

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

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## Electronic Supplementary Information (ESI<sup>†</sup>)

### Experimental

#### Materials

Monomers **(2)**~**(4)** were synthesized according to the procedures in our previous publications as shown in Scheme S2.<sup>1</sup> All of other reagents were purchased from commercial companies and used as received. All of the solvents used in this communication were purified according to standard method prior to use.

#### Measurements

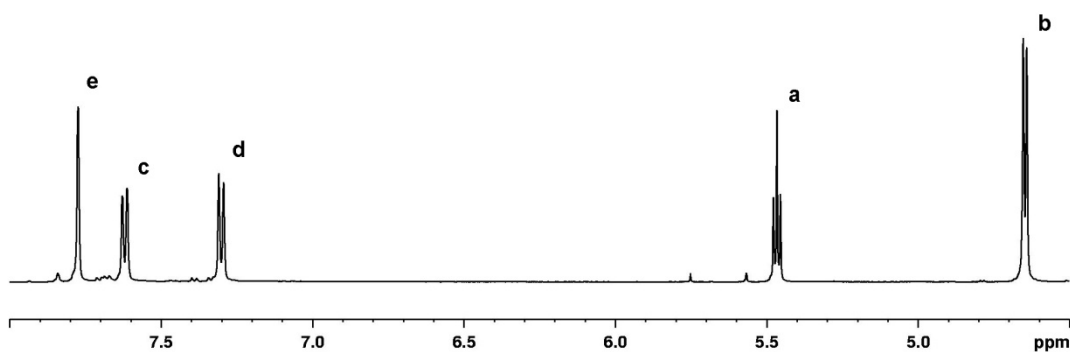
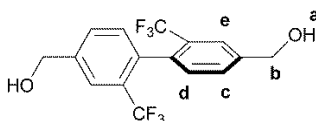
All melting points were determined on a Mel-Temp capillary melting point apparatus. <sup>1</sup>H-NMR spectra were measured at 500 MHz on a Bruker Avance-500 spectrometer. Mass spectroscopy was conducted on a Finnigan TSQ 700 mass spectrometer. Elemental analyses were performed on Heraeus Vario analyzer. Molecular weights were measured on a JASCO GPC system (PU-980) equipped with an RI detector (RI-930), a Jordi Gel DVB Mixed Bed column (250 mm x 10 mm) column, using dimethylacetamide (DMAc) as the eluent and calibrated with polystyrene standards. Thermal gravimetric analyses (TGA) were performed in nitrogen with a TA TGA Q500 thermogravimetric analyzer using a heating rate of 10 °C min<sup>-1</sup>. Differential scanning calorimeter (DSC Pyris 1) was used to measure the glass transition temperatures under nitrogen at a heating rate of 10 °C min<sup>-1</sup>. UV-visible measurements were carried out on a Cary-100 UV-Visible spectrometer.

