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Poly(thioether imide)s via chloro-displacement polymerization

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Summary

Thioether containing polyimides were prepared by displacement of chlorine groups from substituted imides by aromatic and aliphatic sulfur nucleophiles. The all-aromatic monomers and polymers had poor solubility which led to precipitation during synthesis and low molecular weight polymers. However, these polymers were thermally stable up to 400 °C and had T_g's ranging from 212 °C to 233 °C. Poly(thioether imide)s prepared from 1,3-propanedithiol and 2-mercaptoethyl sulfide had good solubility but lower thermal stability, showing TGA loss onset temperatures of 297 °C and 298 °C, respectively.

Introduction

Nucleophilic aromatic substitution of nitro and halo-disubstituted bisimides by the dianions of bisphenols has been well investigated (1,2,3). This synthetic route allows formation of the imide ring first, followed by ether formation through displacement polymerization. The alternative route is substitution first to give precursors to dianhydrides, followed by formation of poly(amic acid) and cyclization to polyimides (4). The latter method has disadvantages of monomer instability and poor shelf life of the poly(amic acid) intermediates.

Poly(thioether imide)s via displacement polymerization have gained little attention due to side reactions and limited material availability (5,6). In model compound studies of nitro, fluoro and chloro-substituted phthalimides, it was found that thiophenoxide was at least 100 times more reactive than phenoxide and substituent activity was in the order $NO_2 > F > Cl$ (5). Although the best combination for reaction appears to be the nitro-substituted phthalimide with thiophenoxides, these systems yielded appreciable amounts of disulfides (5). The high reactivity of sulfur nucleophiles does allow polymerizations to occur between bisthiophenols or sodium sulfide and dichloro-substituted bisimides that don't polymerize well with bisphenol dianions. This article describes our investigation of several new poly(thioether imide)s prepared from alkyl and aryl thiolates with chloro-substituted phthalimides.

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Experimental

Materials

All chemicals were purchased from Aldrich Chemical Company. Pyromellitic dianhydride and 3,3',4,4'-benzophenonetetracarboxylic dianhydride were recrystallized from acetic anhydride. 4,4'-Oxydianiline (ODA) was recrystallized from ethanol and sublimed. Anhydrous sodium sulfide was prepared from the nonahydrate form by storing under vacuum in the presence of P_2O_5 and gradually increasing the temperature to 105 °C. 1,3-Propanedithiol and 2-mercaptoethyl sulfide were distilled. *N,N*-Dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidinone (NMP) were purified by vacuum distillation from calcium hydride.

Characterization

Solution NMR spectra were obtained on a Bruker AC-300 using standard parameters and DMSO-d_6 or $CDCl_3$ as solvents and secondary standards. FTIR spectra were taken on a Perkin-Elmer 1600A spectrometer. Differential scanning calorimetry was conducted on a TA Instruments 2920 DSC module (2100 data station) at a heating rate of 10 °C/min. The glass transition temperature was taken as the inflection point of the ΔT vs. temperature curve. Thermogravimetric analyses were performed with a TA Instruments 2960 TGA module (2100 data station) at a heating rate of 10 °C/min in nitrogen and air atmospheres. Elemental analysis was performed by M-H-W Laboratories, Phoenix, AZ.

4-Chlorophthalic anhydride (1)

The monosodium salt of 4-chlorophthalic acid (44.7 g, 0.201 mol, tech.) was suspended in 500 mL of water. Concentrated HCl (52 mL) was added in one portion turning the solution transparent brown. Extraction with ether, followed by drying over $MgSO_4$ and solvent evaporation yielded a cream colored solid. This solid was reacted with 25 mL of refluxing acetic anhydride for 4 h. The mixture was cooled to ambient temperature upon which crystallization occurred. The tan solid was filtered and vacuum dried at 40 °C for 8 h. The solid was dissolved in CH_2Cl_2, extracted with a cold $NaHCO_3$ solution, dried over $MgSO_4$ and the solvent removed under vacuum. The solid was dried under vacuum and recrystallized from CCl_4; yd 20.6 g (56%); mp 95-97 °C (lit. (7) mp 94-96 °C).

