NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2014, 5 (6), P. 829–835

NEW ROUTE TO POLY (2,6-DIIMIDAAZO(4,5-b: 4’,5’-e) PYRIDINELENE-1,4(2,5-DIHYDROXY)-PHENYLENE) (PIPD) AND HIGH MODULUS FIBER ON IT BASIS

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PACS 81.07.Lb

A novel entry toward poly(2,6-diimidazo(4,5-b: 4’,5’-e)pyridinylene-1,4(2,5-dihydroxy)-phenylene) (PIPD) has been elaborated. A strategy based on a new route to monomers: a sequential nitration of 2,6-diaminopyridine with KNO_3/H_2SO_4 gives 2,6- diamino- 3,5-dinitro pyridine (DNDAP) in moderate yield and its hydrogenation with Raney nickel as catalyst leads to 2,3,5,6-tetraaminopyridine (TAP) in high yield. The second monomer 2,5-dihydroxyterephthalate (DHTA) was synthesized in high yield as product of sulfur-mediated aromatization of dimethyl succinoyl succinate with subsequent base hydrolysis. PIPD was synthesized by step-by-step heating in polyphosphoric acid with molecular weights of 19 – 25 kilodaltons. The macromolecule of PIPD can be seen as lap-join chain form nano-sized rigid fragment. The as-polymerized liquid crystalline PIPD solution was used for fiber spinning. The tensile strength of PIPD fibers were 1.28 – 1.99 GPa and depended on the molecular weight of the polymer used for spinning.

Keywords: Nano-sized rigid polymer, synthesis, fiber spinning, mechanical properties, liquid crystallinity.

Received: 13 October 2014
Revised: 5 November 2014

1. Introduction

The development of polymer composites over the last 50 years has seen the emergence of new materials that are lightweight and have exceptional mechanical properties. The composite properties depend on filler fiber properties. Traditional inorganic fiber (glass, metal etc) composites deliver exceptional stiffness and stress but can often have a limited extensibility and poor damage tolerance, especially at low operating temperatures. Unlike carbon and inorganic fibers, rigid-rod polymeric fibers do not show catastrophic failure under compressive stress. That fact stimulated researchers to create stiffer rigid-rod-like polymeric materials. The best result was been obtained with synthesis of poly (p-phenylene benzobisoxazole) (PBO) [1]. PBO has very impressive tensile properties but its performance under compression is disappointing [2]. The traditional way to solve this problem in polymer chemistry is cross-linking macromolecules in the fiber by introducing double bonds into the macromolecule or Υ-irradiation [2]. An alternative route to increase the lateral strength of the PBO fiber is introducing intermolecular hydrogen bonds [3]. This choice was realized by the synthesis of poly(2,6-diimidazo(4,5-b: 4’,5’-e)pyridinylene-1,4(2,5-dihydroxy)-phenylene) (PIPD) [4]. This polymer forms in fiber intermolecular bonds in two dimensions and has the highest compressive strength (1 – 1.7 GPa) of any polymeric fiber to date [5]. However, the synthetic pathway to this polymer is laborious and expensive in preparation and purification. The aim of present work is to optimize a procedure for PIPD synthesis with a view to enhancing of monomer yield, improve the polymerization to increase the polymer molecular mass, spin a fiber directly from the polymerization solution without polymer precipitation or redissolution by dry-jet wet spinning method, and investigate the performance of the obtained nano- and macro-sized fibers.

2. Materials and Methods

All used reagents are commercial products were purchased from National medicine Co. Ltd., China, and were used without additional purification. Prior to use, al solvents were distilled. Hydrogen was purified by passing though columns with a nickel/chromium catalyst and molecular sieves.

2.1. Nitration 2,6-diaminopyridine

7 g of KNO_3 was mixed with 25 ml of conc. sulfuric acid, and to this was added 3 g of 2,6-diaminopyridine. The mixture was stirred at 80 °C for 2 h and then at120 °C for 1 h. The reaction mixture was then poured into 500 ml of water and cooled to 5 °C. The solution was neutralized by 20% NaOH, and precipitated 2,6- diamino- 3,5-dinitro pyridine (DNDAP) was collected after 24 h at 5 °C as yellow powder. DNDAP was recrystallized from water-DMSO (7:1 v/v). Yield 4.2 g (76.7). Purity by HPLC 95.8% IR, cm^{-1}: 3473/3359, 1621, 1554,1508, 1371, 1322. ^1H NMR, (DMSO-d6), δ, ppm : 8.28; 8.44 (2), 9.00 (4). 13C NMR, (DMSO-d6), δ, ppm: 155.21 (ortho), 120.66 (meta), 136.03 (para).

