PII: S0032-3861(96)00026-8

*Polymer* Vol. 38 No. 12, pp. 3129–3133, 1997

0032-3861/97/$17.00 + 0.00

# Crosslinked networks based on trimethoxysilyl functionalized poly(amic ethyl ester) chain extendable oligomers

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*(Received 4 October 1996; revised 4 December 1996)*

We report here the synthesis and characterization of poly(amic ethyl ester) oligomers functionalized with trimethoxysilyl end-groups. The oligomers were prepared via the condensation of 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane, diethyldichloromellitate and *p*-aminophenyltrimethoxysilane. The *p*-aminophenyltrimethoxysilane was used to control both molecular weight and end-group functionality. These oligomers were thermally cured to form crosslinked networks. The resulting networks possessed $T_g$ in excess of 450°C and thermal decomposition temperatures in the proximity of 500°C. The formation of networks was confirmed by swelling studies. These oligomers offer an attractive processing alternative as low viscosity precursors to crosslinked polyimide networks. © 1997 Elsevier Science Ltd.

**(Keywords: poly(amic ethyl ester) chain extendable oligomers; networks; high $T_g$ (>400°C); swelling measurements)**

## *Introduction*

Aromatic polyimides represent an important class of high temperature polymers. They are characterized by the presence of the phthalimide and/or pyromellitimide structure in the backbone and exhibit excellent thermo-oxidative stability and good thermal and mechanical properties. Consequently, polyimides have been employed in a variety of diverse commercial applications such as aerospace, adhesive and microelectronics industries[1–4].

The utility of polyimide thin films as dielectric insulators for microelectronics applications has been widely reported[5]. They have been found to possess useful properties in a wide variety of applications in the semiconductor industry. These include intermetal dielectrics for integrated circuits, electronic packaging and passivation protection layers. Polyimides also serve as planarizing layers to aid in the fabrication of microelectronic structures and as masks in dry etching processes[6,7].

Polyimides can be prepared via a number of different methods. The most commonly employed technique is the classical two-step synthesis comprising the synthesis of a poly(amic acid) followed by subsequent cyclodehydration to the polyimide. The cyclization can be effected by solution, chemical or thermal routes.

An inherent drawback of the poly(amic acid) approach is the poor hydrolytic stability of both the dianhydride monomer and the resulting poly(amic acid)[8]. Alternatively, the poly(amic alkyl ester) route provides a precursor with a long shelf-life that can be reformulated in a suitable solvent and thermally cyclized. This pathway has also been reported for the design of low molecular weight chain extendable polyimide precursor formulations with improved planarization[8]. In addition, the onset of thermal imidization of the poly(amic ethyl esters) occurs at a significantly higher temperature (~ 250°C) than the analogous poly(amic acids).

The present work deals with the synthesis of isolable trimethoxysilyl terminated poly(amic ethyl ester) oligomers which can subsequently be thermally cyclized and crosslinked into insoluble networks. The trimethoxysilyl end-groups serve as sites for network formation. The resulting polyimide network is expected to display most of the desirable thermal and mechanical properties of the linear analogue as well as improved solvent resistance.

## *Experimental*

*Materials.* *N*-Methyl-2-pyrrolidone (NMP) was purchased from Aldrich and distilled under vacuum over $P_2O_5$. Methylene chloride was purchased from Aldrich and used as supplied. Pyridine was stored over potassium hydroxide and distilled prior to use. Diethyldichloropyromellitate was prepared according to literature procedures[9,10] and was used as an isomeric mixture comprising 99% *meta* and 1% *para* isomer[11]. 1,1-Bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA) was prepared according to the literature procedure[12]. *p*-Aminophenyltrimethoxysilane was purchased from Gelest Inc. and was used as supplied. This monomer was an isomeric mixture comprising 95% *para* and 5% *meta*, as estimated by $^1$H n.m.r. and g.l.p.c.

