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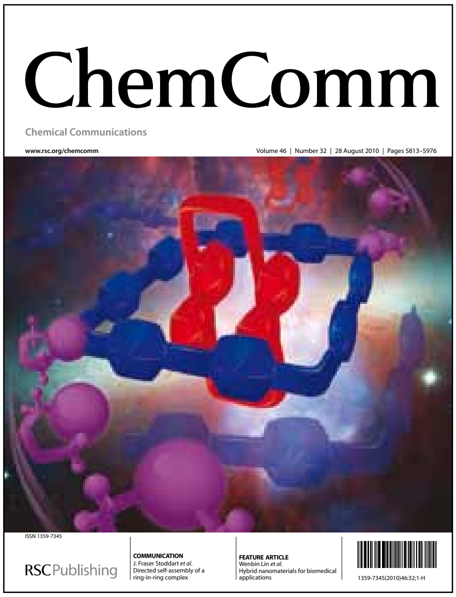

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FEATURE ARTICLE
Wenbin Lin *et al.*
Hybrid nanomaterials for biomedical applications

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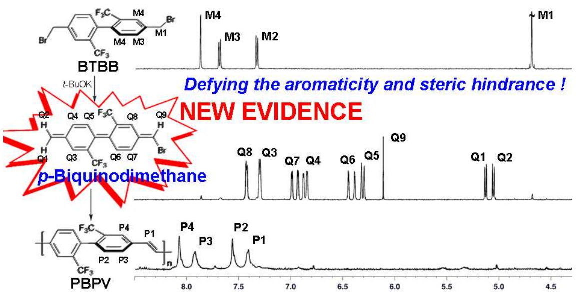

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New Evidence Supporting the Mechanism of Gilch Polymerization from an Extremely Twisted Biphenyl Monomer

Jyh-Chien Chen,* Chi-Jui Chiang, Jen-Chun Chiu and Jyh-Jong Ju

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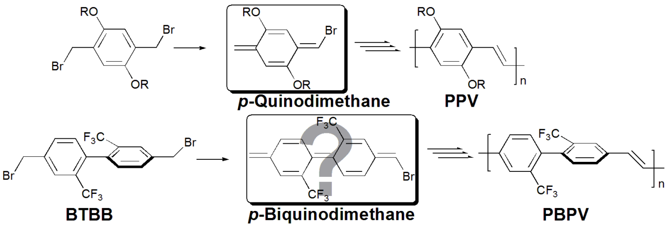
A *p*-biquinodimethane species formed during Gilch polymerization of an extremely twisted biphenyl monomer has been identified by in-situ ^{1}H-NMR spectroscopy for the first time. From the identification of structure defects, we conclude that the chain growth reactions during Gilch polymerization of biphenyl type monomers are both free-radical and anionic in nature.

Since the discovery of electrical conductivity of doped polyacetylene in the last century, much effort has been focused on the synthesis of new π-conjugated polymers and investigations on their opto-electronic properties associated with versatile applications in organic electronics.[1] Among these π-conjugated polymers, poly(*p*-phenylenvinylene) (PPV) is the first polymer reported to exhibit electroluminescence.[2] Therefore, its synthetic procedures have been studies in detail. Many organic reactions such as sulfinyl,[3] sulfonyl,[4] Wessling,[5] Gilch,[6] Heck,[7] Suzuki,[8] ring-opening metathesis,[10] Wittig,[11] and Horner-Emmons[12] approaches have been exploited to prepare PPVs. Gilch polymerization is one of the most widely used methods because of the relatively simple treatment on easily accessible monomers (1,4-bis(halomethyl)benzene) with inexpensive *t*-butoxide as base. No expensive catalysts are required.

Although the issue regarding the anionic or radical chain-growth mechanism of Gilch route is still a central debate, it is generally accepted that the first step in Gilch polymerization is 1,6-dehydrohalogenation of 1,4-bis(halomethyl)benzene-type monomer, leading to the formation of *p*-quinodimethane species as shown in Scheme 1 and ESI† Scheme S1.[6] Consequently, the feasibility to form *p*-quinodimethane species is obviously vital in Gilch polymerization. The existence of the *p*-quinodimethane species has been reported by Rehahn and co-workers using in-situ NMR spectroscopy.[12]

A few articles regarding Gilch- and Gilch-like-polymerized PPVs with biaryl and hetero-biaryl moieties have also been published.[13] It is reported that a dihedral angle is generated by the steric hindrance between the two neighboring rings. If the formation of *p*-biquinodimethane species is the necessity of Gilch polymerization as suggested by the mechanism, the non-coplanar biaryls and hetero-biaryls would be forced to form the coplanar *p*-biquinodimethane species by destroying the aromaticity and overcomimg the large steric hindrance as shown in Scheme 1. However, *p*-biquinodimethane species has never been observed or reported.



