Investigation of novel polytriazole resins

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ABSTRACT

2,4,6-Tri(4-propargyloxy-phenyl)pyridine (POPP) was made from 2,4,6-tri(4-hydroxyphenyl)pyridine (HPP) and propargyl bromide. The chemical structures of POPP and HPP were well characterized by means of FTIR, 1H-NMR, 13C-NMR, and elemental analysis. Novel polytriazole resins (P-PTA resins) were prepared from POPP and azide compounds via 1,3-dipolar cycloaddition reaction and characterized by solubility, FTIR, DSC, and TGA analyses. The P-PTA resins show good solubility in common solvents. The resins could be cured at 80 °C. The glass transition temperature ($T_g$) and the 5% weight loss temperature ($T_{wt}$) of the cured P-PTA-33 resin arrive at 310 and 365 °C in nitrogen atmosphere, respectively.

Introduction

Polytriazole (PTA) resins are a kind of high-performance polymers, which are synthesized from alkynyl compounds and azide compounds by the 1,3-dipolar cycloaddition. The cycloaddition reaction was found by Michael in 1893. [1–3] PTA resins have good processing properties, whose curing reaction occurs at the temperature as low as 70 °C without any release of volatile substances.[1,4,5] The polytriazole thermosets have good thermal stability and mechanical properties. [6,7] However, their performances depend on molecular structure and curing process.[2,6,8]

The triazole ring as a rigid heterocyclic structure in the molecular chains would enhance heat resistance of resins.[4,6,9,10] In this paper, 2,4,6-tri(4-propargyloxy-phenyl)pyridine (POPP) was made from 2,4,6-tri(4-hydroxyphenyl)pyridine (HPP) and propargyl bromide. Novel polytriazole resins (P-PTA resins) were prepared from POPP and azide compounds via 1,3-dipolar cycloaddition reaction. The structures and properties of the produced resins were investigated.

Experimental

Materials

Tetrabutyl ammonium bromide (A.R.), $p$-hydroxyacetophenone, $p$-hydroxybenzaldehyde (A.R., Acros) were purchased from Aladdin; Propargyl bromide was purchased from Shanghai Bangcheng Chemical Institute; ammonium acetate, sodium hydroxide, tetrahydrofuran (THF), ethanol, methanol, and acetic acid (A.R.) were purchased from Jiangsu Yonghua Chemical Reagent Co., Ltd. 1,1-Bisazidomethyl-4,4′-biphenyl (BAMBP) and 1,3,5-tris(azidomethyl)-2,4,6-trimethylbenzene (TAMTMB) were synthesized according to a previously published procedure.[2,3] All solvents were purified by distillation before use.

Instruments and characterization

1H-NMR and 13C-NMR spectra were recorded on a Bruker Avance 500 spectrometer (Bruker, Billerica, MA, USA) at room temperature in DMSO or CDCl$_3$ with Si(CH$_3$)$_4$ as an internal standard. Fourier Transform Infrared (FTIR) spectra were recorded with a Nicolet 5700 spectrometer (Nicolet, USA). The elemental analysis was performed with Vario EL III elemental analyzer (Elementar, Germany). Differential Scanning Calorimetry (DSC) analyses were performed with a Q2000 (TA, USA) at a heating rate of 10 °C min$^{-1}$ and a nitrogen flow rate of 15 cm$^3$ min$^{-1}$. Thermogravimetric Analysis (TGA) was performed on a Mettler TGA/SDTA 851 analyzer (Mettler-Toledo, Columbus, OH, USA) at a heating rate of 10 °C min$^{-1}$ in nitrogen from 40 to 800 °C. Dynamic Mechanical Analysis (DMA) was carried out on a DMA 1 (Mettler Toledo, Swiss) in the dual cantilever clamp mode under heating at the frequency of 11 Hz with a programmed heating rate of 3 °C min$^{-1}$.
**Synthesis of 2,4,6-tri(4-propargyloxyphenyl)pyridine (POPP)**

