

SYNTHESIS AND CHARACTERIZATION OF GRAFT COPOLYMERS BASED ON POLY(*p*-PHENYLENE TEREPHTHALAMIDE) BACKBONE AND WELL-DEFINED POLYSTYRENE SIDE CHAINS*

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Abstract A novel dualfunctional monomer, 2-(2',2',6',6'-tetramethyl-piperidinyl-1'-oxy)methylbenzene-1,4-dioyl chloride hydrochloride, with two acid chloride groups for step-growth polymerization and a nitroxide group for the mediation of living radical polymerization was synthesized. It was first copolymerized with terephthaloyl chloride and *p*-phenylenediamine at a feed molar ratio of 1:3:4 in *N*-methyl-2-pyrrolidone containing 10 wt% calcium chloride at –10°C to yield a poly(*p*-phenylene terephthalamide) based macroinitiator, which initiated radical polymerization of styrene at 125°C to obtain a series of poly(*p*-phenylene terephthalamide)-*g*-polystyrenes. A combinatory analysis of proton nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, elementary analysis, thermogravimetry and gel permeation chromatography indicated that the macroinitiator induced the radical polymerization of styrene to proceed in a well-controlled way. The molecular weight of side-chains increased with an increase of monomer conversion, and the molecular weight distribution index remained lower than 1.5. The graft copolymers showed a remarkably improved solubility in *N*-methyl-2-pyrrolidone and much depressed crystallinity in bulk.

Keywords: Dualfunctional monomer; Graft copolymer; Nitroxide-mediated living free radical polymerization; Polycondensation; Wholly aromatic polyamide.

INTRODUCTION

Poly(*p*-phenylene terephthalamide) (PPTA) represents one of the most important wholly aromatic polyamides^[1–5]. Its fiber product, Kevlar, which is spun from liquid crystalline solutions, has excellent thermal stability, high chemical resistance, low flammability and exceptional tensile strength and modulus. The successful commercialization and the deep fundamental insights into the structure-property relationship of Kevlar fiber stimulated the intensive scientific and applied researches on stiff-chain polymers that have lasted for almost half a century. Nevertheless, PPTA is generally processed from rather harsh or environmentally damaging solvents because it tends to decompose during or before melting and does not dissolve in usual organic solvents.

To improve the processability of PPTA, either substituents or structural irregularities have been incorporated into its structure^[6–13]. PPTAs with a dense periphery of substituent (notably flexible alkyl chains) are known as hairy-rod polymers. Covalent connection of side-chain to backbone enhances the solubility of polymer in common organic solvents and causes melting point depression without loss of rigidity of the

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backbone, and melt or solution processability is thus achieved. On the other hand, flexible alkyl side-chains also improve the compatibility of rigid-chain polymers with other flexible polymers, which is of particular interest in molecular composites^[14]. Furthermore, like block copolymers, hairy-rod polymers tend to aggregate into nanoscale ordered structures in either bulk or solution. For example, hairy-rod polymers have been processed into ultrathin films as elements of construction for larger scale molecular devices^[15]. Finally, the introduction of substituents also makes it possible to endow the polyamide with different functions. Besides N-substituted polyamides and polyaramides substituted with pendant groups through phenyl rings, such kind structures have also been realized in other types of polymers, such as polyazomethines^[16], polypeptides^[17], poly(*p*-phenylene)s^[18], polyfluorenes^[19], polyesters^[20], polyimides^[21] and polyetherimides^[22].

Another synthetic strategy to modify PPTA is appending flexible polymer chains rather than relatively short alkyl groups to rigid backbone. Kim *et al.* substituted the amide groups of PPTA with Nylon 6 *via* anionic graft copolymerization of ϵ -caprolactam^[23]. Aharoni grafted Nylon 6 onto PPTA by employing amine or carboxy group functionalized monomers^[24]. Yamada^[25], Abdel-Bary^[26] and their coworkers attached vinyl polymers as side-chains to Kevlar 49 chopped fibers *via* plasma- or gamma radiation-graft polymerization of styrene (St), glycidyl methacrylate and acrylamide, respectively. Nevertheless, due to the uncontrolled nature of the graft polymerization employed, all the side-chains in these modified PPTA were not well-defined. Their molecular weights (MWs) could not be attained as desired and the molecular weight distribution indices (PDIs) were quite large. The development of living radical polymerization provides us with a useful tool to obtain graft polymers with well-defined side-chains. Recently, poly(pentafluorostyrene) brushes were grafted on the fluorinated polyimides by using a functionalized monomer, 2,4-diaminophenyl-2-bromoisobutyrate. With the similar method, poly(poly(ethylene glycol) methyl ether methacrylate)-*b*-poly(2,2,2-trifluoroethyl methacrylate) brushes were linked to the surface of poly(ether imide) membrane. The initiation site was introduced *via* chloromethylation^[27, 28]. Hawker and Hedrick prepared a diaminoterminated polystyrene (PSt) through nitroxide mediated living radical polymerization (NMP)^[29], which copolymerized with 1,2,4,5-benzenetetracarboxylic dianhydride and 2-bis(4'-aminophenyl)-2-phenyl-1,1,1-trifluoroethane to give a polyimide-*g*-polystyrene. These beautiful grafting-from methods require the introduction of initiating site suitable for living radical polymerization on the polymer backbone and have not been achieved in PPTA yet.

In this communication, we report an efficient method to prepare a novel graft copolymer consisting of a rigid PPTA main-chain and well-defined PSt side-chains *via* a combination of polycondensation and NMP. The initiating site of NMP was introduced onto PPTA backbone by employing a newly synthesized dualfunctional monomer, 2-(2',2',6',6'-tetramethyl-piperidiny-1'-oxy)methylbenzene-1,4-dioyl chloride hydrochloride. Proton nuclear magnetic resonance and Fourier transform infrared spectroscopy, elementary analysis, thermogravimetry and wide-angle X-ray diffractometry were employed to characterize the macroinitiator and graft copolymers, while gel permeation chromatography to characterize the PSt side-chains obtained from hydrolyzation. The grafted PPTAs showed quite different physical properties from the homopolymer.