#### Monomer Synthesis:

##### *2,2'-Bis(trifluoromethyl)-4,4'-bis(hydroxymethyl)biphenyl (7)*

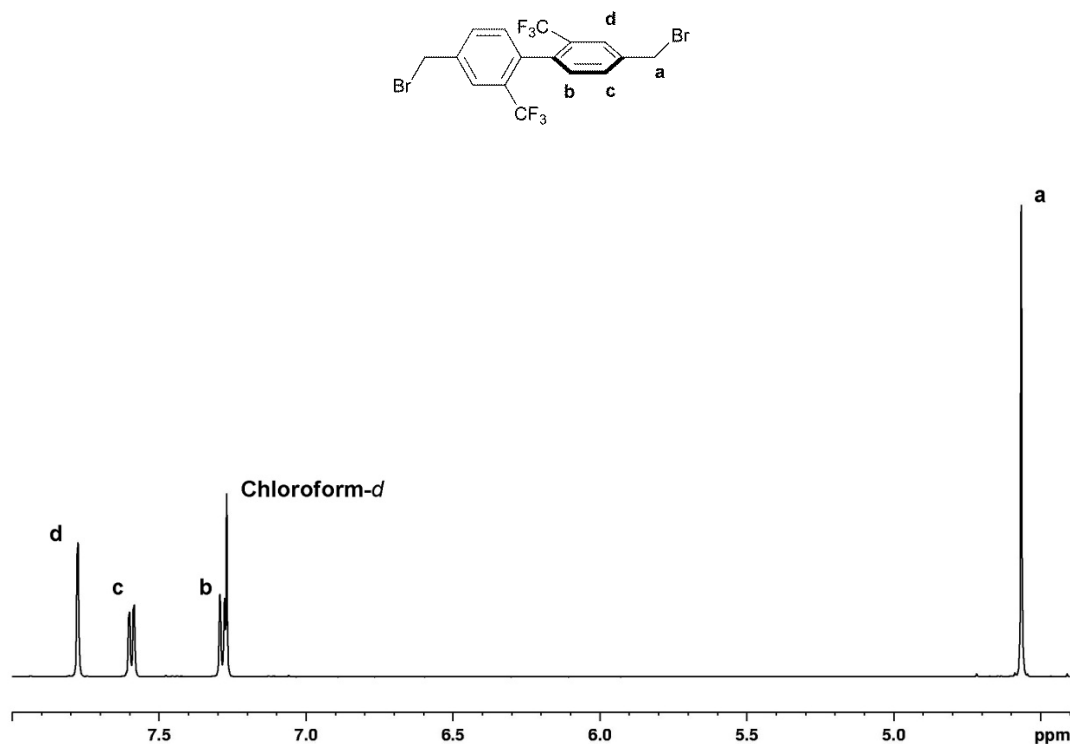
To a 100 mL, three-necked, round bottomed flask were added 1.00 g (2.89 mmol) of 2,2'-bis(trifluoromethyl)-4,4'-biphenylcarbaldehyde (**6**), 1.51 g (0.04 mmol) of

$\text{NaBH}_4$ , 60 mL of THF and 45 mL of methanol. The reaction mixture was stirred at room temperature for 24 hours. After the solvent was removed, 50 mL of dichloromethane was added to the reaction mixture. The dichloromethane solution was then poured into 2M  $\text{HCl}_{(\text{aq})}$  and stirred for 1 hour. The solution was extracted by dichloromethane. The organic layer was washed with water, dried with magnesium sulfate and then evaporated under reduced pressure at 70 °C overnight to afford 0.90 colorless crystals (89%). The colorless crystals were used for the next step without further purification.  $^1\text{H-NMR}$  (500MHz,  $\text{DMSO-d}_6$ ,  $\delta$ , ppm): 7.77 (s, 2H, Ar- $\text{H}_e$ ), 7.62 (d,  $J=7.8$  Hz, 2H, Ar- $\text{H}_c$ ), 7.30 (d,  $J=7.8$  Hz, 2H Ar- $\text{H}_d$ ), 5.45 (t,  $J=5.8$  Hz, 2H, - $\text{OH}_a$ ), 4.64 (d,  $J=5.8$  Hz, 4H, Ar- $\text{CH}_{b2}$ -).



#### *2,2'-Bis(trifluoromethyl)-4,4'-bis(bromomethyl)biphenyl (BTBB)*

To a 100 mL, three-necked, round bottomed flask were added 0.27 g (0.77 mmol) of 2,2'-bis(trifluoromethyl)-4,4'-bis(hydroxymethyl)biphenyl (**7**) and 47 mL of  $\text{HBr}_{(\text{aq})}$  (48%). The reaction mixture was heated to reflux for 6 hours, and then poured into water. The solution was extracted by ether. The organic layer was dried with magnesium sulfate and then evaporated under reduced pressure to afford 0.31g crude brown oil-like product. The crude product was further purified by column chromatography using n-hexane as eluent to afford 0.26 g white solid (71%): mp = 61-62 °C.  $^1\text{H-NMR}$  (500MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.75 (s, 2H, Ar- $\text{H}_d$ ), 7.57 (d,  $J=8.0$  Hz, 2H, Ar- $\text{H}_c$ ), 7.26 (d,  $J=8.0$  Hz, 2H, Ar- $\text{H}_b$ ), 4.54 (s, 4H, Ar- $\text{CH}_{a2}$ -). EIMS ( $m/z$ ): Calcd. for  $\text{C}_{16}\text{H}_8\text{F}_6\text{O}_2$ : 474.0 ; Found: 474.0  $[\text{M}]^+$ . Anal. Calcd for  $\text{C}_{16}\text{H}_8\text{F}_6\text{O}_2$ : C: 40.36%, H: 2.12% ; Found: C: 40.67%, H: 2.07%.

