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Cycloaddition Approach to the Curing of Polyimides via Precursor Containing Thiophene-*S*,*S*-dioxide

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ABSTRACT: *A new method for linear polymerization of maleimides via the Diels–Alder reaction has been developed. This method involves use of a new cross-linking agent, benzene-3,4-dimethylenesuccinimide, which can be generated in situ from its thiophene precursor, benzene-2,5-dihydrothiophene-3,4-dicarboximide-S,S-dioxide. This new cross-linking agent is reasonably reactive, readily prepared, and stable at room temperature. A controlled molecular weight oligomer has been synthesized and applied to the polymerization to yield a highly thermal stable polyimide.* DOI 10.1002/hc.20249

INTRODUCTION

The special requirements of the aerospace and electronics industry for thermally stable, lightweight, and high-strength materials has resulted in an explosion of efforts toward the so-called high-performance polymers. Premier among these are the polyimides [1]. Polyimides are commonly synthesized through a condensation process involving an arene diamine, e.g., *p*-phenylenediamine, and a tetracarboxylic dianhydride. Processing generally takes place at the intermediate polyamic acid stage, and curing involves thermolysis to expel water and produce the imide linkage.

Processing of polyimides presents a conundrum. That is, their desirable characteristics are a combination of strength and impermeability, two properties which are antithetical to conventional processing via melt spinning or solution-casting techniques. One solution to this conundrum is the use of polyamide resins which are terminated with a cross-linking group, e.g., a maleimide, which can undergo addition polymerization at elevated temperatures or cross-linking with an added "enophile," e.g., an alkane dithiol, via the Michael addition [2]. Polyimide resins with terminal maleimide groups are readily available [3]. Because there are a variety of bismaleimide derivatives and commercially available dithiols, the polymer properties of the resulting materials range from those rubber-like elastomers to those of high-melting thermoplastics [4]. Thermogravimetric analysis (TGA) indicates that most of those polyimides decompose at 325–360°C or below [5]. Moreover, the polymer produced through such cross-linking exhibits significantly deteriorated tensile strength [6,7],presumably because car-sulfur bonds are weaker than carbon–carbon bonds. Ottenbrite et al. [8] and others [9] have

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introduced another approach to this problem, i.e., linear polymerization by Diels–Alder reactions between carbon–carbon double bonds of terminal maleimide groups and dienes, although no information on mechanical properties is given, and similar considerations may apply here as to the sulfur cross-linked polymers. Thus, the ultimate solution to this conundrum requires use of a cross-linking technique, which maintains the functional integrity of the rod polymer.

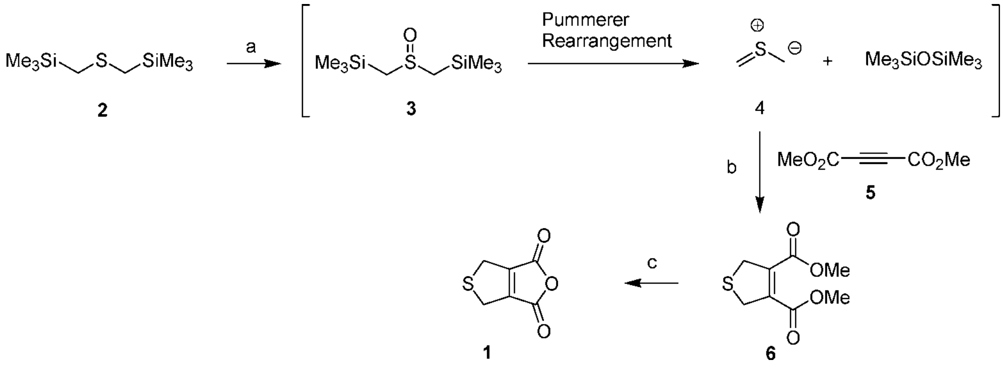
We now report the development of an alternative Diels–Alder method for consolidation of polyimides using 2,5-dihydrothiophene-3,4-dicarboxylic anhydride (**1**) as an end-capping agent, then oxidation to its *S*,*S*-dioxide which serves as a source of 1,4-butyldiene in the Diels–Alder reaction to react with maleimides as a dienophile during chain-extension. Polymers produced with this method not only have thermal properties better than that from the conventional polyamide, but also hold promise as candidates for synthesizing block polyimide copolymers.