Scheme 1 Formation of *p*-quinodimethane and motive of this research.

In this communication, we report the in-situ ^{1}H-NMR evidence of *p*-biquinodimethane structure that formed during Gilch polymerization of an extremely twisted biphenyl monomer, 2,2'-bis(trifluoromethyl)-4,4'-bis(bromomethyl)biphenyl **(BTBB)**. We also discuss the characteristics (anionic or radical) and defects that formed during chain growth reaction.

This monomer **(BTBB)** was designed to be extremely twisted by the intense steric hindrance resulted from the bulky trifluoromethyl groups at the 2 and 2' positions of 4,4'-biphenyl. It was synthesized by a seven-step synthetic route as shown in ESI† Scheme S2. Compounds **(2)** ~ **(6)** as shown in ESI†Scheme S2 were prepared according to our previous publication.[14] The chemical structures and properties were well characterized (Fig. 1 and ESI†). Gilch polymerization was carried out through the general process (ESI†) to obtain **PBPV-1** (yield: 60%, Mn: 149,000, PDI: 2.19 (ESI† Table S1)). The solubility and thermal properties of **PBPV-1** are summarized in ESI† Table S2 and S3.

It is generally believed that the first and the vital step in the Gilch polymerization is 1,6-dehydrohalogenation of monomer, leading to the formation of *p*-quinodimethane species. And the diradical-type initiator is formed by the spontaneous self-dimerization of 2 moles of *p*-quinodimethanes. This active species then polymerized immediately to generate the non-eliminated prepolymer. *p*-Quinodimethane can also be initiated by *t*-BuOK present in the reaction mixture to form the prepolymer through anioic polymerization. The prepolymers were finally converted into PPV by macromolecular elimination cascade (ESI† Scheme S1).[6]

As far as we know, all the mechanistic studies of Gilch polymerization were based on the phenyl-type monomers.[6,12] In the case of **BTBB**, the biphenyl is extremely twisted. We are curious about the possibility of forming the coplanar *p*-biquinodimethane species by defying aromaticity and extremely

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large steric hindrance. However, the successful preparation of the corresponding twisted **PBPV-1** by Gilch polymerization implied the existence of *p*-biquinodimethane species as suggested by the mechanism (Scheme 1 and ESI† Scheme S3).

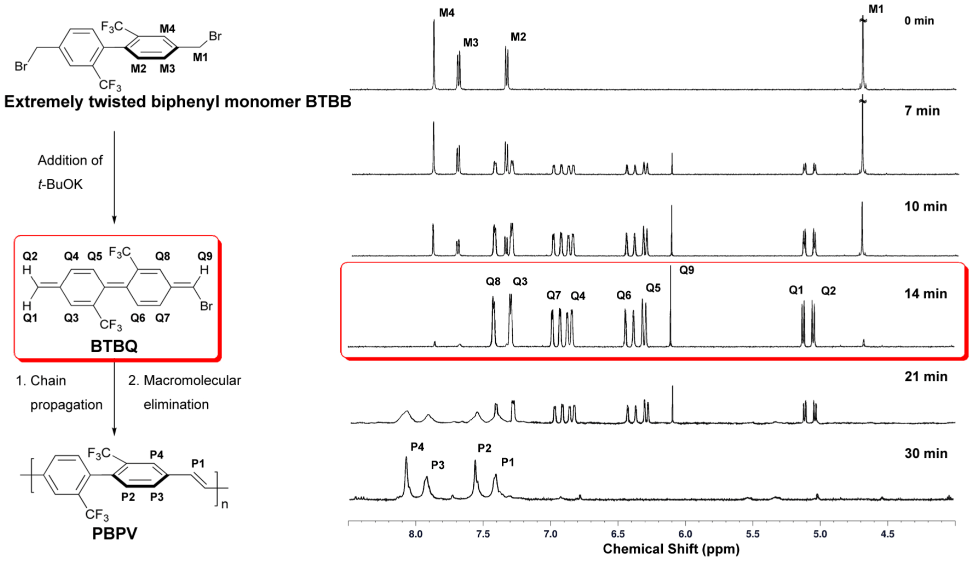

Fig. 1 In-situ ^{1}H-NMR spectra at -50 ℃ with different reaction time in THF-d_8.