EXPERIMENTAL

Materials

Dimethyl 2-methylbenzene-1,4-dioate was synthesized according to the method reported previously by us^[30]. *N*-methyl-2-pyrrolidone (analytical reagent; Beijing Chemical Co.) and pyridine (analytical reagent; Beijing Chemical Co.) were dried by stirring with KOH pellets and distilled out under reduced pressure. Calcium chloride (CaCl₂; analytical reagent; Beijing Chemical Co.) was dried at 180°C in oven for 6 h before use. Terephthaloyl chloride (TPC; analytical reagent; Beijing Chemical Co.) was used after recrystallization twice from petroleum ether. *p*-Phenylenediamine (PPD; analytical reagent; Beijing Chemical Co.) was sublimated twice under vacuum before use. Tetrahydrofuran (THF; HPLC grade; Fisher Chemical Co.) was directly used for the gel permeation chromatography (GPC). Cuprous bromide (CuBr; 98%; Aldrich) was purified by stirring overnight in acetic acid. After filtration, it was washed with ethanol and ether and then dried under vacuum. Styrene (analytical reagent; Beijing Chemical Co.) was purified by the passage through a basic alumina column

to remove the inhibitors and then vacuum distillation. *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA; 99%; Aldrich), 2,2,6,6-tetramethyl-piperidiny-1-oxyl (TEMPO; 99%; Acros) and all other reagents and solvents were used as received unless otherwise specified.

Monomer Synthesis

Dimethyl 2-(bromomethyl)benzene-1,4-dioate (**V**)

To a round-bottomed flask were added dimethyl 2-methylbenzene-1,4-dioate (6.25 g, 0.03 mol), *N*-bromosuccinimide (NBS, 5.87 g, 33.3 mmol), benzoyl peroxide (BPO, 0.1 g, 0.41 mmol) and tetrachloromethane (CCl₄, 60 mL), and the mixture was refluxing for 1.5 h. After cooling to room temperature, the mixture was filtered and the filtrate was evaporated to dryness under vacuum. The crude product was further purified by recrystallization from petroleum ether and afforded 7.75 g of white solids. Yield: 90%.

¹H-NMR (400 MHz, CDCl₃, δ): 3.95–3.97 (d, 6H; –CH₃), 4.96 (s, 2H; –CH₂–), 8.01, 8.02, 8.12 (m, 3H; Ar). FT-IR: 1718 (–C=O), 2956 cm^{–1} (–CH₃). MS: *m/z* = 286 (M⁺). C₁₁H₁₁BrO₄ (287.1): Calcd. C 46.02, H 3.86; Found C 45.94, H 3.74.

Dimethyl 2-(2',2',6',6'-tetramethyl-piperidiny-1'-oxy)methylbenzene-1,4-dioate (**IV**)

To a round-bottomed flask were added **V** (2.87 g, 0.01 mol), TEMPO (1.56 g, 0.01 mol), Cu (0.71 g, 0.01 mol), CuBr (1.45 g, 0.01 mol), PMDETA (1.79 g, 0.01 mol) and *N,N*-dimethylformamide (DMF, 30 mL). The mixture was stirred at 65–70°C under nitrogen atmosphere for 6 h and then poured into 200 mL of deionized water. The mixture was extracted with dichloromethane by 3 × 200 mL portions. The combined organic layers were dried over anhydrous sodium sulfate and evaporated to dryness under vacuum. The crude product was further purified by recrystallization from petroleum ether and afforded 1.56 g of white solids. Yield: 43%. Melting point: 81.1°C.

¹H-NMR (400 MHz, CDCl₃, δ): 1.18–1.19 (d, 12H; –CH₃), 1.33–1.62 (m, 6H; –CH₂–), 3.91–3.96 (d, 6H; –O–CH₃), 5.21 (s, 2H; –O–CH₂–), 7.94–7.98, 8.43 (m, 3H; Ar). FT-IR: 1721 (–C=O), 2849, 2924, 2871, 2961 cm^{–1} (–CH₂– & –CH₃). MS: *m/z* = 363 (M⁺). C₂₀H₂₉NO₅ (363.5): Calcd. C 66.09, H 8.04, N 3.85; Found C 66.10, H 8.01, N 3.76.

2-(2',2',6',6'-Tetramethyl-piperidiny-1'-oxy)methylbenzene-1,4-dioyl dichloride hydrochloride (**III**)

Into a round-bottomed flask were placed **IV** (9.3 g, 25.6 mmol), sodium hydroxide (NaOH, 20.7 g, 0.52 mol) and 200 mL of water and methanol mixed solvent (3:1, *V/V*). The mixture was stirred at 40°C for 2 days and acidified by dilute hydrochloric acid until pH = 2. The white precipitates were collected and recrystallized from acetic acid. The TEMPO-functionalized terephthalic acid was obtained as white solids (7.38 g, Yield: 86%).

¹H-NMR (400 MHz, DMSO-*d*₆, δ): 1.14–1.47 (m, 18H; –CH₂– & –CH₃), 5.14 (s, 2H; –O–CH₂–), 7.94 (s, 2H; –Ar), 8.30 (s, 1H; Ar), 13.34 (s, 2H, –COOH). FT-IR: 1713 (–C=O), 2500–3000, 3463 cm^{–1} (–OH).

Into a round-bottomed flask were placed the above obtained diacid (8.4 g, 25.0 mmol), 60 mL of thionyl chloride and 3 drops of DMF as a base. The mixture was stirred at 40°C until the suspended solids disappeared completely. Unreacted thionyl chloride was removed by distillation under vacuum and the residue was recrystallized twice from 1,2-dichloroethane. After drying under vacuum, 8.2 g of diacid chloride was obtained. Yield: 80%.