N-(4-Mercaptophenyl)-4-chlorophthalimide (2)

Anhydride **1** (17.04 g, 93.34 mmol) was dissolved in 60 mL of glacial acetic acid and chilled to 0 °C with an ice bath. 4-Aminothiophenol (14.28 g, 102.7 mmol, 90 % purity) was added along with 40 mL of glacial acetic acid. The mixture was gradually heated under a nitrogen atmosphere to a temperature of 130-155 °C and held there for 23 h. Upon cooling, a lemon-colored precipitate formed which was filtered, washed with water and dried under vacuum at 100 °C. Recrystallization from glacial acetic acid gave 17.4 g (64%) of product; mp 191-193 °C; IR (KBr): 2571 cm^{-1} (S-H), 1775 and 1723 cm^{-1} (C=O), 1384 cm^{-1} (C-N), 738 cm^{-1} (imide ring); ^1H NMR (DMSO-d_6): δ 5.67 (s, 1H), 7.31 (d, 2H, J = 8 Hz), 7.44 (d, 2H, J = 8 Hz), 7.94-7.95 (m, 2H), 8.01 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 166.1, 165.7, 139.4, 134.7, 134.4, 133.6, 133.1, 130.1, 128.5, 127.9, 125.1, 123.4.

*Polymerization of **2** to give **3***

Monomer **2** (0.7047 g, 2.432 mmol) was dissolved in 10 mL of DMAc and 5 mL of toluene under nitrogen. Upon addition of NaH (0.0620 g, 2.585 mmol), a vigorous evolution of H_2 occurred while a clear brown solution formed. The reaction mixture was heated at 155 °C for 18 h. During the course of polymerization, the solution color gradually turned yellow and a precipitate formed. After cooling, the heterogenous solution was poured into 300 mL of CH_3OH, filtered, washed with hot CH_3OH and vacuum dried at 80 °C; yd 0.6025 g (98%); T_g 212 °C. The polymer was soluble in H_2SO_4, partially soluble in m-cresol and NMP, and insoluble in HCO_2H, DMF, DMSO, o-dichlorobenzene and $(CF_3)_2COH$; IR (KBr): 1775 and 1723 cm^{-1} (C=O), 1384 cm^{-1} (C-N), 738 cm^{-1} (imide ring).

*Bis(4-chlorophthalimide) of ODA (**6**) (8)*

Anhydride **1** (9.13 g, 50.0 mmol) was dissolved in 190 mL of glacial acetic acid and 95 mL of DMAc under a N_2 atmosphere. ODA (5.006 g, 25 mmol) was added in one portion and the mixture was heated at 150 °C for 15 h. Upon cooling, a yellow precipitate formed which was filtered, washed with water and dried under vacuum. The product was recrystallized from DMSO; yd 10.0 g (76%); mp 235-236 °C; IR (KBr): 1779 and 1720 cm^{-1} (C=O), 1383 cm^{-1} (C-N), 1242 cm^{-1} (C-O-C), 741 cm^{-1} (imide ring); ^1H NMR ($CDCl_3$): δ 7.19 (d, 4H, $J = 9$ Hz), 7.42 (d, 4H, $J = 9$ Hz), 7.77 (dd, 2H, $J = 8$ Hz and 2 Hz), 7.91 (d, 2H, $J = 8$ Hz), 7.94 (d, 2H, $J = 2$Hz). Anal. Calcd. for $C_{28}H_{14}Cl_2N_2O_5$: C, 63.53; H, 2.67; Cl, 13.40; N, 5.29; Found: C, 63.38; H, 2.71; Cl, 13.59; N, 5.12.

*Polymerization of **6** with Na_2S to yield **7***

Anhydrous Na_2S (0.1051 g, 1.347 mmol) and bisimide **6** (0.660 g, 1.247 mmol) were reacted in 10 mL of DMAc and 5 mL of toluene at reflux for 12 h under N_2. During the polymerization, the solution turned red and then yellow in color. After cooling, the mixture was added to 350 mL of dilute HCl in water. The precipitate was filtered, refluxed in acetone for 1 h, filtered and dried under vacuum to yield 1.08 g (87%); T_g 233 °C. Intrinsic viscosity of the polymer in m-cresol at 30 °C was 0.43 dL/g. The polymer was marginally soluble in m-cresol and NMP, partially soluble in DMAc and insoluble in acetone and DMSO; IR (KBr): 1774 and 1724 cm^{-1} (C=O), 1370 cm^{-1} (C-N), 1240 cm^{-1} (C-O-C), 740 cm^{-1} (imide ring).