In order to prove the existence of *p*-biquinodimethane species during Gilch polymerization of **BTBB**, we monitored the polymerization with in-situ ^{1}H-NMR experiments at -50 ℃. Monomer **BTBB** (20 mg, 0.04 mmol) in THF-d_8 (0.4 mL) was added into an NMR tube and pre-cooled at -50 ℃. The pre-cooled base solution (*t*-BuOK, 18 mg, 0.16 mmol in 0.8 mL of THF-d_8, at -50 ℃) was injected slowly into the tube, which was then transferred into the pre-cooled NMR spectrometer. ^{1}H-NMR spectra were recorded at different time intervals. Fig. 1 shows some of the spectra. Spectrum at the start (0 min) demonstrates the chemical structure of monomer **BTBB**. After 7 min, some new peaks are detected between δ= 5.0 and 7.5 ppm. These new peaks become more prominent as absorption peaks attributed to **BTBB** monomer diminish with time. At 14 min, except the new peaks, all the peaks attributed to **BTBB** monomer disappear. The newly formed peaks were gradually replaced by a set of peaks attributed to **PBPV-1** from 21 min to 30 min.

Closer examination on the chemical shifts, splitting, coupling constants and integral area of peaks appearing in spectrum at 14 min confirms the chemical structure of *p*-biquinodimethane species as α-bromo-2,2'-bis(trifluoromethyl)-*p*-biquinodimethane **(BTBQ)**. This is the first time that *p*-biquinodimethane species is observed and identified by ^{1}H-NMR spectrum. It proves that *p*-biquinodimethane species can be formed regardless the aromaticity and steric hindrance. It further confirms the validity of the mechanism of Gilch polymerization, not only for phenyl-type monomers but also for biphenyl-type monomers even with large steric hindrance. On the contrast to Gilch polymerization of phenyl-type monomers, there are no peaks that could correspond to the cyclic byproducts[15] were observed in Fig. 1.(ESI†)

An unsuccessful attempt to observe the *p*-biquinodimethane species in temperature-dependent ^{1}H-NMR experiments (from -70 ℃ to 0 ℃ with an interval of 10 ℃) might be due to the relatively short life-time of *p*-biquinodimethane species. The life time might be shorter than the time required for NMR spectrometer to reach thermal equilibrium. Therefore, the formed *p*-biquinodimethane species might have been converted to the polymer before measurement started. The large driving force to restore aromaticity and alleviate the steric hindrance by forming a non-coplanar polymer conformation might be responsible for the short life time.

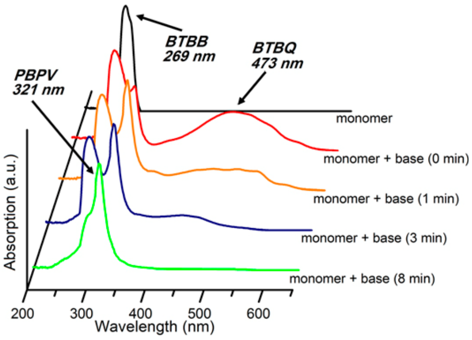

Fig. 2 In-situ UV-vis spectra with different reaction time in THF at -20 ℃.

In order to reconfirm the existence of *p*-biquinodimethane, UV-vis spectrometer was also used to monitor the Gilch polymerization of **BTBB** in THF at -20 ℃. Fig. 2 shows the UV-vis spectra of monomer **BTBB** (10^{-4} M in THF) in the presence of *t*-BuOK (4 equivalents) recorded at different reaction time. Immediately after the addition of *t*-BuOK solution to the **BTBB** in anhydrous THF, a new absorption peak around 473 nm was observed. This peak quickly diminished, followed by the simultaneous growth of absorption peak resulted from the formed polymer **PBPV** at 321 nm with the reaction time. After 8 min, only absorption peak of **PBPV** was observed. Thus, the absorption peak at 473 nm can be assigned to the *p*-biquinodimethane species **BTBQ** due to longer conjugation length. The results of UV-vis experiment combined with in-situ ^{1}H-NMR examination are the direct evidence to support the proposed mechanism of Gilch polymerization, even for monomer with extremely twisted biphenyl structure.

The nature of chain propagation in Gilch polymerization remains to be controversial until today. Some authors are in favour of the free-radical mechanism while others anionic one. Therefore, we added free-radical scavenger 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) during the Gilch polymerization of **BTBB** to corroborate the free-radical pathway. As shown in ESI† Table S1, the molecular weight and yield of **PBPV-2** (Mn=15,000 g/mol, yield=42%) decrease drastically when 0.5 equivalent of TEMPO was added. Furthermore, when a large excess of TEMPO (1.5 equivalents) was added, only oil-like oligomer with molecular weight less than 1,000 g/mole can be obtained. Their SEC chromatograms are shown in ESI† Fig. S1.