**Synthesis of 2,4,6-tri (4-hydroxyphenyl)pyridine (HPP)**

14.30 g p-hydroxy-acetophenone (105 mmol), 6.10 g p-hydroxyl-benzaldehyde (50 mmol), 50.10 g ammonium acetate (0.65 mol), and 70 mL acetic acid were charged into a 100-mL four-necked flask under nitrogen atmosphere. The mixture was kept at 120 °C for 6 h.\[11–14\] When cooled to room temperature, the solution was poured into 125 mL water to get a viscous solid. The solid was washed with deionized water till pH of the washed water was 7.\[11,12,15,16\] The yellow powder was obtained by recrystallization using 70% alcohol (ethanol: water = 7:3). The powder was filtered and dried at 60 °C under vacuum to afford a pale yellow powder, 2,4,6-tri (4-hydroxyphenyl)pyridine (HPP), in yield of 65%. Its melting point is 208 °C determined by DSC. Analyses of HPP: FTIR (KBr, cm⁻¹): 3390 (–OH stretching); 3057 (C–H stretching on phenyl); 1605, 1543, 1518, 1446 (Ar skeleton vibration); 1402 (C–N bending); 1235 (Ar–O stretching); 837, 761, 692 (C–H bending on Ar).¹H-NMR (400 MHz, DMSO-d₆, δ (ppm)): 6.89–6.93 (d, 6H), 7.83–7.88 (m, 4H), 8.13–8.15 (m, 4H), 9.72 (s, 2H), 9.80 (s, 1H).¹³C-NMR (DMSO-d₆, 400 MHz, δ (ppm)): 113.9 (d, C6), 115.9 (d, C2), 116.3 (d, C10), 128.7 (d, C3), 128.9 (d, C9), 129.1 (s, C8), 130.6 (d, C4), 149.3 (s, C7), 156.6 (s, C5), 158.9 (s, C1), 159.0 (s, C11; see Scheme 1). Elemental content (%): Calculated for C₂₃H₁₇NO₃: C 77.75, H 4.79, N 3.94; found: C 77.32, H 4.63, N 3.71.

**Synthesis of POPP**

In a 100-mL three-necked flask with thermometer, mechanical stirrer, and reflux condenser, 45 mL of sodium hydroxide solution (20%), 13.56 g HPP (0.04 mol), and 1.29 g tetrabutyl ammonium bromide (0.004 mol) were added and mixed.\[11,15,16\] About 16.06 g propargyl bromide (0.135 mol) was slowly added in a drop-wise manner within 30 min.\[11,17,18\] This mixture was gradually heated to 50–55 °C and kept at the temperature for 6 h. Then, the products were filtered and washed with cold methanol and water. After dried at 60 °C under vacuum, white powder of 2,4,6-tri(4-propargyloxy-phenyl)pyridine (POPP) was obtained in the yield of 95% with m.p. of 107 °C (determined by DSC).

**The preparation of novel P-PTA resins**

P-PTA resins were prepared from the newly synthesized POPP and azide compounds (1,1-bisazidomethyl-4,4′-bi-phenyl (BAMBP) and 1,3,5-tris(azidomethyl)-2,4,6-trimethyl-benzene (TAMTMB)).\[2,4,19\] POPP and azide compounds with the molar ratio 1.00:1.05 of azide group to alkyne group ([N₃]/[C≡C]) were mixed in acetone with a solid content of 50% and stirred at 55 °C till the mixture became homogeneous. The liquid resins were obtained after acetone was removed. The resin prepared from POPP and BAMBP is named as P-PTA-23 and from POPP and TAMTMB as P-PTA-33. The liquid resins were put into a vacuum oven for removing the residual acetone and embedded air, thereafter, poured into a mold.

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**Scheme 1. Synthesis route of POPP.**
P-PTA-23 and P-PTA-33 resins were cured at 80 °C for 6 h. The obtained cured resins were postcured in the following procedure: 120 °C/2 h + 150 °C/2 h + 180 °C/2 h for P-PTA-23; 120 °C/2 h + 150 °C/2 h + 180 °C/2 h + 200 °C/2 h for P-PTA-33.

**Results and discussion**

**Synthesis and characterization of POPP**

The procedures for synthesizing a novel propargyl ether monomer, POPP, by two steps are shown in Scheme 1, which is referred to those publications for the synthesis of 4-phenyl-2,6-bis(4-propargyloxyphenyl)pyridine (P-PHPP). [11,20] Firstly, the triphenol compound (HPP) was synthesized from p-hydroxyacetophenone and p-hydroxybenzaldehyde. And then the propargyl ether-terminated compound (POPP) was synthesized by the nucleophilic substitution reaction between HPP and propargyl bromide in the presence of tetrabutylammonium bromide as a phase transfer catalyst.

Figure 1 shows the FTIR spectrum of POPP. The disappearance of hydroxyl bands at 3390 cm⁻¹ and the appearance of alkynes bands at 3290 cm⁻¹ (≡C–H) and 2105 cm⁻¹ (C≡C) confirm the nucleophilic displacement reaction and all hydroxyl groups are replaced to alkyne functionalities. The spectrum exhibits characteristic absorption bands at 1608, 1545, 1512, 1432 cm⁻¹ for Ar skeleton vibration, 1392 cm⁻¹ for C–N stretching, 1221 and 1030 cm⁻¹ for Ar–O–C stretching vibration. The absorption band at 3400 cm⁻¹ is assigned to –OH due to absorption of humidity during sample prepared.

