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Characterization and Thermo-stability of Alkylated Poly*para*phenylene

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Summary

Alkylated polyparaphenylenes are synthesized with isoamyl bromide and isopropyl bromide via $AlCl_3$-catalyzed Friedel-Crafts alkylation. The molecular structures of alkylated polyparaphenylenes are characterized using CHN elemental analysis, FT-IR, UV-Vis, NMR, SEC and WXRD. The thermal properties are investigated by TGA. The results show the thermal stability of alkylated polyparaphenylenes is inferior to PPP.

Introduction

Polyparaphenylene (PPP) has high thermal stability, thermo-oxidation stability, very wide conductive range and interesting optical properties, considerable interest has been drawn due to its potential commercial applications in electrode materials [1,2], active layers in light-emitting diodes [3-5], support materials for cobased catalysts [6], filler in rubber stock [6], etc.

However, PPP is infusible and insoluble in common organic solvents [7], so its application is quite limited. Alkyl PPP is one of the soluble PPPs. Alkyl PPP can be obtained by two different ways. The first is oxidizing and coupling polymerization with monomer (alkyl benzene) [8] or Ni-catalyzing coupling of aromatic dichlorides [9]. More reaction steps are needed in this method. The second is alkylation of PPP under Friedel-Crafts conditions. Kovacic *et al* synthesized alkyl PPP with *n*-propyl bromide and *n*-propyl chloride [10]. However, the thermal properties of alkylated PPP have not been reported.

In this article, the synthesis of soluble alkylated PPPs with isoamyl bromide and isopropyl bromide under Friedel-Crafts conditions is reported. The structures of alkylated PPPs are studied by a combination of CHN elemental analysis, Fourier transform infrared spectroscopy (FT-IR), ultraviolet and visible spectroscopy (UV-Vis), nuclei magnetic resonance spectroscopy (NMR), wide-angle X-ray diffraction (WXRD), size exclusion chromatography (SEC). The thermal properties of alkylated PPPs and PPP are studied by thermo-gravimetric analysis (TGA).

Experimental

Materials

Benzene is from Tianjin Baishi Chemical Co. Hydrochloric acid, $CaCl_2$, anhydrous $AlCl_3$, anhydrous $FeCl_3$ are from Shanghai experiment reagent Co. Isoamyl bromide, isopropyl bromide are purchased from Tianjin Chemical Reagent Co.

Alkylation with Isoamyl Bromide or Isopropyl Bromide

Catalyzed by $AlCl_3$

The method used for preparation of alkylated PPP is in accordance with the method proposed by Kovacic and co-workers [10]. A three-necked, round-bottomed flask equipped with thermometer and condenser, $CaCl_2$ drying tube are added 0.3 g of purified PPP and 1.5 g of anhydrous $AlCl_3$ under a nitrogen atmosphere. Into the suspension 11 mL of alkyl bromide is added dropwise. The mixture is stirred and refluxed for 11 h, for isoamyl bromide the temperature at 120 ˚C and for isopropyl bromide at 59 ˚C. After 18% HCl is added, the mixture is filtered. The residual product is repeatedly extracted by acetone using Soxhlet extractor. Deep orange-red powder is collected by evaporation. The solid is dried overnight at 110~120 ˚C. The weight of recovered polymer is 178% for isoamyl bromide. CHN elemental analysis indicates the quantity in percent: (found) C92.03, H7.97; (calc) C91.89, H8.11 $(C_{17}H_{18})_n$. The IR spectrum (KBr pellet, cm^{-1}) of the product exhibits bands at 2957, 2926, 2868, 1454, 1375, 999, 860 and 814. ^{1}H NMR (300 MHz, $CDCl_3$) indicates that δ=7.24-7.85 (br., m), 2.33-2.66 (t, 2H, $PhCH_2$-), 1.25 (m, 2H, $PhCH_2CH_2$-), 1.15-1.02(m, 1H, -CH<), 0.83-0.88 (d, 6H, -CH_3). UV-Vis spectrum (λ_{max}, nm, $CHCl_3$): 244, 288, 336, 356.