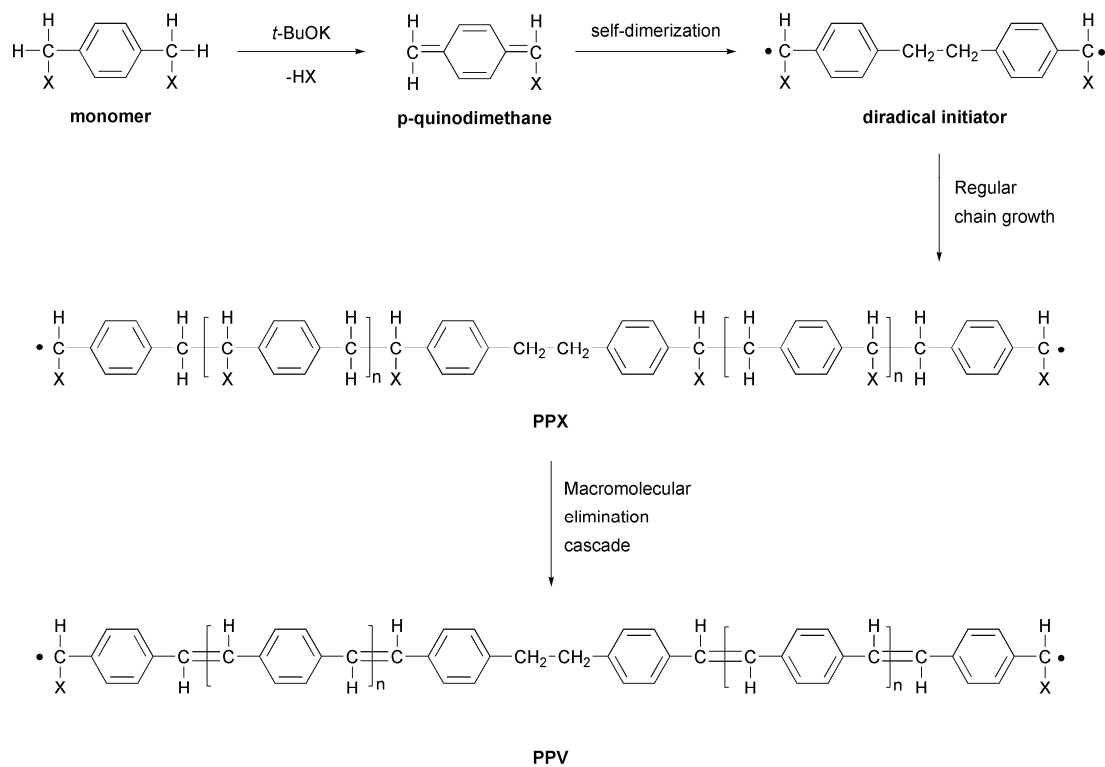


### Optimization of the synthetic route for monomer BTBB

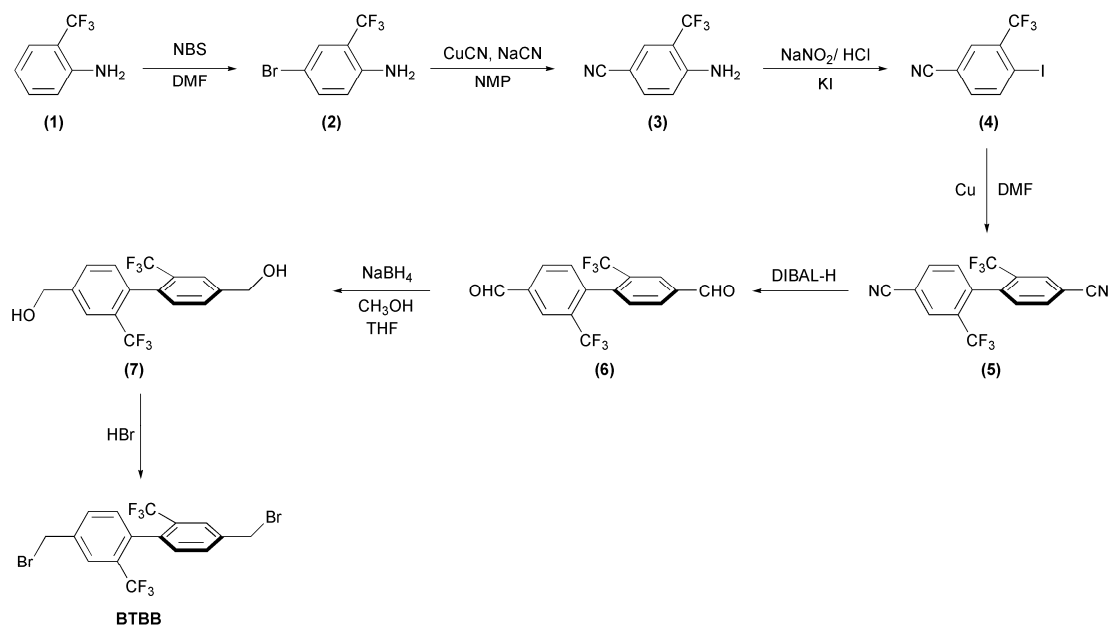
Several attempts to simplify the synthetic route have been carried out without success. For example, the attempt to direct bromomethylation of the 2,2'-bis(trifluoromethyl)-4,4'-biphenyl by HBr and paraformaldehyde was unsuccessful. It might be resulted from the presence of strong electron-withdrawing trifluoromethyl group.

### Polymer Synthesis

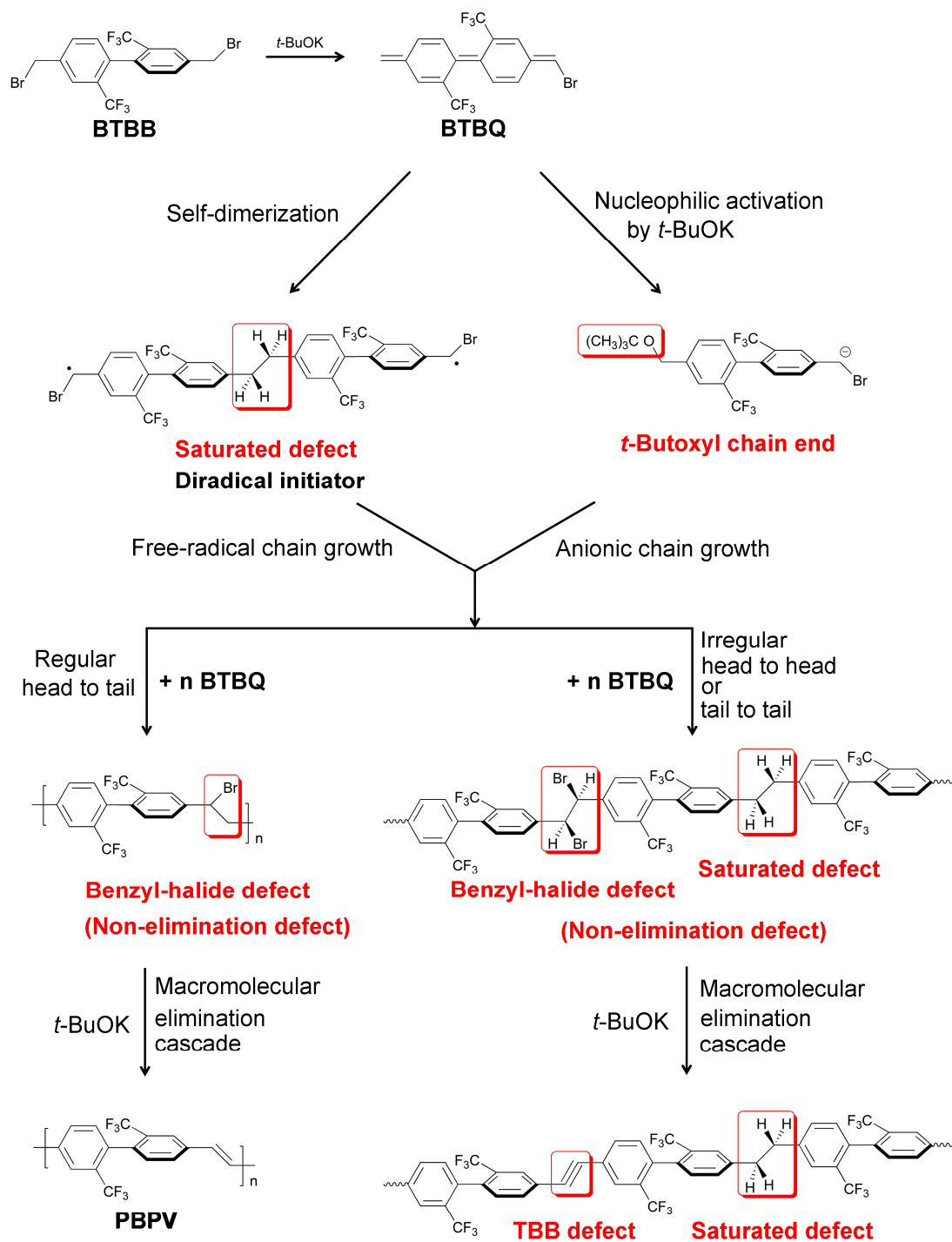
Gilch polymerization was carried out in vigorously stirred anhydrous N,N-dimethylformamide (DMF) containing BTBB and 4 equivalents of potassium *t*-butoxide (*t*-BuOK) under N<sub>2</sub> atmosphere at room temperature for 24 hours. The reaction mixture was poured into methanol. The formed polymer PBPV-1 was collected by filtration and washed by hot ethanol with Soxhlet apparatus. PBPV-1 was prepared in 60% yield with number-averaged molecular weight (M<sub>n</sub>) 149,000 g/mole and molecular weight distribution (PDI) 2.19 as shown in Table S1. PBPV-2 was prepared by the same procedure in the presence of 0.5 equivalent of TEMPO. The thermal properties and solubility of PBPV-1 and PBPV-2 are summarized in Table S2 and S3.