*Synthesis of poly(amic ethyl ester) oligomers (*Scheme *1).* All oligomers employed in this study were synthesized via typical step growth polymerization techniques by co-reacting AA and BB type monomers with or without a monofunctional end-capper. The stoichiometry of the reaction was dictated by the targeted number average molecular weight $\langle M_n \rangle$. The latter was predicted by the use of Carother's equation. The stoichiometry calculations were designed with consideration for the specific end-functionality required. For example, to synthesize trimethoxysilyl functionalized oligomers, a stoichiometric equivalent of the diamine was substituted with the monofunctional

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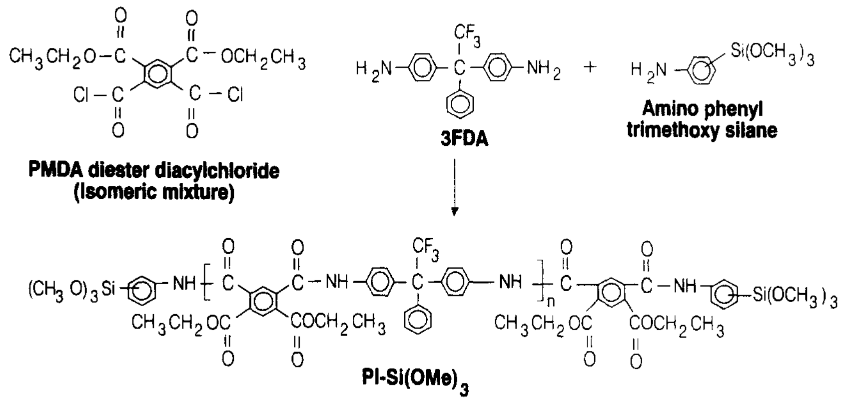

**Scheme 1** Synthesis for trimethoxysilane functionalized PMDA-3FDA poly(amic ethyl ester)

**Table 1** Characterization of poly(amic ethyl ester) oligomers and their corresponding cured polyimide films

| | Poly(amic ethyl ester) | | | Cured polyimide[a] | | | |
|---|---|---|---|---|---|---|---|
| | Target $\langle M_n \rangle$ (g mol$^{-1}$) | $\eta_{inh}$ NMP, 30°C dl g$^{-1}$ | $\langle M_n \rangle$ $^1$H n.m.r. (g mol$^{-1}$) | T.g.a.[b] 5% wt loss (°C) | $T_g$ (d.s.c.) 10°C min$^{-1}$ (°C) | $T_g$ (d.m.t.a.) 10 Hz, 10°C min$^{-1}$ (°C) | Swelling in NMP at 25°C for 72 h |
| PI-Si(OCH$_3$)$_3$ | 10 000 | 0.17 | 8900 | 542 | ND | 491 | 500% |
| | 20 000 | 0.24 | 17 000 | 546 | ND | 485 | 1000% |
| PI-COOH | 10 000 | 0.19 | — | 540 | ND | — | dissolves |
| | 20 000 | 0.27 | — | 539 | ND | 440 | dissolves |

[a] Cured for 1 h each at 200, 300 and 400°C
[b] Dynamic t.g.a. at 10°C min$^{-1}$
ND: not detected

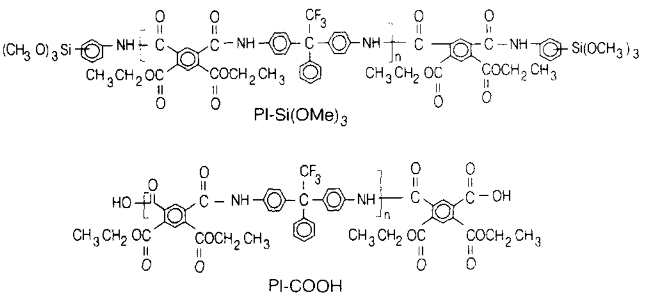

**Figure 1** Poly(amic ethyl ester) oligomers

end-capper. Alternatively, a stoichiometric excess of the diacid chloride diester monomer was used to synthesize carboxy terminated oligomers.

