

Novel Propargylether-Terminated Monomers Containing Pyridine and Phenyl Pendent Group: Synthesis, Cure, and Properties

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ABSTRACT: Two novel propargylether-terminated resins containing pyridine and bulky phenyl pendent group were prepared from propargyl bromide and different diphenols, and highly thermal stable polymers were obtained by the thermal cure of the monomers. The chemical structures of these novel monomers were well confirmed by FTIR, ¹H-NMR and elemental analysis. Curing and thermal behavior of the resins were investigated using differential scanning calorimetry (DSC) and dynamic thermogravimetry in argon atmosphere. DSC curves of these two monomers showed a single endothermic peak corresponding to the conformation of chromene ring and homopolymerization of the chromene ring. The temperature at 5% weight loss (T_{d5}) was higher than 440°C under argon and the highest glass transition temperature (T_g) reached 362°C. The rheological behavior and solubility of the monomer were also investigated. The monomers showed excellent flow-ability, broad processing window, and great solubility. These results showed that the two resins could be ideal candidates for high-temperature resistant resins. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2014, 131, 40469.

KEYWORDS: resins; thermosets; thermal properties; synthesis and processing; properties and characterization

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INTRODUCTION

Since 1990, Dirlikov has reported a series of novel thermosetting materials named propargyl-terminated resins. The cured products exhibited numerous advantages, e.g. low water absorption, excellent thermal stability, dielectric, and mechanical properties.¹ Propargyl ether resin appeared to be a very attractive candidate for epoxy resin in advanced composites, electronics, adhesives, and coatings. Therefore, propargyl-containing polymers, such as bis propargyl ether bisphenol,² propargyl ether novolak,^{3,4} polybenzoxazines,^{5,6} polyarylether ketones⁷ as well as poly-phthalimide⁸ and other materials⁹ were synthesized, and the thermal properties of the resins were also investigated. However, the processability and solubility of the propargyl-containing resins were less studied. Recently, with the fast development of high technology fields just like in aerospace and microelectronics industry, the demand for polymers materials with excellent combined properties including excellent heat resistance, easy processing, and lower water uptake increased sharply. Thus, improving the processability and solubility of propargyl resins while maintaining the heat resistance is important and interesting.

Pyridine is a heteroaromatic molecule with polarizability and rigidity. New kinds of dianhydride, diamine, or other monomers

within pyridine unit were designed and synthesized, and the novel linear polymers containing pyridine with good thermostability and processability were obtained as well.^{10–18} Pyridine ring would offer contributions for the thermal stability, chemical stability, retention of mechanical property of the resulting polymer at elevated temperature, because of the rigidity based on symmetry and aromaticity of pyridine. Because of the polarizability of nitrogen atom in pyridine ring, monomers containing pyridine always have good solubility in organic solvent.^{19,20} At the same time, the incorporation of bulky pendent groups into polymers can provide beneficial effects for solubility because of separation of molecular, lowering of chain packing with a gain of free volume and weakening of intermolecular hydrogen bonding.^{21–28} Furthermore, bulky pendent groups with $-\text{CF}_3$ can not only provide enhanced solubility but also offer other merits such as good thermal oxidative stability, low water uptake, excellent electrical insulating, and dielectric properties.^{13,29–34} However, most of the polymers containing pyridine or phenyl pendent group were linear and thermoplastic, and thermoset polymers containing pyridine or phenyl pendent group were poor.

In this article, the method of molecular design was used to synthesize new structure propargyl ether monomer with advantages

of propargylether-terminated, pyridine, and bulky phenyl pendent groups. Two kinds of propargyl ether monomers containing pyridine and bulky phenyl pendent groups were synthesized and their thermal curing behavior was examined and discussed at the same time. The monomers exhibited good solubility in organic solvent, excellent rheological properties and the obtained cured products exhibited high thermal stability.

EXPERIMENTAL

Materials

Bromopropyne, *p*-hydroxyacetophenone, benzaldehyde, *p*-trifluoromethyl benzaldehyde (A.R., Acros) were used as received; Tetrabutyl ammonium bromide (A.R.) was used as received from Tianjin Fine Chemical Institute (China). Dichloromethane (DCM), tetrahydrofuran (THF), ethanol, methanol, acetic acid, and hydrochloric acid (A.R., Beijing Chemical Plant) were purchased from Beijing Chemical Plant. All solvents were purified by distillation before using.

Instruments and Characterization

FTIR spectra were recorded with a Nicolet model NEXUS-470 FTIR Spectrometer in solid state as KBr pellets in a range of 4000–400 cm^{-1} . The resolution was 4 cm^{-1} with 32 accumulated scans. Liquid state $^1\text{H-NMR}$ spectra were recorded on a JEOL model FX-90Q spectrometer operating at 400 MHz in DMSO- d_6 or CDCl_3 . Differential scanning calorimetry (DSC)–thermogravimetric analysis (TGA) were carried out in argon atmosphere on a NETZSCH model STA 449C Jupiter simultaneous thermal analyzer with heating rate 10°C/min or 20°C/min. The temperature range of DSC was between room temperature and 450°C, and temperature range of TGA was between room temperature and 900°C. Bohlin Instrument model Gemini 200 Advanced Rheometer was used to study the rheological properties of the resins with a shear rate of 0.1 s^{-1} at the heating rate of 5°C/min between 100°C and 300°C. The elemental analysis was performed by Vario EL III elemental analyzer.

