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Synthesis and properties of polyimides from 1,3–bis(4-piperidino-1,8-naphthalic anhydride)propane

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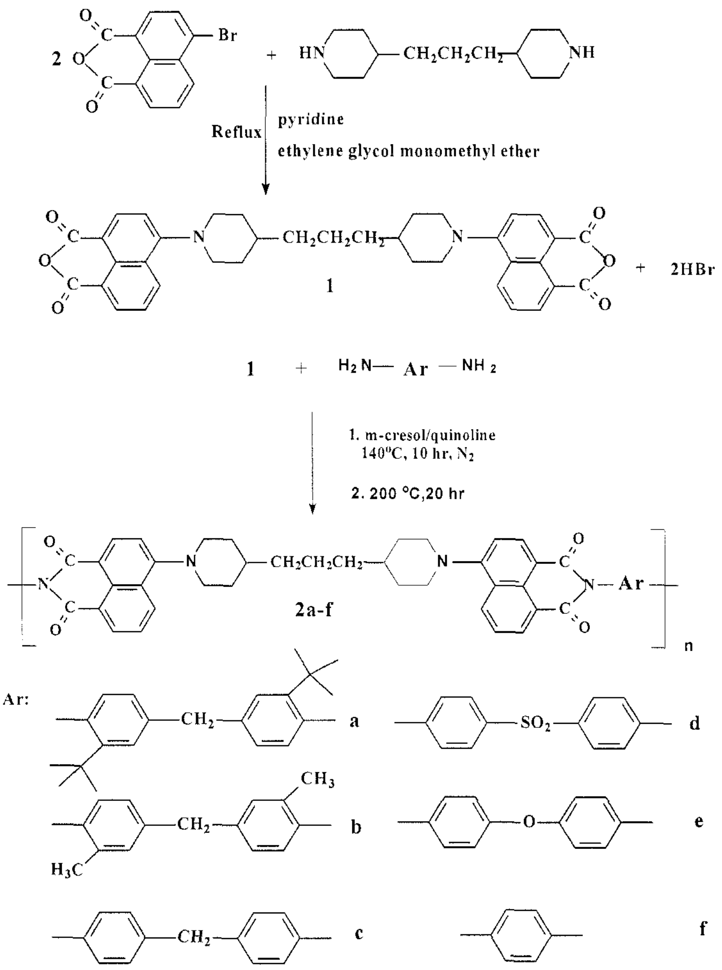
Summary

A novel dianhydride containing nathphalene units was prepared by Ullmann reaction of 4-bromo-1,8-nathphalic anhydride with trimethylenedipiperidine and polymerized with various aromatic diamines in one-pot polycondensation at high temperature in m-cresol. All the polyimides are soluble in organic solvents and form transparent yellow thin films by solution casting. Their inherent viscosities were ranged in 0.17 – 0.68 dL /g (in m-cresol at 25□). The glass transition temperatures were from 202.7□ to 263.6□ by DSC. These polymers did not show appreciable decomposition up to 380□ in N_2 by TGA and can emit strong green fluorescence in solution and in solid state. They may be potential light emitting and solar energy conversion materials.

Introduction

Aromatic polyimides have been widely investigated because of their high thermal stability, good mechanical and excellent electronic properties[1-3]. Recent years more attention has been paid to synthesize soluble polyimides containing naphthalene units. Almost all of the naphthalene containing dianhydrides used for the synthesis of soluble polyimides are derived from 1,8-naphthalene dicarboxylic anhydride which is linked by a hinge such as oxygen, carbonyl, arylene ether/sulfone[4-6]. Simultaneously some organic small molecules 4-substituted-1,8-naphthalimide derivatives are very interesting in view of their usage as fluorescent dyes for solar energy collectors[7], organic light-emitting diodes[8] and laser active media[9]. These make us be interesting to choose some "special hinge molecule" to connect two 1,8-naphthalene dicarboxylic anhydrides in order to introduce 4-substituted-1,8-naphthalimide derivatives into the polymer main chain and hope them having some special properties. In this paper we described the preparation of a series new fluorescence aromatic polyimides containing naphthalene units in main chain and soluble in organic solvent. By molecular design, a novel aromatic dianhydride monomer (1,3–bis(4-piperidino-1,8-naphthalic anhydride)-propane) was prepared from 4,4'-trimethylenedipiperidine and 4-bromo-1,8-naphthalic anhydride according to Ullmann condensation reaction[11-12] and was used to synthesize polyimides with various aromatic diamines by one-pot procedure as shown in Scheme 1. The physical, thermal and fluorescence properties of these polyimides are investigated.



