]paracyclophane-type cyclic dimers such as **19** and **20** were identified as the most prominent side products (Scheme 8).[20] In conclusion, there is strong evidence of radical chain propagation under standard Gilch conditions, but there are also some serious arguments around that might possibly support anionic chain propagation. Nevertheless, the arguments for anionic chain growth are not particularly compelling and represent rather indirect proof while, on the other hand, even careful validation of current knowledge does not provide any suggestions of undeniable conflicts with radical chain growth. Therefore, radical chain growth seems more probable, but further studies are required to really ascertain this point.

3. Results and Discussion

3.1. The Standard Gilch Procedure. For profound investigation of both the mechanistic pathway of the Gilch polymerization process and the effect of additives, it is essential to select an appropriate standard procedure for the planned studies. Moreover, constitution, molar mass, and molar-mass distribution have to be analyzed precisely for the reference polymers formed under these standard conditions. On the basis of what was known from the literature as well as from our preceding studies,[20−23] 5-methoxy-2-(*β*-ethylhexyloxy)-1,4-bis(chloromethylene)ben-

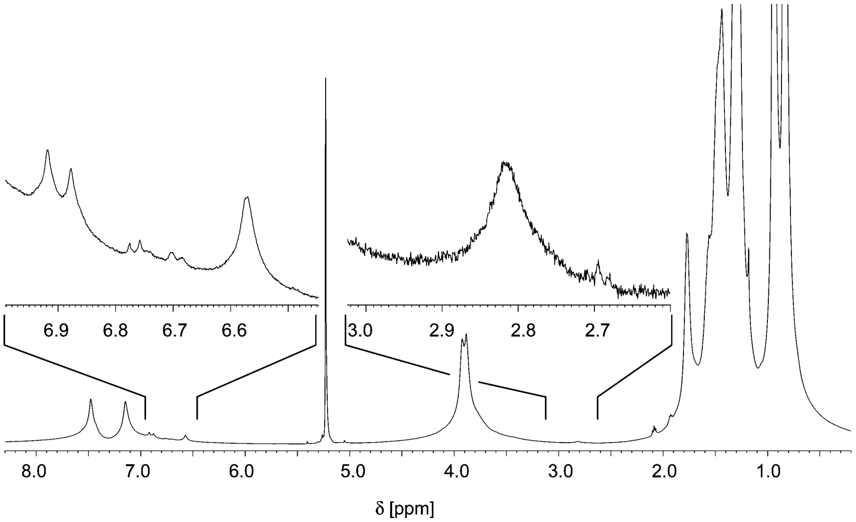
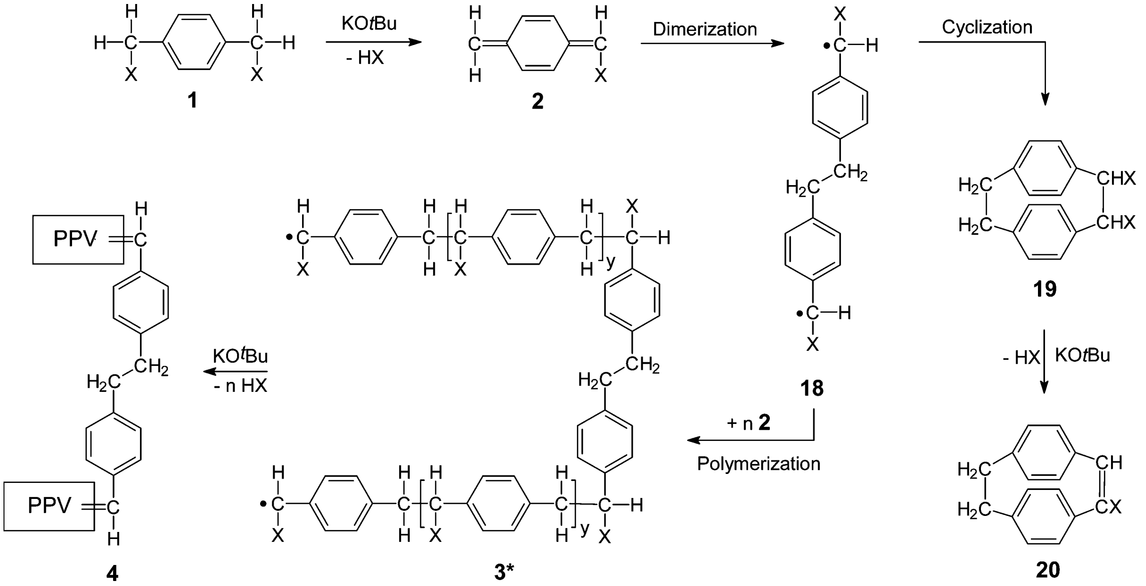
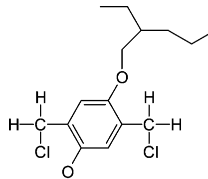


Figure 1. ^{1}H NMR spectrum, and (inserts) enlarged sections thereof, of a reference PPV **4b** obtained under standard conditions (measurement in $CDCl_3$ at room temperature). The small absorptions point toward characteristic defect structures. For details, see text.

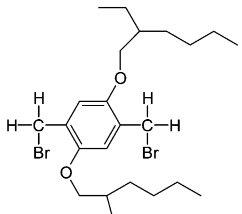
Scheme 8. Current Understanding of the Partial Steps in the Alternative Radical Gilch Polymerization, Proceeding via Growing α,ω-Macro-Diradical 3* Created by Dimerization of 2 Leading to Diradicals 18



zene **1a** and 2,5-bis(β-ethylhexyloxy)-1,4-bis(bromomethylene)-benzene **1b** were chosen as the starting materials.



1a



1b

KO^{t}Bu was used as the base, and dry THF was the solvent. Standard monomer concentration was 10 mmol L^{-1}, and the number of moles of **1** used in an entry was defined as “1 equiv”. With respect to that, 4 equiv of KO^{t}Bu were applied throughout to ensure quantitative dehydrohalogenation of the starting material and precursor polymer. Standard polymerization temperature was 0 °C, and all reaction mixtures were stirred for 24 h. If an entry was gel-like after that time, stirring was continued at room temperature for 1 more day. After that, the reaction mixtures were poured into a large excess of methanol. The precipitated polymer as well as all the material that remained in solution were isolated for further characterization. Figure 1 shows a representative ^{1}H NMR spectrum of a PPV **4b** obtained under these standard conditions. The observed broad and unstructured absorptions are characteristic of the repeating units of high-molecular weight PPVs **4** being predominantly in the trans configuration: at $\delta \approx 7.1$ and 7.5 ppm, one observes the phenylene and vinylene protons, at $\delta \approx 3.9$ ppm those of the $O-CH_2$ protons of the side chains, and above $\delta = 2.0$ ppm there appears all other protons of the 2-ethylhexyloxy substituents. Moreover, there are further absorptions of minor intensity detectable at, for example, $\delta \approx 2.8$, 6.6, 6.7−6.8, and 6.9 ppm. They underlie the existence of some defects within the chains such as the well-known ethylene and ethinylene bridges or cis-configurated vinylenes.[14−19] The molecular weight of these reference PPVs **4** was determined using SEC. The values of M_n were typically of the order of $(5 \times 10^5)-(2 \times 10^6)$ Da; polydispersities were around 2.5−3.0.