¹H-NMR (400 MHz, CDCl₃, δ): 1.37–1.80 (m, 18H; –CH₂– & –CH₃), 2.62 (m, 1H; –NH⁺), 6.09 (s, 2H; –O–CH₂–), 8.30–8.35 (m, 3H; Ar). FT-IR: 1769, 1782 (Cl–C=O), 1900–2700 (NH⁺), 2854, 2924, 2881, 2961 cm^{–1} (–CH₂– & –CH₃).

C₁₈H₂₄NCl₃O₃ (408.8): Calcd. C 52.89, H 5.92, N 3.43; Found C 52.82, H 6.11, N 3.43.

N,N'-bis(4-methoxyphenyl)-2-(2',2',6',6'-tetramethyl-piperidiny-1'-oxy)methylbenzene-1,4-diamide (**MI**)

Into a round-bottomed flask containing 4-methoxybenzenamine (1.17 g, 9.5 mmol), THF (20 mL) and a drop of DMF, a solution of **III** (1.86 g, 5 mmol) in 15 mL THF was added dropwise with rapid stirring at 0°C. After the diacid chloride solution was added, the reaction was allowed to continue at room temperature over night. After evaporation of solvent, the crude product was recrystallized from toluene and afforded 2.15 g of white solids.

Yield: 82%.

$^1\text{H-NMR}$ (400 MHz, D_2SO_4 , δ): 0.81–1.65 (m, 18H; $-\text{CH}_2-$ & $-\text{CH}_3$), 3.81 (s, 6H; $-\text{O}-\text{CH}_3$), 5.25 (s, 2H; $-\text{O}-\text{CH}_2-$), 6.65–8.15 (m, 11H; Ar). FT-IR: 1648 ($-\text{N}-\text{C}=\text{O}$), 2854, 2924, 2881, 2961 ($-\text{CH}_2-$ & $-\text{CH}_3$), 3290 cm^{-1} ($-\text{NH}-$).

$\text{C}_{32}\text{H}_{39}\text{N}_3\text{O}_5$ (545.7): Calcd. C 70.44, H 7.20, N 7.70; Found C 70.36, H 7.29, N 7.69.

Copolycondensation

Into a round-bottomed flask equipped with drying tube and nitrogen inlet and outlet, a mixture of finely ground and dried CaCl_2 (6.23 g), PPD (1.83 g, 16.9 mmol), pyridine (1.33 g) and *N*-methyl-2-pyrrolidone (50 mL) were introduced and stirred until the suspension mixture was converted into a clear solution. The resulting solution was cooled to -10°C . Subsequently, with continued cooling and vigorous stirring, a mixture of **III** (1.60 g, 4.0 mmol) and TPC (2.61 g, 12.9 mmol) was quickly added into the reaction system. Stirring was continued for 30 min and the temperature rose to about 30°C for 6 h. The reaction mixture was poured into 500 mL of methanol/water mixture (1:1, *V/V*), and the precipitated polymer was collected by filtration and washed thoroughly with hot distilled water and dried at 60°C for 48 h under vacuum to afford 4.69 g of macroinitiator (**II**) as yellow solids. Yield: 98%.

Inherent viscosity (η_{inh}) = 2.83 dL g^{-1} (96 wt% H_2SO_4 , $c = 0.5$ g dL^{-1} , 30°C).

$^1\text{H-NMR}$ (400 MHz, D_2SO_4 , δ): 0.81–1.95 (m, 18H; $-\text{CH}_2-$ & $-\text{CH}_3$), 5.24 (s, 2H; $-\text{O}-\text{CH}_2-$), 6.86–8.55 (m, Ar). FT-IR: 1651 ($\text{C}=\text{O}$), 2932 ($-\text{CH}_2-$), 2975 ($-\text{CH}_3$), 3314 cm^{-1} ($\text{CON}-\text{H}$). $[(\text{C}_{24}\text{H}_{29}\text{N}_3\text{O}_3)_{0.25}(\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2)_{0.75}]_n$ (277.2) $_n$: Calcd. C 70.62, H 4.97, N 11.39; Found C 70.25, H 5.53, N 11.00.

Nitroxide-mediated Radical Polymerization

The graft copolymers (**I-n**, *n* represents the number average degree of polymerization of side-chain) were obtained *via* NMP of St induced by the macroinitiator **II**. In order to monitor the growth of side chain easily, a model compound **M1** was employed together with **II** to initiate NMP of St. In a typical run, **II** (47.8 mg, 4.26×10^{-5} mol), **M1** (Chart 1, 5.8 mg, 1.06×10^{-5} mol), St (1.07 g, 1.03×10^{-2} mol) and *N*-methyl-2-pyrrolidone (containing 4 wt% CaCl_2) (16 g) were introduced into a glass reaction tube. After three freeze–pump–thaw cycles, the tube was sealed off under vacuum and put into a thermostatic oil bath at $(125 \pm 2)^\circ\text{C}$ for 8 h. The polymerization was stopped by cooling to room temperature and the tube was broken. The mixture was diluted with 10 mL of *N*-methyl-2-pyrrolidone and added into 200 mL of water/methanol (2:5, *V/V*) under rapid stirring. The precipitated polymers were collected by filtration. The operations of dissolution in *N*-methyl-2-pyrrolidone and precipitation in methanol were repeated three times to remove the unreacted monomer. After drying at 50°C under vacuum for 2 days, 0.21 g of white powders were obtained. Yield: 19.2%. The polymers thus obtained were the mixture of the target graft copolymer and St homopolymer (**hPSt**), which were derived from **II** and **M1**, respectively. They were separated by extraction with cyclohexane.

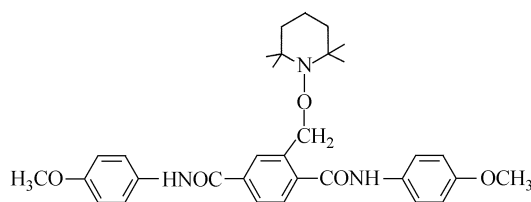


Chart 1 Chemical structure of model compound **M1**

The NMP of St initiated by the model compound **M1** was carried out in a similar way.