Figure 2 shows ¹H-NMR spectrum of the obtained POPP. The peak at 7.26 ppm is for d-CHCl₃ solvent. The ¹H-NMR spectrum of POPP displays the characteristic alkyne protons (–CH₂– and ≡C–H) at 4.8 and 2.6 ppm and pyridinyl protons at 7.8 ppm, whereas the resonances for aromatic protons (Ar–H) at 7.15–8.19 ppm are still observed. The ¹³C-NMR spectrum of POPP is shown in Figure 3. The solvent signal for d-CHCl₃ is at 77.2 ppm. Figure 3 shows characteristic ethynyl groups (C12, C13 at 71.1–73.8 ppm) and methylene protons (C14 at 51.1 ppm). The peaks at 110.7(C6), 144.7(C7), 151.9(C5) ppm are assigned to pyridinyl protons, whereas the peaks of aromatic protons are at 110.2(C2, C10), 123.7(C3, C9), 127.5(C8), 128.4(C4), 153.6(C1, C11) ppm.

Table 1 shows elemental analysis results of POPP. As shown in the table, the measured contents of element N, C and H for POPP are 2.87, 81.76 and 4.82%, respectively, which accord with the calculated values based on the formula C₃₂H₂₃NO₃. All results of FTIR, ¹H-NMR, ¹³C-NMR spectra, and elemental analysis above demonstrate that POPP have been successfully synthesized.
Table 1. Elemental analysis result for POPP.

| Elements | N   | C   | H   |
|----------|-----|-----|-----|
| Calculated (%) | 2.99 | 81.88 | 4.90 |
| Found (%)     | 2.87 | 81.76 | 4.82 |

**Preparation of P-PTA resins**

P-PTA resins are prepared by 1,3-dipolar cycloaddition reaction between POPP and azide compounds as shown in Scheme 2. Figure 4 shows FTIR spectra of the obtained P-PTA-23 and the mixture consisting of POPP and BAMBP. The absorption at 3295 cm\(^{-1}\) is due to the stretching vibration of \(\equiv C-H\), and the signals at 2095 cm\(^{-1}\) is attributed to the stretching vibration for \(-N_3\) and \(C\equiv C\). As shown in the figure, the peaks at 2095 and 3295 cm\(^{-1}\) on the spectrum of the P-PTA-23 disappear completely. In addition, a new absorption band appears at 3136 cm\(^{-1}\), representing the hydrogen on the triazole ring. This indicates that the triazole ring in polymer chains has formed. The FTIR spectra of P-PTA-33 are similar with those of P-PTA-23. The results demonstrate that 1, 3-dipolar cycloaddition reaction of the azide group and propargyl group has taken place and formed poly(1,2,3-triazole)s at 55 °C.

**Solubility of P-PTA resins**

The solubility of the resins in common organic solvents has an influence on the processability. The solubility of P-PTA resins in several common organic solvents with 3.0 wt % is shown in Table 2. The P-PTA resins are soluble in chlorinated hydrocarbon solvents such as chloroform, dichloromethane, and strong polar aprotic solvents such as DMSO, but insoluble in nonpolar solvents or weak polar solvents. P-PTA-23 has better solubility than P-PTA-33. The difference of the resins in solubility could be explained by their structure. The functionality of monomers and the spatial symmetry of P-PTA-33 are higher than those of P-PTA-23. The good solubility facilitates the processing of the resins.

**Curing behavior of P-PTA resins**

The curing behavior of the P-PTA resins is investigated by DSC at a heating rate of 10 °C min\(^{-1}\) under argon atmosphere as shown in Figure 5. Obviously, the DSC curves of two P-PTA resins show the similar curing behavior with two exothermic peaks. Two exothermic peaks (a large peak and a small peak) can be observed in the range...
of 90–300 °C. A large exothermic peak appeared in the range of 90–150 °C is an exothermic peak for the P-PTA resins curing. There is a small exothermic peak appearing in the range of 270–300 °C, which is a cross-linking reaction peak of excessive alkyne groups.[11] The DSC curves show the temperature of cure initiation for P-PTA-23 resin is at about 72 °C while that is about 82 °C for P-PTA-33. The exothermic peaks centered at 133 °C and the heat is 836 J g⁻¹ for curing for P-PTA-23. The peak temperature of DSC for P-PTA-33 (138 °C) is a little higher than that of P-PTA-23, which probably results from the steric effect of TAMTMB in P-PTA-33. The heat of curing for P-PTA-33 is 876 J/g which is higher than that of P-PTA-23. This can be explained by the fact that there are more functional groups in the P-PTA-33 resin.