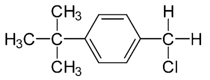
The above standard conditions were used predominantly in the following studies focused on the effect of additives on the

Gilch reaction. However, to highlight specific details, or to valuate the robustness of an experimental setup, further PPVs **4** were also prepared under slightly modified conditions: for example, the concentration of starting material **1** was decreased (down to 5 mmol L^{-1}) or increased (up to 30 mmol L^{-1}) or conversions were carried out at room temperature or 60 °C. As a general trend, it was found that the results obtained under modified conditions were very similar to those found for the standard procedure. The only really significant parameter was concentration of starting material **1**: when this was increased, there was a clearly increasing trend toward gel formation, and it took much longer to redissolve a gel fraction. On the other hand, when the concentration of **1** was decreased, the yield of polymer decreased.

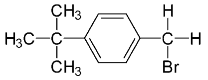
3.2. The Effect of Extra Protons or Carbanions. A central aspect which has to be taken into account right from the beginning in any discussion concerning carbanionic chain growth is that significant amounts of protic species are formed intrinsically during every Gilch polymerization, even if the reaction is started under strictly aprotic conditions. This is because monomer activation **1** → **2** as well as conversion of precursor PPX **3** into PPV **4** proceed via dehydrohalogenation, converting successively the KO^{t}Bu into ^{t}BuOH and KCl. Finally, 2 mol of protic ^{t}BuOH are present per mole of starting material. Thus, the progress of the Gilch reaction is associated with a tremendous increase in proton activity. Anionic chain propagation, therefore, is only possible if the involved carbanions are highly inert toward protic species. A huge excess of protons is already available after activation of only a small fraction of starting material **1**, which is orders of magnitude larger than the hypothetical overall number of growing carbanionic chains; this can be verified easily by taking into account the average molar masses of the formed PPVs **4**. Nevertheless, in order to make really sure experimentally that the polymerization mechanism and the products formed right at the beginning of a Gilch reaction do not differ from those at later stages of the conversion, up to 2 equiv of ^{t}BuOH were added right at the beginning, corresponding to the full amount of ^{t}BuOH present after complete conversion. As expected, almost no difference was found in all these polymerizations with respect to the reference syntheses carried out in the absence of extra alcohol: the polymerizations seemed to be slightly retarded, but once started, the characteristic color of the PPV appeared very fast. Moreover, gelation of the entries as well as redissolution of the formed gels was observed, and the PPVs were obtained in the usual yields of around 80%. Also, the NMR spectra did not indicate any difference compared to those of the reference PPVs. Only in SEC, minor variations were found: while the overall shape of the distribution curves was unchanged, the average molar mass of the PPV samples produced in the presence of extra alcohol was slightly below what was found for the reference PPVs. In combination with the slightly retarded start of the process, this might be interpreted as the consequence of a lower rate of initial monomer activation **1** → **2** caused by the extra ^{t}BuOH, but no evidence is found which supports a change of the propagation mechanism. To conclude, this first set of experiments did not provide any evidence of anionic chain propagation.

Nevertheless, one might argue that the involved carbanions are sufficiently inert toward ^{t}BuOH. Therefore, in a second set of trial experiments, we studied the consequences of extra carbanions of different reactivity when added very slowly to ongoing Gilch reactions: highly diluted solutions of *n*-, *sec*-, and *tert*-butyllithium as well as triphenylmethyl lithium were added at various rates, in different quantities, and at different temperatures to progressing Gilch reactions. Evaluation of these studies led to the conclusion that all tested carbanions were deactivated immediately and quantitatively by the ^{t}BuOH if there was a sufficient quantity of protic species available at the respective time. NMR analysis of the PPV obtained under these conditions showed that the organolithium compounds did not affect the Gilch polymerization in any respect. However, if the organolithium compounds were in excess with respect to the already formed ^{t}BuOH at any time during the conversion, the reaction mixtures changed their color immediately from yellowish-orange to deeply reddish-brown and ill-defined products were obtained from the entry. These studies showed that all tested carbanions are much too reactive to induce regular chain propagation, and it is reasonable to assume that the same applies to the hypothetical carbanions residing at the chain termini of growing PPV chains. Hence, already these initial studies allowed the conclusion that it is really hard to imagine that carbanions are the decisive species in the Gilch process. Nevertheless, we decided to also analyze the effect of monofunctional benzylhalogenides, which is taken as the main support of anionic chain growth by some authors.

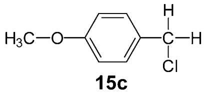
3.3. The Effect of Monofunctional Benzylhalogenide Additives. It has been reported that monofunctional benzylhalogenides **15** suppress gel formation during the Gilch synthesis of PPVs, prevent appearance of insoluble polymer fractions and systematically lower the PPV's molar masses. These effects were interpreted as an indication of anionic chain growth.[43−45] As stated above, doubts exist concerning this explanation.[60] On the other hand, if these "additives" really interfere with the Gilch process as chemically active species, the way they contribute is certainly indicative of the understanding of the whole chain propagation. It was therefore the next issue to verify the reported effects of the additives under the above standard conditions. As monofunctional benzylhalogenides, compounds **15a**−**e** were selected in order to cover a broader range of additive reactivity. They were added in quantities ranging from 0.5 to 4 equiv with respect to **1**. Such quite large quantities were applied to ensure perceptible changes in process and/or products even if the effects possibly induced by compounds **15** are only weak.



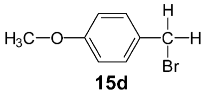
15a



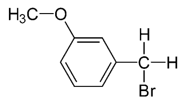
15b



15c



15d



15e

In fact, the first experimental observations were in full agreement with the literature: significant reduction or even complete suppression of gel formation was found in polymerization experiments when carried out in the presence of one of these above additives. If some gel appeared, moreover, it clearly redissolved faster and more completely. It also became evident that the efficiency of gel suppression depends not only on additive concentration but more significantly on its substitution pattern: 4-*tert*-butylbenzylchloride **15a** was the less efficient additive within the tested series, high concentrations were required to achieve reliable gel prevention. 4-*tert*-Butylbenzyl-

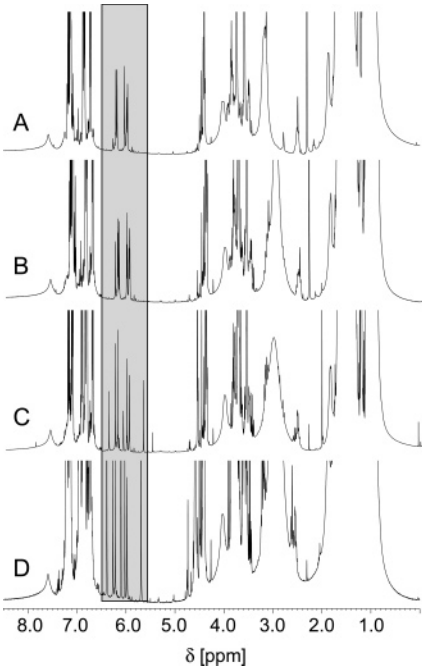


Figure 2. Representative ^{1}H NMR spectra of the reaction mixtures of a series of Gilch reactions using **1b** as the starting material, carried out in the presence of (A) 0.5, (B) 1.0, (C) 2.0, and (D) 4.0 equiv of *m*-methoxybenzylbromide **15e**; THF-d_8, room temperature. An enlargement of the underlayed area is shown in Figure 3.

