

Synthesis and Characterization of Novel Highly Branched Block Copoly(urethane-imide)s Based on Pentaerythritol, Different Diisocyanate and Aromatic Dianhydride

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Received 29 April 2009; accepted 7 March 2010

DOI 10.1002/app.32398

Published online 13 May 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this work, we for the first time prepared a series of novel highly branched block copoly(urethane-imide)s (CoPUIs) successfully by the condensation polymerization of star-like prepolymers and dianhydrides, (including pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenonetetracarboxylic dianhydride, and 4,4'-oxydiphthalic anhydride) and the star-like prepolymers were synthesized from pentaerythritol (PAT) and toluene-2,4-diisocyanate (TDI) or isophorone diisocyanate. Our results revealed that it took about 40 min to complete the prepolymerization of PAT and TDI at 40°C. In addition, the imidization of the prepolymer and PMDA was successfully carried out at 120°C for 2 h. The X-ray diffractometer patterns exhibited that the resulting CoPUIs presented heterogenous structure with the *d*-spac-

ing around 0.40 nm. Differential scanning calorimeter curves showed that the T_g of these CoPUIs ranged from 214 to 229°C in N₂ atmosphere. Thermogravimetric analyzer curves indicated that these synthesized CoPUIs had obviously two steps of weight loss in N₂ atmosphere due to the used monomers which decomposed at 230–235°C and 602–644°C, respectively. The solubility testing results showed that the highly branched block CoPUIs had desirable solubility in several strong polar aprotic solvents and exhibited a strong resistance to dilute acid corrosion. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 99–104, 2010

Key words: copoly(urethane-imide)s (CoPUIs); condensation polymerization; polyimides; dianhydrides; synthesis

INTRODUCTION

In recent years, aromatic polyimides have attracted an increasing attention of many investigators due to their excellent heat resistance, superior mechanical properties, and electrical and durable performance. They are widely used in aerospace industry, electronic and electric industry, machinery industry, chemical industry, and national defense military industry.^{1–3} However, the major limitations of aromatic polyimides for the versatile applications are their high melting points and insolubility in organic solvents.⁴ To improve their poor fusibility and solubility without sacrificing other performances, various approaches have been used. One of the acceptable methods to improve the processability of polyimides is the chemical modification of their structure by blending or copolymerization with urea,⁵ amide,⁶ sulfone,⁷ ether,⁸ aromatic heterocyclic linkages,⁹ and

metal ions.¹⁰ By introducing some flexible groups such as urethane groups, it can endow the polyimides with remarkable abrasion resistance, elastomers, and plastics performances. Various attempts to incorporate urethane groups into polyimides have been made. The reaction of –NCO terminated PU prepolymer with acid dianhydride is one of the methods most often used to introduce urethane function into PI backbone.^{11–13} Most poly(urethane-imide) block copolymers obtained by this method are linear, resulting in poor solvent resistance to ordinary organic solvents.

However, to the best of our knowledge, few studies are reported on the block copoly(urethane-imide)s (CoPUIs) with highly branched structure. In this article, we for the first synthesized a series of novel highly branched block CoPUIs from Pentaerythritol (PAT), various diisocyanates and dianhydrides by two-step methods. Thus, obtained copolymers exhibits some unique properties, such as no chain entanglement, less or no crystallization, high solubility, low solution, and melt viscosity due to its highly branched molecular structure.¹⁴ We discussed the optimized parameters required for the prepolymerization and

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imidization based on PAT, toluene-2,4-diisocyanate (TDI), and pyromellitic dianhydride (PMDA). Furthermore, the chemical structure and some general physical properties of the obtained block CoPUIs with highly branched structure were studied by FTIR, $^1\text{H-NMR}$, X-ray diffractometer (XRD), Differential scanning calorimeter (DSC), thermogravimetric analyzer (TGA), and solubility testing.

EXPERIMENTAL PROCEDURE

Materials

PAT, PMDA, 3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA), and 4,4'-oxydiphthalic anhydride (ODPA) were obtained commercially from Sigma-Aldrich (USA), Sinopharm Chemical Reagent (Shanghai, China), Alfa Aesar (USA), and Shanghai Research Institute of synthetic resins (Shanghai, China), respectively, and dried under vacuum after purified. TDI and isophorone diisocyanate (IPDI) were purchased from Tianjing Yuanli Chemical (Tianjing, China) and Fluka (Germany). They were used as received. *N,N*-Dimethylformamide (DMF) was refluxed in the presence of calcium hydride, distilled under reduced pressure, and dehydrated with 4 Å molecular sieves before use.

