

Synthesis of Soluble Poly(*p*-phenylene methylene) from Tribenzylborate by Acid-Catalyzed Polymerization

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ABSTRACT: An acid-catalyzed polymerization of tribenzylborate (TBB) is described for the synthesis of soluble poly(phenylene methylene) (PPM). The polymerization proceeds via carbocationic mechanism with first-order kinetics with respect to TBB and 0.7th order with respect to acid concentration. The structure of PPM was characterized by ¹H and ¹³C NMR analysis. Thermal properties of PPM were investigated by TGA and DSC, and thermally stable polymers displayed completly amorphous structure, which was attributed to nonrestricted rotation of the phenyl rings around bridged methylene units in the rodlike structure. PPM exhibits a broad fluorescence emission band with a maximum at 422 nm arising from the benzonoid transition. The extremely low dielectric constant of PPM suggests that these polymers can be used as polymer insulators.

Introduction

Poly(phenylene alkylene)s possessing alkyl-bridged phenyl rings in the repeating units are considered to be chemically inert polymers.¹ These polymers have found commercial interest because of their low dielectric constant, thermal stability, high solvent resistance, and good barrier properties.^{1,2} Poly(*p*-xylene), also called poly(paracyclophane), is a well-known example of this class of polymers. This polymer is obtained by the vacuum deposition polymerization (VDP) technique. In this technique, cyclodimer of *p*-xylene (paracyclophane) is thermally decomposed under vacuum to give xylidyl diradical, which in turn forms polymer by spontaneous combination on the cold surfaces.³ Pinhole-free coatings with uniform thickness on interior parts of metal goods can readily be obtained by using this methodology.²

Structurally similar polymer, namely, poly(p-phenylene methylene) (PPM), has also found considerable interest since the first report of Friedel and Crafts on the reaction of benzyl chloride with aluminum chloride in 1885.⁴ Various Friedel-Crafts catalysts have been studied for polymerization of a wide variety of benzyl derivatives including benzyl halides, benzyl alcohol, and benzyl ethers.⁵ However, all of those attempts were failed in preparing soluble PPM. For instance, the reaction of benzyl alcohol with sulfuric acid yielded partially dioxane soluble polymer possessing one terminal hydroxyl group per chain.⁶ The resulting polymer with an average polymerization degree (DP) of about 9 exhibited a softening point in the temperature range of 85-100 °C. Polymerization proceeds via benzylic carbocation mechanism, and polymers are formed through ortho, meta, and para linkages.⁷⁻⁹ Itoh et al. successfully prepared polymers possessing phenylenemethylene and biphenylene-ethylene repeating units by VDP of disulfone analogue of paracyclophane.¹⁰ They demonstrated that the thermal decomposition results in sulfur dioxide elimination yielding benzylic and phenylenic type biradicals. The combination of such biradicalic species essentially produces amorphous films. ¹H NMR spectra of the polymers thus formed indicated the presence of biphenyl ethylene structures in addition to the benzylic repeating units. Cianga and Yagci reported the successful synthesis of poly(p-xylene) by the polymerization of p-dibromo xylene, a typical atom transfer radical polymerization (ATRP)

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bifunctional initiator, under atom transfer radical coupling (ATRC) conditions.¹¹

Herein, we wish to present the first report for the synthesis of entirely soluble PPM starting from boron ester of benzyl alcohol (tribenzylborate, TBB) (Scheme 1).

Results and Discussion

Attempts to bulk polymerization of TBB with 0.2 to 0.3 mL of H₂SO₄ ([H₂SO₄]/[TBB] 1/50) at room temperature resulted in explosions in each case, indicating highly exothermic nature of the polymerization. Low-molecular-weight polymer ($M_{\rm p}$: 960) isolated by precipitation in aqueous NaOH solution (3%) was shown to be entirely soluble in a wide range of organic solvents including CHCl₃, CH₂Cl₂, toluene, benzene, and THF but insoluble in water, methanol, and ethanol. To avoid the explosion, the polymerization was conducted at 0 °C under bulk conditions. However, explosion still took place in a few cases. Nevertheless, the polymerization can be conducted in a controlled manner using CH2Cl2 as the diluting solvent at room temperature. The results of polymerization of TBB (20% w/w) in CH₂Cl₂ under different reaction conditions are presented in Table 1. To inspect the explosion limit of the reaction, the polymerization mixture with CH₂Cl₂ was deliberately heated to 40-60 °C. The reactions resulted in explosion within 1 to 2 h. Fortunately, no explosion was observed in the reactions conducted at room temperature. As can be seen, the prolonged reaction times did not bring about significant increase in the molecular weight when the polymerization was conducted in the absence of P₂O₅.