The recovered weight is 180% for isopropyl bromide. CHN elemental analysis indicates the quantity in percent: (found) C90.927, H9.073; (calc.) C90.85, H9.15 $(C_{30}H_{36})_n$. The IR spectrum (KBr pellet, cm^{-1}) of the product exhibits bands at 2957, 2922, 2866, 1454, 1377, 872 and 827. UV-Vis spectrum (λ_{max}, nm, $CHCl_3$): 241, 271, 322, 353.

Catalyzed by $FeCl_3$

In order to test effect of $FeCl_3$ as catalyst, similar experiment is done. $AlCl_3$ is replaced by 1.5 g of anhydrous $FeCl_3$. For isoamyl bromide or isopropyl bromide, no color and weight changes are observed. The IR spectrum (KBr pellet) of the products gives a very weak absorption at 2954 cm^{-1}.

Instrumentation and Measurement

Infrared spectra are recorded on a Fourier transform infrared spectrometer (IRprestige-21 FT-IR, Shimadzu, Japan) as a KBr pellet. The data are collected over 20 s scans with a resolution of 4 cm^{-1}.

UV–Vis absorption spectra for the alkylated PPPs solution are taken with a TU-1901 UV–visible spectrophotometer (PGENERAL, China).

^{1}H NMR (300 MHz) spectrum is measureded on a Bruker AVANCE 300 instrument (Bruker, Switzerland) using $CDCl_3$ signal as an internal reference.

Element analysis is performed using a PerkinElmer 2400CHN analyzer (PE, America).

SEC is performed with Waters-Breeze Gel Permeation Chromatograph (Waters, America) at 30 ˚C using THF as the eluent at a flow rate of 0.4 mL.min^{-1}.

WXRD patterns are carried out on an X-ray diffraction instrument (D/Max-3c, Rigalcu, Japan) with Cu Kα radiation (λ=1.5405 Å) at 40 kV and 30 mA with a scan rate of 4°/min^{-1}. The diffraction angle ranges from 5 to 70°.

Thermo-gravimetric analyses are obtained using a SDT Q600 TGA analyzer (TA, America) in the nitrogen atmosphere. The heating rate was 10 ˚C/min.

Results and Discussion

Alkylation

Alkylation of PPP is successful with isoamyl bromide and isopropyl bromide using AlCl$_3$ catalyst. The effects of the reaction times and reactants ratio on the recovered weight for the isoamyl bromide are investigated. The results are given in Table1 and Table 2 for AlCl$_3$ catalyst. It is seen from Table 1 that the recovered weight (%) of the isoamyl PPP increases with alkylation reaction time. Table 2 shows that the recovered weight of the isoamyl PPP varies with the amount of added isoamyl bromide.

Table 1. The recovered weight for isoamyl bromide *vs* reaction time

	Reactive time (h)	The recovered weight (%)
1	4	148
2	8	150
3	11	176
4	24	180

Table 2. The recovered weight for isoamyl bromide *vs* reactants ratio (0.3g of PPP)

	Volume of isoamyl bromide (mL)	The recovered weight (%)
5	4	141
6	6	145
7	8.8	150
8	13	178

The isoamyl PPP and isopropyl PPP are soluble in CHCl$_3$, THF.

It is worthwhile to note that the alkylation of PPP is unsuccessful with isoamyl bromide and isopropyl bromide in the presence of FeCl$_3$ as catalyst.

Structure

IR and ^{1}H NMR

Figure 1 shows the FT-IR spectrum of isoamyl PPP (KBr pellet). The strong bands are observed at 2957 cm^{-1}, 2926 cm^{-1}, 2868 cm^{-1} and assigned to C-H stretching vibration of CH$_3$ and CH$_2$ groups. The absorption bands at 1454 cm^{-1}, 1375 cm^{-1} rises from the in-the-plane bending vibration absorption bands of C-H. The ^{1}H NMR spectrum displays 5 groups of peak. These results indicate the characteristic of isoamyl group.

As is shown in Figure 1, characteristic absorption bands of tri- or tetra-substituted phenyl units (out-of-plane C-H deformation) are at 860 cm^{-1} and 814 cm^{-1}. Substitution beyond tetraalkyl is rather difficult, because the steric hindrance would be very great. According to the results of the IR spectrum, ^{1}H NMR spectrum and the results of CHN elemental analysis, the structure of the isoamyl substituted PPP is depicted in Figure 3.