Measurements

The $-\text{NCO}$ content in PU prepolymer was determined by di-*n*-butylamine back-titration method.¹⁵ Conversion of $-\text{NCO}$ was calculated by $100(1-C/C_0)$, where C_0 (wt %), the initial content of $-\text{NCO}$ in the reaction mixture, is 7.35%, and C (wt %) is the content of $-\text{NCO}$ at a certain time determined. FTIR spectra were performed on KBr pellets with a Perkin-Elmer (USA) Spectrum One FTIR spectrometer. $^1\text{H-NMR}$ spectrum was characterized on a Varian Residuey spectrometer at 600 MHz (USA) with tetramethylsilane as reference and $\text{DMSO-}d_6$ as solvent. XRD patterns were recorded on a Rigaku D-Max IIC (Japan) X-ray diffractometer with pattern from 2° to 60° (2θ) using Cu K_α radiation. DSC and TGA curves were obtained respectively by a TA Instruments (USA) Q-100 DSC and a Perkin-Elmer (USA) DETLASERIES TGA7 thermogravimetric analyzer with a same heating rate of $20^\circ\text{C}/\text{min}$ in N_2 atmosphere. Solubility of CoPUIs was measured in the relevant solvents at 2.5% (w/v) at both room temperature and an elevated temperature.

Synthesis of highly branched block CoPUIs

A diisocyanate (10 mmol) was dissolved in DMF (5 mL) in a thoroughly dried 100-mL four-neck flask in N_2 with continuous magnetic stirring. A solution of

PAT (2.5 mmol) in DMF (10 mL) was added dropwise into this solution at 40°C with a duration of 0.5 h. After the reaction was conducted for 10 min, a solution of dianhydride (5 mmol) in DMF (10 mL) was dropped into it in 0.5 h. It was maintained at 80°C for 1.5 h and 120°C for 2 h after further conducted for 0.5 h at 40°C , respectively. After removing most of the solvent under reduced pressure, the highly viscous solution was cast onto a glass plate and dried at 80°C until the residual solvent evaporated completely. (Except $\text{CoPUI}_{\text{TPP}}$, which was conducted as reported in the following article).

RESULTS AND DISCUSSION

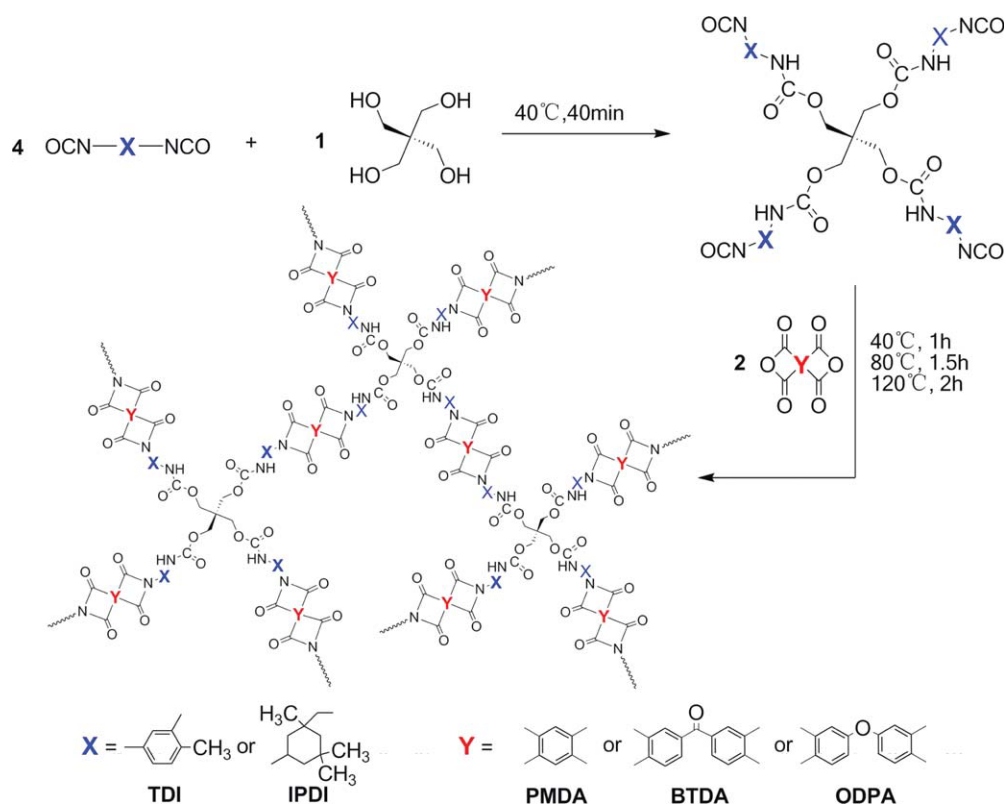
Synthesis of highly branched block CoPUIs