This was attributed to dehydrating effect of the sulfuric acid catalyst on the boric acid formed during the polymerization. The condensed water most likely induces an inhibiting effect on the acid catalyst. The chain growth eventually ceases, and the molecular weight does not further increase. To avoid the possible deteriorating effect of the water, the polymerization was performed in the presence of P_2O_5 as water scavenger. In this case, a significant increase in the molecular weight was noted. (See Table 1.)

The structure of the polymer was confirmed by both ¹H and ¹³C NMR analysis. The ¹H NMR spectrum of the isolated polymer (Figure 1) represents a quite simple pattern in which

Scheme 1. Synthesis of PPM from Tribenzylborate by Acid-Catalyzed Polymerization



 Table 1. Molecular Weight Characteristics of PPM Obtained under Different Synthetic Conditions^a

run	[H ₂ SO ₄]/[TBB] (mol)/(mol)	[P ₂ O ₅]	time (min)	$M_{ m n} \ ({ m g/mol})^b$	$M_{ m w}/{M_{ m n}}^b$
1^c	1/50	_	< 10 min	960	1.73
2	1/10	_	24 h	1200	2.80
3	1/10	_	36 h	1300	2.50
4	(with TFA) ^{d}	_	18 h	1750	2.10
5	1/10	+	12 h	2300	4.71
6	1/10	+	48 h	8600	4.26
7	1/15	+	24 h	4400	4.50
8	1/35	+	36 h	3750	3.71

^{*a*} Polymerization was conducted in CH₂Cl₂ at room temperature. ^{*b*} By GPC. ^{*c*} Polymerization was carried out under bulk conditions, and explosive polymerization was noted. ^{*d*} TFA (trifluoromethane sulfonic acid) was used as catalyst.



Figure 1. ¹H NMR spectrum of PPM in CDCl₃.

intense singlets appearing at 7.1 and 3.8 ppm associated with aromatic and methylene protons respectively were noted.

Approximately 2:1 integral ratio of these peaks clearly confirms the expected structure. The molecular weight ($M_{n,NMR}$ = 930 g/mol) estimated from the integration of the terminal CH₂ protons appearing at 4.9 ppm to that of either methylene or aromatic protons of the repeating unit is in fairly good accord with that determined by GPC calibrated with polystyrene standard ($M_{p,GPC}$ = 960 g/mol).

The 13 C NMR spectrum of the polymer (Figure 2) shows aromatic carbon signals around 128 ppm and aliphatic carbon signal at 39–41 ppm, whereas the signal of the methylol carbon at the chain end is invisible. Another weak signal centered at 138 ppm must be due to aromatic quaternary carbons of the phenyl rings.

Although multiplicity of the carbon signals is common for the ¹³C NMR spectra of the polymers,¹² the multiple carbon signals of the polymer could be a sign of some branching during the polymerization as a result of the reaction also at ortho position.

¹³C NMR spectra of poly(phenylene methylene) are scarcely treated. Baumberger and Woolsey reported that polymerization of benzyl chloride by using SnCl₄ catalyst yields partially soluble poly(phenylene methylene). The ¹³C NMR spectrum of the soluble portion represents multiple signals lying in 34–44 ppm range for the carbon of the bridged methylene group. Similar multiple signals have been observed in 134–144 and 124–134 ppm ranges for the quaternary aromatic carbons and the





Figure 2. ¹³C NMR spectrum of PPM in CDCl₃.