2.2. 2,3,5,6-tetraaminopyridine (TAP)

In a 200 ml autoclave, 10 g of DNDAP, 50 ml of water and 10 ml of 85% phosphoric acid with 1 g of Raney nickel were slurried; the air was displaced with nitrogen and 1.3 kPa of hydrogen was supplied; the hydrogen pressure was increased to 0.1 MPa and then to 0.5 MPa; the temperature was kept at RT and stirring was continued with the supply of hydrogen at 0.5 MPa until the hydrogen consumption ceased (10 h). Without the introduction of air, 20 ml of 37% hydrochloric acid was added, and mixture was extruded through the filter from autoclave; to filtrate were added 50 ml of THF and and 25 ml of conc. HCl. The precipitate was filtered off and dried, yielding 12.9 g $TAP{\cdot}HCl{\cdot}H_2O$ (93%) with HPLC purity of 99.7%. IR, cm^{-1}: 3500 – 2500, 1654, 1610, 1320. ^1H NMR, (D_2O), δ, ppm : 7.70 (1), 8 – 9 (NH_2). ^{13}C NMR, (D_2O), δ, ppm: 147.56 (ortho), 102.77 (meta), 131.22 (para).

2.3. Dimethyl 2,5-dihydroxyterephthalate

In a 2 l four-necked flask with stirrer, reflux head, dropping funnel and thermometer were placed 500 ml of water and 240 ml of glacial acetic acid and in this mixture was dispersed 44 g of dimethyl succinyl succinate. The dispersion was heated in a stepwise manner with stirring to 80, 85 and 110 °C, and 1 g of each iodine and potassium iodine were added. Without external heating was added 20 ml of 30% hydrogen peroxide in a course of 20 min at temperature 110 °C. After ten minutes the 40 ml of warm and than 40 ml of cold water were stirred through reaction mixture. After cooling to RT, the slurry was filtered off and washed twice with water. After drying, yield 32.7 g (75%), m.p. 153 °C.

2.4. 2,5-dihydroxyterephthalate (DHTA)

In a 1 l four-necked flask with stirrer, reflux head, dropping funnel and thermometer were placed 20 g of NaOH dissolved in 160 ml of water. 32.7 g of dimethyl 2,5-dihydroterephtalate was slurried into 100 ml of warm water, and slurry was added to alkali. The solution was heated under stirring to 95 °C and after 2 h, 45 ml of 37% HCl was added to the boiling solution. After cooling to RT, the precipitated DHTA was filtered off and dried to yield 18.5 g (65%) with HPLC purity of 99.8%. IR, cm^{-1}: 3300 – 2500, 1650, 1491, 1429, 1290, 1201, 894, 843, 695, 525. ^1H NMR, (DMSO-d6), δ, ppm: 7.21 (2), 11.7 (OH). ^{13}C NMR, (DMSO-d6), δ, ppm: 117.78, 119.95, 152.48. 170.80.

2.5. Preparation of PIPD Fiber

Into a 1 l glass reactor with powerful anchor-type stirrer was step-by-step added 71.5 g of 115% polyphosphoric acid (PPA) and 30.5 g of 85% phosphoric acid in a stepwise manner. The mixture was heated to 100 °C and 40 g of solid $TAP{\cdot}HCl{\cdot}H_2O$ added. The reactor was closed and air was displaced by argon by repeated evacuation and argon blanketing. After homogenization for 1 h, to the mixture was added 29.7 g of DHTA and 88.5 g of P_2O_5. The reaction mixture was stirred for 48 h at 100 °C, 2.5 h at 150 °C, 2.5 h at 160 °C, and finally 19 h at 185 °C. The reaction mass became opalescent at 150 °C. The bottom part of the reactor was removed and the polymer solution was transferred into the cylinder of a piston-type fiber spinning machine. The intrinsic viscosity of the obtained PIPD polymers ranged from 10.9 to 19.1 dL/g. The obtained PIPD/PPA dopes were directly spun into fibers via dry-jet wet-spinning process. Fibers were completely washed in running water, and dried at 100 °C in vacuum.