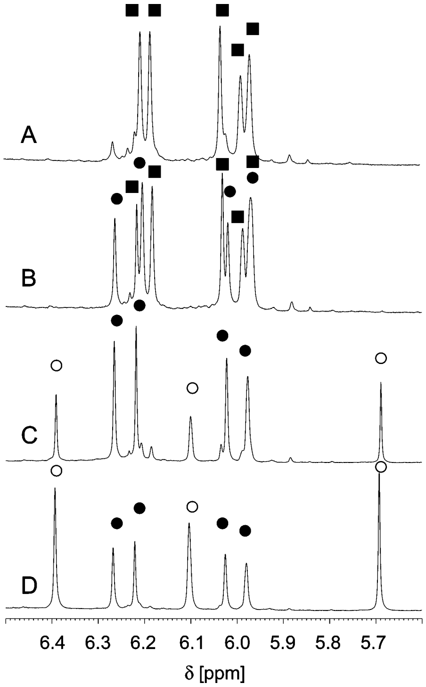


Figure 3. Sections of the ^{1}H NMR spectra shown in Figure 2 of a series of Gilch reactions using **1b** as the starting material, carried out in the presence of (A) 0.5, (B) 1.0, (C) 2.0 and (D) 4.0 equiv of *m*-methoxybenzylbromide **15e**; measurement in THF-d_8 at room temperature. The signal assignment is as follows: ○, [2.2]paracyclophane **19b**; ●, [2.2]paracyclophane-ene **20b**; ■, [2.2]paracyclophane ether **22**.

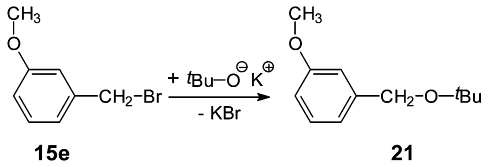
bromide **15b** proved to be slightly more efficient, however, at the expense of decreasing polymer yield: only 50−70% of the theoretically expected PPV **4** was formed while it was 70−90% for entries without an additive. Much higher efficiency was found for methoxy-substituted benzylhalogenides **15c**−**e**: even when added in small quantities, the reaction mixtures remained homogeneous solutions over the whole time of conversion (for standard concentration of **1**) or intermediately formed gels redissolved soon upon further stirring (for a monomer concentration of 30 mmol L^{-1}). On the other hand, application of these additives was accompanied by an even stronger decrease of polymer yield: PPVs were typically obtained in less than 40% yield when ≥2 equiv of a methoxy-substituted additive were present. To conclude, monofunctional benzylhalogenides **15** are appropriate for tackling the problem of gel formation during Gilch syntheses, and methoxy substituents clearly increase their efficiency. However, high efficiency in gel prevention was directly correlated with decreasing polymer yields.

The next task was to analyze whether the PPVs formed in the presence of additives **15** differ in any respect from PPVs obtained without additives. The polymer end groups were of particular interest here: if deprotonated **15** acts as an initiator for anionic chain propagation, it must appear as a chain terminus in the final polymer. However, the NMR spectra of PPVs produced in the presence of **15** were identical to the NMR spectra of the reference materials: there was absolutely no absorption detectable that might correspond to *tert*-butylphenyl or methoxyphenyl chain termini, even if the spectra were enlarged considerably. One might argue that lack of those absorptions is due to very high chain lengths and vanishing intensity of end group signals. Therefore, some PPVs were fractionated by careful precipitation, and the low-molecular weight fractions were analyzed once again using NMR. Even then, no indication was found of the expected additive-based chain termini. Also, the methanol-soluble fractions obtained when the formed PPVs were precipitated from the original reaction mixtures did not contain any oligomeric PPV fractions that bear the expected end groups.

A further characteristic feature, often reported in the context of anionic chain growth, is the systematic reduction of the PPV's molar masses with increasing amounts of monofunctional benzylhalogenides **15**. Therefore, all produced PPVs were analyzed using SEC. Very surprisingly, and in clear contrast to what has been published, there was no change at all observable in the SEC elugrams depending on constitution or quantity of **15** present during polymer synthesis, except some few entries containing very large amounts of **15c**−**e** where the apparent molar masses were even higher. In all other cases, neither the maxima of the distribution curves shifted nor was their shape modified in any respect. Instead, proper monomodal products were obtained. This result was not restricted to conversions at 0 °C but could be reproduced for polymerizations at room temperature and 60 °C as well. This is in unbridgeable conflict with the concept of anionic chain propagation induced by deprotonated **15**.

Since verification of these conclusions might have considerable consequences, it was our duty to be absolutely sure of the latter point. Therefore, we improved the performance of our experimental setup further: a series of polymerization experiments was carried out in a glovebox usually reserved for block copolymer synthesis via living anionic polymerization, and very dry and degassed THF-d_8 was applied as the solvent to enable NMR characterization of the reaction mixtures without intermediate workup or contact with ambient conditions. Concentrated solutions (30 mmol L^{-1})[61] of starting material **1b** were prepared, and 0.5, 1.0, 2.0, or 4.0 equiv of either **15d** or **15e** were added: these two additives were selected since they had shown the strongest effects in all previous experiments. Finally, 4.0 equiv of KO^{t}Bu were added to the vigorously stirred solutions at room temperature. After that, it took less than 1

Scheme 9. Ether Formation Is One of the Identified Side Reactions during Gilch Syntheses in the Presence of Monofunctional Benzylhalogenide Additives and Excess of KO^{t}Bu



min until the reaction mixtures had reached their final reddish-orange color, indicating very rapid polymerization which is apparently finished within a few minutes. And also in full agreement with the preceding reactions carried out at high monomer concentrations, all entries became gel-like within approximately 5 min: first those with lower quantities of additive but slightly later also all others. Therefore, stirring at room temperature was continued for 24 h. Within this period, one entry after the other changed back into a homogeneous solution, strictly following the order given by the quantity of additive present. Finally, the reaction mixtures were transferred into tightly closing NMR tubes equipped with screw caps, and full sets of NMR spectra were recorded. As a representative example, the proton NMR spectra recorded for a series containing 0.5, 1.0, 2.0, and 4.0 equiv of *m*-methoxybenzylbromide **15e** are shown in Figure 2. In all spectra, one can easily identify the broad and unstructured absorptions of PPV **4**. Moreover, the intense and well-resolved absorptions of unchanged **15e** are also visible as well as those of one additional derivative thereof. Comprehensive NMR analysis led to the conclusion that this second additive-based species is the ether **21**, which is formed via conversion of **15e** with excess KO^{t}Bu, as shown in Scheme 9.