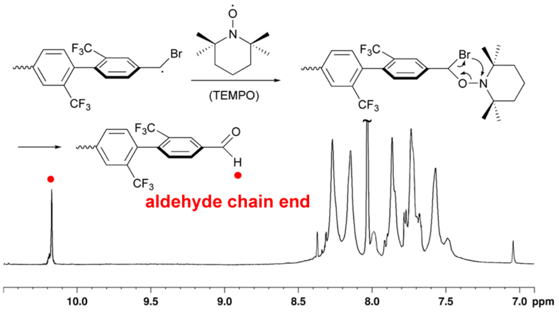

Fig. 3 ^{1}H-NMR spectrum of PBPV with 1.5 equivalent of TEMPO in DMF-*d*$_7$.

Fig. 3 shows the ^{1}H-NMR spectrum of this oil-like oligomer. A peak at δ=10.18 ppm, corresponding to aldehyde group, was observed. The radical chain end generated by Gilch polymerization can react with TEMPO as shown in Fig. 3. The formed nitroxide is not stable and will lead to the formation of aldehyde chain end. The TEMPO equivalent-dependent molecular weights and the formation of aldehyde chain end provide us the strong evidence of free-radical chain growth in Gilch polymerization.

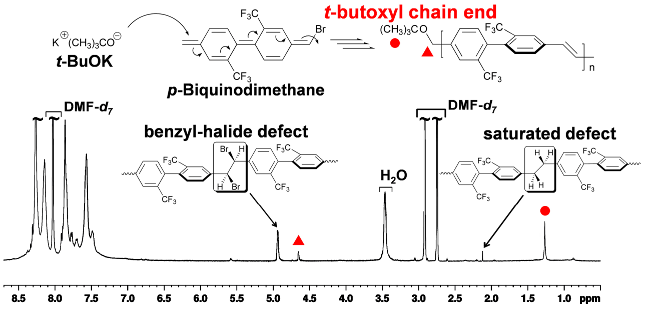

Fig. 4 ^{1}H-NMR spectrum of PBPV-2 in DMF-*d*$_7$.

However, this is not enough to exclude anionic chain growth pathway. Fig. 4 shows the ^{1}H-NMR spectrum of **PBPV-2**. Based on the proposed mechanism of Gilch polymerization for **BTBB** monomer as shown in ESI† Scheme S3, peaks at δ=2.12 and 4.95 ppm are assigned to the saturated and benzyl halide defects, respectively. Astonishingly, two peaks at δ=1.28 and 4.65 ppm have never been reported before. By investigating their chemical shifts and integral area, we believe that these two peaks should be *t*-butoxyl group (δ=1.28 ppm) and the benzyl group (δ=4.65 ppm) at the chain end. It is possible only if the chain growth reaction is anionic in nature as shown in Fig. 4.

From the TEMPO equivalent-dependent molecular weights and formation of aldehyde group combined with *t*-butoxyl and benzyl chain end, it is reasonable that the nature of chain growth reactions of Gilch polymerization for an extremely twisted biphenyl monomer should be free-radical and anionic as well.

In conclusion, we successfully obtain the direct in-situ ^{1}H-NMR evidence of the twisted biphenyl-based *p*-biquinodimethane species at -50 ℃. To the best of our knowledge, it is the first article to prove the feasibilities to form coplanar *p*-biquinodimethane **BTBQ.** It proves that *p*-biquinodimethane species can be formed regardless the aromaticity and steric hindrance. It further confirms the validity of the mechanism of Gilch polymerization, not only for phenyl-type monomers but also for biphenyl-type monomers even with large steric hindrance. Moreover, from the identification of aldehyde, *t*-butoxyl, and benzyl chain ends combined with TEMPO-equivalent dependent molecular weight, it is concluded that the Gilch polymerization of twisted **BTBB** monomer proceeds simultaneously by free-radical and anionic chain growth.

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† Electronic Supplementary Information (ESI) available: Experimental details, synthesis, polymerization, spectroscopic characterization, solubility and thermal properties. See DOI: 10.1039/b000000x/

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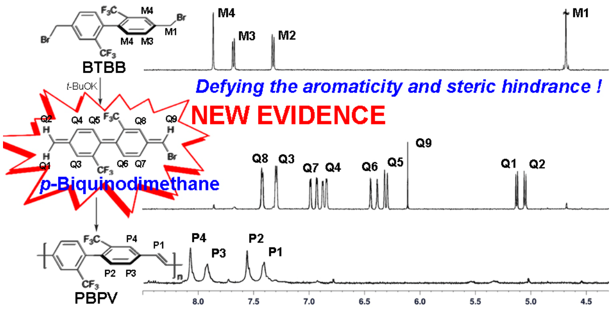

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