The synthesis of highly branched block CoPUIs includes two steps, as illustrated in Scheme 1. The first step is the synthesis of the $-\text{NCO}$ terminated star-like PU prepolymer with PAT and excess toluene-2,4-diisocyanate (2,4-TDI) or IPDI. The following step is the imidization of the prepolymer and PMDA, BTDA, or ODPA. The yields of these highly branched block CoPUIs were listed in Table I.

For $\text{CoPUI}_{\text{TPP}}$, the effect of reaction time on the conversion of $-\text{NCO}$ in the first step was shown in Figure 1. The conversion of $-\text{NCO}$ increased rapidly until the addition of PAT completed. During the course, PAT reacted with excess highly active TDI to form a star-like PU prepolymer with $-\text{NCO}$ terminated, and then the reaction became gently with around 50% conversion of $-\text{NCO}$. As a result, the optimal reaction time of prepolymerization at 40°C should be about 40 min.

Gelation would be observed immediately when the temperature was increased to 120°C in the second step of highly branched $\text{CoPUI}_{\text{TPP}}$. Therefore, a film was prepared at 80°C in an air oven for 24 h and 120°C for 2 h after the reaction solution concentrated.

The reaction of $-\text{NCO}$ of the prepolymer and PMDA in the second step of $\text{CoPUI}_{\text{TPP}}$ was investigated by FTIR spectra at 80 and 120°C , respectively. It can be found that the bands around 1785 ($\text{C}=\text{O}$ asymmetrical stretching), 1724 ($\text{C}=\text{O}$ symmetrical stretching), 1380 ($\text{C}-\text{N}$ stretching) and 725 cm^{-1} ($\text{C}=\text{O}$ bending) were the characteristic absorption bands of imide groups in highly branched $\text{CoPUI}_{\text{TPP}}$.¹⁶ In addition, the bands around 3350 and 1538 cm^{-1} were attributed to the association stretching and variable-angle stretching of the $\text{N}-\text{H}$ of urethane groups. However, the band at 2265 cm^{-1} of $\text{CoPUI}_{\text{TPP}}$ at 80°C was the characteristic absorption band of free $-\text{NCO}$, which indicated that the $-\text{NCO}$ of star-like PU prepolymer did not react with



Scheme 1 Synthesis of novel highly branched block CoPUIs. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

anhydride groups of PMDA completely at 80°C for 1.5 h. While such characteristic absorption band of —NCO of $\text{CoPUI}_{\text{TPP}}$ at 120°C disappeared, it confirmed that the imidization in the second step was completely carried out after 120°C for 2 h. In addition, it also demonstrated that the imidization process was a two-step reaction, including the formation of a sevenmembered ring intermediate from the reaction of isocyanate with anhydride at a lower temperature (80°C), and an imide ring structure with the release of CO_2 at a higher temperature (120°C).⁷

No gelations appeared when the highly branched $\text{CoPUI}_{\text{TPB}}$, $\text{CoPUI}_{\text{TPO}}$, $\text{CoPUI}_{\text{IPP}}$, $\text{CoPUI}_{\text{IPB}}$, and

$\text{CoPUI}_{\text{IPO}}$ were conducted at 120°C in the second step. It possibly ascribes to the better chain flexibility of BTDA residue and ODPA residue than the PMDA residue, and the same as IPDI residue and TDI residue.