Figure 3. TGA thermogram of PPM.

other aromatic carbons bearing hydrogen atoms, respectively.¹³ Hasan and Tsonis developed a semiempirical procedure to estimate the ratio of ortho or meta to para linkages in polybenzyls by assuming additive deshielding effects of di-, tri-, and tetra substitutions on ¹³C NMR signals of the phenyl rings.¹⁴ In those reports, NMR spectra of the partially soluble polybenzyls have been considered only from the positional isomerism viewpoint. However, reliability of the reported NMR methods for the assignment of the distribution of ortho to para isomers is debatable.¹⁵ However, there is no report dealing with sterostructural aspect of polybenzyls. In view of these reported studies, the presence of some ortho linkages in the polymer prepared in this work can also be suggested. To clarify this dilemma, we have attempted to employ the chemical method of Shriner and Berger⁶ for sequential analysis of polybenzyls based on oxidation of the polymer with nitric acid and followed alkaline fusing of the polyketone. This procedure did not yield any detectible terephtallic or phatalic acid to assign the ratio of para to ortho linkages. However, more convincing evidence to confirm the proposed structure was obtained from the careful evaluation of thermal gravimetric analysis (TAG). Interestingly, poly(phenylene methylene) prepared by using TBB shows a TGA pattern completely different from those given in the previous reports (Figure 3).

Notably, TGA analysis revealed reasonably high decomposition temperature (\sim 540 °C), as high as those of poly(*para*-xylenes).¹⁶ The polymer sample with 3750 Da of molecular weight decomposes almost completely around 600 °C and yields negligible chary residue under a nitrogen atmosphere. It is important to note that the TGA curve represents a single and sharp decomposition, suggesting one type of connection between the repeating units in the polymer. In complete contrast, TGA curves reported for the polybenzyls obtained by acid or metal catalysts possess at least two inflection points below 500 °C, implying two or more different chemical linkages between the phenyl rings. In view of the simplicity of the TGA pattern, the multiple peaks in the ¹³C NMR spectrum of the polymer can hardly be ascribed to ortho and para isomerism. Instead,



Figure 4. First-order kinetic plots for the polymerization of the solutions with various initial acid contents ($[H_2SO_4]/[TBB]$: 1/10, 1/17, 1/21).



Figure 5. Double logarithmic plot of the apparent rate constant versus proton concentration in the polymerization mixture.

these peaks might be originating from different stereochemical arrangement of the repeating units. From this viewpoint, the carbon signals of the methylene bridging group at 39 and 41 ppm can be ascribed to *mm* and *mr* sequences of the triads. Nearly equal intensity of the peaks implies equal density of meso and racemic triads forming an atactic polymer structure.

In light of the above spectroscopic investigations, a carbocationic mechanism based on proton attack on the oxygen atom of TBB was proposed. In this mechanism, benzylic carbocation liberated concomitantly with boric acid reacts with the aromatic ring of another boron ester at the para position.

In this connection, it should be pointed out that a similar mechanism was proposed for the polymerization of benzyl halides and benzyl esters by Friedel–Crafts catalysts.^{7–9}

To investigate the polymerization kinetics, we performed a series of reactions at room temperature using reaction mixtures with [H₂SO₄]/[TBB] 1/10, 1/17, and 1/21 molar ratios. Conversion—time plots derived from each set were evaluated. It was shown that the polymerization followed first-order kinetics with respect to TBB, as inferred from the linearity (regression factors, R = 0.98 to 0.99) of the semilogarithmic plots presented in Figure 4.

The overall rate of the polymerization, *Rp* can be written as follows

$$Rp = k_0 \times [\text{acid}]^a \times [\text{TBB}] \tag{1}$$

Because the acid is not consumed in the reaction, integration of this equation yields

$$\ln(1/(1-p)) = k_0 \times [\operatorname{acid}]^a \times t \tag{2}$$

where $k_0 \times [acid]^a$ can be defined as apparent rate constant, k.

A plot of ln k versus ln[acid] yields a straight line (Figure 5) with a slope, a = 0.71 and an intercept



Figure 6. X-ray powder diffraction patterns of PPM.