The IR spectrum in Figure 2 and CHN elemental analysis indicate the chemical structure of isopropyl PPP (Figure 3). The structure differs from **3** (Figure 3), which was assumed by Kovacic [10].
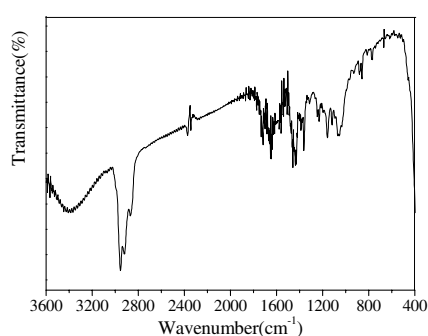

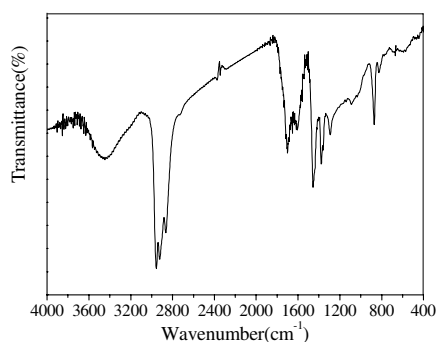**Figure 1.** IR spectrum of the isoamyl PPP

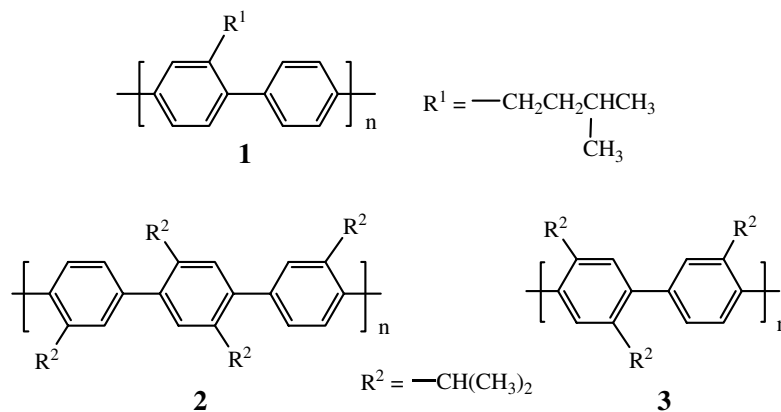**Figure 2.** IR spectrum of the isopropyl PPP

Figure 3. Chemical structure of isoamyl PPP and isopropyl PPP

Molecular Weight

Table 3 gives the SEC analysis for isoamyl PPP and isopropyl PPP. The number-average molecular weight (M_n) of isoamyl PPP and isopropyl PPP is found at 1400, 1680, respectively. The polymerization degree of PPP was 12.2, which is determined by IR spectra [11,12]. From the structure of alkylated PPP, M_n of isoamyl PPP and isopropyl PPP is calculated as 1361, 1627, respectively. The results are close to M_n of SEC analysis.

Table 3. Molecular weight of alkylated PPPs

Substituted PPP	M_n	M_w	PDI
Isoamyl PPP	1400	2450	1.8
Isopropyl PPP	1680	2900	1.7