*Trimethoxysilyl functionalized poly(amic ethyl ester) oligomers* ($M_n = 10\,000\,g\,mol^{-1}$) (*Scheme 1*). To a three-neck flask equipped with an overhead stirrer, nitrogen inlet and additional funnel was charged 3.2456 g (9.48 mmol) 3FDA, 0.2218 g (1.04 mmol) of amino-phenyltrimethoxysilane, 2 g (25 mmol) of pyridine and 50 ml of distilled NMP. The reaction mixture was maintained under a positive nitrogen pressure and cooled to 0°C. The PMDA diethylester diacylchloride (3.4716 g, 10 mmol) was dissolved in ~ 100 ml of methylene chloride, quantitatively transferred to the additional funnel and added dropwise to the cold, stirred reaction mixture. After the addition was complete, the polymerization was allowed to proceed overnight at room temperature. The poly(amic ethyl ester) oligomer was isolated by precipitation under high shear conditions (Waring blender) in methanol, filtered and dried in a vacuum oven at 60°C. An oligomer ($\langle M_n \rangle = 20\,000\,g\,mol^{-1}$) was synthesized likewise employing the appropriate stoichiometry.

*Carboxy-terminated poly(amic ethyl ester) oligomers* ($M_n = 10\,000\,g\,mol^{-1}$) (*Scheme 1*). To a three-necked flask equipped with an overhead stirrer, nitrogen inlet and additional funnel was charged 3.2456 g (9.48 mmol) of 3FDA, 2 g (25 mmol) of pyridine and 50 ml of distilled NMP. The reaction mixture was cooled to 0°C and PMDA diethylester diacyl chloride (10 mmol, 3.4716 g) was added dropwise as a solution in methylene chloride. After the addition, the reaction was allowed to proceed overnight at room temperature. The oligomer was isolated by precipitation under high shear conditions (Waring blender) in methanol. Likewise, a higher molecular weight oligomer ($M_n = 20\,000\,g\,mol^{-1}$) was synthesized using the appropriate stoichiometry.

*Thermal imidization.* The poly(amic ethyl ester) oligomers were dissolved in NMP at 10–20% (w/v) solids and the solutions cast onto glass plates. Imidization was effected by heating the polymer films for 1 h each at 200, 300 and 400°C under a $N_2$ atmosphere. The cured polyimide films were then cooled slowly to room temperature.

*Characterization.* The poly(amic ethyl ester) oligomers were characterized by their inherent viscosities as well as by $^1$H n.m.r. and *FT*i.r. spectroscopy. The inherent viscosities were obtained with 0.5 g dl$^{-1}$ solutions in NMP at 30°C employing a Cannon Ubbelohde viscometer and were calculated from an average of five different runs. $^1$H n.m.r. spectra were obtained on a Bruker AC 250 MHz n.m.r. spectrometer in either $CDCl_3$ or deuterated DMSO and are reported in ppm ($\delta$) downfield from TMS. In the case of the