Cleavage of Side-chains

In a typical reaction, 0.1 g of **I-112** was added into a mixture containing 20 mL of 5 wt% KOH methanol solution and 30 mL of THF. The reaction mixture was refluxed for 1 week. When the solution was cooled to room temperature, concentrated hydrochloric acid was added to adjust the pH value to 7. The mixture was

extracted with chloroform and washed with water. The solvent was evaporated under reduced pressure. The remaining solids were dried under vacuum at 60°C and afforded 0.09 g of white powders.

Measurements

¹H-NMR (400 MHz) measurements were run on a Bruker ARX 400 spectrometer at ambient temperature. Mass spectra were obtained on a Micromass Finnigan MAT ZAB-HS mass spectrometer. Infrared (IR) spectra were recorded on a Bio-Rad FTS-65A Fourier transform infrared spectroscope. Inherent viscosities were determined using an Ubbelohde viscometer at a concentration of 0.5 dL g⁻¹ in 96 wt% H₂SO₄ at (30 ± 0.2)°C. Thermogravimetric analyses (TGA) were carried out on a TA Q600 SDT instrument under nitrogen atmosphere at a heating rate of 20 K min⁻¹ up to 800°C. Crystallographic data of **IV** were collected at room temperature on a Rigaku AFC6S diffractometer with graphite-monochromatic Mo K_α (λ = 0.071073 nm) radiation by using the ω-2θ scan method. A PSI absorption correction was applied using the teXsan program. The structures were solved with direct methods and refined on *F*² with full-matrix least-squares methods using SHELXS-97^[31] and SHELXL-97^[32] programs, respectively. All nonhydrogen atoms were refined anisotropically. Hydrogen atoms attached to carbons were added by calculated positions. One-dimensional wide-angle X-ray diffraction (1D WAXD) powder experiments were performed on a Philips X'Pert Pro diffractometer with a 3 kW ceramic tube as the X-ray source (Cu K_α) and an X'celerator detector. The sample stage was set horizontally. The reflection peak positions were calibrated against silicon powder (2θ > 15°) and silver behenate (2θ < 10°). Background scattering was recorded and subtracted from the sample patterns. The number-average molecular weight (*M*_n), weight-average molecular weight (*M*_w) and polydispersity index (PDI, *M*_w/*M*_n) of the polystyrene side-chains were estimated by gel permeation chromatography (GPC) equipped with a Waters 515 HPLC pump and a Waters 2410 refractive-index detector. Three Waters Styragel columns with a 10 μm bead size were connected in series. Their effective molecular weight ranges were 100–10000 for Styragel HT2, 500–30000 for Styragel HT3, and 5000–600000 for Styragel HT4, respectively. The pore sizes were 50, 100, and 1000 nm for Styragels HT2, HT3 and HT4, separately. THF was used as the eluent at a flow rate of 1.0 mL min⁻¹ at 35°C. Calibration was made against a series of mono-dispersed polystyrene standards.

RESULTS AND DISCUSSION

Scheme 1 depicts the synthetic route of the macroinitiator (**II**) and the target graft copolymers (**I-n**). The synthesis started with the bromination of dimethyl 2-methylbenzene-1,4-dioate by NBS. The resultant benzyl bromide coupled with TEMPO under the catalysis of Cu/CuBr/PMDETA complex to yield the key intermediate **IV**. After hydrolyzation under alkaline condition and chlorination by thionyl chloride, **IV** was converted to the dualfunctional monomer **III**. This compound copolymerized with commercially available TPC and PPD at a feed molar ratio of 1:3:4 in *N*-methyl-2-pyrrolidone containing 10 wt% CaCl₂ at -10°C to produce a PPTA based macroinitiator **II** with an inherent viscosity (η_{inh}) of 2.83 dL g⁻¹ measured in concentrated sulfuric acid. Five poly(*p*-phenylene terephthalamide)-*g*-polystyrenes (**I-n**) were obtained through the NMP of St induced by **II** at 125°C (Table 1).

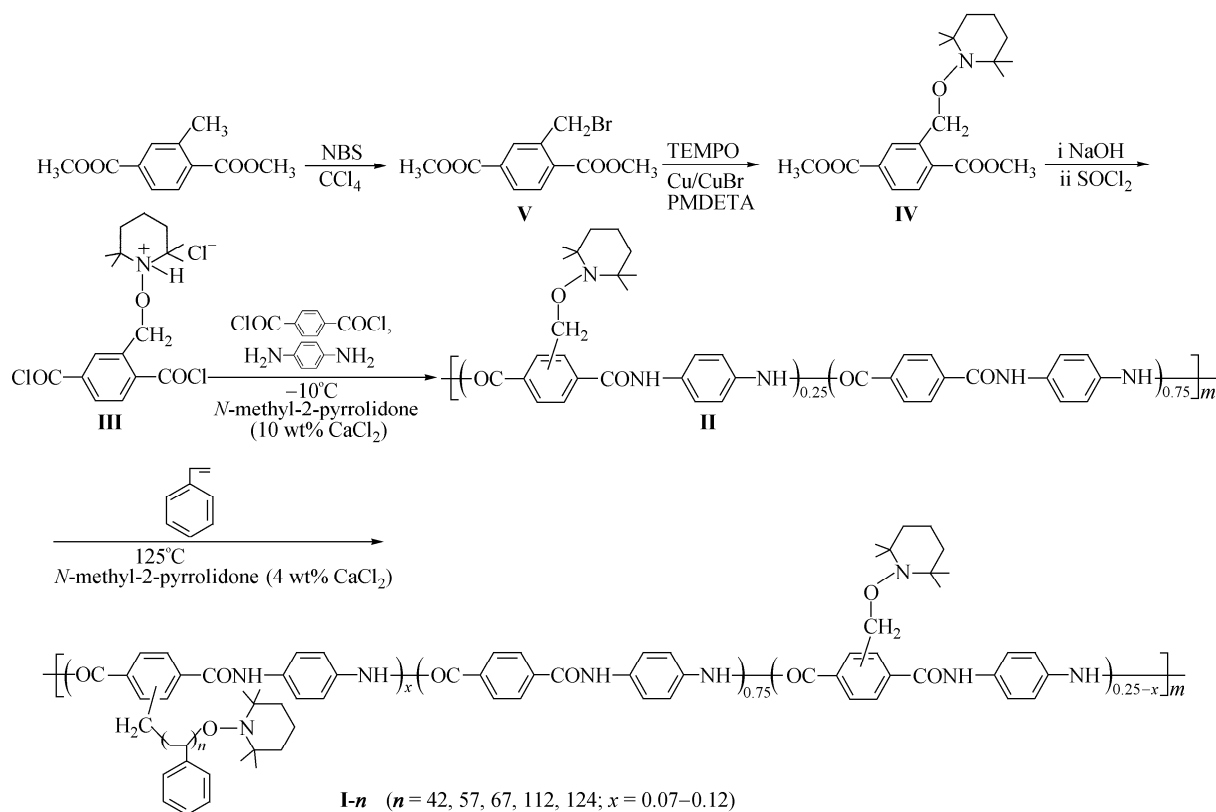
Table 1. Simultaneous nitroxide-mediated radical polymerization of St induced by macroinitiator **II** and **M1**, respectively