Synthesis of 4-Phenyl-2,6-bis[4-hydroxy-phenyl]pyridine

A 250-mL three-necked flask fitted with a nitrogen inlet, a reflux condenser, and a mechanical stirrer was charged with a mixture of *p*-hydroxyacetophenone (14.30 g, 105 mmol), benzaldehyde (5.31 g, 50 mmol), ammonium acetate (37.50 g), and acetic acid (125 mL). The mixture was heated under reflux with stirring under N_2 for 4 h. Then the solution was cooled to room temperature and poured into 125-mL water, to give a viscous semi-solid which was washed with warm water and dissolved with 100 mL ethanol. The yellow powder was obtained by adding 15 mL 35% aqueous HCl into the ethanol solution. The powder was filtered off, washed with water and ethanol. The yellow powder was dissolved with 40 mL 10% KOH solution and then added an excess of glacial acetic acid to the solution to get yellow precipitate. The precipitate was washed with DCM and recrystallized with 2 : 1 petroleum ether/THF then dried at 60°C under vacuum to obtain a pale yellow powder 4-phenyl-2,6-bis[4-hydroxy-phenyl]pyridine (PHPP), yield: 65%, m.p.: 228°C (determined by DSC).

FTIR (KBr): cm^{-1} = 3378 (—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).

$^1\text{H-NMR}$ (DMSO- d_6 , 400 MHz): δ (ppm) = 6.90–6.92 (d, 4H), 7.50–7.58 (m, 3H), 7.96–8.02 (m, 4H), 8.15–8.18 (d, 4H), 9.74 (s, 2H).

Synthesis of 4-(4'-Trifluoromethyl)phenyl-2,6-bis[4-hydroxy-phenyl] pyridine

A 250-mL three-necked flask fitted with a nitrogen inlet, a reflux condenser, and a mechanical stirrer was charged with a mixture of *p*-hydroxyacetophenone (14.30 g, 105 mmol), *p*-trifluoromethyl benzaldehyde (8.70 g, 50 mmol), ammonium acetate (37.50 g), and acetic acid (125 mL). The mixture was heated under reflux with stirring under N_2 for 5 h. Then the solution was cooled to room temperature and poured into 135 mL water, to give a viscous semi-solid which was washed with warm water and dissolved with 100 mL ethanol. The yellow powder was obtained by adding 15 mL 35% aqueous HCl into the ethanol solution. The powder was filtered off, washed with water, and then with ethanol. The yellow powder was dissolved with 40 mL 10% KOH solution and then added an excess of glacial acetic acid to the solution to get yellow precipitate. The precipitate was washed with DCM and recrystallized with 3:1 petroleum ether/THF then dried at 60°C under vacuum, to obtain a pale yellow powder 4-(4'-trifluoromethyl)phenyl-2,6-bis[4-hydroxy-phenyl]pyridine (FPHP), yield: 62%, m.p.: 256°C (determined by DSC).

FTIR (KBr): cm^{-1} = 3356 (—OH stretching), 3063 (C—H stretching on phenyl), 1609, 1546, 1521, 1430 (Ar skeleton vibration), 1389 (C—N bending), 1226 (Ar—O stretching), 1110 (C—CF₃ skeleton-stretching vibration), 833, 758, 667 (C—H bending on Ar).

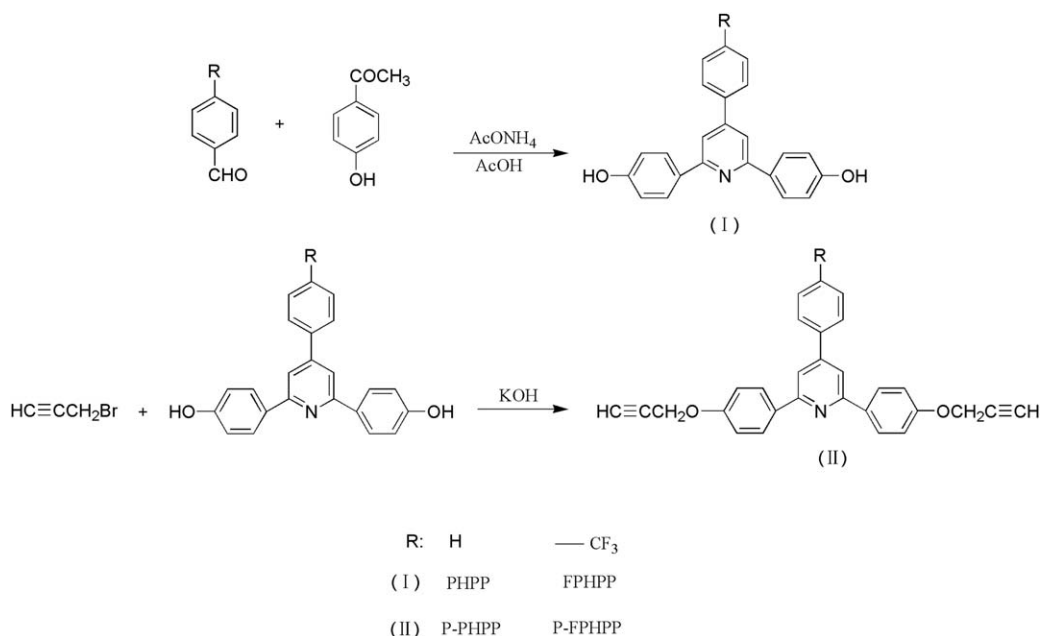
$^1\text{H-NMR}$ (DMSO- d_6 , 400 MHz): δ (ppm) = 6.91–6.93 (d, 4H), 7.90–8.03 (m, 4H), 8.17–8.20 (d, 4H), 8.22–8.24 (d, 2H), 9.75 (s, 2H).