Scheme 1 The synthesis routine of monomer and polymers

Experimental

Materials

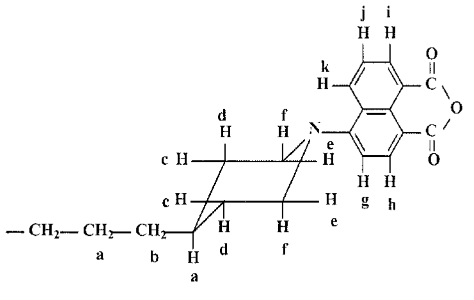
4,4'-Trimethylenedipiperidine (Aldrich) was used directly. 4-Bromo-1,8-naphthalic anhydride (Aldrich) was recrystallized from ethyl acetate before used. 4,4'-Methylenebis -(2-tert-butylaniline) was prepared by our laboratory according reference[13]. P-phenylenediamine, 4,4'-diaminodiphenylether, 4,4'-diaminodiphenylsulfone, 4,4'-diaminodiphenyl-methane and 4,4'-methylenebis(2-methylaniline) were purchased from domestic chemical market and recrystallization or sublimation before used. Quinoline, methanol, acetic anhydride and other solvents were purchased from the domestic chemical market and used without further purification. N, N'-Dimethylformamide and *m*-cresol were bought from the domestic chemical market and purified by vacuum distillation before used.

Measurements

Elemental analyses were run in a Perkin-Elmer Model 2400 C, H, N instrument; IR spectra were recorded on a Perkin-Elmer FT/IR spectrometer; ^1H NMR and ^{13}C NMR spectra were measured on a 300 MHz Bruker NMR spectrometer; The fluorescence spectra of the polyimides in solution or solid state were recorded on Luminescence Spectrometer LS50B; Thermogravimetric analysis (TGA) was performed under nitrogen on a PE Pyris-7 thermal analyzer at a scan rate 20℃/min. Differential scanning calorimetric studies were conducted under nitrogen on PE Pyris-1 (DSC) thermal analyzer at a scan rate 20 ℃/min. The molecular weight was measured by EuroOsmo 7000 Vapor Phase Osmometer(VPO) and the inherent viscosity was determined by an Ubbelohde dilution viscometer (0.5g polyimide in 100 mL m-cresol at 25±0.1℃).

Monomer preparation

1,3–bis(4-piperidino-1,8-naphthalic anhydride)propane (1): 50 ml ethylene glycol monomethyl ether, 5 ml pyridine, 6.6564 g (0.024 mol) 4-bromo-1,8-naphthalic anhydride were added into a 150 ml four-neck flask equipped with a mechanical stirring, a reflux condenser, a drop funnel and a nitrogen inlet. Under the stirring the mixture was heated to reflux temperature until 4-bromo-1,8-naphthalic anhydride dissolved in ethylene glycol monomethyl ether completely. After 2.10 g (0.01 mol) 4,4'-trimethylenedipiperidine was dissolved in a mixture solvent completely (5 ml ethylene glycol monomethyl ether and 2 ml pyridine), it was dropped into the reaction mixture in 1 h and kept the reaction mixture on this condition. In the reaction process more and more yellow powder appeared. The hot slurry mixture was filtrated when no more yellow powder increased. The total reaction time was about 10 h. The resulting yellow powder was washed by warm ethylene glycol monomethyl ether twice and then the yellow powder was further purified by recrystallization from the mixture solvent of DMF and acetic anhydride twice. The pure 1,3–bis(4-piperidino-1,8-naphthalicanhydride)propane is a sort of crystal as red orange needles.