RESULTS AND DISCUSSION

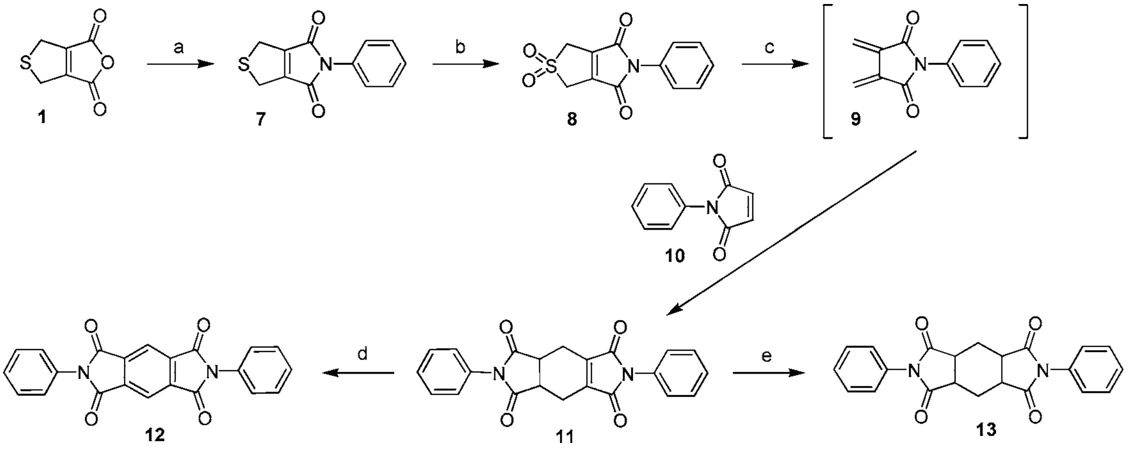
2,5-Dihydrothiophene-3,4-dicarboxylic anhydride (**1**) could be synthesized in six steps using a literature route [10] from commercially available carbomethoxymethyl 2-carbomethoxyethylsulfide with utilizing liquid HCN in a key step [10]. Because it is very dangerous to use liquid HCN in large quantity (e.g., 20 mL), we have felt that we needed an alternative approach to avoid that. A much more efficient three-step sequence has been developed (Scheme 1). Bis(trimethylsilylmethyl)sulfide (**2**) is a commercial available regent, and it was oxidized with *m*-chloroperoxybenzoic acid (mcpba) in CH_2Cl_2 at −78°C to afford **3**. Sulfoxide **3** was a very labile compound, which underwent the Pummerer rearrangement to give **4** in a polar solvent (DMPU). It is crucial to heat **3** in the presence of excess amount of dimethyl acetylenedicarboxylate (**5**) so that in situ formed **4** would be immediately reacted with **5** to form the desired product **6**. Otherwise, sulfoxide **3** would be further rearranged to its byproduct, $Me_3Si\text{-}O\text{-}CH_2SCH_2SiMe_3$, which will not react with **5**. Hydrolysis of **6** followed by dehydration gave rise to **1** in good yield (71%).

The feasibility of using thiophene **1** to build a building block as a precursor of diene in the Diels–Alders reaction, and hence the value of developing a synthesis of polyimide, was first explored with a simple system (Scheme 2), in which all compounds were characterized by full spectroscopic data.

The synthesis was initiated by reacting **1** with phenyl amine followed by imidization with acetic anhydride to give **7**. Oxidation of **7** with mcpba afforded the sulfone **8** as a stable intermediate. By thermogravimetric analysis (TGA), we observed facile loss of SO_2 from **8** to form diene **9** at about 100°C. After well-mixing **8** with **10**, the mixture was heated at 210°C without any solvent. Upon releasing sulfur dioxide, newly formed diene **9** efficiently reacted with dienophile **10** to give the desired Diels–Alder adduct **11** (88%), which was confirmed by both ^1H an ^{13}C NMR analyses. Due to the electron-withdrawing carbonyl groups attached to the 2 and 3 positions of diene **9**, vigorous conditions (210°C and 48 h) for the Diels–Alder reaction were required. To prevent retro Diels–Alder reaction for **11** and enhance its thermostability, there is a need to transform the newly formed double bond in **11** either into a part of aromatic ring (as in **12**) by oxidation, or into an alkane (as in **13**) by reduction. A number of oxidation reagents [12] were used to aromatized **11** to **12**, but the yields were generally poor (15–27%) with numerous byproducts. On the other hand,



SCHEME 1 Reagents and conditions: (a) mcpba, CH_2Cl_2, −78°C; (b) **5**, DMPU, 100°C; (c) (1) NaOH, (2) $SOCl_2$, PhH, reflux.