Figure 7. Dielectric spectrum and loss tangent of the polymer (Mn: 3750) within the 10 kHz to 13 MHz frequency range.

Therefore, the explicit form of the polymerization rate would be

$$Rp = 3.4 \times 10^{-4} \,\mathrm{s}^{-1} \times [\mathrm{H}^+]^{0.71} \times [\mathrm{TBB}] \,\mathrm{mol} \,\mathrm{L}^{-1} \,\mathrm{s}^{-1} \quad (4)$$

Such a reaction order seems to be unusual and implies somewhat deviation from simple carbocation mechanism. However, the proton concentration in this relationship is based on the concentration of sulfuric acid added to the reaction mixture in the beginning. Besides this, P_2O_5 added to the reaction mixture would yield phosphoric acid by dehydration of boric acid formed during the reaction. Therefore, because of additional contribution of the phosphoric acid, first-order kinetics with respect to the proton concentration is more likely to be on the order of 0.7.

DSC traces of the polymers showed no glassy transition within the 0-300 °C temperature range. This must be due to absence of side chains in the polymer structure. Broad depletion in the DSC curves (endothermic) within the 85–105 °C range represents melting of the polymers, as evidenced by separate meltingpoint tests. The broad melting range can be ascribed to the high polydispersities (PDI) of the resulting polymers.

Interestingly, the XRD patterns of the polymers disclosed a completely amorphous structure (Figure 6). This is in complete contrast with the observation of Yamamoto and coworkers, who reported partially soluble crystalline PPM.¹⁸ However, their synthetic methodology was different and based on Wurtz coupling of 1-chloro-4-(chloromethyl)benzene. Because of the high reactivity of chloromethyl groups, this reaction is expected to yield bis(p-chlorophenyl)ethane in the first step. The subsequent reactions with aromatic halides must yield poly(biphenyl ethylene) rather than PPM. The π -stacking of the biphenyl groups present in the structure can induce some crystallinity. The amorphous nature of the polymers in our case might be due to nonrestricted rotation of the phenyl rings around bridged methylene groups in the rodlike structure. This observation is also in accordance with the above spectral analysis, indicating that the polymers constitute mostly with one to four phenylene methylene repeating units because of sterical hindrance of the boron-oxygen bond for the reaction of benzylic cation through the ortho position.

The dielectric spectrum of the polymer presented in Figure 7 shows that, ε' (real part of the dielectric constant) is extremely



Figure 8. Excitation and fluorescence emission spectra of PPM in THF ($\lambda_{exc} = 370 \text{ nm}$).

small (1.8 to 1.9) in the 10 kHz to 13 MHz range and almost independent of frequency, indicating the absence of polar or ionic groups in the polymer structure.¹⁹

Small depletion at high frequencies must be due to distortion of π -electron clouds of the phenyl rings under the electrical field. This insulating behavior is comparable to those of typical polymer insulators such as polyethylene and polypropylene having ε' values 2.1 and 2.1 to 2.3, respectively.^{20,21} The isothermal (25 °C) tangential dielectric loss curve (Tg $\delta = \varepsilon''/\varepsilon'$) (Figure 7) shows a maximum at 1.39, which implies 3.2×10^{-3} s of upper limit for the relaxation period of the polymer under an electrical field.

It is important to note that THF solutions of the light-yellow polymers exhibit green-yellow fluorescence, which is visually observable. Figure 8 shows excitation and fluorescence emission (PL) spectra of PPM sample (M_n : 4400 g/mol) in THF solution. A broad fluorescence emission band with a maximum at 422 nm is observed by excitation at 370 nm of wavelength. The broad and intense absorption band in the 320–410 nm range is associated with benzenoid transition of the polymer and implies reasonable UV filtering effect of the polymer.

In conclusion, acid-catalyzed reaction of TBB at room temperature results in the formation of poly(1,4-phenylene methylene) with the molecular weight in the range of $M_n = 1000-8600$ g/ mol. The polymerization proceeds via carbocationic mechanism, with first-order kinetics with respect to TBB and 0.7th order with respect to proton concentration. The resulting amorphous polymers that consist of the ¹H NMR and ¹³C NMR spectral analysis evidencing 1,4-phenylene methylene repeating units show high thermal stability (polymer degradation temperature: 540 °C) and very low dielectric constant ($\varepsilon' = 1.8$ to 1.9), as in the case for poly(*para*-xylene) and related poly(phenylene alkylene)s. The polymers obtained this way are expected to find potential applications in block copolymerization or further functionalization because they contain functional methylol end groups. Further studies in this line are now in progress.