*Polymerization of **6** with 1,3-propanedithiol to yield **8***

1,3-Propanedithiol (0.257 g, 2.37 mmol) was slowly added to a suspension of NaH (0.124 g, 5.17 mmol) in 4 mL of DMF under N_2. Vigorous evolution of H_2 occurred and the resulting cream-colored suspension was stirred for 1 h. Bisimide **6** (1.257 g, 2.375 mmol) was added followed by 5 mL of DMF. The solution color immediately changed to red. The reaction mixture was heated at 125-150 °C for 24 h. During the course of polymerization, the color of the mixture gradually turned orange and eventually to a pale brown. The polymer was isolated by precipitating into 350 mL of CH_3OH, washing with additional CH_3OH and drying under vacuum; yd 0.790 g (59%); T_g 163 °C. The intrinsic viscosity in m-cresol at 30 °C was 0.11 dL/g. The polymer was very soluble in m-cresol, NMP, and H_2SO_4, and marginally soluble in DMAc, DMF, and DMSO; IR (KBr): 3066 cm^{-1} (=C-H), 2925 cm^{-1} (-C-H), 1774 and 1724 cm^{-1} (C=O), 1370 cm^{-1} (C-N), 1240 cm^{-1} (C-O-C), 740 cm^{-1} (imide ring); ^{13}C NMR (DMSO-d_6): δ 166.6, 155.8, 145.7, 134.4, 132.6, 129.2, 127.8, 127.3, 123.8, 120.5, 119.0, 29.7, 27.5.

*Polymerization of **6** with 2-mercaptoethyl sulfide to yield **9***

Preparation of this polymer was analogous to the previous one; yd. 77%; T_g 148 °C; intrinsic viscosity in m-cresol at 30 °C 0.18 dL/g. The polymer was very soluble in m-cresol, NMP, and H_2SO_4, and marginally soluble in DMAc, DMF, and DMSO; IR (KBr): 3053 cm^{-1} (=C-H), 2917 cm^{-1} (-C-H), 1772 and 1716 cm^{-1} (C=O), 1377 cm^{-1} (C-N), 1241 cm^{-1} (C-O-C), 740 cm^{-1} (imide ring); ^{13}C NMR (DMSO-d_6): δ 166.2, 155.6, 145.4, 134.4, 132.2, 128.5, 127.7, 127.1, 123.5, 120.9, 118.7, 32.1, 30.4.

Results and Discussion

The synthesis of *N*-(p-mercaptophenyl)-4-chlorophthalimide (**2**) and it's conversion to poly(thioether imide) (**3**) are shown in Figure 1. The A-B monomer was synthesized from 4-chlorophthalic anhydride (**1**) and p-aminothiophenol in 55% yield after recrystallizing from acetic acid. The monomer was unstable in air and polar aprotic solvents such as DMSO, DMF and NMP in which disulfides formed. Polymerizations were carried out in DMF with NaH, although polymer precipitated during polymerization. The polymer was isolated in quantitative yields by filtering and removing the salt with CH_3OH / water wash. Figure 2 shows the first and second DSC scans of the polymer. A T_g of 187 °C and T_m of 413 °C was observed in the first scan. In the second scan, as well as third, a much more pronounced T_g was observed at 212 °C and the T_m disappeared, probably due to kinetically slow crystallization from the melt. Due to limited flexibility, this polymer was only soluble in sulfuric acid. Viscosity measurements were not acquired due to polymer decomposition in this solvent.

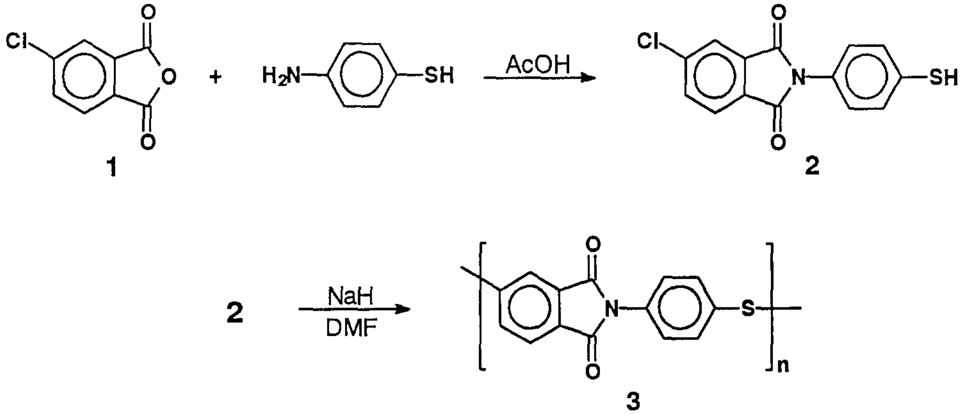

Figure 1:
Synthesis of *N*-(p-mercaptophenyl)-4-chlorophthalimide (**2**) and it's poly(thioether imide) (**3**).