The absorption of the characteristic functional groups of the resins in the FTIR spectra changes during the process of polymerization as shown in Figure 6 ((a):P-PTA-23) and ((b):P-PTA-33). The characteristics peaks of –N₃, ≡C–H and –C≡C– are obvious before curing. The absorption peaks at 3293 and 2103 cm⁻¹ assigned to the stretching vibrations of –C≡C–H, –C≡C–, and N₃, respectively, decrease, whereas a new absorption peak at 3137 cm⁻¹ corresponding to the stretching vibration of hydrogen on the triazole ring appears, which shows that the polymerization reaction of –N₃ and –C≡C– occurs at 80 °C. With the increase in polymerization temperature, the superposition peak intensity of azide group and –C≡C– stretching vibration at 2103 cm⁻¹ gradually weakens and completely disappears at 180 °C for P-PTA-23 (200 °C for P-PTA-33). The results show that the POPP and azide compounds do react completely in the thermal process.

The curing degree of the resins was evaluated by DSC analyses at a heating rate of 10 °C min⁻¹ under argon atmosphere. The DSC curves of the cured P-PTA resins are shown in Figure 7. There is a small exothermic peak at about 275 °C. The exothermic peak contributes to the curing peak of excessive alkyne groups. This means the reaction between alkyne and azides is completed at 180–200 °C. Combining the analysis results of DSC and FTIR analyses, the post curing procedure could be determined: 120 °C/2 h + 150 °C/2 h + 180 °C/2 h for P-PTA-23 and 120 °C/2 h + 150 °C/2 h + 180 °C/2 h + 200 °C/2 h for P-PTA-33.

**Thermal properties of cured P-PTA resins**

Thermal properties of cured P-PTA resins are determined by DMA and TGA techniques. The heat resistance of cured

| Table 2. Solubility of P-PTA resins. |
|--------------------------------------|
| Solvent                          | P-PTA-23 | P-PTA-33 | Solvent                  | P-PTA-23 | P-PTA-33 |
|-----------------------------------|----------|----------|--------------------------|----------|----------|
| Tetrahydrofuran                   | +        | +        | Acetone                  | +        | +        |
| Petroleum ether                   | ×        | ×        | Ethyl ether              | +        | +        |
| Ethanol                           | ×        | ×        | Toluene                  | ×        | ×        |
| Chloroform                        | +        | +        | Dimethylacetamide        | +        | +        |
| Dichloromethane                   | +        | +        | Dimethyl sulfoxide       | +        | +        |
| 1,2-Dichloroethane                | +        | ×        | Dimethylformamide        | +        | +        |

Notes: +: soluble, ×: insoluble.
P-PTA resins is determined by DMA at a heating rate of 3 °C min⁻¹ under argon atmosphere. The test results are shown in Figure 8. As seen from the figure, the high \( T_g \) of cured P-PTA-23 (249 °C see Figure 8(a)) and P-PTA-33 (310 °C see Figure 8(b)) illustrate that the polytriazole resins incorporating pyridine and bulky phenyl group provide good heat resistance. The \( T_g \) of cured P-PTA-33 is higher than the \( T_g \) of cured P-PTA-23 due to the denser cross-linking network which could reduce the motion of the chain segments in the cross-linked network. These all indicate that the improved thermal performance results from the contribution of the cross-linked structure and the rigid structure of pyridine ring connected with bulky phenylene.

Table 3 lists the glass transition temperatures of some polytriazole resins. As shown in the table, \( T_g \) of the resins are influenced by the cross-linked density of the resins, the functionality of monomers, and chain flexibility. The higher the functionality, the higher the \( T_g \) would be. The \( T_g \) for cured P-PTA-33 and cured PTA-33 \([6,8]\) resins are higher than those for cured P-PTA-23, PTA-23 \([6,8]\), and PTA32 \([21]\) resins. When the average functionality of the PTA resins is 3, the cured P-PTA-33 resin and cured PTA-33 resin have a close \( T_g \). The length of PTA-33 resin segments between the...
Conclusion

The new kind of propargyl ether monomer, 2,4,6-tri(4-propargyloxy-phenyl)pyridine (POPP), was prepared in overall yields of about 62%. The novel P-PTA resins derived from POPP have good solubility in common solvents. The novel resins containing pyridine and bulky phenyl group exhibit the similar curing behavior and could be cured at a temperature as low as 80 °C. The cured polytriazole resins have high glass transition temperatures and thermal decomposition temperatures. The glass transition temperature and decomposition temperature at 5% weight loss for cured P-PTA-23 are 249 and 356 °C, respectively. The $T_g$ of cured P-PTA-33 increases by 61 °C as compared with that of cured P-PTA-23. TGA data reveal slightly higher $T_d5$ of P-PTA-33 as compared with P-PTA-23.

Disclosure statement

No potential conflict of interest was reported by the authors.

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