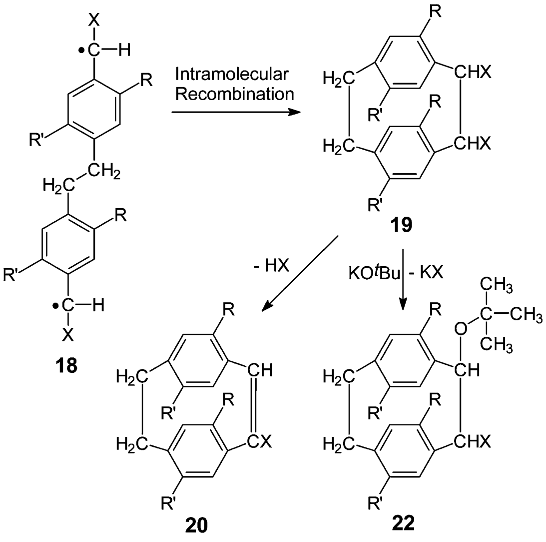
The relative amounts of **15e** and its ether derivative **21** change systematically with increasing amounts of additive present in the respective reaction mixture: when only 0.5 equiv of **15e** was added, it is almost quantitatively converted into the ether **21**, while with increasing quantities of **15e** more and more benzylbromide remains unchanged. Obviously, there is insufficient KO^{t}Bu present in the latter cases to achieve complete etherification of **15e**.

For the next step, let us ignore the absorptions discussed above. If so, further series of well-resolved signals remain in the spectra, especially in the range of $\delta = 5.6-6.5$ ppm. For more convenient visualization, Figure 3 shows an enlargement of the most relevant sections of the ^{1}H NMR spectra shown in Figure 2.

Some of these absorptions seemed well-known from previous studies,[20,23] others were obviously new, resulting from still unidentified species. Moreover, it was also evident that the intensities of all these latter signals change systematically with changing amounts of additive. Therefore, a careful analysis was carried out in order to safely assign all these absorptions.

Comprehensive analysis of the ^{1}H, ^{13}C, and 2D NMR spectra led to the conclusion that for 4.0 equiv of **15e**, [2.2]paracyclophane **19b** is the dominant side product (absorptions assigned by ○ in Figure 3). Moreover, there is a minor fraction of [2.2]-paracyclophane-ene **20b** (●) formed under these conditions, presumably via dehydrobromination of that fraction of **19b** which has the required configuration at its CHBr−CHBr bridge. With decreasing amounts of **15e**, the intensity of the signals of [2.2]paracyclophane **19b** decreases, while that of [2.2]paracyclophane-ene **20b** increases. Moreover, a third set of absorptions appears (■). The compound causing these new absorptions was identified to be the [2.2]paracyclophane ether **22b** (Scheme 10). It is obviously formed via substitution of one bromine substituent of [2.2]paracyclophane **19b** by a ^{t}BuO$^-$ moiety.

Scheme 10. Side Products Observed for Gilch Polymerizations When Performed in the Presence of Additives 15 and an Excess of KO^{t}Bu, Together with the Assumed Ways of Their Formation



a: X = Cl, R = OC_8H_{17}, R' = OCH_3, **b**) X = Br, R = R' = OC_8H_{17}

How can we interpret the changing composition of the various product mixtures as a function of the added quantity of additive **15**? Here, it is worthwhile analyzing the relative rates of the involved processes: there are two classes of reactions when Gilch reactions are performed in the presence of additives **15**, some reactions are very fast, others significantly slower. One of the fastest conversions is dehydrohalogenation of starting material **1**. This is evident, for example, because no indication could be found of remaining starting material **1** in any of the NMR spectra recorded in the course of these studies. Moreover, chain propagation of **2** leading to precursor PPX **3** as well as cyclodimerization of **2** leading to paracyclophanes such as **19** are also very fast processes, certainly finished within the first few minutes under the applied conditions. Last but not least, dehydrohalogenation of the intermediate precursor PPX **3**, leading to the final PPV **4**, must be assumed to be of a comparably high rate. This is because in all NMR spectra, whenever recorded in the course of a Gilch reaction carried out in the presence of sufficient quantities of KO^{t}Bu, we could never find absorptions indicating remaining $-CHX-CH_2-$ bridging units within the formed polymers.

In addition to the four fast reactions, there are at least three slow processes. The first (and presumably fastest in this series) is etherification of **15** by excess KO^{t}Bu, which is left over from dehydrohalogenation of **1** and **3**.[62] The second is dehydrohalogenation of [2.2]paracyclophane **19**. This reaction seems hampered compared to dehydrohalogenation of **1** and **3** due to considerable ring strain already existing in **19**, which is further increased by this elimination event leading to **20** due to the shorter C=C double bond. The third slow reaction is etherification of **19**. This reaction might compete with dehydrohalogenation **19** → **20**, or it might be the indicated reaction pathway for isomers of **19** which have an inappropriate configuration (1,2-*trans*-dihalogenide) for dehydrohalogenation.[63] Therefore, the latter two reactions of the paracyclophanes can take place to a significant extent only if KO^{t}Bu is left over after Gilch synthesis and conversion of **15** into its ether. Moreover, further small absorptions in the spectra also seem to correspond to paracyclophanes, presumably additional isomers. However, a precise constitutional analysis was not possible in those cases

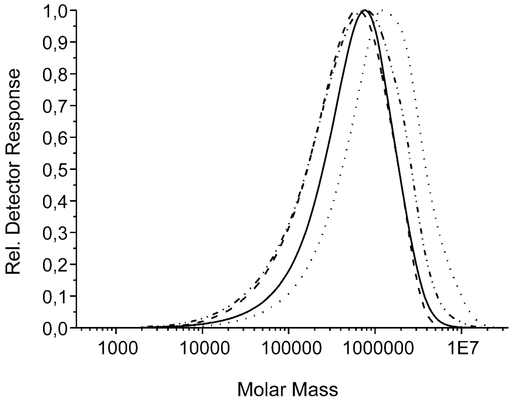


Figure 4. Molar mass distribution curves measured for Gilch PPVs **4b** synthesized in the presence of 0.5 (—), 1.0 (-----), 2.0 (-••-••-), and 4.0 (•••••••) equiv of additive **15e** from **1b** as the starting material.

because of their small quantities, which would require chromatographic enrichment. As this effort seemed unnecessary for the purpose of this work, this time-consuming procedure was not carried out.

In addition to the composition of the product mixtures, further relevant information can be derived from the NMR spectra, such as the yield of polymer formed in the respective entry. With knowledge of the constitution of all major side products, comparison of signal intensities allows estimation that the yield of PPV drops down from roughly 70% for 0.5 equiv of **15e** to 40% for 4.0 equiv of **15e**. Vice versa, the quantities of paracyclophanes increase with increasing amounts of additive from 30% to approximately 60%. This finding is in full agreement with our initial studies where a very similar decrease in polymer yield was observed with increasing quantities of methoxy-substituted additives **15**.