Synthesis of 4-Phenyl-2,6-bis[4-propargylether-phenyl]pyridine

In a 100-mL three-necked flask, 45 mL of 20% the aqueous solution of sodium hydroxide, 13.56 g (0.04 mol) of PPHP and 1.29 g (0.004 mol) of tetrabutyl ammonium bromide were mixed. The mixture was stirred at room temperature for about 1 h in order to form the phenolate. About 10.94 g (0.09 mol) of propargyl bromide was slowly added dropwise to the resulting mixture for 20 min, then heated at 50–55°C with stirring for 5 h. Then the products were filtered, washed with water and cold methanol. After drying at 60°C under vacuum, light yellow powder was obtained 4-phenyl-2,6-bis[4-propargylether-phenyl]pyridine (P-PHP), yield: 96%, m.p.: 117°C (determined by DSC).

FTIR (KBr): cm^{-1} = 3277 ($\equiv\text{CH}$ stretching), 3041 (C—H stretching on phenyl), 2919 (C—H stretching on CH_2), 2113 ($\text{C}\equiv\text{CH}$ stretching), 1606, 1542, 1515, 1449 (Ar skeleton vibration), 1395 (C—N bending), 1223 (Ar—O stretching), 1172 (O—C stretching), 837, 764, 695 (C—H bending on Ar).

$^1\text{H-NMR}$ (CD_3Cl , 400 MHz): δ (ppm) = 2.55–2.56 (t, 2H), 4.77–4.78 (s, 4H), 7.10–7.12 (d, 4H), 7.47–7.55 (m, 3H), 7.73–7.74 (m, 4H), 8.16–8.18 (d, 4H).



Scheme 1. Synthesis of P-PHPP and P-FPHPP.

Elemental analysis: Calculated for C₂₉H₂₁NO₂: C, 83.86%; H, 5.06%; N, 3.37%. Found: C, 83.99%; H, 5.15%; N, 3.38%.

Synthesis of 4-(4'-Trifluoromethyl)phenyl-2,6-bis[4-propargylether-phenyl]pyridine

4-(4'-Trifluoromethyl)phenyl-2,6-bis[4-propargylether-phenyl]pyridine (P-FPHPP) was prepared according to the same procedure except that PHPP was replaced by FPHPP. P-FPHPP was obtained as a light yellow solid, yield: 92%, m.p.: 106°C (determined by DSC).

FTIR (KBr): cm⁻¹ = 3286 (≡CH stretching), 3054 (C—H stretching on phenyl), 2925 (C—H stretching on CH₂), 2115 (C≡CH stretching), 1603, 1546, 1508, 1430 (Ar skeleton vibration), 1389 (C—N bending), 1216 (Ar—O stretching), 1175 (O—C stretching), 1113 (C—CF₃ skeleton-stretching vibration), 827, 754, 692 (C—H bending on Ar).

¹H-NMR (CD₃Cl, 400 MHz): δ (ppm) = 2.55–2.57 (t, 2H), 4.78–4.79 (s, 4H), 7.11–7.13 (d, 4H), 7.77–7.79 (m, 4H), 7.82–7.86 (d, 2H), 8.16–8.18 (d, 4H).

Elemental analysis: Calculated for C₃₀H₂₀NO₂F₃: C, 74.53%; H, 4.14%; N, 2.90%. Found: C, 74.42%; H, 4.23%; N, 2.88%.

RESULTS AND DISCUSSION

Synthesis of P-PHPP and P-FPHPP

The propargyl ether monomers containing pyridine and bulky phenyl pendent group P-PHPP and P-FPHPP were synthesized by a two-step synthesis route as shown in Scheme 1. Firstly, the diphenol compounds (I) were obtained via a modified Chichibabin reaction³⁵ between *p*-hydroxy-acetophenone with benzaldehyde or *p*-trifluoromethyl benzaldehyde. Then compounds (I) were coupled with propargyl bromide in the presence of tetrabutylammonium bromide as phase transfer catalyst to yield the propargylether-terminated compounds (II).

Figure 1 shows the FTIR spectra of the two monomers. The two aromatic bispropargyl ether monomers contained some

analogous groups with similar IR absorption locations. FTIR spectra of the two monomers exhibited characteristic absorption bands near 3280 cm⁻¹ (C≡C—H stretching vibration), 2115 cm⁻¹ (C≡C stretching vibration), 1605, 1545 cm⁻¹, 1510 cm⁻¹,

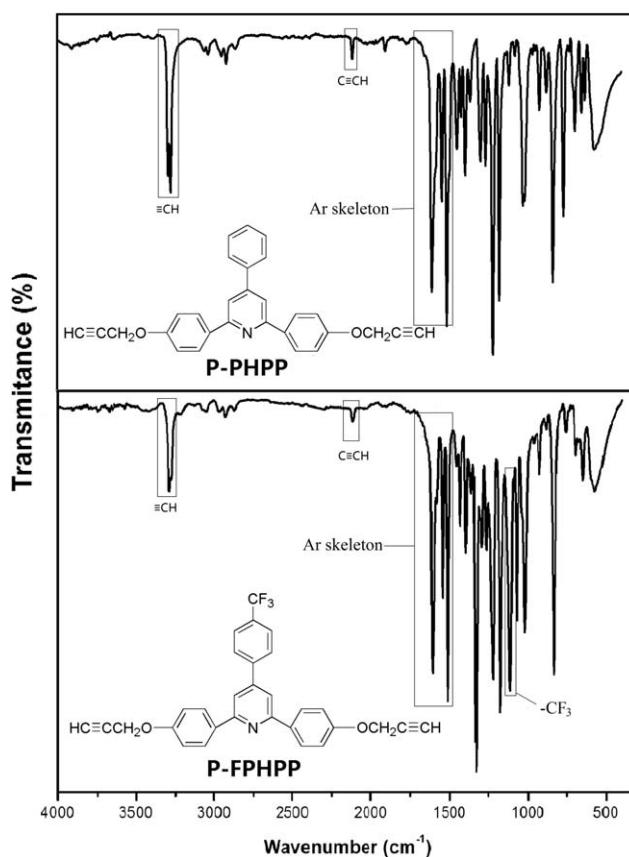


Figure 1. FTIR spectra of P-PHPP and P-FPHPP.