Sample ID	Conv. (%) ^a	hPSt ^b		scPSt ^c		Grafting yield (%) ^d	<i>x</i> (%) ^e	Char yield (%) ^f
		<i>M</i> _n	PDI	<i>M</i> _n	PDI			
PPTA								47.0
II								39.2
I-42	2.9	6600	1.38	4400	1.45	50.4	28	32.9
I-57	8.9	7700	1.39	5900	1.48	65.2	36	28.8
I-67	14.2	8300	1.38	7000	1.40	75.4	49	20.7
I-112	19.2	8400	1.43	11600	1.42	80.4	40	17.1
I-124	23.7	8900	1.39	12900	1.37	84.7	48	11.7

^a Monomer conversion; ^b St homopolymer initiated by **M1**; ^c PSt side-chain of copolymer obtained by hydrolysis;

^d Grafting yield based on elementary analysis; ^e Initiation efficiency evaluated from the grafting yield and *M*_n of scPSt;

^f Residual yield at 800°C obtained from TGA experiments



Scheme 1 Synthetic route of poly(*p*-phenylene terephthalamide)-*g*-polystyrene

The subscript n denotes the number average polymerization degree of side chain, while the subscripts x , $0.25 - x$, and 0.75 denote the molar fraction of each repeating unit.

The structures of all the intermediates and the dualfunctional monomer were confirmed by ^1H -NMR, mass spectroscopy and elementary analysis. The molecule **IV** readily formed sizable single crystal from petroleum ether solution. Figure 1 shows its X-ray single crystal structure. It was evident that **IV** crystallized in a monoclinic fashion and four molecules stacked in a unit cell. The unit cell parameters calculated were $a = 1.6103(3)$ nm, $b = 0.80269(16)$ nm, and $c = 1.6732(3)$ nm with $\beta = 112.18(3)^\circ$.

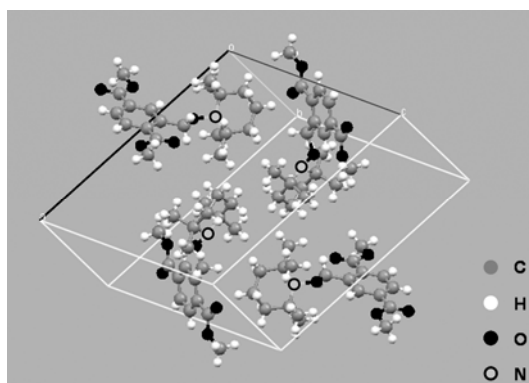


Fig. 1 X-ray single crystal structure of the key intermediate **IV**

In order to shed light on the feasibility that the macroinitiator **II** effectively induces NMP of St and find a spectator to watch the process of graft copolymerization, a model compound **M1** (Chart 1) was prepared and used to initiate the radical polymerization of St. Figure 2 displays the variations of M_n and PDI of PSt with monomer conversion. The fact that M_n increased linearly with monomer conversion and PDI kept less than 1.32 suggested a well-controlled polymerization process.

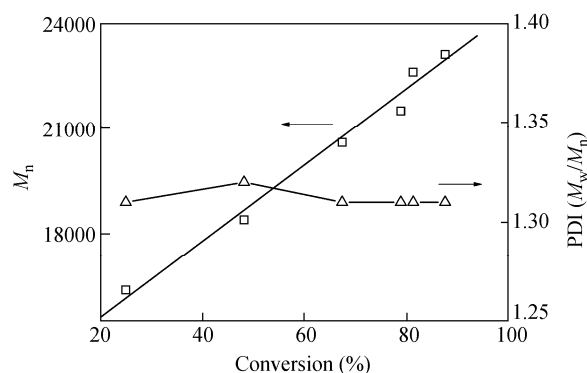


Fig. 2 Dependence of molecular weight and molecular weight distribution on the conversion of styrene
Reaction condition: [St] = 4.0 mol L⁻¹; Temperature, 125°C; Solvent, *N*-methyl-2-pyrrolidone containing 4 wt% CaCl₂