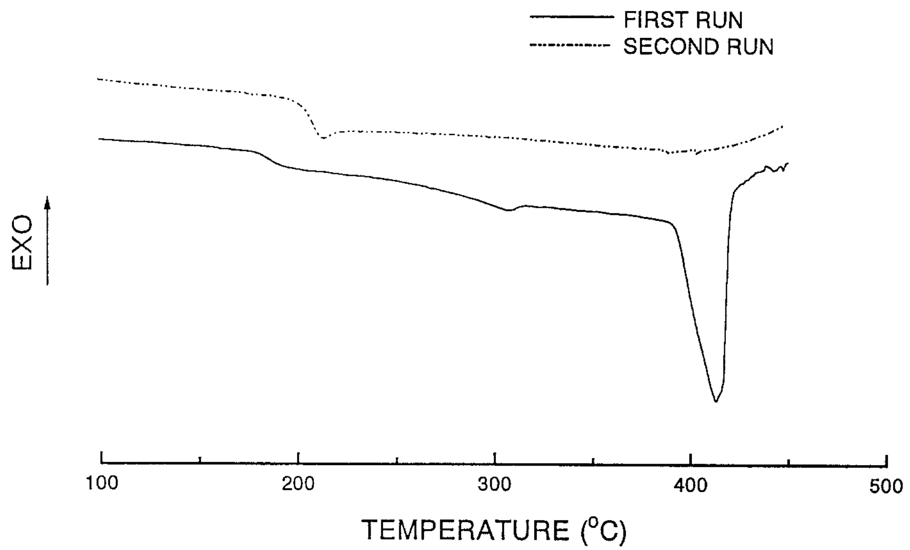

Figure 2:
DSC scans of poly(thioether imide) **3**.

Figure 3 shows the synthesis of dimercapto-substituted bisimides **4** and **5** from p-aminothiophenol with pyromellitic and benzophenone dianhydrides, respectively. Both reaction mixtures were initially homogeneous at ambient temperature, but almost immediately a bright yellow precipitate formed and the mixture remained heterogeneous throughout the reaction. We were unable to purify the monomers due to their poor solubility and instability. Attempted polymerizations of monomers **4** and **5** with dichloro-substituted bisimide (**6**) were heterogeneous and gave low molecular weight, infusible solids.

Dichlorobisimide **6** was synthesized from 4-chlorophthalic anhydride with 4,4'-oxydianiline, and polymerized with sodium sulfide, 1,3-propanedithiol and 2-mercaptoethyl sulfide (Figure 4). The polymerization of **6** with anhydrous sodium sulfide has been reported and was repeated for comparison to the alkyl-containing polymers (8,9). The stoichiometric amount of sodium sulfide was difficult to obtain due to the trapped impurities within the salt. The polymerization mixture was heterogenous. High molecular weight polymer **7** was obtained by analyzing the initial polymerization product by NMR to determine the percent of unreacted chlorine positions, and then compensating with additional Na_2S in a second-stage polymerization. Polymer **7** had a T_g of 233 °C and good thermal stability in both nitrogen and air atmospheres (Table 1). The intrinsic viscosity of polymer **7** in m-cresol at 30 °C was 0.43. This polymer was also soluble in NMP and H_2SO_4.

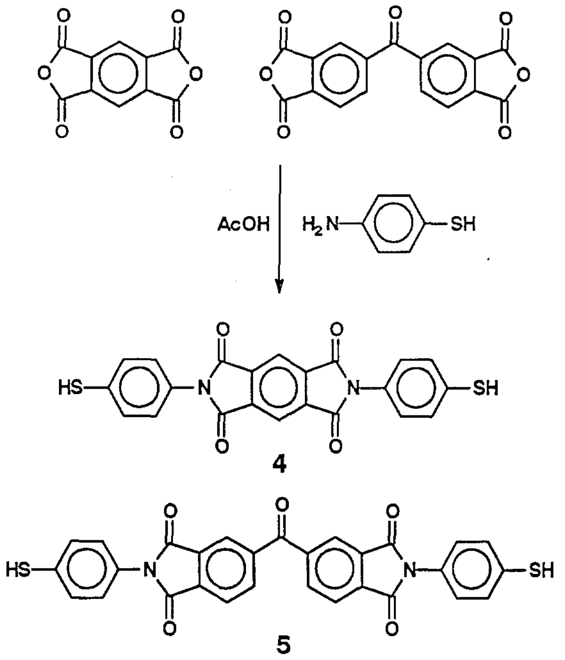

Figure 3:
Synthesis of dimercapto-functionalized bisimides **4** and **5**.