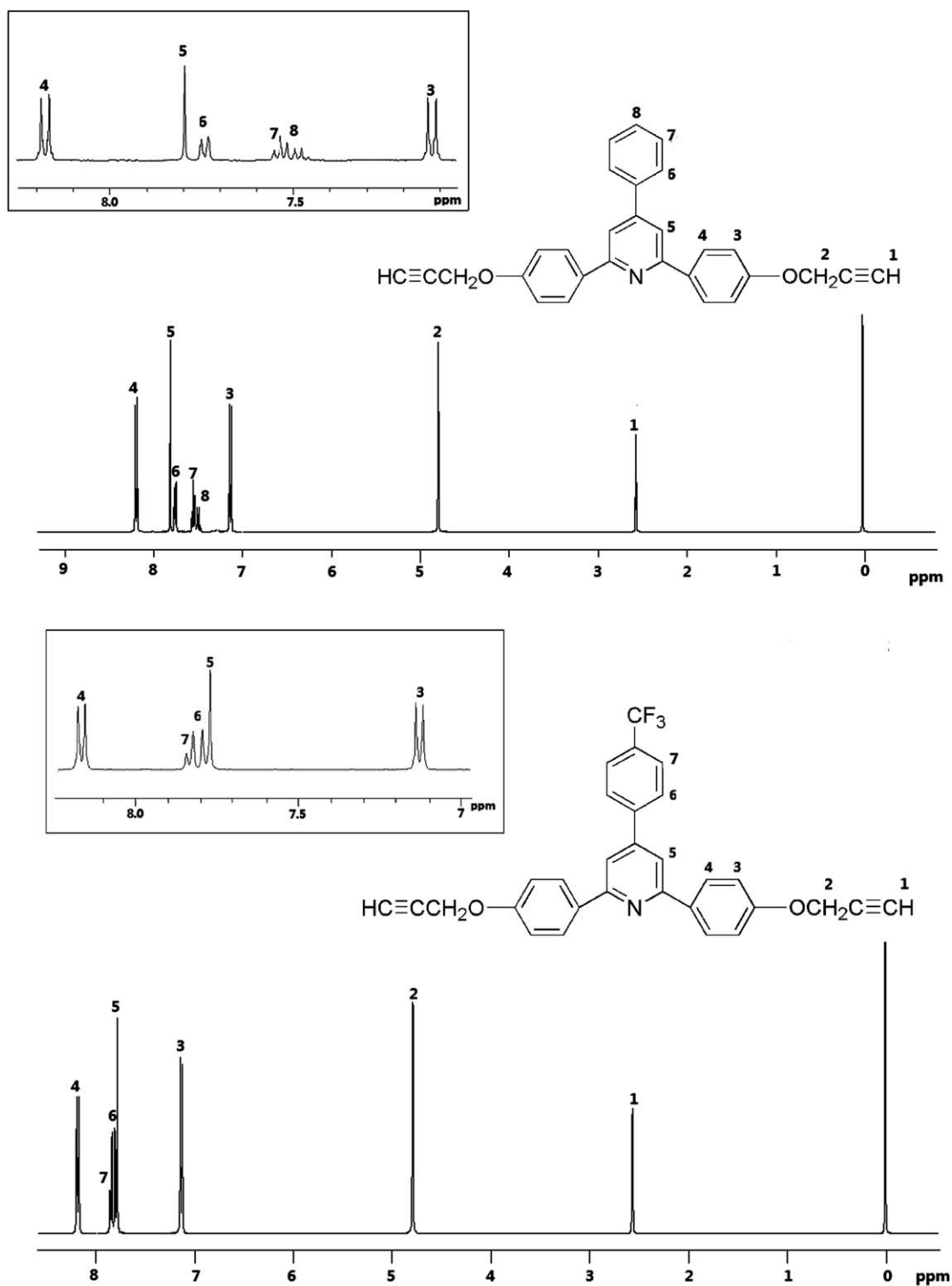


Figure 2. ¹H-NMR spectra of P-PHPP and P-FPHPP.

1440 cm^{-1} (Ar skeleton vibration), 1390 cm^{-1} (C—N stretching), 1220 cm^{-1} , 1175 cm^{-1} (Ar—O—C stretching vibration). In addition, the spectrum of P-FPHPP showed characteristic absorption bands at 1113 cm^{-1} owing to C—CF₃ skeleton-stretching vibration.