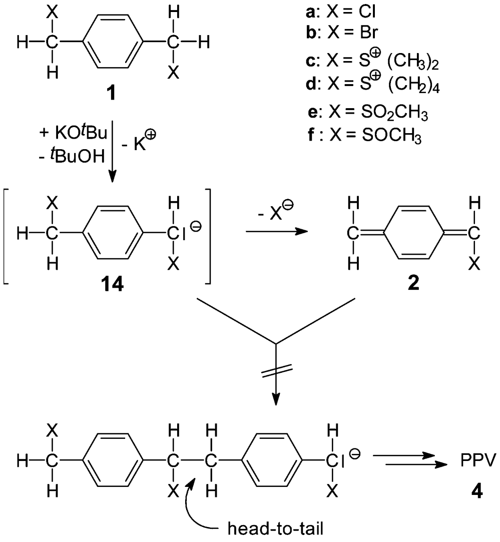
Finally, it was of interest whether there is any change of molar masses and/or molar mass distributions of the PPVs formed in the deuterated solvents and caused by the additives **15** under the highly inert glovebox conditions. Therefore, representative parts of the obtained reaction mixtures were added to a large excess of methanol, and the precipitated PPVs were analyzed using SEC. Figure 4 shows the SEC plots for the series where the *m*-methoxybenzylbromide **15e** was used as the additive; the corresponding SEC traces obtained in the case of additive **15d** were almost identical. As it became evident from these measures, it is a nicely consistent result that for both additives, **15d** and **15e**, almost all SEC elugrams coincide exactly, as was also the case before in the conventional lab experiments: there is neither a decrease in average molar mass nor any relevant change in the molar mass distribution curves caused by the additives. On the contrary, for the highest added quantities of additives (4.0 equiv), the SEC curves are slightly shifted to even higher molar masses, in contrast to what was expected based on the current understanding of the effect of these additives. All together, therefore, these glovebox studies fully supported what we had established before in the other Gilch experiments under "conventional" conditions.

To conclude, there is now a nicely consistent picture available of what the consequences are of the presence of additives **15** during the Gilch process: first, there is certainly no direct incorporation of additive fragments into the PPV chains. Second, there is no other chemical modification observable for the formed PPVs: constitution, configuration, and all detectable defects in the formed PPV chains remain unchanged with respect to the reference PPVs. Third, the same applies to the byproducts: irrespective of the presence of additives **15**, the only significant side-reaction of the *p*-quinodimethane monomers **2** is cyclodimerization leading to [2.2]paracyclophanes **19** and derivatives thereof. Fourth, it is also evident now that additives **15** influence neither directly nor indirectly the chain propagation event: average chain length, polydispersity, and in particular the molar mass distribution are very sensitive toward any change in chain-growth conditions, but the additives clearly change neither the initiation event nor the concentration of active monomers **2** in the relevant phase of the Gilch reaction. Also, concentration of growing chains, propagation mechanism, and termination process remain unaffected. Fifth, the only identified chemical reaction of additives **15** is etherification via conversion with excess KO^{t}Bu. However, this process is much slower than all other reactions found during the Gilch reaction, i.e., dehydrohalogenation processes **1** → **2** and **3** → **4**, chain propagation **2** → **3**, and cyclodimerization **2** → **19**. These reactions are finished long before etherification of **15** follows. These findings ultimately disprove the role of monofunctional benzylhalogenide additives as initiators of carbanionic polymerization of **2**. Decrease of the PPV's chain length with increasing quantities of additives **15,** as was reported by other groups, has to be traced back instead to impurities present in these monofunctional benzylhalogenides.[64]

3.4. The Gelation Mystery. Everything would be fine now if there were not these two mysterious, but experimentally clearly verified, modifications in the presence of increasing amounts of additives **15**, i.e., suppression of gel formation (or its accelerated redissolution) and higher amounts of [2.2]-paracyclophane byproducts. First of all, we should emphasize that there is clear evidence that gelation is not due to chemical crosslinking but must rather be a purely physical phenomenon. The most remarkable support of this statement is provided by the fact that the gel, once formed in the reaction mixture, redissolves even at low temperatures (0 °C) and in the dark upon prolonged stirring. Under these conditions, it is hard to imagine a chemical reaction that might be able to lead back from a chemically crosslinked state to a homogeneous solution. Moreover, as we could show, the gel suppression effect provided by additives **15** is not due to lowering the molar masses of the resulting PPVs. Also, simple dilution is certainly not an appropriate explanation: if so, the efficiency of an additive in suppressing gel formation, and also the extent of cyclodimerization leading to [2.2]paracyclophanes, must not depend on the constitution of the respective additives [^{t}Bu (**15a**,**b**) vs methoxy (**15c**−**e**) in this study]. The only reasonable explanation of both effects which we can provide so far points toward (i) strong attractive ($\pi-\pi$, donor−acceptor or dipolar) interactions between additive molecules and chain segments, leading to preferential solvation of the polymer chains by the additive molecules, and/or (ii) retardation of the macromolecular dehydrohalogenation reaction **3** → **4**. Why should these effects be in operation here? This is because, in contrast to conventional polymerization reactions, the PPV chains are formed in very high molar masses and additionally have coil dimensions and entanglement densities far away from the equilibrium state immediately after their formation. This is presumably effected by the extremely rapid chain propagation, which includes regular 1,6-type radical monomer addition steps as well as polyrecombination events of the growing α,ω-macro-diradicals. Moreover, immediately after this very rapid chain growth, which especially does not consider preferred coil dimensions and entanglement densities in later states, the PPX intermediates **3** undergo the final dehydrohalogenation step. This macromolecular elimination reaction is very rapid as well, according to preliminary studies it is not much slower than the chain growth itself, and converts the rather flexible PPX **3** into an only semiflexible and rather rodlike PPV species **4**. It is immediately evident that the chain and segment motions of these very high-molecular weight polymers cannot follow these tremendously rapid changes by adapting the overall shape instantaneously, and a much too high entanglement density survives the polymer formation, in particular when the polymerization was carried out at high concentration and without stirring (introduction of momentum). Macroscopically, this temporarily physically crosslinked system is manifested by the appearance of a gel state. Subsequently, de-entanglement processes proceed up to an extent which is in accordance with thermodynamics, and the homogeneous solution is formed again. Without extra support (heating, stirring, additives), this needs a considerable amount of time in the highly viscous systems and this is why prolonged stirring and (sometimes) heating is required to achieve a polymer solution again. On the other hand, the rate of de-entanglement is certainly a function of chain dynamics and segment−segment interaction at the molecular level, and these two parameters might be addressed by additives such as **15**. They might weaken the otherwise strong segment−segment interactions in the high-molecular weight chains, replace them at least partially by segment−solvent contacts, and moreover they might retard, at least to a certain extent, the conversion of the flexible PPX precursor **3** into the only semiflexible and thus much less dynamic PPV **4**. This explanation is supported by the reproducible observation that gel formation can be prevented efficiently without additives when the reaction mixtures are vigorously stirred, using mechanical stirrers instead of magnetic bars, while in the opposite case, when the reaction mixtures are not stirred at all, as in the case of conversions in NMR tubes, the formed gel is very hard to redissolve. Moreover, the additives might support closer chain conformations, which additionally support de-entanglement processes. The same effect might also be the reason for the clearly increasing amounts of cyclodimerized products with increasing quantities of additives: they might increase the probability of assuming the (otherwise energetically unfavorable) stacked conformation of **18**, which is required for ring closure. Clearly, these explanations are still rather speculative and will require further verification, but to the best of our knowledge they represent the only consistent rationalization of the full set of experimental information obtained in this as well as in many previous studies. Therefore, we believe it is worthwhile mentioning these considerations and conclusions even if they were not the main focus of the present study.