**Scheme S1.** Mechanism of Gilch polymerization for phenyl-type monomer.<sup>2</sup>



**Scheme S2.** Synthetic route for monomer **BTBB**.



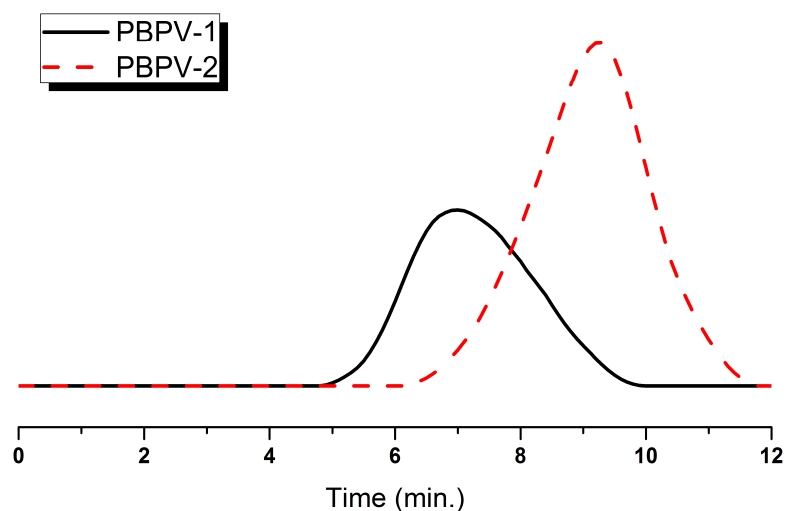
**Scheme S3.** Detailed mechanism of defect formation.

**Table S1.** Effect of TEMPO equivalent on the molecular weights of polymers.

Polymer	Equiv. of TEMPO	Yield	$M_n^a$ (g/mole)	PDI <sup>*</sup>
<b>PBPV-1</b>	0.00	60 %	149000	2.19
<b>PBPV-2</b>	0.50	42 %	15000	1.70

<sup>a</sup> Number-averaged molecular weight measured by GPC calibrated by polystyrene standard with dimethylacetamide (DMAc) as eluent at 40 °C.