2.6. Fiber Properties

Tensile Strength and Young's Modulus of Fibers was tested according to the standard of ASTM C1557-14. A fiber was selected randomly from the fiber bundle and the two ends of the fiber were grasped between the clamps of the tester. Tensile properties were measured using a UTS 10 device (UTStestsysteme, Germany). No less than 5 specimens were taken for each sample to obtain an average value. Arithmetical mean measurement error was less than 0.03 GPa for tensile strength and 1.5 GPa for Young's modulus.

3. Techniques

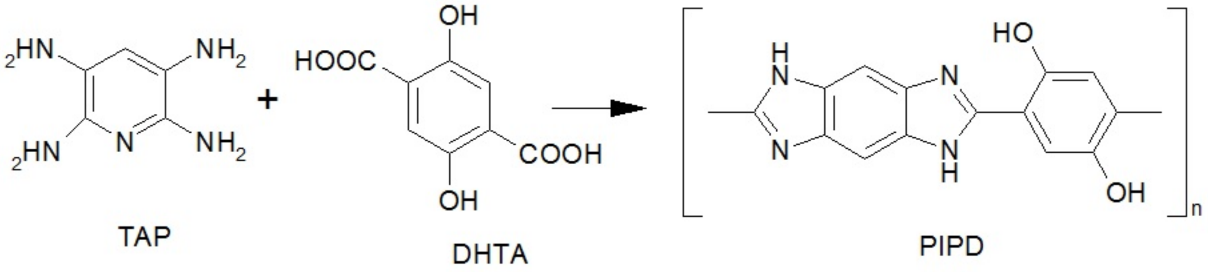
^1H- and ^{13}C NMR spectra were recorded on a Bruker AV400 spectrometer. IR spectra were obtained on a Nexus 670 (Nicolet) infrared spectrometer (liquid on KBr disk or in KBr tablets for powder). HPLC was performed on Agilent 1100 instrument using a phosphate buffer as a solvent on 6890/5973N Agilent column. Scanning electron microscope (SEM) images was obtained using a Carl Zeiss Supra55VP scanning electron microscope.

4. Result and discussion

4.1. Monomer synthesis

The synthesis of PIPD was achieved by polymerization of 2,5- dihydroxyterephthalic acid with 2,3,5,6-tetraaminopyridine (TAP) (see the scheme).

To achieve a fiber with optimal mechanical properties, it is necessary to have a polymer with high molecular weight and without defects in the chemical structure. This necessitates the elaboration of versatile procedures for the synthesis of monomers and optimization of polymerization conditions. The main problem in the synthesis of TAP is their oxidative lability as free base. This problem can be solved if the synthetic route using the salt of TAP (for



example with hydrochloric acid) that avoids any handling of the TAP free base. Such synthetic procedure was described by Sikkema in [4] and in a number of patents [6–8]. This synthetic pathway included the nitration of commercially-available 2,6-diaminopyridine to 2,6-diamino-3,5-dinitropyridine and its reduction to TAP salt by hydrogenation in solution using different catalysts. The best results were obtained using 10 % Pd/C. The yield of final product with polymer grade purity was about 85% [4]. We used a new route to DNDAP: a sequential nitration of 2,6-diaminopyridine with KNO_3/H_2SO_4 gives a DNDAP in moderate yield. We modified the Sikkema procedure to avoid using a palladium catalyst and replace it by the inexpensive Raney nickel. This allowed us to increase the yield of TAP salt to 93% with an HPLC purity of 99.7%. The second monomer for PIPD synthesis, DHTA, was used in polymer chemistry, particularly in the synthesis of 'hairy rod' liquid crystalline polymers [9]. The workable procedure for DHTA synthesis was suggested by Sikkema [4] and was used by us with minor modification. As a result, DHTA was obtained in 65% yield in 99.9% purity as determined by HPLC analysis. Hence, the new synthetic route we developed for PIPD monomers allowed to obtain both monomers in polymerization-grade purities with high yields.

4.2. Polymerization

For the synthesis PIPD, we used the traditional method with step-by-step heating of monomers in weak acid (polyphosphoric acid- PPA). The high-purity monomers allowed us to obtain the polymer (Fig. 1) with high molecular weight (MW) in amounts sufficient for fiber spinning.