Experimental Section

Materials. Benzyl alcohol (99.5%, Merck) and ε -caprolactone (97%, Aldrich) were distilled under reduced pressure before use. Dichloromethane (99.8%, LABSCAN) was distilled over P₂O₅. All other chemicals, namely, boric acid (99.5%, Merck), toluene (99.0%, Merck), P₂O₅ (97%, Merck), sulfuric acid (96%, J. T. Baker), and tetrahydrofuran (99.5%, Merck) were used as purchased.

Preparation of Tribenzylborate. This was prepared according to general procedure for the synthesis of boron esters.²² The clear liquid was redistilled under vacuum 220–225 °C (5 mm) for purification. Yield: 86.6%. ¹H NMR (CDCl₃, δ): 7.6 (m, 15 H, aromatic), 5.3 (s, 6H, CH₂).

Synthesis of Poly(1,4-phenylene methylene). A solution of 10.6 g of TBB (32 mmol), 30 mL of CH_2Cl_2 , and 4.8 g of P_2O_5 (34 mmol) was charged in a 100 mL volume flat-bottomed flask

placed in an ice bath. To this mixture, 0.15 g (1.47 mmol) of sulfuric acid (96%) was added dropwise while being stirred vigorously. The mixture was stirred for 1 h at 0 °C, and stirring was continued for 24 h at room temperature. A marked increase in viscosity was observed within 30 min. The mixture was poured in 250 mL of ice water. The organic layer at the bottom was separated, washed with 150 mL of NaOH solution (3%), and water (150 mL). The solvent, CH_2Cl_2 , was removed by rotaevaporator. The residue was dissolved in 50 mL of THF precipitated in 150 mL of NaOH (3%). The crude product was dissolved again in THF (30 mL) and centrifuged at 3500 rpm to remove trace amounts (ca. 1 to 2%) of inorganic impurities. The light-yellow polymer was reprecipitated in water and collected by filtration. The polymer was dried under vacuum at 50 °C for 12 h. The overall yield was 8.1 g (93.9%).

Kinetics of the Polymerization. Similar conditions were employed in the kinetics experiments in which conversions were monitored by progressive mass increases in the polymers precipitated from the aliquots taken appropriate time intervals (i.e. 1-4 h). To inspect the effect of acid concentration, we repeated the kinetic experiments at different [H₂SO₄]/[TBB] molar ratios (1/10, 1/17, 1/21).

Characterizations. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ solvent using a 250 MHz Bruker DPX 250 spectrometer. FT-IR spectra were taken by a Perkin-Elmer FT-IR Spectrum One B. The molecular weights were assigned by gel permeation chromatography (GPC) using Agilent 110 operating with RI and UV detectors and four Waters Styragel columns (HR 5E, 4E, 3, 2). Measurements were carried out in THF solvent at 30 °C with a flow rate of 0.3 mL/min.

X-ray diffraction (XRD) spectra were obtained from a Rigaku D/Max-Ultima+/PC XRD apparatus. Dielectric spectra were taken from solvent (THF) cast films (\sim 0.5 mm) on Al cells at 25 °C using Hewlett-Packard/4192A impedance analyzer operating in the 10 kHz to 13 MHz frequency range. We carried out the fluorescence (PL) emission measurements by using Varian Cary Eclipse Fluorescence Spectrophotometer at the 90° position.

Thermogravimetric analyses (TGA) were carried out under a nitrogen atmosphere with Perkin–Elmer Diamond TA/TGA instrument at a heating rate of 10 °C/min. Differential scanning calorimeter traces were obtained by the use of Perkin–Elmer Diamond DSC under nitrogen flow in -30 to 300 °C with a heating rate of 10 °C/min.

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