Table 1 summarizes the results of simultaneous graft copolymerization and homopolymerization of St induced by **II** and **M1**, respectively, in the same reactor. Thanks to the distinct solubility of graft copolymer and St homopolymer (**hPSt**) in cyclohexane, the latter was easily separated from the former by extraction. The graft yields (content of side-chains) of copolymers were estimated based on the nitrogen content obtained from elementary analysis. To characterize the macromolecular parameters of side-chains (**scPSt**), the copolymers were first hydrolyzed under alkaline condition and then subjected to GPC measurements. The graft yield increased with monomer conversion. Moreover, the M_n s of both **scPSt** and **hPSt** increased also with monomer conversion and had relatively narrow distributions (PDI < 1.5), an indicative of a well-mediated polymerization process. The M_n s of **scPSt** and **hPSt** were close to each other, implying the probability of using **M1** and the **hPSt** derived from it as a spectator to monitor the process of graft copolymerization. It was notable that the M_n of **scPSt** was lower than that of **hPSt** when the monomer conversion was less or equal to 14.2%. It might be attributed to the lower mobility of macroinitiator compared to **M1**. However, the tendency was completely opposite when the monomer conversion was higher than 14.2%, this might be caused by slight intramolecular crosslinking.

Pure PPTA obtained under a completely identical condition with **II** showed an η_{inh} value of 5.78 dL g⁻¹ in concentrated sulfuric acid, much larger than that of **II**. In fact, the higher the content of TEMPO containing unit, the lower the η_{inh} value of the macroinitiator obtained (data not shown). It suggested that the bulky substituent depressed the reactivity of diacid chloride toward diamine.

The introduction of bulky substituent on PPTA backbone improved its solubility remarkably. PPTA could not be dissolved in *N*-methyl-2-pyrrolidone containing 4 wt% CaCl₂. However, the macroinitiator **II** dissolved in the solvent at a concentration of 3.5 mg/mL, although a little light scattering was discernible when laser light (635 nm) passed through the solution, which suggested the presence of some aggregates. All the copolymers gave completely clear solutions in the same solvent and at the same concentration.

The initiation efficiency of **II** was evaluated from the graft yield and M_n of side-chain. As shown in Table 1, the initiation efficiency of **II** was generally quite low and increased slightly with graft yield. This might be ascribed to the aggregation of **II** in the graft polymerization system and the improved solubility of graft copolymers.

Figure 3 exhibits the ¹H-NMR spectra of **M1** and **II**. The assignments of protons were made on the spectra

and agreed well with the expected structures. We had tried to characterize the structure of copolymers by $^1\text{H-NMR}$. Unfortunately, all the efforts failed due to the lack of suitable deuterated solvent that dissolves both main- and side-chain. So we turned to FT-IR for characterization of the graft copolymers.

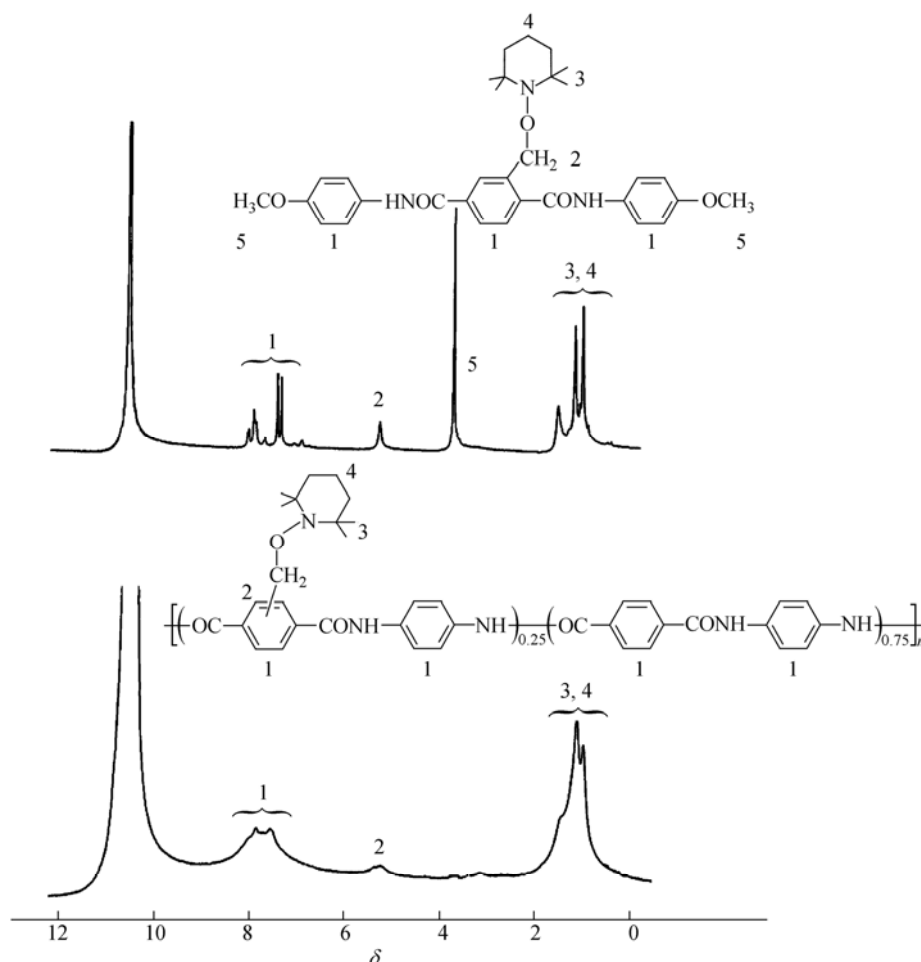


Fig. 3 $^1\text{H-NMR}$ spectra of model compound **M1** (upper part) and macroinitiator **II** (lower part) (in D_2SO_4)