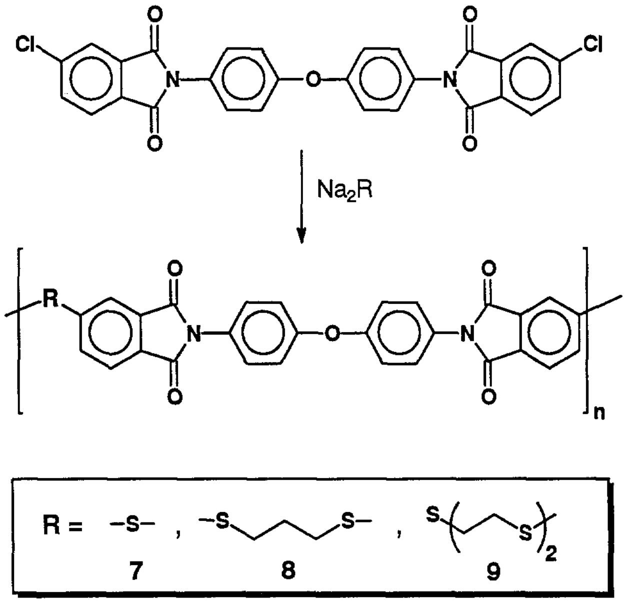

Figure 4:
Polymerization of dichloro-substituted bisimide (**6**) with bisthiolates to give polymers **7**-**9**.

The alkyl bisthiols were converted to the bisthiolates by addition to a suspension of NaH in DMF. Once hydrogen gas bubbles ceased, dichlorobisimide (**6**) was added to the mixture and polymerization occurred. Polymers **8** and **9** were isolated by precipitating into methanol. These poly(thioether imide)s had T_g's of 163 °C and 148 °C, respectively. Both polymers showed good solubility in m-cresol, DMF, DMSO and NMP, but thermally degraded in both air and nitrogen at approximately 300 °C in the TGA (Table 1). Intrinsic viscosities ranged from 0.11 to 0.18, confirming polymer formation.

Table 1:
Polyimide viscosities and thermal properties.

POLYIMIDE	$[n]^a$	T_g^b (°C)	TGA[b] Onset (°C)	
			N_2 atm.	Air atm.
3	---[c]	212	435	439
7	0.43	233	516	490
8	0.11	163	297	299
9	0.18	148	298	296

[a] Measured in m-cresol at 30 °C.
[b] Measured at heating rate of 10 °C/min.
[c] Insoluble.

Conclusions

Poly(thioether imide)s were prepared by chlorine displacement of substituted phthalimides by aromatic and aliphatic thiolates. The prepared mercapto monomers were difficult to purify due to their instability and low solubility. The fully aromatic polymers had good thermal stability, but poor solubility for the more rigid polymers. Incorporating aliphatic groups into the polymers enhanced solubility but lowered thermal stability. Overall, use of nucleophilic aromatic substitution for aryl thioether formation during step-growth polymerization is feasible, although problems exist with aryl sulfide oxidation and low solubility of the forming polymers which limit molecular weights obtainable.

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References

1. White, D. M.; Takekoshi, T.; Williams, F. J.; Relles, H. M.; Donahue, P. E.; Klopfer, H. J.; Loucks, G. R.; Manello, J. S.; Matthews, R. O.; Schluenz, R. W. (1981) J. Polym. Sci.: Part A: Polym. Chem. 19: 1635
2. Wirth, J. G.; Heath, D. R. (1974) U.S. Patent 3 787 364
3. Williams, F. J.; Relles, H. M. (1981) U.S. Patent 4 297 474
4. Takekoshi, T.; Kochanowski, J. E.; Manello, J. S.; Webber, M. J. (1985) J. Polym. Sci.: Part A: Polym. Chem. 23: 1759
5. Williams, F. J.; Donahue, P. E. (1978) J. Org. Chem. 43(2): 250
6. Williams, F. J. Canadian Patent (1979) 1 049 696
7. Zweig, A.; Epstein, M. (1978) J. Org. Chem. 43(19): 3690
8. Williams, F. J. (1976) German Patent 2 537 305
9. Teshirogi, T.; Kato, M.; Ota, S.; Sakota, K. (1991) Japanese Patent 02 229 829