3.5. Simulation Studies. The above experimental results clearly disprove any anionic chain propagation in the Gilch synthesis. What precisely is the reason for that, and why do not we find side products pointing toward at least a minor extent of anionic initiation steps in the oligomeric fractions? In order to gain a deeper insight into these questions, the relevant steps of initiation were additionally analyzed by means of computational simulation studies.

Scheme 11. General Reaction Scheme for the Anionic Mode of Polymerization Leading to PPVs



In the absence of monofunctional benzylhalogenide additives **15**, there are two possible ways of creating initiating carbanionic species. These are in addition to KO^{t}Bu as a nucleophile to the active monomer **2** and deprotonation of starting material **1** (see Scheme 6). In the presence of additives like **15**, moreover, there might be additionally deprotonated species **16** which act as extra anionic initiators (Scheme 7). The apparently simplest way of forming carbanions is deprotonation of starting material **1** without simultaneous elimination of the halogenide leaving group. This process, however, requires that monomer activation **1** → **2** is an E_{1cb} two-step process, composed of initial individual deprotonation and subsequent dehalogenation events. For the Wessling route, it could be shown that this option exists. However, the corresponding anion has neither been reported for the Gilch reaction itself, nor for other Gilch-related processes. Therefore, it was of interest whether simulation studies also lead to the conclusion that dehydrohalogenation of **1** leading to *p*-quinodimethane **2** is a concerted E_2 process. In a first attempt to model the anionic mode of polymerization (Scheme 11), we focused on the features of the anionic intermediate **14**. However, all attempts to fully optimize its molecular geometry by ab initio (HF/6-311G(d)) or DFT methods (B3LYP/6-311G-(d)) resulted in spontaneous loss of the corresponding halide anions and formation of the neutral α-substituted *p*-quinodimethane **2** only, without any apparent transition barrier at all. This behavior proved to be independent of various initial structures as well as the quality of the basis sets (6-311G(d) vs 6-311++G(d,p) and aug-cc-pVTZ) used. Even the latter very large basis set calculations uniformly resulted in barrier-free dissociation.

As solvent effects may be considered crucial to the stabilization of the highly polar anionic intermediates, we have included solvents of different polarity (toluene, THF, CH_3CN, and DMSO) by polarizable continuum models in the electronic structure calculations. Despite these refinements, no optimized and stable geometry of **14a**,**b** could be obtained in any case. Instead, all models resulted in an essentially unchanged process of spontaneous dissociation. Additionally, all attempts to characterize stable intermediates emerging from the direct anionic coupling of **14a**,**b** and **2a**,**b** (Scheme 11) with different modes of regioselectivity (head-to-tail and head-to-head) or spatial arrangements (gauche and trans orientation of the phenyl rings with respect to the central carbon−carbon bond formed) failed. Invariably, all configurations displayed the pronounced tendency toward loss of one halide anion at varying positions depending on the mode of coupling. In any case, we were not able to identify a single stable anionic intermediate, nor any corresponding transition state for the anionic mode of the Gilch polymerization. In this context, we looked specifically at the initial mode of deprotonation of **1a** by KO^{t}Bu. In Figure 5, the configurations of the starting materials and the products, along with the transition state **1a*** connecting both configurations **1a** → **2a** are depicted. Although the chlorine atom is still bonded to the carbon atom in the transition state with an only

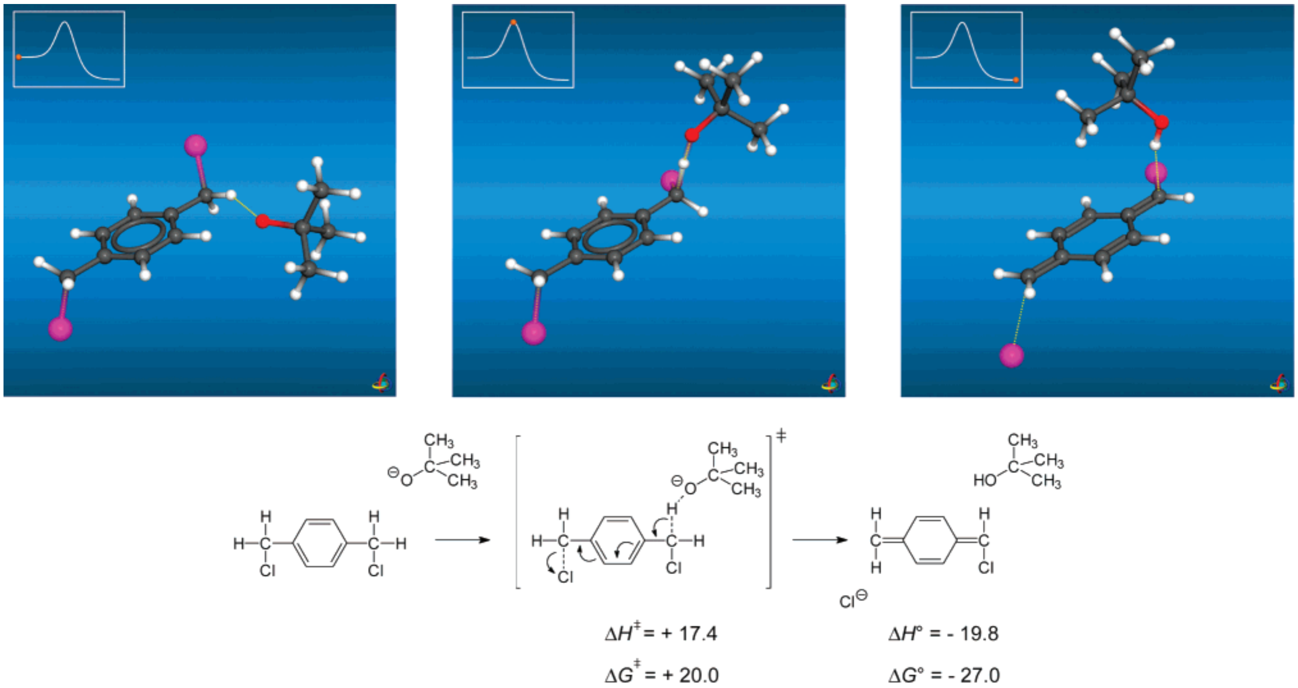


Figure 5. Reaction coordinate modeling of the deprotonation of 1,4-bis(chloromethyl)benzene **1a** by *tert*-butanolate (left, starting materials; center, transition state; right, products). The E_2 type mechanism results in the simultaneous formation of ^{t}BuOH, the chloride anion, and the *p*-quinodimethane **2a** (all structures B3LYP/6-311G(d); energies in kJ mol^{-1} relative to the starting materials); similar results were obtained with larger basis sets (B3LYP/6-311++G(d,p) and B3LYP/aug-cc-pVTZ), though the exact zero-point energy (ZPE) corrected energies were not determined in these cases.

slightly increased bond length of 1.918 Å as compared to 1.841 Å in the initial geometry, it is continuously removed immediately after surmounting the energy barrier, until finally the chloride anion, *tert*-butanol, and the *p*-quinodimethane **2a** are formed.