Scheme 2 The peak assignment of the monomer 1 in ^1H NMR

Yield: 36.8%; m.p.: 275.6℃ by DSC; IR (KBr,cm^{-1}): 1766, 1722 (C=O, naphthalic dianhydride); ^1H NMR (pyridine-d_5, ppm): 1.17(d), 1.29(a), 1.39(b), 1.63-1.67(c), 2.36-2.73(f), 3.36-3.43(e), 4.74(H_2O in solvent pyridine-d_5), 6.97(j), 7.38-7.53(g), 8.27-8.30(i), 8.36-8.41(h), 8.43-8.50(k); ^{13}C NMR (pyridine-d_5, ppm): 24.05, 32.70, 35.96, 36.99, 53.84, 111.52, 115.37, 119.97, 125.92, 126.21, 132.32, 132.60, 132.96, 134.76, 158.09, 161.13, 162.01; Elem. Anal. $C_{37}H_{34}N_2O_6$: Calc. C 73.75 H 5.65 N 4.65 Found C 73.75 H 5.82 N 4.87; MS: (m+1)/e = 603.2 (100%)

Polyimide synthesis:

A typical polymerization process as fellows: A 100 ml three-necked flask equipped with a nitrogen inlet, a condenser and a mechanical stirring was charged with equimolar diamine and dianhydride, 10 ml m-cresol and 15 drops quinoline. The solution was stirred and heated to 140℃ until the solids dissolved completely and kept at this temperature for 10 h. Then the temperature was raised slowly to 190-200℃ and the reaction mixture was stirred for 20 h at 190-200℃. After cooling to the room temperature, the transparent reaction mixture was poured slowly into 300 ml vigorously stirring methanol, giving rise to a yellow powder precipitate. The precipitated polymer was washed with hot methanol several times and dried under vacuum at 100℃ for 24 h.

2a) IR (KBr,cm^{-1}):1700, 1656 (C=O, imide), 1356 (C-N-C, imide);Elemental analysis for $(C_{58}H_{48}N_4O_4)_n$ Calc. C 79.45 H 6.84 N 6.39 Found C 78.71 H 6.53 N 6.34

2b) IR (KBr,cm^{-1}): 1701, 1654 (C=O, imide), 1362 (C-N-C, imide);Elemental analysis for $(C_{52}H_{48}N_4O_4)_n$ Calc. C 78.79 H 6.06 N 7.07 Found C 79.23 H 5.79 N 6.85

2c) IR (KBr,cm^{-1}): 1703, 1657 (C=O, imide), 1356 (C-N-C, imide)Elemental analysis for $(C_{50}H_{44}N_4O_4)_n$ Calc. C 78.53 H 5.76 N 7.33 Found C 76.81 H 5.71 N 7.24

2d) IR (KBr,cm^{-1}): 1705, 1660 (C=O, imide), 1363 (C-N-C, imide) Elemental analysis for $(C_{49}H_{42}N_4O_6S)_n$ Calc. C 72.24 H 5.16 N 6.88 S 0.04 Found C 72.01 H 5.21 N 6.94 S 0.13

2e) IR (KBr,cm^{-1}):1699, 1660 (C=O, imide), 1362 (C-N-C, imide)Elemental analysis for $(C_{49}H_{42}N_4O_5)_n$ Calc. C 76.76 H 5.85 N 7.31 Found C 75.78 H 5.35 N 7.29

2f) IR (KBr,cm^{-1}): 173, 1659 (C=O, imide), 1363 (C-N-C, imide) Elemental analysis for $(C_{43}H_{38}N_4O_4)_n$ Calc. C 76.56 H 5.64 N 8.31 Found C 75.63 H 5.28 N 7.81

Results and discussion

Monomer synthesis

The synthetic routine of the monomeric dianhydride 1 outlined in Scheme 1. The classic Ullmann condensation reaction of aryl halides with amines is traditionally carried out under high temperature with the catalysts copper powder or copper salt in the presence of some inorganic bases such as potassium carbonate or hydroxide. Therefore the high boiling point solvent ethylene glycol monomethyl ether was used as reaction medium in this work. It is considered that the raw reagent 4-bromo-1,8-naphthalic anhydride is very sensitive to inorganic bases, some organic tertiary amines such as pyridine, triethylamine etc are chosen as the bases to neutralize the byproduct HBr and this measure can improve the yield of monomeric dianhydride 1. On the other hand the reactive activity of the second amine 4,4-trimethylene-piperidine is very high so that no copper catalysts need to be used here to eliminate some side reactions and the purity of monomeric dianhydride 1 can be improved. In order to assure 4,4-trimethylenepiperidine reacted with 4-bromo-1, 8-naphthalic anhydride completely, the mole ratio of 4-bromo-1,8-naphthalic anhydride and 4,4-trimethylenepiperidine should be greater than 2. In the reaction process, the monomeric dianhydride 1 (yellow orange powder) appeared more and more in hot reaction mixture. However, the excessive 4-bromo-1,8-naphthalic anhydride can keep dissolving in hot reaction mixture. Therefore the hot slurry reaction mixture was filtrated to remove the unreacted 4-bromo-1,8-naphthalic anhydride when no more monomeric dianhydride 1 powder appeared. This method decreased the yield of monomeric dianhydride 1, but its purification can be improved. Then monomeric dianhydride 1 was further purified by recrystallization from the mixed solvents (DMF and acetic anhydride) to form red orange needle crystal. Its structure was confirmed by the elements analyses, IR, MS, ^{1}H NMR and ^{13}C NMR. DSC analysis indicated that it displayed a sharp endothermic peak at melting point 275.6℃. The yield was not very high (36.8%).