For spinning, three samples were selected with MW according capillary viscometry 19.1, 22.0 and 25.5 kilodaltons respectively. For calculating the MW, we used the Mark-Kuhn-Houwink equation:

$$[\eta] = KM^{\alpha},$$

where for K was accepted value 2.27×10^{-7} and for α 1.8. The selection constants in the Mark-Kuhn-Houwink equation were based on values recommended for rigid-rod polymers capable of forming H-bonds in solution for viscosity measurements [10]. Capillary viscometry was carried out in a solution of methanesulfonic acid, which suggests the possibility of a polyelectrolitic effect and as a result, the increase of the calculated values for MW relative to their true value. However, the high tensile strength of spinning fibers supports the high MW of synthesized PIPD simples. Theoretically calculated values for persistence length was in the range of 22 – 65 nm [11–13], which is in good agreement with experimental data for cis-PBO, which was found to range from 20 – 30 nm [14] or 50 nm [10]. Hence, the macromolecule of PIPD can be seen as lap-join chain form nano-sized rigid fragment [11].

The solubility limit of PIPD in the reaction mixture is about 20% for high MW polymer. This allowed spinning from the polymerization solution without polymer precipitation and redissolution by dry-jet wet spinning method. It should be noted that solution of PIPD in PPA

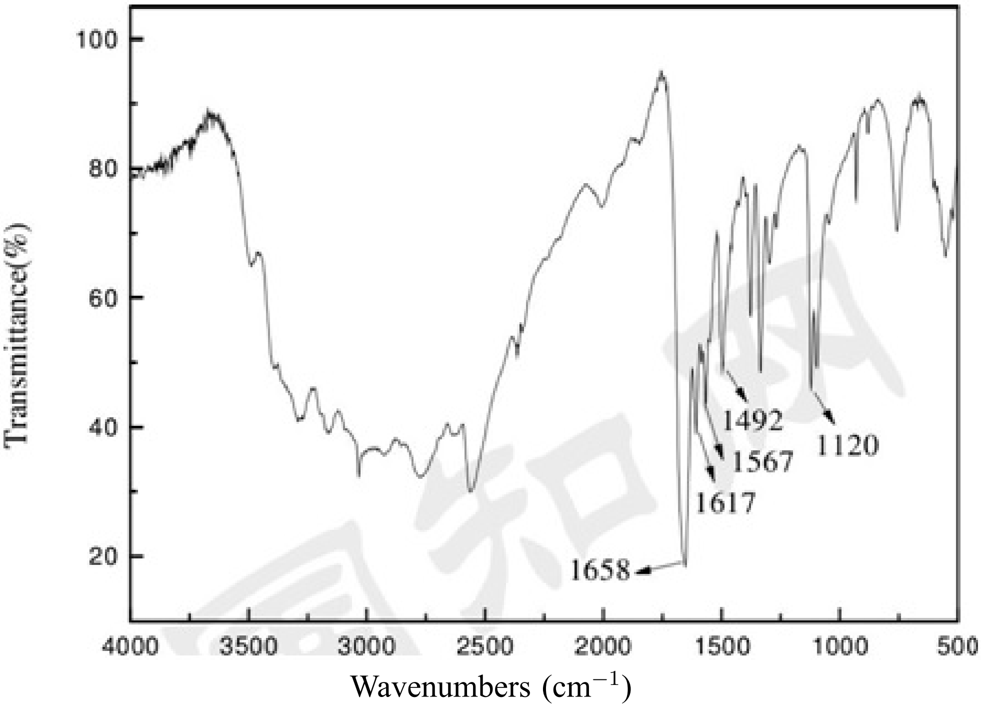


FIG. 1. IR spectrum of PIPD

with polymer contain higher than 18 wt% is lyotropic nematic [6] that contribute any specifics in spinning process. Liquid crystallinity offers desirable properties, which make it possible to efficiently spin a thread from such a rigid macromolecule as PIPD.