Summarizing, it must be concluded that the initial formation of *p*-quinodimethanes **2** from the starting materials **1** by reaction with KO^{t}Bu does not represent a stepwise E_{1cb} (or E_1) elimination but must follow a concerted E_2 type mechanism. Obviously, any putative anionic species proved unstable under the conditions considered here, and only inert solvents of high polarity − solvent molecules may even have to be included explicitly rather than by continuum models in the structure calculations, which, in turn, become prohibitively expensive − may contribute to the stabilization of anionic intermediates. Obviously, the formation of the halide ions represents a major driving force for the process of generating the *p*-quinodimethanes.

It should be noted that we have seen a similar tendency toward spontaneous fragmentation for alternative PPV precursors derived from phenyl bis-sulfonium salts ($X = -S^+(CH_3)_2$ **1c** and $-S^+(CH_2)_4$ **1d**). However, the anions generated from bis-sulfonyl ($X = -SO_2CH_3$, **1e**) or bis-sulfinyl ($X = -SOCH_3$, **1f**) substituted benzene derivatives proved to be more stable, and an anionic type of polymerization mechanism cannot be excluded from the corresponding precursors routes toward PPVs.

An alternative way for carbanion formation is direct attack of KO^{t}Bu to the *p*-quinodimethane monomer **2**. Of course, this process is highly improbable from the energetic point of view, and no evidence of its occurrence has been found so far. However, one might argue that the associated aromatization of the *p*-quinodimethane motif bridges the gap in energy and that there might still be a finite probability of addition of KO^{t}Bu to the *p*-quinodimethane **2**. This process was therefore also simulated, and the associated energies were calculated.

Although the primary addition of *tert*-butanolate to *p*-quinodimethane **2a** is exothermic, this bimolecular process is calculated to be slightly endergonic at room temperature ($\Delta G_{calcd} \approx +8$ kJ mol^{-1}, despite the aromatization of the π-system, Figure 6) with an activation barrier of about $\Delta G^* \approx +80$ kJ mol^{-1} in THF (solvent used in the computational model). However, on the basis of the computational results, the process is surmised to be followed by a rapid protonation step of the resulting anion by ^{t}BuOH, which is also present in the reaction mixture, resulting in an energy gain of approximately 40 kJ mol^{-1}. The same result was already anticipated on the basis of the relative pK_a values (see discussion above) of the benzyl halides in relation to ^{t}BuOH, and the overall process would correspond to a 1,6-addition of *tert*-butanol to the *p*-quinodimethane. In summary, this protonation step would lead to very rapid deactivation of the corresponding anions, thus effectively preventing the anionic mode of polymerization in the presence of excess protic species, which is clearly not the case for the Gilch process.

In the presence of monofunctional benzylhalogenides **15**, a special option of anionic chain initiation is carbanion formation by deprotonation of the additive leading to **16**. In the light of the above results, the corresponding anions are certainly not stable in the presence of alcohols but would undergo rapid deactivation by excess *tert*-butanol. In total, the computational results must be interpreted such that no supporting evidence could be obtained for stable anionic species as active polymerization reagents in the mechanism of the Gilch process. To conclude, the simulation studies as well are in clear conflict with any relevance of anionic chain growth, not only for the standard Gilch process but also for those carried out in the presence of additives or in usual solvents.

4. Conclusions

From the studies reported in this paper, the key conclusions are the following: (i) addition of extra ^{t}BuOH to the reaction

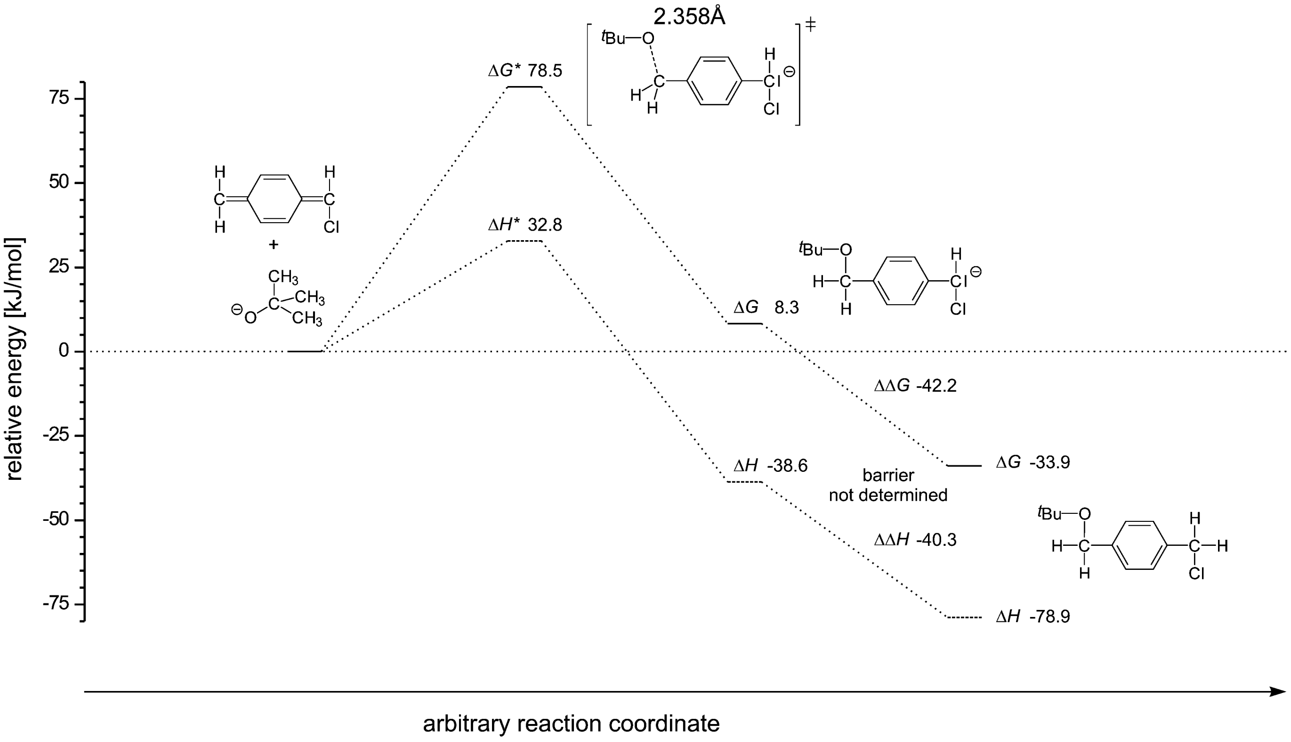


Figure 6. Energies Δ*H* and Δ*G* (298 K) for the reaction of *p*-quinodimethane **2a** with *tert*-butanolate; all B3LYP/6-311G++(p,d) ZPE corrected energies in kJ mol^{-1} (solvent: THF represented using the polarizable continuum model).