The FT-IR spectra of PPTA, **II** and **I-n** are shown in Fig. 4. The pure PPTA displayed a broad absorption peak centered at 3300 cm^{-1} due to hydrogen-bonded NH groups and three peaks attributable to amide I, II, and III bands at 1654 cm^{-1} ($\nu_{\text{C=O}}$), 1516 cm^{-1} (coupling between $\nu_{\text{C-N}}$ and δ_{CH}), and 1310 cm^{-1} (coupling between $\nu_{\text{C-N}}$ and δ_{CH}), respectively. The macroinitiator **II** exhibited not only absorptions of hydrogen-bonded NH groups and amide I, II, and III bands of PPTA main chain but also new absorptions at $2860\text{--}2967\text{ cm}^{-1}$, indicating the presence of CH_3 and CH_2 groups of TEMPO. A broad absorption peak centered at 3300 cm^{-1} and peaks of amide I and II were present in the spectra of **I-n**. Moreover, they also presented new absorptions due to aromatic and methylene groups in the side-chains at $690\text{--}710\text{ cm}^{-1}$ (δ_{CH}), $1680\text{--}2000\text{ cm}^{-1}$ (octave of δ_{CH}), $3000\text{--}3120\text{ cm}^{-1}$ (ν_{CH}) and $2860\text{--}2967\text{ cm}^{-1}$ ($\nu^{\text{as}}_{\text{CH}}$, $\nu^{\text{s}}_{\text{CH}}$, and ν_{CH}), respectively, the intensities of which increased with increasing the length of side-chain.

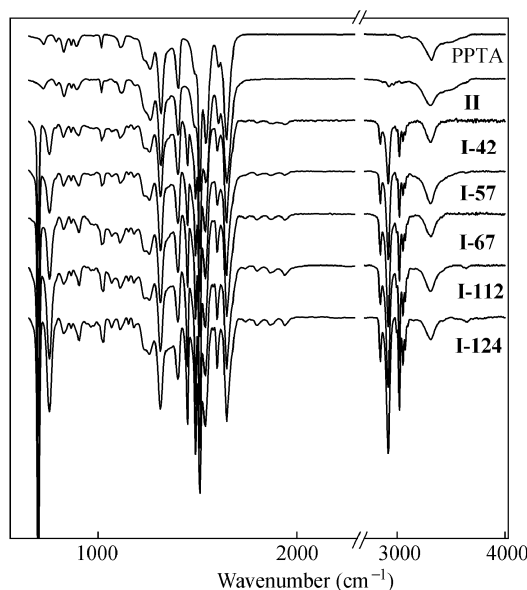


Fig. 4 IR spectra of PPTA, macroinitiator **II** and graft copolymers **I-*n***

Figure 5 represents TGA thermograms of pure PPTA, **II**, and various graft copolymers under inert atmosphere. Pure PPTA was quite thermal stable and had a 5% weight loss temperature of 550°C and a single step thermal decomposition. In a sharp contrast to PPTA, **II** and **I-*n*** began to decompose at temperatures much lower than that of PPTA and displayed three stages. The first at about 120°C was attributed to the leakage of TEMPO, while the second to the decomposition of PSt side-chains. The last one, which took place at about 450°C, was coincided with the decomposition of polyaramid main-chain. The longer the PSt side chains, the lower the char yield.

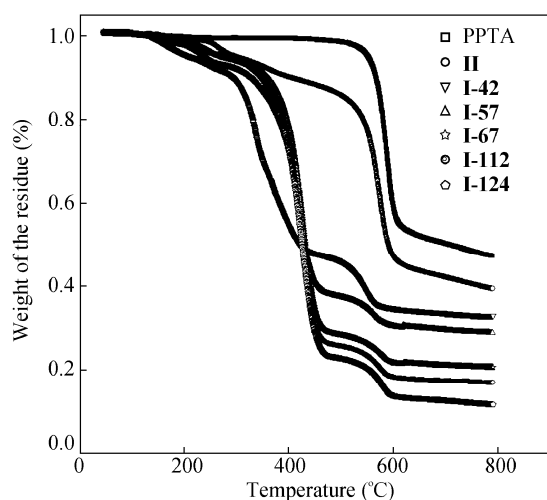


Fig. 5 TGA curves of PPTA, macroinitiator **II** and graft copolymers **I-*n***

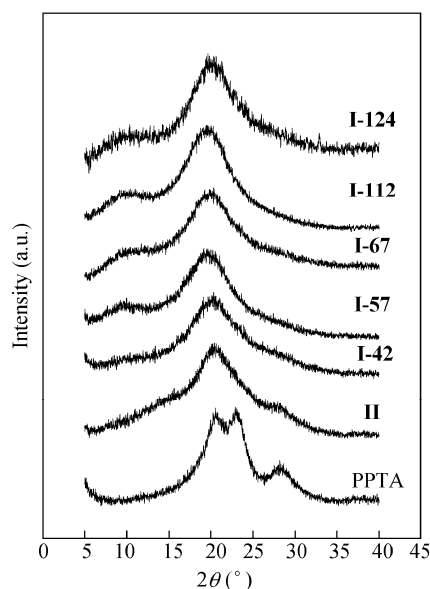


Fig. 6 X-ray powder diffractograms of PPTA, macroinitiator **II**, and graft copolymers **I-*n*** recorded at room temperature

The 1D WAXD patterns of PPTA, **II**, and **I-n** recorded at room temperature are shown in Fig. 6. PPTA presented three sharp peaks at $2\theta = 20.9^\circ$ ($d = 0.42$ nm), 23.6° ($d = 0.39$ nm), and 28.5° ($d = 0.31$ nm), which were indexed as the (110), (200) and (004) diffractions, respectively^[33, 34]. The macroinitiator **II** displayed a diffused halo and two weak shoulders located at $2\theta = 20.5^\circ$ ($d = 0.43$ nm), 15.6° ($d = 0.57$ nm), and 28.0° ($d = 0.32$ nm), respectively, indicating the presence of bulk substituents significantly disrupted the ordered packing of PPTA. In the case of the graft copolymers, only diffractions of PSt were observed, suggesting a completely amorphous packing of macromolecules.