Figure 2 shows ¹H-NMR of P-PHPP and P-FPHPP. The two aromatic bispropargyl ether monomers contained some identical groups with similar resonance peaks in the ¹H-NMR spectra. The resonance peaks at 7.10–8.18 ppm were assigned to the aromatic protons (Ar—H), whereas the resonance peaks of protons

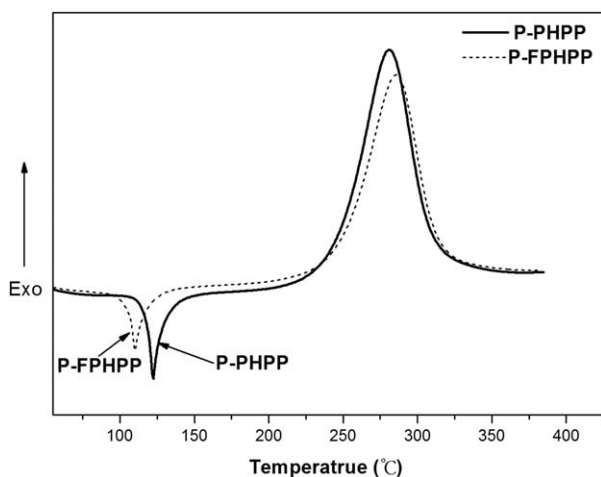


Figure 3. DSC curves of P-PHPP and P-FPHPP.

for methylene groups (CH_2) appeared near 4.78 ppm. The signals for protons of ethynyl groups ($\text{C}\equiv\text{C}-\text{H}$) were found near 2.55 ppm. Furthermore, the elemental analysis values of the two monomers were in good agreement with the calculated ones. All the above characterizations demonstrated that the two propargyl ether monomers synthesized herein were consistent with the proposed structures.

Thermal Curing of P-PHPP and P-FPHPP

The curing behavior of the monomers was examined by DSC at a heating rate of $10^\circ\text{C}/\text{min}$ under argon atmosphere as shown in Figure 3. Obviously, a sharp melt endothermic peak was observed from each DSC curve. The m.p. for P-FPHPP was 105°C , whereas for P-PHPP it was 115°C . Because of the introduction of the trifluoromethyl group, the packing density and the regularity of molecules for P-FPHPP were lower than that for P-PHPP. The temperatures of cure initiation for P-PHPP and P-FPHPP were about 245°C . The DSC curves displayed endothermic peaks centered at 280°C for P-PHPP, 286°C for P-FPHPP, respectively. The curing process of the two monomers was the Claisen type sigmatropic rearrangement of the terminal propargyl ether groups into a chromene ring, and homopolymerization of the chromene ring.^{36,37} The reaction mechanism of terminal propargyl ether groups is proposed in Scheme 2. The Claisen-type sigmatropic rearrangement of the terminal propargyl ether groups was electrophilic in nature, which was retarded by the presence of electron-withdrawing groups on the benzene ring, and the curing process was also influenced by steric hindrance of the groups. The peak temperature of DSC exotherm for P-FPHPP was higher than that of P-PHPP, which was attributed to the stronger electron withdrawing of trifluoromethyl group in P-FPHPP and the large volume of trifluoro-

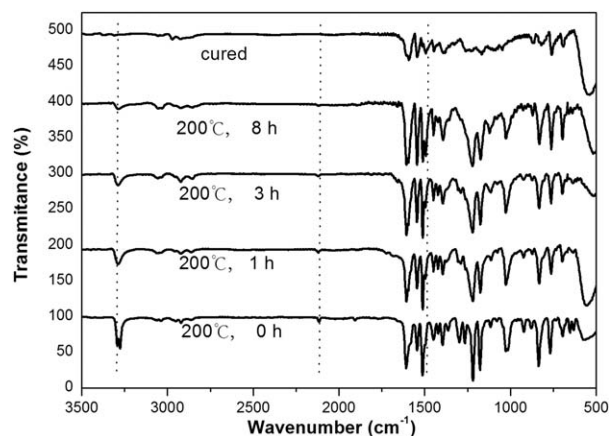


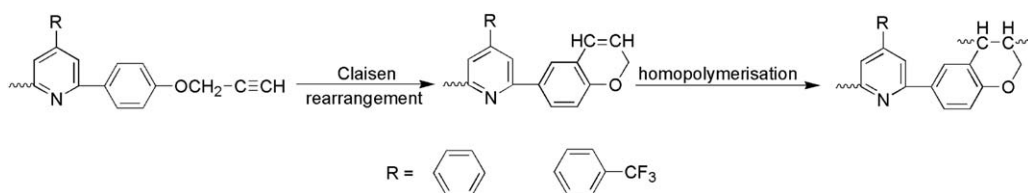
Figure 4. FTIR spectra of P-PHPP after being cured at 200°C for different time.

methyl group. The exothermic heats (ΔH) of curing of P-PHPP and P-FPHPP were 348 kJ/mol and 355 kJ/mol respectively, depending on the different structures of the aromatic bispropargyl ethers. Because the steric effect of P-FPHPP was stronger than that of P-PHPP, the ΔH of P-FPHPP was more than that of P-PHPP in the curing reaction.

The FTIR spectra of P-PHPP after being cured at 200°C for different durations of curing are given in Figure 4. After being cured for 1 h, 3 h, 8 h at 200°C , we could see that the infrared absorption strength of $\equiv\text{C}-\text{H}$ at 3280 cm^{-1} and of $\text{C}\equiv\text{C}$ at 2115 cm^{-1} decreased. What is more, the new absorption peak near 1493 cm^{-1} was ascribed to the aromatic ring of 2*H*-chromene. After the resin was cured absolutely, the absorption peak of 2*H*-chromene at 1493 cm^{-1} disappeared, which showed that the homopolymerization of 2*H*-chromene occurred. The results of FTIR spectra characterization verified the Claisen rearrangement reaction and the chromene homopolymerization. The curing behavior and reaction of P-FPHPP were similar with that of P-PHPP.