4.3. Spinning

Conventional air gap wet spinning of the as-polymerized PIPD solution was performed at 180 °C in a steam bath for fiber production. As result, filaments with diameter 18 – 20 μm (Fig. 2) were obtained, which were further washed to low phosphorus content and dried to produce final, high-modulus fibers. In PIPD solutions used for spinning, a high degree of molecular orientation of the polymer chains with respect to the local director can be expected. During the spinning process the local directors are aligned in the direction of flow by the shear flow in the capillaries of the spinneret and by the elongation flow in the entrance zone above the spinneret and in the air gap. The high degree of the orientation of the director together with the high degree of local molecular order implies that the PIPD macromolecules are highly-oriented. Assuming that this orientation order is merely ‘frozen-in’ during the coagulation process, the high modulus of PIPD fiber obtained can be predicted. It was supported by our measurements. The average data for tensile strength of three samples with different MW are 1.28, 1.49 and 1.99 GPa. Young’s moduli were 101, 120 and 161 GPa correspondingly. Elongation before break for all samples was about 1%. Hence, this strong dependence of tensile strength on MW shows that polymerization grade of our samples is relative low. However, the absolute value of tensile strength is high compared with literature data [15].

5. Conclusion

A novel entry toward PIPD has been elaborated. A strategy based on a new route to monomers: a sequential nitration of 2,6-diaminopyridine with KNO_3/H_2SO_4 gives a DNDAP in moderate yield and its hydrogenation with Raney nickel as catalyst leads to TAP in high

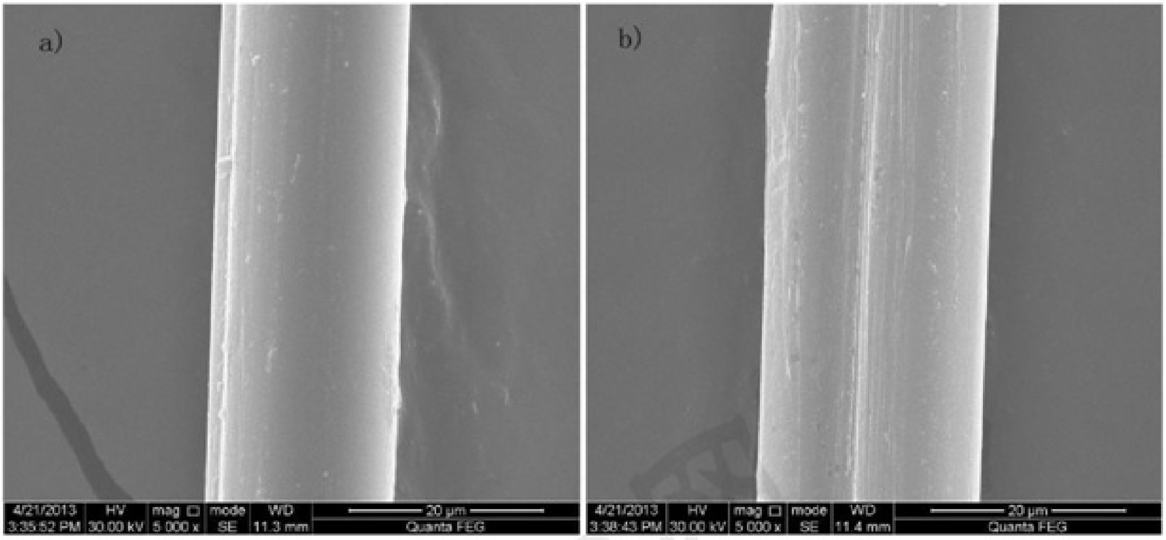


FIG. 2. SEM images of PIPD fiber ($MW = 25.5 \cdot 10^3$) in two directions

yield. Second monomer (DHTA) was synthesized in high yield as product of sulfur-mediated aromatization of dimethyl succinoyl succinate with following base hydrolysis. PIPD was synthesized in a stepwise manner by heating in polyphosphoric acid with MW 19 – 25×10^3. The macromolecule of PIPD can be seen as lap-join chain form nano-sized rigid fragment. The as-polymerized liquid crystalline PIPD solution was used for fiber spinning. The tensile strength of PIPD fibers were 1.28 – 1.99 GPa in dependence on MW polymer used for spinning. PIPD is light as well as strong. Its strength approaches and even exceeds that of typical high strength engineering steel (1.3 GPa). However, the PIPD have a significantly lower relative density (1.7) [6] than steel (7.8). Compared on a weight basis, PIPD is thus by far the stronger material.

Acknowledgements

The research reported in this paper was partly supported by RFBR-NNSFC grant No. 14-03-91152-a, by National Natural Science Foundation of China (NNSFC) (grant No. 51203034), Research Fund for the Doctoral Program of Higher Education of China (grant No. 20122302120038), Special Foundation of China Postdoctoral Science (grant No. 2013T60379), Supported by China Postdoctoral Science Foundation (grant No. 2013M541392).

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