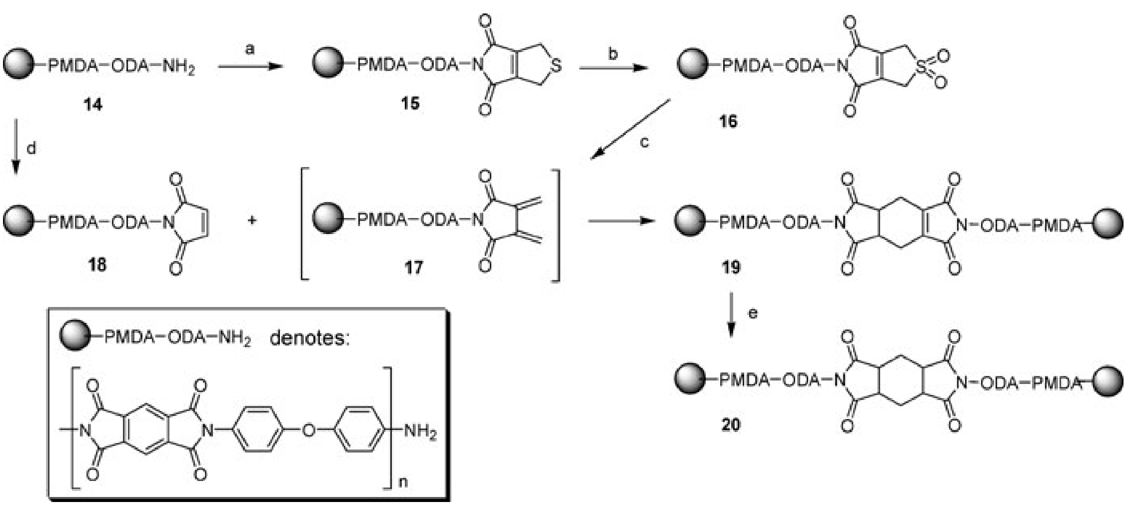
SCHEME 2 Reagents and conditions: (a) (1) aniline, $CHCl_3$, (2) AcONa, Ac_2O; (b) mcpba, CH_2Cl_2, rt; (c) **10**, xylene, 210°C; (d) DDQ, dioxane, reflux; (e) diimide, rt.

reduction of **11** with diimide [13] afforded **13** in excellent yield (91%). Because the purpose of developing this method was for polymer synthesis, the catalytic hydrogenation was ruled out, although some of them resulted in good yields (85–98%) for product **13**.

The overall sequence is straightforward, which includes incorporation **1** with an amine to form a sulfide then a sulfone. Upon heating, a diene was formed; the Diels–Alder reaction followed by reduction yields desired imide. At this point, we envisioned that if we applied one polyimide in the place of **7** whereas another in the place of **10**, we could obtain an even larger polyimide.

Finally, synthesis of about 2000 molecular weight oligomer containing terminal amine groups (**14**) was achieved by the known methods [11] using an excess of oxydianiline (ODA) to react with pyromellitic dianhydride (PMDA), whereas the oligomer containing terminal maleimide groups (**18**) was obtained by using an excess of oxydianiline (ODA), pyromellitic dianhydride (PMDA), and meleic anhydride (Scheme 3). Using a procedure similar to that used for preparation of **7**, compound **14** reacted with **1** to give sulfide **15** then to **16** with the treatment with hydrogen peroxide. This oligomer **17** was allowed to react with **18** at 210°C to yield the polymer **19**, in which the double bond was subsequently reduced, and a new polyamide **20** was formed.

TGA studies revealed a remarkable increase in decomposition temperature from 350°C (for **14**) to ca. 550°C (for **20**). This clearly indicates that a polymer with longer chain has been obtained.



SCHEME 3 Reagents and conditions: (a) **14**, NMP, **1**, Ac_2O, AcONa; (b) mcpba, CH_2Cl_2, rt; (c) **18**, xylene, 210°C; (d) maleic anhydride, AcONa; (e) diimide, rt.

CONCLUSION

Use of the previously unreported 2,3-dimethylenesuccinimide moiety as a Diels–Alder cross-link agent provides a new versatile method for consolidation of polyimides. Use of this moiety on one type of oligoimide and maleimide end groups on another oligoimide provides ready entry into a number of polyamide block copolymers. Further studies on mechanical properties and block copolymer formation are underway and will be reported in due course.

EXPERIMENTAL

General

All reactions were conducted under a nitrogen atmosphere. All NMR data were obtained at 400 MHz for proton and 100 MHz for carbon spectra, in $CDCl_3$ unless otherwise noted, using TMS as an internal standard. Melting points are uncorrected. Column chromatography was performed using 230–400 mesh silica gel. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer TGA series 7. Oxydianiline (ODA) and pyromellitic dianhydride (PMDA) were either purchased as Gold Label zone-refined quality or were sublimed prior to use.