The structure of the other highly branched block CoPUIs were characterized by FTIR spectra. It can be found that the characteristic absorption bands based on the urethane groups and imide groups can be observed. Furthermore, the FTIR spectra of $\text{CoPUI}_{\text{TPP}}$, $\text{CoPUI}_{\text{TPB}}$, and $\text{CoPUI}_{\text{TPO}}$ has weak absorption bands at 2960 and 1380 cm^{-1} belonging to the methyl groups in TDI residues. While the FTIR spectra of $\text{CoPUI}_{\text{IPP}}$, $\text{CoPUI}_{\text{IPB}}$, and $\text{CoPUI}_{\text{IPO}}$ presented

TABLE I
Yields and Thermal Properties of Novel Highly Branched Block CoPUIs

Sample	Diisocyanate-pentaerythritol-dianhydride	Yield (%)	T_g^a (°C)	$T_{d,1}^b$ (°C)	$T_{d,2}^b$ (°C)
$\text{CoPUI}_{\text{TPP}}$	TDI-PAT-PMDA	87.8	229	231	632
$\text{CoPUI}_{\text{IPP}}$	IPDI-PAT-PMDA	88.6	216	230	644
$\text{CoPUI}_{\text{TPB}}$	TDI-PAT-BTDA	89.2	—	234	610
$\text{CoPUI}_{\text{IPB}}$	IPDI-PAT-BTDA	88.9	—	232	616
$\text{CoPUI}_{\text{TPO}}$	TDI-PAT-ODPA	90.5	221	235	602
$\text{CoPUI}_{\text{IPO}}$	IPDI-PAT-ODPA	89.7	214	233	605

^a T_g measured by DSC at a heating rate of 20°C/min in N_2 atmosphere.

^b $T_{d,1}$ and $T_{d,2}$, the first and the second decomposition temperature measured by TGA at a heating rate of 20°C/min in N_2 atmosphere.

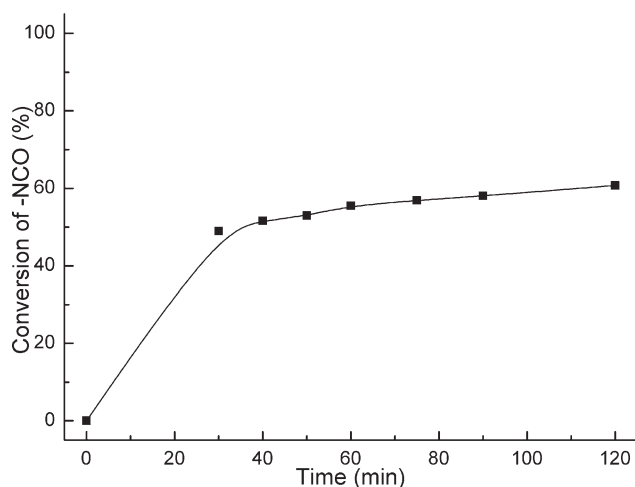


Figure 1 Effect of reaction time on conversion of $-NCO$ in prepolymerization of highly branched $CoPUI_{TPP}$.

strong absorption bands of methyl groups in the same range and methylene groups at 1460 cm^{-1} due to the IPDI residues.

The 1H -NMR spectrum of highly branched $CoPUI_{TPP}$ could not be characterized for its insolubility in $DMSO-d_6$. As a result, the soluble $CoPUI_{IPP}$ was characterized on a Varian Residue spectrometer at 600 MHz with tetramethylsilane as reference. The multisplit peaks ranging from 8.2 to 8.7 were assigned to protons of PMDA residues, while the multiple overlapped peaks in the range of 4.3–3.8 were attributed to protons of PAT residues, and the peaks in the range of 2.0–0.9 ascribed to protons of IPDI residues. The broad peaks at 7.0 and 5.5 corresponded to the protons of urethane groups and free hydroxyl groups in PAT residues, respectively. The multiple peaks ranging from 2.9 to 2.7 were assigned to protons of methylene bonded with urethane groups and methine bonded with imide groups in IPDI residues. The further structural verification, such as ^{13}C -NMR spectra, was not provided here to calculate the degree of branching values of these highly branched block $CoPUI$ s. Because it was difficult to verify the highly branched structure of the block $CoPUI$ s which was induced by the reaction of various diisocyanates and PAT via A_2+B_4 approach. In this work, the reaction degree of the hydroxyl groups of PAT and the $-NCO$ of IPDI in the first step was investigated by evaluating the integration of the peaks for free hydroxyl groups in PAT residues and methine in PMDA residues ($-NCO$ of PU prepolymers were supposed to react completely with anhydrides in the second step). As a result, it confirmed that about 70% of the hydroxyl groups of PAT reacted with the $-NCO$ of IPDI in the first step.