Polymerization and characterization

In general polyimides can be prepared from the condensation of a diamine and a dianhydride through either two-step method or one-pot approach. The two-step method is very useful for high reactive monomers. At the first step, a polyamic acid is formed at low temperature, and then the intermediate converts into the polyimide by way of thermal or chemical imidization. The one-pot method is suitable for some low reactive monomers to synthesize soluble polyimides because the polycondensation should be implemented at high temperature. In this study one-pot solution polycondensation at high temperature was adopted because of the low reactivity of the six-numbered ring dianhydride 1. At first, the reactive mixture should be heated to 140℃ slowly to form a yellow transparent solution and kept at this temperature for 10 h. Then the temperature was raised to 190~200℃ in 1 h and kept at this temperature for another 20 h. The viscosity of the yellow transparent solution increased continuously during the polycondensation process, and the polymerization solution remained homogenous if the solid content in the raw materials was kept around 10 % (w/w). The byproduct (H_2O) in the reaction system could be removed rapidly by a nitrogen flow in order to destroy the equilibrium between water and the imide groups.

The structure of the polyimides was confirmed by element analysis and FT-IR. FT-IR spectra of the polyimides showed imide carbonyl peaks at around 1770 and 1660 cm^{-1} which are typical values for the naphthalimide and lower than that for the phthalimide (e.g. 1770 and 1720 cm^{-1}), indicating the complete imidization during polycondensation. The polyimide 2a is soluble in $CHCl_3$ and THF so that its number-average molecular weight (M_n) was about 7763 estimated by VPO. Because of lower reactivity of the hindered aromatic diamine monomer 4,4'-methylenebis(2-tertbutylanilina) and six-membered ring dianhydride monomer 1, the molecular weight of the obtained polyimide 2a was not high. The molecular weight of other polyimides can not be measured by VPO because of their lower solubility in low boiling point solvents, but their inherent viscosities were ranged from 0.25 ~ 0.68 dL/g and higher than that of the polyimide 2a 0.17 dL /g. That is to say, their number-molecular weights may be higher than that of the polyimide 2a.

Table 1 Characterization of the polyimides

Polymer number	T_g	η	Solubility [a]					
			p-chlorophenol	m-cresol	DMAc	DMF	THF	$CHCl_3$
2a	202.7	0.17	+	+	+	+	+	+
2b	216.2	0.25	+	+	±	±	–	–
2c	238.2	0.49	+	+	±	±	–	–
2d	213.4	0.36	+	+	±	±	–	–
2e	263.5	0.68	+	+	±	±	–	–
2f	214.8	0.37	+	+	–	–	–	–

[a] + Soluble; ± partly soluble; – insoluble at room temperature

The solubility of these polyimides was tested in various solvents. It is well known that the polyimides containing naphthalene units are usually insoluble or poorly soluble in organic solvents. These novel polyimides can dissolve in common organic solvents. Especially the polyimide 2a can be dissolved in tetrahydrofuran, cyclohexanone and chloroform at room temperature. The improvement of its solubility can be attributed to the bulky tert-butyl groups of the aromatic diamine that reduced the interaction between polyimide chains. But for other polyimides, their solubility was improved due to the flexible chain block (thrimethylene group) was introduced into the polyimide main chain. These novel polyimides can be processed to form yellow transparent film by solution casting.