M_w is the weight-average molecular weight, PDI= M_w / M_n

X-ray Diffraction

Figure 4 displays the XRD patterns of PPP and alkylated samples. The three main diffraction peaks of PPP for 2θ are centered at 19.6°, 27.9° and 43.2°, which accord with one of the references [13,14]. The intensity of peaks decreases and broadens after alkylatation. The diffraction lines of isoamyl PPP at 19.7°, 27.4° and 43.1° shift as compared to that of PPP. The peak of isopropyl PPP moves to 16.3°. The X-ray diffraction plot indicates a distinct decrease in crystallization as a result of substituting of alkyl, and the alkylated PPPs are amorphous. The changes are caused by the diminishing regularity of macromolecular array. The isoamyl substituted PPP is an isoamyl in every two rings, so that the steric interference is small. However, it is 1.3 isopropyls per ring in the isopropyl substituted PPP in average, so the steric hindrance is very obvious.
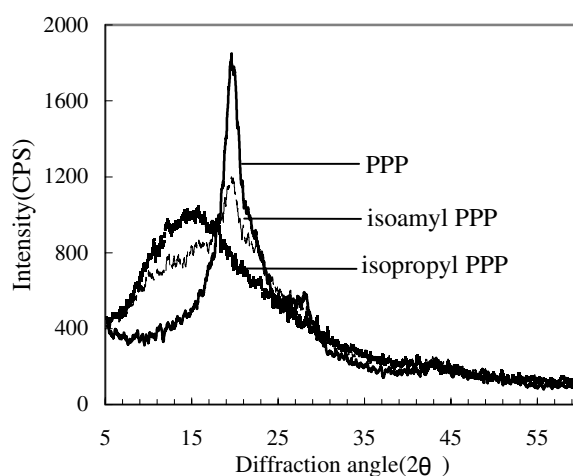
Figure 4. Wide-angle X-ray diffractograms of PPP and alkylated PPPs

Thermo-stability

The results of thermo-gravimetric analysis for PPP powder and alkylated PPPs purified are shown in Figure 5. These results indicate that the thermo-stability of alkylated PPPs is worse than that of PPP. The initial temperature of thermal degradation for the alkylated PPPs is around 174 °C, but it is around 650 °C for PPP. The lower heat-resistance of alkylated PPPs, as compared to PPP, can be explained by the presence of alkyl side chains, which are well known as vulnerable to elevated temperatures.
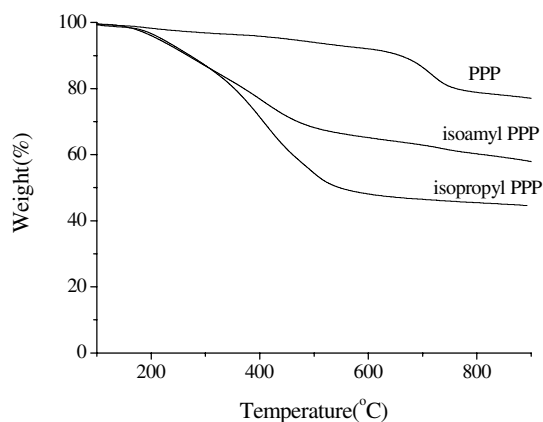
Figure 5. Thermogravimetric analysis of PPP and alkylated PPPs

However, the weight loss of PPP and alkylated PPPs are almost constant at 800 ˚C. The remnant weight (%) of PPP is 78.86%. The remnant weight for isoamyl PPP and isopropyl PPP is 60.25%, 45.67%, respectively. This experimental value is associated with the loss of alkyl linked to the phenyl ring and degradation of polyphenylene backbone. The weight loss in the case of PPP is the degradation of polyphenylene backbone. The weight loss for alkylated PPPs consists of alkyl groups and polyphenylene backbone degradation. Taking into account the fact that the residue of PPP decomposed is highly thermo-stable or changed very little, the difference between alkylated PPPs and PPP can be used to calculate the content of alkyl groups. The results are summarized in Table 4. The weight percent corresponds to a side group per 2 rings for isoamyl PPP, 4 side groups per 3 rings for isopropyl PPP, which agree with CHN elemental analysis and IR spectra.

Table 4. Percent of the phenyl core and side group weight

Alkyl	Weight of Phenyl core (%)[A]	Weight of Side group (%)[B]
C_5H_{11}-	76.4	23.6
C_3H_7-	57.9	42.1

A is the remanent weight of alkyl PPP divided by the remanent weight of PPP, B=(100-A) %

Conclusions

Polyparaphenylene is alkylated with isoamyl bromide and isopropyl bromide in the presence of $AlCl_3$ catalyst. $FeCl_3$ can hardly be used as catalyst for the alkylation. The two alkyl PPPs are soluble in chloroform. The structure of isoamyl PPP is illustrated by CHN elemental analysis, IR, ^{1}H NMR, UV-Vis, WXRD, SEC and TGA. Analysis for thermal stability indicates that PPP is more stable than alkylated PPPs.

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