Solubility of P-PHPP and P-FPHPP

For thermally stable resins, solubility in common organic solvents before curing is a very important factor for their processability. The solubility of the two propargyl ether monomers and corresponding diphenols in several common organic solvents at 3.0% (wt/vol) is shown in Table I. The two propargyl ether monomers were readily soluble in most semi-polarity and low boiling point solvents, such as toluene, acetone, THF, DCM, chloroform, and ethanol. And both P-PHPP and P-FPHPP showed good solubility in stronger polarity-aprotic solvents such as NMP, DMF, DMSO, DMAc. In addition, P-FPHPP had better solubility in ethanol and methanol than P-PHPP due to

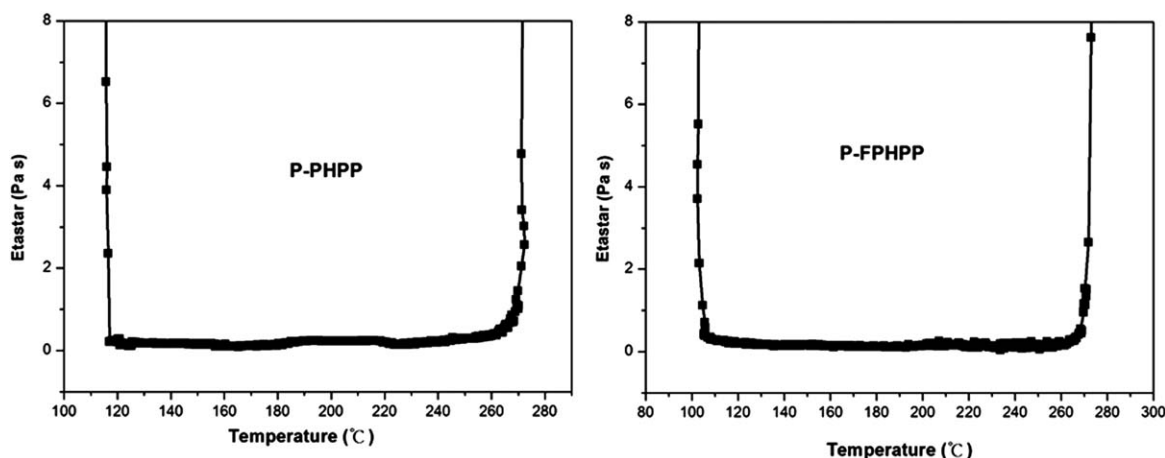


Scheme 2. Curing mechanism of the propargylether-terminated monomers.

Table I. Solubility of the Propargylether-Terminated Monomers

Sample	Solvent										
	NMP	DMF	DMSO	DMAc	THF	Acetone	CHCl ₃	CH ₂ Cl ₂	Toluene	Ethanol	Methanol
P-PHPP	++	++	++	++	++	++	++	++	++	+-	+-
PHPP	++	++	++	++	++	++	--	--	++	++	++
P-FPHPP	++	++	++	++	++	++	++	++	++	+	+
FPHPP	++	++	++	++	++	++	--	--	++	++	++

Qualitative solubility was determined at 3.0% (wt/vol); ++, soluble at room temperature, +, partially soluble at room temperature; +-, soluble on heating; --, insoluble on heating.

**Figure 5.** Viscosity-temperature curves of the P-PHPP and P-FPHPP.

the polarity of trifluoromethyl group in P-FPHPP. As the introduction of propargylether, the solubility of P-PHPP and P-FPHPP in CHCl₃ and CH₂Cl₂ was better than PHPP and FPHPP. The excellent solubility facilitated the processing property of those resins.

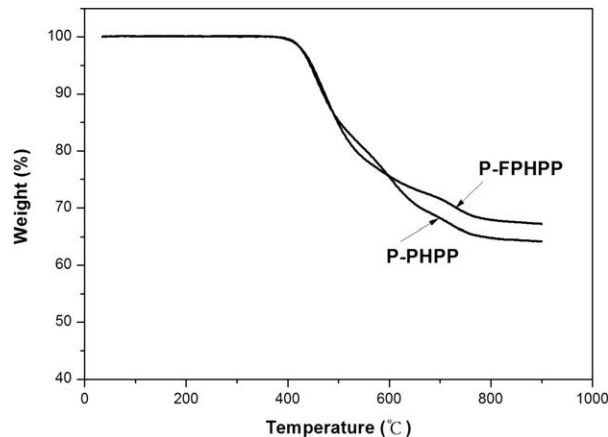
Dynamic Rheological Behavior of the Resulting Resins

The viscosity of P-PHPP and P-FPHPP was measured using the rheometer as shown in Figure 5, which shows that the propargylether-terminated resins containing pyridine and bulky phenyl pendent group exhibited excellent flowability. The viscosity of P-PHPP and P-FPHPP showed an obvious initial sharp decrease with the temperature increasing and melted at 117°C and 106°C, respectively. Then the viscosity both stabilized and finally increased dramatically while the temperature reached about 270°C due to the thermal curing reaction. The melting point of P-FPHPP was lower than P-PHPP, since -CF₃ could decrease the molecular packing density and reduce the regularity of the crystals. Accordingly, the processing windows of P-PHPP and P-FPHPP were 117–272°C and 106–270°C, respectively, whose viscosity were lower than 1 Pa s. Compared with bisphenol A propargylether-terminated resin,³⁸ the two propargylether-terminated resins containing pyridine and bulky phenyl pendent group exhibited excellent flowability and had a broader processing window. It is because the incorporation of bulky phenyl pendent group and -CF₃ into resins could increase the intermolecular distance and decrease the intermolecular

force. With a broad processing window around 160°C and excellent mobility after being melt, P-PHPP and P-FPHPP could be processed by a variety of techniques for fabricating thermo-setting composites.