<sup>\*</sup> Polydispersity index



**Fig. S1.** SEC chromatograms of **PBPV-1** and **PBPV-2**.

On the contrast to the bimodal SEC chromatogram of phenyl-type monomers reported by Vanderzande<sup>3</sup>, only monomodal SEC chromatograms were observed. This may suggest that polymers formed by free-radical and anionic chain propagation have the similar molecular weights.

**Table S2.** Thermal properties of PBPVs.

Polymer	Tg <sup>a</sup> (°C)	Td <sup>b</sup> (°C)	Char yield <sup>c</sup> (wt %)
<b>PBPV-1</b>	234	404	50
<b>PBPV-2</b>	228	390	47

<sup>a</sup> Measured by DSC at a heating rate of 10 °C/min under nitrogen atmosphere.

<sup>b</sup> Measured by TGA at a heating rate of 10 °C/min under nitrogen atmosphere.

<sup>c</sup> Residue weight percentage at 800 °C under nitrogen atmosphere.

**Table S3.** Solubility of PBPVs.

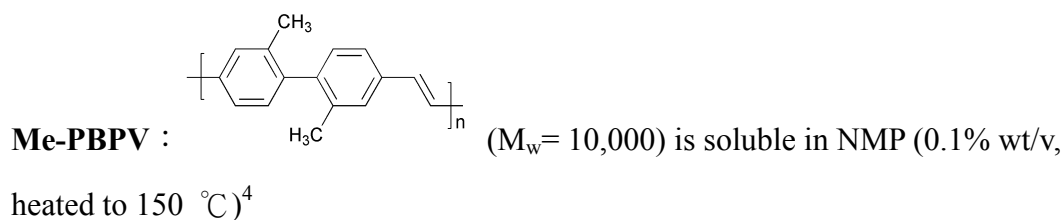
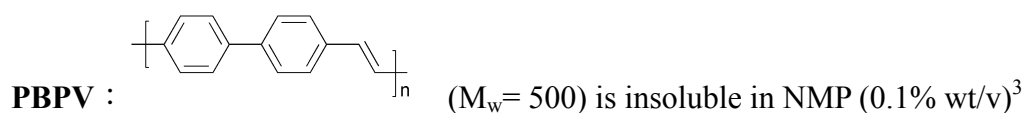
Polymer / Mn (g/mol)	NMP	DMAc	DMF	DMSO	THF
<b>PBPV-1 / 149000</b>	-	-	-	-	-
<b>PBPV-2 / 15000</b>	++	++	++	+/-	+/-
<b>PBPV</b>	-				
<b>Me-PBPV</b>	+				

Abbreviations: NMP, *N*-methyl-2-pyrrolidinone; DMAc, dimethylacetamide; DMF, dimethylformamide; DMSO, dimethylsulfoxide; THF, tetrahydrofuran.

The solubility was determined by using 20 mg of sample in 1 mL of stirred solvent.

++: soluble at room temperature; +: soluble when heated;

+/-: partially soluble when heated; -: insoluble even when heated.



### Cyclization Effect

Rehahn and coworkers found some cyclic isomers (paracyclophane) in the methanol-soluble part of the reaction products (phenyl-type monomer).<sup>5</sup> We did not investigate the chemical structures and the compositions of the methanol-soluble part in this communication. In our case, the polymer yield of Gilch polymerization is around 60% and an appreciable amount of reaction products remains in the methanol. Giving the biphenyl structure with large trifluoromethyl substituents, the formation of cyclic isomers, if not impossible, should be more difficult than that of cyclic isomers resulted from phenyl-type monomers. From our in-situ <sup>1</sup>H-NMR measurements (Fig. 1, all reaction products are in the NMR tube), there are no peaks that could correspond to the possible cyclic isomers. Therefore, it is reasonable to conclude that the methanol-soluble part of biphenyl-type Gilch polymerization products are mainly low molecular weight oligomers.

### References

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