CONCLUSIONS

A PPTA based macroinitiator **II** was obtained *via* the copolycondensation of TPC, PPD and a newly designed TEMPO-functionalized diacid chloride **III**. It induced and effectively mediated NMP of St to yield five novel graft copolymers consisting of a stiffened PPTA backbone and well-defined PSt side-chains. The graft copolymers showed a remarkably improved solubility in *N*-methyl-2-pyrrolidone and much depressed crystallinity in bulk compared to PPTA. They displayed three-step thermal decompositions under inert atmosphere, which were attributed to the leaving of TEMPO, degradation of PSt and PPTA, respectively. This character might find application in the preparation of high performance foams with ordered cavities by a combination of self-assembling of copolymer and sequential thermal degradation.

The presence of bulky TEMPO-substituent on the molecule **III** depressed its reactivity toward amine. Thereafter, the molecular weights of the macroinitiators derived from **III** directly as in this study decreased as the content of **III** was increased. In order to get high molecular weight macroinitiator, optimizations of reaction condition and synthetic route are necessary and are currently under way.

REFERENCES

- 1 Bair, T.I. and Morgan, P.W., 1972, U.S. Pat., 3,673,143
- 2 Bair, T.I. and Morgan, P.W., 1974, U.S. Pat., 3,817,941
- 3 Penn, L. and Larsen, F., J. Appl. Polym. Sci., 1979, 23: 59
- 4 Yang, H.H., "Aromatic high-strength fibers", 1st ed., John Wiley & Sons, New York, 1989, p.128; 227
- 5 Yang, H.H., "Kevlar aramid fibers", 1st ed., John Wiley & Sons, Chichester, New York, 1993, p.25
- 6 Takayanagi, M. and Katayose, T., J. Polym. Sci. Part A: Polym. Chem., 1981, 19: 1133
- 7 Shi, H.F., Zhao, Y., Zhang, X.Q., Zhou, Y., Xu, Y.Z., Zhou, S.R., Wang, D.J., Han, C.C. and Xu, D.F., Polymer, 2004, 45: 6299
- 8 Müller, W.T. and Ringsdorf, H., Macromolecules, 1990, 23: 2825
- 9 Meyer, W.R., Gentile, F.T. and Suter, U.W., Macromolecules, 1991, 24: 642
- 10 Gaudiana, R.A., Minns, R.A., Rogers, H.G., Sinta, R., Taylor, L.D., Kalganarama, P. and McGrown, C., J. Polym. Sci. Polym. Chem. Ed., 1987, 25: 1249
- 11 Calderón, V., García, F.C., de la Peña, J.L., Maya, E.M. and García, J.M., J. Polym. Sci. Part A: Polym. Chem., 2006, 44: 2270
- 12 García, J.M., de la Campa, J.G., Schwarz, G. and de Abajo, J., Macromol. Chem. Phys., 2001, 202: 1298
- 13 García, J.M., García, F., Sanz, R., de la Campa, J.G., Lozano, A.E. and de Abajo, J., J. Polym. Sci. Part A: Polym. Chem., 2001, 39: 1825
- 14 Lin, J.S., Eur. Polym. J., 2002, 38: 79
- 15 Martin, G., Bradley, D.D.C. and Whitehead, K.S., Journal of the Korean Physical Society, 2000, 36: 331
- 16 Park, S.B., Kim, H., Zin, W.C. and Jung, J.C., Macromolecules, 1993, 26: 1627
- 17 Schmidt, A., Lehmann, S., Georgelin, M., Katana, G., Mathauer, K., Kremer, F., Schmidt-Rohr, K., Boeffel, C., Wegner, G. and Knoll, W., Macromolecules, 1995, 28: 5487

- 18 Vanhee, S., Rulkens, R., Lehmann, U., Rosenauer, C., Schulze, M., Köhler, W. and Wegner, G., *Macromolecules*, 1996, 29: 5136
- 19 Lieser, G., Oda, M., Miteva, T., Meisel, A., Nothofer, H.G. and Scherf, U., *Macromolecules*, 2000, 33: 4490
- 20 Wang, D.H., Cheng, S.Z.D. and Harris, F.W., *Polymer*, 2008, 49: 3020
- 21 Shen, Z.H., Jing, A.J., Jin, S., Wang, H.B., Harris, F.W. and Cheng, S.Z.D., *Chinese J. Polym. Sci.*, 2005, 23(2): 171
- 22 Wang, D.H., Shen, Z.H., Cheng, S.Z.D. and Harris, F.W., *Polymer*, 2007, 48: 2572
- 23 Kim, E.Y., An, S.K. and Kim, H.D., *J. Appl. Polym. Sci.*, 1997, 65: 99
- 24 Aharoni, S.M., *Polym. Bull.*, 1993, 30: 149
- 25 Yamada, K., Haraguchi, T. and Kajiyama, T., *J. Appl. Polym. Sci.*, 1996, 60: 1847
- 26 Abdel-Bary, E.M., El-Nesr, E.M. and Helaly, F.M., *Polym. Adv. Technol.*, 1997, 8: 140
- 27 Fu, G.D., Kang, E.T. and Neoh, K.G., *Macromolecules*, 2005, 38: 7593
- 28 Cheng, Z.P., Zhu, X.L., Kang, E.T. and Neoh, K.G., *Macromolecules*, 2006, 39: 1660
- 29 Hawker, C.J. and Hedric, J.L., *Macromolecules*, 1995, 28: 2993
- 30 Liu, Y.X., Zhang, D., Wan, X.H. and Zhou, Q.F., *Chinese J. Polym. Sci.*, 1998, 16(3): 283
- 31 Sheldrick, G.M., SHELXS97, Program for solution of crystal structures, University of Göttingen, Göttingen, Germany, 1997
- 32 Sheldrick, G.M., SHELXL97, Program for the refinement of crystal structure, University of Göttingen, Göttingen, Germany, 1997
- 33 Northolt, M.G., *Eur. Polym. J.*, 1974, 10: 799
- 34 Northolt, M.G. and van Aartsen, J.J., *J. Polym. Sci. B*, 1973, 11: 333