Thermal Properties of the Cured Polymers

T_g values of the cured products were tested by DSC with a heating rate of 20°C/min in argon atmosphere. The thermal stability of the cured resins was evaluated by TGA at a heating rate of 10°C/min under argon atmosphere. The typical TGA thermograms of the resins are depicted in Figure 6. The DSC curves of

**Figure 6.** TGA curves of the cured P-PHPP and P-FPHPP.

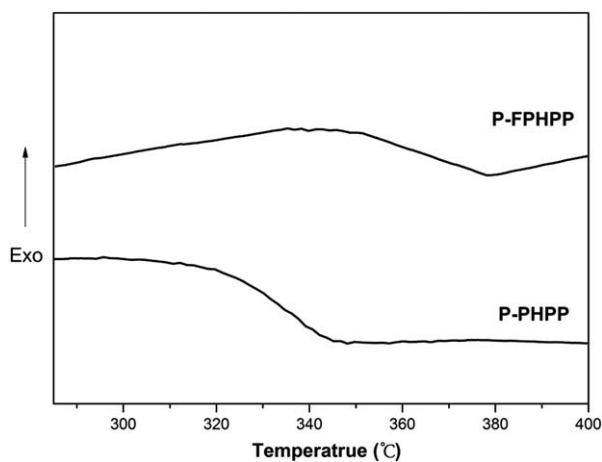


Figure 7. The DSC curves of glass-transition region for cured P-PHPP and P-FPHPP.

glass-transition region for the two cured resins are shown in Figure 7. The detailed thermal data obtained from the TGA and DSC analyses are summarized in Table II. The cured resins showed great thermal stability and high char yields at 900°C under argon atmosphere related to the rigid backbone of the crossing network and high denser crossing network by thermal crosslinking reactions in the curing process. Furthermore, the introduction of $-\text{CF}_3$ into the aromatic propargyl ether resin could increase the thermal stability slightly.

Both of the cured resins exhibited the 5% weight loss temperature (T_{d5}) above 440°C which surpasses the T_{d5} of the cured bisphenol A propargylether-terminated resin³⁸ (DPBPA) and bisphenol AF propargylether-terminated resin³⁹ (DPBPF), because of the introduction of the stable and rigid pyridine and bulky phenyl pendent group into the molecular. In particular, the T_{d5} and T_{d10} in argon of cured P-FPHPP were 447°C and 473°C respectively, which were higher than those of cured P-PHPP, probably due to the greater thermal stability of trifluoromethyl group with the C–F bond. At the same time, the char yield at 900°C of cured P-FPHPP was 67.2%, which was slightly higher than that of cured P-PHPP. In addition, the T_g of cured P-FPHPP was also higher than the T_g of cured P-

Table II. Thermal Analysis Data of the Cured P-PHPP and P-FPHPP

Data	Cured monomers	
	P-PHPP	P-FPHPP
T_g (°C) ^a	332	362
T_{d5} (°C) ^b	445	447
T_{d10} (°C) ^c	470	473
Char yield (%) ^d	64.2	67.2

^a T_g measured by DSC at a heating rate of 20°C/min in argon atmosphere.

^bTemperature at a 5% weight loss at a 10°C/min heating rate in argon atmosphere.

^cTemperature at a 10% weight loss at a 10°C/min heating rate in argon atmosphere.

^dResidual weight (%) at 900°C in argon atmosphere.

PHPP, which was attributed to the introduction of trifluoromethyl as the polar groups that could decrease the activity of the segment in the crosslinking network. These all indicated that we achieved the expected results that pyridine, bulky phenyl pendent group and trifluoromethyl could improve the thermal performance of the propargylether-terminated resin. The high T_g (>360°C) and high T_{d5} (>440°C) illustrated that the propargylether-terminated resins containing pyridine and bulky phenyl pendent group offered good heat resistance and might be applied at high temperature conditions. At the same time, both of them exhibited high char yield (>65%) at 900°C in argon atmosphere, which implied their potential application as ablation materials.

CONCLUSION

Two kinds of propargylether-terminated resins containing pyridine and bulky phenyl pendent group were successfully synthesized and characterized. The obtained monomers could be dissolved in common low boiling-point and polar solvents. The novel monomers containing pyridine and bulky phenyl pendent group exhibited usual crosslinking behavior with the exothermal maximum below 275°C as the common propargyl ether monomers. The dynamic rheological curves showed excellent dynamic rheological property of the resins as well. Extremely high thermal stability was confirmed by TGA. The highest T_{d5} of the cured resins was increased by about 95°C than bispropargyl ether bisphenol A. The char yield at 900°C of cured resins was 67%, which was an outstanding result for thermosetting resins without addition of inorganic filler. At the same time, the incorporation of $-\text{CF}_3$ into the monomers could not only increase the solubility of the resin in common solvent, but also could keep the high heat resistance of the cured polymers. Excellent flowability, solubility, and heat resistance indicate that the resins have the great potential to be used as high-temperature resistant resins such as ablation materials, resin matrix of composites.