X-ray diffraction of highly branched block $CoPUI$ s

The crystallinity of the resulting highly branched block $CoPUI$ s was examined by a Rigaku D-Max III C X-ray diffractometer with pattern from 2° to 60° (2θ) using $Cu\ K_\alpha$ radiation. In general the diffraction patterns of $CoPUI_{TPP}$, $CoPUI_{IPP}$, $CoPUI_{TPO}$, and $CoPUI_{IPO}$ expressed a set of wider diffraction peaks with a single sharp peaks around 22° . It confirmed that the obtained four kinds of $CoPUI$ s mainly had amorphous aggregation structure with a small degree of crystallinity. The heterogenous morphology most likely relate to the highly branched structure and rigidity of aromatic units, whereas the strong chain-to-chain interactions, such as hydrogen bond, leads to a crystalline morphology. Moreover, according to XRD patterns, we could also find 2θ of the diffraction maximum, as listed in Table II, and the d -spacing value was calculated with Bragg's equation,¹⁷ which can be expressed as follows:

$$n \cdot \lambda = 2d \cdot \sin \theta, \quad n = 1, 2, \dots \quad (1)$$

where λ is the X-ray wavelength = 0.154 nm, θ is the Bragg angle ($^\circ$), and d is the d -spacing of the polymer molecules (nm). By calculation, the data of d -spacing value were listed in Table II.

The XRD patterns of the other two highly branched block $CoPUI$ s, $CoPUI_{TPB}$, and $CoPUI_{IPB}$, were not shown here. However, we can conclude that their XRD patterns were similar with the XRD patterns of the four highly branched block $CoPUI$ s mentioned above for their analogous monomers' structure and rigidity.

Thermal properties of highly branched block $CoPUI$ s

Thermal properties of highly branched block $CoPUI$ s were determined by DSC and TGA in N_2 atmosphere, and the measured results were summarized in Table I. The data of thermal behaviors showed that all the four highly branched block $CoPUI$ s displayed a glass transition temperatures (T_g) ranging from 214 to $229^\circ C$, which depended on the chemical structure of diisocyanates and aromatic dianhydrides used in the reaction. Highly branched $CoPUI_{TPP}$ and $CoPUI_{IPP}$ exhibited higher T_g than highly branched $CoPUI_{TPO}$ and $CoPUI_{IPO}$ because of

TABLE II
The Data of XRD Patterns of Highly Branched Block $CoPUI$ s

Samples	$CoPUI_{TPP}$	$CoPUI_{IPP}$	$CoPUI_{TPO}$	$CoPUI_{IPO}$
$2\theta_{max}$ ($^\circ$)	22.80	21.71	22.55	22.00
d (nm)	0.3896	0.4089	0.3938	0.4035

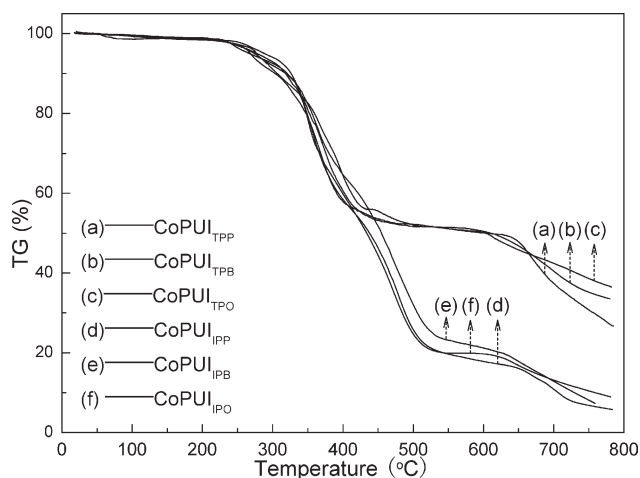


Figure 2 TGA curves of the highly branched block CoPUIs in N_2 atmosphere.