Compound **3**. A solution of 3-chloroperoxybenzoic acid (mcpba, 35 g, 55%, 123 mmol in CH_2Cl_2 (250 mL) was added to a solution of sulfide **2** (20.6 g, 100 mmol) in CH_2Cl_2 (250 mL) at −78°C. After stirring at −78°C for 1 h, the mixture was warmed to 0°C, washed with ice water, $NaHCO_3$, dried over $MgSO_4$, then concentrated under vacuum (at 10°C) to give **3** as an oil, which was used in next without purification. ^{1}H NMR 0.22 (s, 18 H), 2.15 (d, 2H, $J = 13.6$), 2.43 (d, 2H, $J = 13.6$).

*Dimethyl 2,5-Dihydrothiophene-3,4-dicarboxylate (**6**).* A solution of freshly prepared sulfoxide **3** (100 mmol) and dimethyl acetylenedicarboxylate (5, 7.1 g, 50 mmol) in 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU, 10 mL) was added to a heated DMPU (100°C) in 3 min. The resulting mixture was stirred at 100°C for 10 min then poured into ice water. CH_2Cl_2 (100 mL × 5) was washed to extract, and combined organic layer was dried ($MgSO_4$). After the solvent was removed under the vacuum, the product was purified by distillation to give **6** (5.6 g, 59%). bp 93–95°C (0.3 mm); ^{1}H NMR 3.81 (s, 6H), 4.05 (s, 4H).

*2,2,4,4-Tetrahydrothiophene-3,4-dicarboxylic Anhydride (**1**).* A solution of **6** (5.6 g, 30 mmol) in glacial acetic acid (30 mL) and concentrated HCl (30 mL) was stirred at its reflux temperature for 5 h. The mixture was poured into ice water, and 2,2,4,4-tetrahydrothiophene-3,4-dicarboxylic acid was collected by vacuum filtration. After drying, freshly distilled thionyl chloride ($SOCl_2$, 5 mL) and benzene (40 mL) were added. The resulting mixture was heated at its reflux temperature for 30 min then solvent was removed by distillation. The product was recrystallized from benzene to give 1 (3.5 g, 71%). mp 165–166°C; ^{1}H NMR δ 4.05 (s, 4H); ^{13}C NMR δ 37.3, 139.4, 165.2. Anal. Calcd for $C_6H_4O_3S$: C, 46.15; H, 2.58; S, 20.53. Found: C, 46.27; H, 2.73; S, 20.23.

Compound **7**. A solution of aniline (930 mg) in $CHCl_3$ (4 mL) was added to a solution of **1** (1.56 g) and was stirred at 45°C for 0.5 h, then solvent was removed to give a solid. At this point, acetic anhydride (6 mL) and NaOAc (1 g) was added, and the mixture was heated at 100°C for 0.5 h. After cooling to rt, the mixture was poured to ice-water. The crystalline product **7** (1.86 g, 81%) was formed, collected and dried under a high vacuum for 18 h. ^{1}H NMR δ 4.08 (s, 4H), 7.24 (t, 1H, $J = 7.2$), 7.41 (m, 2H), 7.66 (d, 2H, $J = 7.2$); ^{13}C NMR δ 38.2, 121.6, 124.4, 129.0, 132.8, 138.6, 169.8. Anal. Calcd for $C_{12}H_9NO_2S$: C, 62.32; H, 2.92; N, 6.06, S, 13.86. Found: C, 62.44; H, 2.87; N, 6.13, S, 14.01.

Compound **8**. A solution of mcpba (2 g, 55%, 6 mmol) and compound **7** (1.16 g, 5 mmol) in CH_2Cl_2 was stirred at rt for 3 h. The mixture was washed $NaHCO_3$ then dried over $MgSO_4$. Solvent was removed under vacuum, and residue was recrystallized from water to give **8** (0.88 g, 67%). ^{1}H NMR (DMSO-d_6) δ 4.51 (s, 4H), 7.34 (d, 1H, $J = 7.2$), 7.42 (t, 2H, $J = 7.2$), 7.51 (t, 2H, $J = 7.2$). ^{13}C NMR δ 58.1, 121.6, 124.4, 129.0, 132.8, 138.6, 169.8. Anal. Calcd for $C_{12}H_9NO_4S$: C, 54.75; H, 3.45; N, 5.32, S, 12.18. Found: C, 55.01; H, 3.58; N, 5.46, S, 12.24.