REFERENCES

- Dirlikov, S. K. *High Perform. Polym.* **1990**, *2*, 67.
- Reghunadhan Nair, C. P. *Prog. Polym.* **2004**, *29*, 401.
- Bindu, R. L.; Reghunadhan Nair, C. P.; Niman, K. N. *Polym. Int.* **2001**, *50*, 651.
- Bindu, R. L.; Reghunadhan Nair, C. P.; Niman, K. N. *J. Macromol. Sci. Pure Appl. Chem.* **2003**, *40*, 357.
- Agag, T.; Takeichi, T. *Macromolecules* **2001**, *34*, 7257.
- Chernykh, A.; Agag, T.; Ishida, H. *Macromolecules* **2009**, *42*, 5121.
- Kimura, K.; Nishichi, A.; Yamashita, Y. *Polym. Adv. Technol.* **2004**, *15*, 313.
- Furutani, H.; Ida, J. *U.S. Pat.* 5,397,419 (1995).
- Osuna-Jr, J. A.; Dershem, S. M. *U.S. Pat.* 5,714,086 (1998).
- Liu, J. G.; Wang, L. F.; Yang, H. X.; Li, Y. F.; Yang, S. Y. *J. Polym. Sci. Part A: Polym. Chem.* **2004**, *42*, 1845.
- Mehdipour-Ataei, S.; Hani, H. *J. Appl. Polym. Sci.* **2004**, *91*, 22.

12. Tamami, B.; Yeganeh, H. *J. Polym. Sci. Part A: Polym. Chem.* **2001**, *39*, 3826.
13. Banerjee, S.; Madhra, M. K.; Salunke, A. K.; Jaiswal, D. K. *Polymer* **2003**, *44*, 613.
14. Hariharan, R.; Bhuvana, S.; Anitha-Malbi, M.; Sarojadevi, M. *J. Appl. Polym. Sci.* **2004**, *93*, 1846.
15. Yang, H. X.; Li, Y. F.; Liu, J. G.; Yang, S. Y.; Yin, D. X.; Zhou, L. C.; Lin, F. *J. Appl. Polym. Sci.* **2004**, *91*, 3981.
16. Mehdipour-Ataei, S.; Maleki-Moghaddam, R.; Nami, M. *Eur. Polym. J.* **2005**, *41*, 1024.
17. Mehdipour-Ataei, S.; Tareni, F. *J. Appl. Polym. Sci.* **2011**, *121*, 299.
18. Shibayama, Y.; Kawauchi, T.; Takeichi, T. *High Perform. Polym.* **2013**, *25*, 1.
19. Butuc, E.; Gherasim, G. M. *J. Polym. Sci. Polym. Chem. Ed.* **1984**, *22*, 503.
20. Wang, X. L.; Li, Y. F.; Zhang, S. J.; Yin, D. X.; Liu, J. G.; Yang, S. Y. *Hua. Xue. Tong. Bao (Chemistry)*. **2005**, *68*, 329.
21. Tamami, B.; Yeganeh, H.; Kohmareh, G. A. *Eur. Polym. J.* **2004**, *40*, 1651.
22. Jeong, H. J.; Kakimoto, M. A.; Imai, Y. *J. Polym. Sci. Part A: Polym. Chem.* **1994**, *32*, 1057.
23. Liaw, D. J.; Chen, P. S. *J. Polym. Sci. Part A: Polym. Chem.* **1996**, *34*, 885.
24. Kakimoto, M. A.; Negi, Y. S.; Imai, Y. *J. Polym. Sci. Part A: Polym. Chem.* **1986**, *24*, 1511.
25. Yang, C. P.; Oishi, Y.; Kakimoto, M. A.; Imai, Y. *J. Polym. Sci.* **1989**, *27*, 1353.
26. Kalliteis, J. K.; Kakali, F.; Gravalost, K. G. *Macromolecules* **1994**, *27*, 4509.
27. Huh, S. M.; Jin, J. I. *Macromolecules* **1997**, *30*, 3005.
28. Kakali, F.; Kallitsis, J.; Pakula, T. *Macromolecules* **1998**, *31*, 6190.
29. Yang, C. P.; Hsiao, S. H.; Chung, C. L. *Polym. Int.* **2005**, *54*, 716.
30. Miyagawa, T.; Fukushima, T.; Oyama, T.; Iijima, T.; Tomoi, M. *J. Polym. Sci. Part A: Polym. Chem.* **2003**, *41*, 861.
31. Yin, D. X.; Li, Y. F.; Shao, Y.; Zhao, X.; Yang, S. Y.; Fan L. *J. Fluorine Chem.* **2005**, *126*, 819.
32. Park, S. J.; Kim, H. S.; Jin, F. L. *J. Colloid Interface Sci.* **2005**, *282*, 238.
33. Seino, H.; Haba, O.; Ueda, M.; Mochizuki, A. *Polymer* **1999**, *40*, 551.
34. Chung, I. S.; Kim, S. Y. *Macromolecules* **2000**, *33*, 3190.
35. Shang, Y. M.; Fan, L.; Yang, S. Y.; Xie, X. F. *Eur. Polym. J.* **2006**, *42*, 981.
36. Douglas, W. E.; Overend, A. S. *Eur. Polym. J.* **1991**, *27*, 1279.
37. Dirlikov, S.; Feng, Y. *Polym. Prepr.* **1990**, *31*, 322.
38. Reghunadhan Nair, C. P.; Bindu, R. L.; Krishnan, K.; Ninan, K. N. *Eur. Polym. J.* **1999**, *35*, 235.
39. Liu, F.; Li, W. W.; Wei, L. H.; Zhao, T. *J. Appl. Polym. Sci.* **2006**, *102*, 3610.