the effect of the rigidity of diisocyanates among aromatic TDI and aliphatic IPDI. While highly branched CoPUI_{TPP} and CoPUI_{TPO} exhibited higher T_g than highly branched CoPUI_{IPP} and CoPUI_{IPO} due to the difference of rigidity of aromatic dianhydrides among PMDA and ODA. According to XRD patterns, the resulting highly branched block CoPUIs might possess a slight degree of ordering because of the definitive crystalline patterns. However, there were no crystalline melting transitions detected by DSC curves. This probably indicated either that the melting point (T_m) values of the resulting polymers were higher than the measurement range used in the DSC experiments, or that the polymers are predominately amorphous with only a low degree of molecular ordering.

As shown in Figure 2, the six obtained highly branched block CoPUIs showed two steps of weight loss, respectively. The temperatures of the first weight loss ($T_{d,1}$), which were usually considered as the decomposition of urethane groups and PAT residues in the polymer backbones, were between 230 and 235°C. The temperatures of the second weight loss ($T_{d,2}$) ranging from 602 to 644°C corresponded to the decomposition of imide groups and aromatic residues in the polymer backbones. However, CoPUI_{IPP}, CoPUI_{IPB}, and CoPUI_{IPO} exhibited a weight loss immediately followed by the weight loss of urethane groups and PAT residues around 400°C due to the decomposition of aliphatic IPDI residues, while CoPUI_{TPP}, CoPUI_{TPB}, and CoPUI_{TPO} did not show obvious weight loss in this temperature range. Furthermore, the residual weight retentions of CoPUI_{TPP}, CoPUI_{TPB}, and CoPUI_{TPO} at 700°C in N_2 atmosphere ranging from 27 to 36% were higher than those of CoPUI_{IPP}, CoPUI_{IPB}, and CoPUI_{IPO}, which were in the range of 9–11%. It was most likely attributed to the chemical structure of diisocyanates and aromatic dianhydrides.

Solubility of highly branched block CoPUIs

The solubilities of these highly branched block CoPUIs were determined in some common organic solvents and inorganic acid solutions at 2.5% (w/v) at room temperature or an elevated temperature. The results showed that all of these highly branched block CoPUIs could be more or less soluble in DMSO and NMP at room temperature, and soluble in DMAc and DMF upon heating. These highly branched block CoPUIs, CoPUI_{TPO}, CoPUI_{IPB}, and CoPUI_{IPO} with flexible residues could be partially soluble in less polar aprotic solvent such as THF. The resulting highly branched block CoPUIs exhibited good solubility than the analogous polyimides,¹⁸ which were nearly insoluble in any organic solvents. It was most likely due to the flexible urethane group which decreases the interaction of polymer chains. Moreover, the good solubility of block CoPUIs also more or less related to the highly branched structure.¹⁹ However, none of them could dissolve in the little polar aprotic solvents, such as xylene, acetone, methanol, etc. Furthermore, all of them could resist the corrosion of dilute acid solution, such as 10 wt % hydrochloric acid and 10 wt % sulfuric acid. The good solubility of these block CoPUIs in several strong polar aprotic solvents was useful for the processing and molding.

CONCLUSIONS

In this study, novel highly branched block CoPUIs based on PAT and various diisocyanates and dianhydrides were successfully synthesized and characterized for the first time. The resulting highly branched block CoPUIs presented heterogenous morphology with the d -spacing values ranging from 0.3896 to 0.4089 nm. The obtained polymers exhibited T_g in the range of 214–229°C caused by the effect of chemical structure of diisocyanates and aromatic dianhydrides used in the polymerization. Our results revealed that these polymers exhibited obviously two steps weight loss with $T_{d,1}$ around 230°C and $T_{d,2}$ around 620°C in N_2 atmosphere, and that the highly branched block CoPUIs showed definite solubility in various polar aprotic solvents and a strong resistance to dilute acid corrosion.

This work was financially supported by the Natural Science Foundation of Hubei Province. Authors also acknowledge the Ministry-of-Education Key Laboratory for the Green Preparation and Application of Functional Materials for providing necessary facilities.

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