Compound **11**. A mixture of sulfone **8** (190 mg, 1 mmol) and **10** (123 mg, 1 mmol) in xylene (3 mL) was heated at 210°C in a resealable reaction vial for 48 h to afford **11** (151 mg, 59%) after crystallization from $CHCl_3$. ^{1}H NMR δ 2.82 (m, 4H), 3.65 (m, 2H), 7.32 (d, 4H, $J = 8.4$), 7.40 (t, 2H, $J = 8.4$), 7.49 (t, 4H, $J = 7.8$); ^{13}C NMR δ 26.8, 34.2, 121.6, 124.4, 129.0 135.4, 174.4. Anal. Calcd for $C_{22}H_{16}N_2O_4$: C, 70.96; H, 4.33; N, 7.52. Found: C, 70.88; H, 4.56; N, 7.38.

Compound **12**. The compound **11** (26 mg) was oxidized to **12** (6.8 mg, 27%) based on a literature condition [12]. For **12**: ^{1}H NMR δ 7.05 (t, 2H,

$J = 7.2$), 7.35 (m, 4H), 7.60 (d, 4H, $J = 7.2$), 9.05 (s, 2H); ^{13}C NMR δ 121.6, 124.4, 125.3, 129.0, 132.8, 135.6, 167.1. Anal. Calcd for $C_{22}H_{12}N_2O_4$: C, 71.74; H, 3.28; N, 7.61. Found: C, 71.65; H, 3.50; N, 7.78.

Compound **13**. The compound **11** (26 mg) was oxidized to **13** (23.7 mg, 91%) based on a literature condition [13]. For **13**: ^{1}H NMR δ 2.21 (m, 4H), 2.65 (m, 4H), 7.05 (t, 2H, $J = 7.2$), 7.30 (m, 4H), 7.60 (d, 4H, $J = 7.2$); ^{13}C NMR δ 26.8, 34.2, 121.6, 124.4, 129.0 135.4, 174.4. Anal. Calcd for $C_{22}H_{18}N_2O_4$: C, 70.58; H, 4.85; N, 7.48. Found: C, 70.66; H, 4.77; N, 7.42.

Compound **14**. A suspension of oxydianiline (ODA, 714 mg, 3.37 mmol), PMDA (650 mg, 2 mmol) in *N*-methyl-2-pyrrolidone (NMP) was stirred at 60°C for 1 h. Acetic anhydride (2 mL) and AcONa (1 g) was added, and the mixture was heated to 90°C for 4 h. The mixture was poured into water, and solid was collected by vacuum filtration to give **14** (1.1 g, 96%) after drying.

Compound **15**. A solution of 2,2,4,4-tetrahydrothiophene-3,4-dicarboxylic anhydride (**1**, 0.5 g, 3.5 mmol) in $CHCl_3$ (8 mL) was added to a suspension of **14** (1 g, 3 mmol) in NMP (15 mL) at ambient temperature. After being stirred for 0.5 h, sodium acetate (0.5 g, 5 mmol) was added. The mixture was stirred at 100°C for 0.5 h then poured into a vigorously stirred ice water. Yellow crystals were collected, washed with water, and dried to yield **15** (0.9 g, 86%). mp: >300°C; ^{1}H NMR (solid state) δ 4.09 (s), 7.10 (m), 7.46 (m), 8.88 (s).

Compound **16**. A solution of MCPBA (1.6 g, 55%) in CH_2Cl_2 (10 mL) was added to a suspension of **15** (900 mg) in CH_2Cl_2 (5 mL). After stirring at room temperature for 3 h, the solid was collected and washed with saturated aqueous $NaHCO_3$ (10 mL × 2). After drying under a high vacuum, a solid (**16**) was obtained (880 mg, 97%). ^{1}H NMR (solid state) δ 4.51 (s), 7.34 (m), 7.67 (m), 8.91 (s).

Compound **18**. A suspension of **14** (1 g) and maleic anhydride (0.5 g) in NMP (10 mL) was stirred at 60°C for 1 h. AcONa (1 g) was added, and the mixture was heated to 90°C for 4 h. The mixture was poured into water, and solid was collected by vacuum filtration to give **18** (1.11 g, 95%) after drying.

Synthesis of Cross-Linked Copolymer **20**

A suspension of disulfone **16** (0.1 g) and oligomer **18** (1.0 g) in xylene was sealed and heated at 210°C for 2 days to form **19**, which was further treated with diimide (5 mL) to reduce the double bond resulting from the Diels–Alder reaction. The final product was purified by Soxhlet extraction (acetone, 100 cycles) to remove small molecules. The residue was dried under a high vacuum for 24 h to give the desired polymer **20** (0.9 g, 89%).

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