mixture of a Gilch synthesis right at the beginning changes neither the process nor the obtained products; (ii) extra carbanions, when added in the course of a Gilch reaction, are either destroyed immediately by the protic ^{t}BuOH already existing or, if added in excess with respect to available protic species, destroy starting materials, intermediates, and products involved in the regular Gilch synthesis; moreover, (iii) the reported suppression of gel formation during Gilch syntheses in the presence of monofunctional benzylhalogenide additives **15** could be verified, but (iv) increasing amounts of **15** correlate with clearly lower yields of PPV. A corresponding increase of cyclodimerization was observed (up to 60% overall yield!), leading to [2.2]paracyclophanes. (v) NMR spectra of products and byproducts are nearly identical for polymerizations with and without additives **15**, and, very remarkably, (vi) there is (almost) no dependency of the molar masses and polydispersities of the PPVs on the quantity and efficiency of the monofunctional benzylhalogenide additives **15**. (vii) According to the theoretical analysis, and in full agreement with our experiments, it is reasonable to assume that the process of activation of starting material, **1** → **2**, is an E_2 type elimination. Thus, no indication was found toward the existence of any stable anion in the theoretical analysis either. The driving force for the appearance of such a carbanion might be the formation of KCl and KBr, but the acidity of the ^{t}BuOH is clearly higher than that of the benzylhalogenides. (viii) Fully in line with that, the addition of ^{t}BuO$^-$ to the *p*-quinodimethane also has an insufficient driving force according to the theoretical calculations, despite the associated aromatization of the *p*-quinodimethane moiety. The reaction's driving force was sufficient only when protonation of the hypothetical carbanion was additionally included in the calculations. However, the corresponding products were never observed in practice.

To conclude, it is not possible to formulate a convincing process leading to carbanions in the Gilch synthesis of PPV. Hence, anionic chain growth certainly does not play a role here. Instead, the process is a radical chain polymerization, mainly driven by conventional 1,6-type monomer addition to the radical chain termini. It is superimposed to a certain, not yet quantified, extent by polyrecombination events of the α,*ω*-macro-diradicals **3*** which do not terminate individual chain growth due to their diradical character, in contrast to conventional radical polymerizations. One consequence is the very high molar mass that can be achieved by the Gilch synthesis; another consequence is obviously that the chains are very highly entangled immediately after their formation. This presumably gives rise to the frequently observed gelation of the reaction mixtures during the Gilch reactions which is obviously purely physical crosslinking due to the numerous entanglements and additionally due to the final additional stiffening of the very long chains via the macromolecular elimination process PPX **3** → PPV **4**. Therefore, de-entangling needs much more time than usual, and this gelation is thus found to be maintained over longer periods of time. In this respect, the effect of the benzylhalogenide additives **15** is obviously that of a preferred solvent, which weakens the segment−segment interactions of the polymers and thus supports de-entangling. Moreover, they might additionally slow down the final conversion **3** → **4** to a certain extent, thereby additionally supporting increased chain mobility. In agreement with these explanations, increasing quantities of [2.2]paracyclophane side products were found for increasing quantities, and increasing gel-prevention efficiencies, of the additives **15**. Clearly, these interpretations require further verification. Nevertheless, to the best of our knowledge, the picture presented here is the only one available so far which does justice to all experimental findings known so far.

5. Experimental Section

5.1. Materials. All chemicals and solvents were purchased from Acros, Aldrich, and Strem and used without further purification. General procedures were as described recently.[20−23] THF-d_8 was purchased from Deutero GmbH, Kastellaun, Germany, and used as received.

5.2. Methods. NMR spectra were recorded using a Bruker ARX 300 NMR spectrometer working at 300 MHz (^{1}H NMR) and 75

MHz (^{13}C NMR) and on a Bruker DRX 500 NMR spectrometer working at 500 MHz (^1H NMR) and 125 MHz (^{13}C NMR). δ values are given relative to tetramethylsilane as the internal standard.

5.3. General Procedure for Gilch Reactions. Under an atmosphere of nitrogen, starting material **1** (200 mg, 10 mmol L^{-1}) is dissolved in dry and degassed THF (sometimes fully deuterated THF was used, see text). At 0 °C, 4 equiv of KO^{t}Bu, dissolved in dry THF (3.3 mol L^{-1}), is added at once. Stirring at 0 °C is continued for another 4 h. Subsequently, the reaction mixture is allowed to warm up to room temperature and to stir for another 24 h. The obtained solution is poured into methanol. The formed solid is collected and dried in vacuum. The methanol solution is also carefully rotoevaporated and then dried. Without additives, the yield of PPV is around 70% (**4a**) and 80% (**4b**). In the presence of additives, it may drop down to less than 40%, depending on the constitution and the quantity of the additives. Spectroscopic data of the obtained polymers and oligomeric fractions are as described in the text and a recent publication.[20−23]

5.4. Calculation Methods. Ab initio and DFT (B3LYP)[51−54] computations were carried out using the Gaussian 03[55] suite of programs. All structure setups, analysis protocols, and molecular graphics were prepared using the MolArch$^+$ utility.[56] All electronic structure calculations employed the 6-311G(d) basis set[57,58] unless stated otherwise in the text. Solvation effects were included by the polarizable continuum model (PCM) for solvents of different polarity: toluene ($\epsilon = 2.4$), THF ($\epsilon = 7.6$), CH_3CN ($\epsilon = 36.6$), and DMSO ($\epsilon = 46.7$).[55] All stationary points identified (energy minima vs transition states as first-order saddle points) were verified by thermal frequency analysis. All calculations were performed on AMD Opteron 846 based 64-bit Linux computer systems of the Frankfurt Center for Scientific Computing.

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(59) It has to be emphasized that gel formation during the Gilch synthesis of PPVs as well as redissolution of once formed gel upon prolonged stirring were still a kind of mystery when we started our research program: chemical crosslinking was unlikely because of the observed reversibility of gel formation under very mild conditions. Physical crosslinking, on the other hand, might explain reversible gelation, but there was no conventional interaction evident which might be strong enough to cause the observed effects.

(60) Although the process of deprotonation of species like **15**, as depicted in Scheme 7, seems plausible at first sight, a rough estimate of the protonation−deprotonation equilibria, i.e., **15** vs **16**, in the presence of ^{t}BuOH must be based on the approximate pK_a value of the species under consideration (^{t}BuOH $\approx$ 16, Ph−CH$_2$X $>$ 20). Yet these values on their own indicate that the formation of **16** is highly improbable.

(61) This high monomer concentration was indicated to obtain well-resolved NMR spectra directly from the reaction mixtures with a resonable number of scans not only for proton spectra but also for carbon and 2D NMR experiments,

(62) This should be a rather slow S$_N$1 type reaction, in particular because KO^{t}Bu is almost inappropriate to undergo the clearly faster S$_N$2 pathways.

(63) It is assumed that the ether **22** is formed following an elimination−addition mechanism. This is because the two alternative pathways leading to its formation seem rather unlikely, the S$_N$2 option for sterical reasons and the S$_N$1 option because of the lack of mesomeric stabilization of the carbenium intermediate due to its inappropriate geometry in the bridging unit.

(64) We will describe the most probable reason of these effects in a subsequent paper.

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