The thermal stability of these polyimides was tested by TGA under nitrogen atmosphere and their typical TGA curves are shown in Figure 1. These polyimides were stable up to 380 ℃ and the temperature of 10 wt% loss was higher than 440 ℃ . Their glass transition temperatures (T_g) measured by DSC were ranged from 202.6℃ to 263.5℃. Thus the flexible chain block (thrimethylene group) introduced into the polyimides main chain can considerably improve the solubility of the polyimides without detriment to their thermal stabilities.

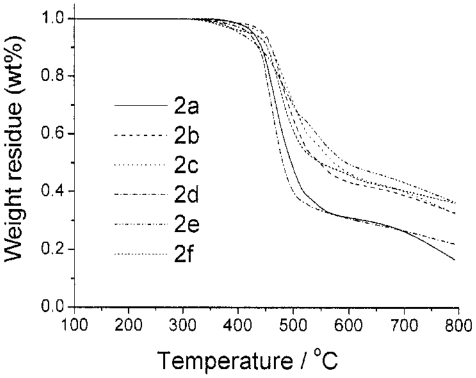


Figure 1 The TGA curves of the polyimides

The UV-spectra of the monomer 1 and the polyimide 2a in $CHCl_3$ solution are shown in Figure 2. From the UV-spectra, the absorption peak types are similar with each other but only a little ultraviolet shift of the polyimide 2a than the monomer 1 was found. This may be caused by the chemical structure change from naphthalic anhydride to polyimide. No fluorescence of 4-bromo-1,8-naphthalic anhydride in $CHCl_3$ solution was found in visible light range. However, when the bromide of 4-bromo-1,8-naphthalic anhydride was substituted by the piperidino group, it can emit very strong green fluorescence because the conjugated structure was formed between the naphthalene ring and piperidine ring. The fluorescence of the polyimides in solid state was shown in Figure 3. The peak type of the polyimides fluorescence spectrum is similar with that in solution but a little more red shift was found in solid state. The high fluorescence emission properties of these polymers can be exploited for the realization of organic light-emitting devices by using them as electron transport and emission materials in our further investigation.

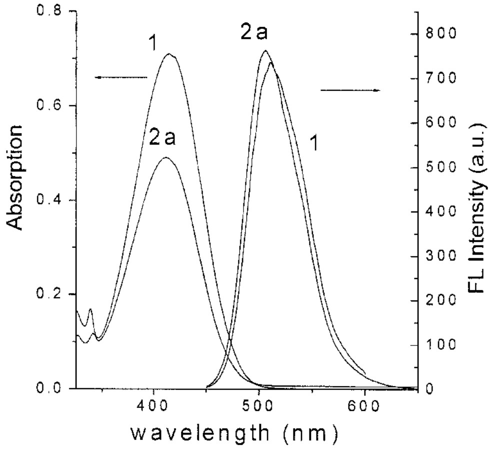


Figure 2 The UV-spectra and FL spectra of the monomer 1and polyimide 2a in $CHCl_3$ solution

Conclusion

The novel monomer 1,3–bis(4-piperidino-1,8-naphthalic anhydride)-propane was synthesized and used to prepare polyimides with some aromatic diamines by high temperature one-pot polycondensation in m-cresol. These polyimides are soluble in organic solvents and form transparent yellow thin films by casting from solution. Their inherent viscosities were ranged in 0.17 – 0.68 dL /g. The glass transition temperatures were from 202.7 ℃ to 263.6℃ by DSC. These polymers did not show appreciable decomposition up to 380℃ in N_2 by TGA and can emit strong green fluorescence in DMF solution (the maximum band around 530 nm) and in solid state (the maximum band around 540 nm). They may be potential light emitting and solar energy conversion materials.

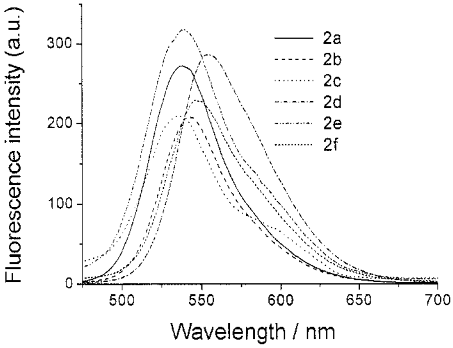


Figure 3 The fluorescence spectra of the polyimides in solid state

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