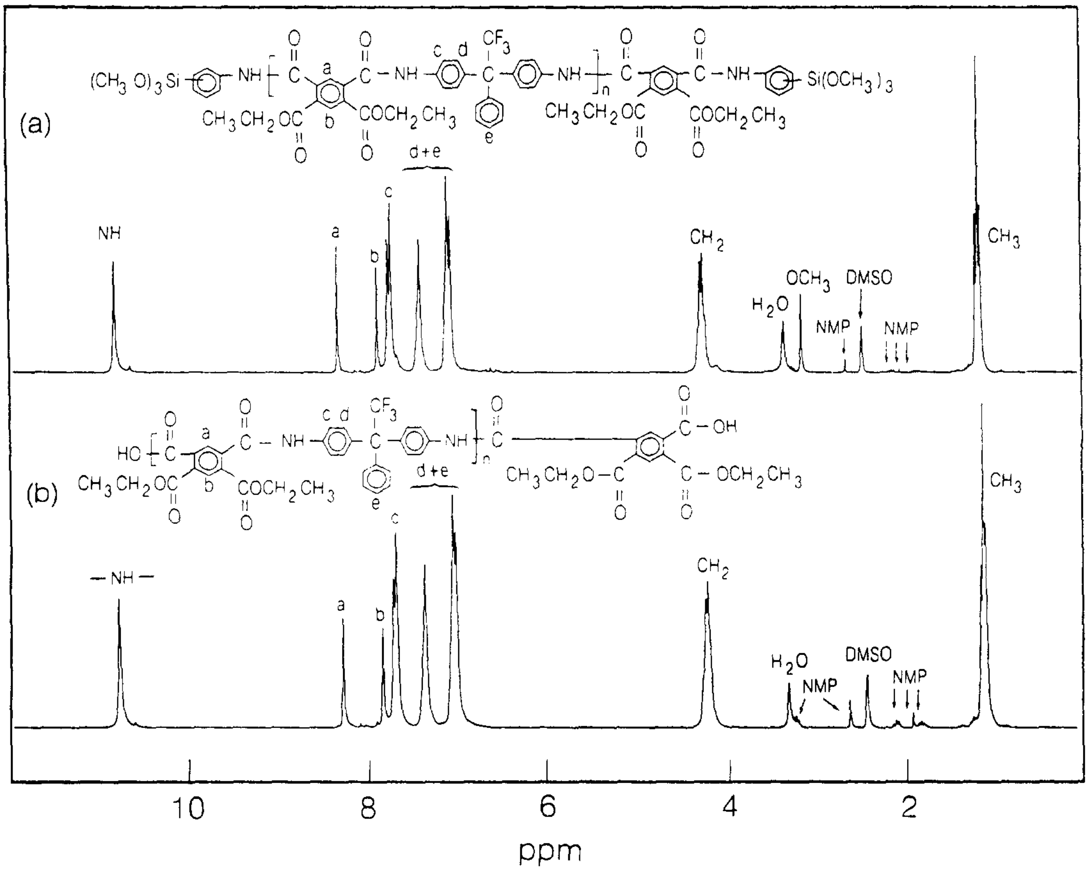

**Figure 2** $^1$H n.m.r. (250 MHz, $d_6$-DMSO) of $\langle M_n \rangle = 10\,000\,\mathrm{g\,mol^{-1}}$: (a) PI-Si(OCH$_3$)$_3$ and (b) PI-COOH poly(amic ethyl ester) oligomers

trimethoxysilyl functionalized oligomers, the number average molecular weights were estimated from the ratio of the methyl protons of the ester functionality to the methoxy protons of the trimethoxysilyl end-group. *FT*i.r. analyses were carried out on a Nicolet *FT*i.r. on films prepared from a solution of poly(amic ethyl ester) in THF on NaCl plates. The cured polyimide films were characterized by thermogravimetric analysis (t.g.a.), differential scanning calorimetry (d.s.c.), *FT*i.r., dynamic mechanical thermal analysis (d.m.t.a.) and solvent swelling techniques. Dynamic t.g.a. was performed on a Perkin-Elmer TGA-7 in air at a heating rate of 10°C min$^{-1}$. Dynamic d.s.c. was carried out on a DuPont 1090 instrument at 10°C min$^{-1}$. A Polymer Labs DMTA operating in the tension mode at 10 Hz and a heating rate of 10°C min$^{-1}$ was employed for dynamic mechanical analysis. *FT*i.r. analyses of the cured polyimides were carried out on 2–4 $\mu$ thick films sandwiched between NaCl plates. Swelling studies of the cured films were performed in NMP at 25°C for 72 h.

## *Results and discussion*

*Table 1* summarizes the characterization data on the poly(amic ethyl ester) oligomers (*Figure 1*) and the resulting cured polyimide films. Representative $^1$H n.m.r. spectra of the poly(amic ethyl ester) oligomers PI-Si(OCH$_3$)$_3$ and PI-COOH are shown in *Figure 2*. The singlet at $\delta$ 3.16 in *Figure 2a* corresponds to the methyl protons of the trimethoxysilyl group of the PI-Si(OCH$_3$)$_3$ terminated oligomers. This peak was absent in the $^1$H n.m.r. spectrum of the PI-COOH oligomers (*Figure 2b*). The number average molecular weight of the trimethoxysilyl functionalized oligomers was estimated by the ratio of the methyl proton signal of the ethyl ester centred at $\delta$ 1.7 to the trimethoxysilyl protons at $\delta$ 3.16. The calculation was based on the assumption that there were two such end-groups per chain. Trends in inherent viscosities in the case of the PI-Si(OCH$_3$)$_3$ and PI-COOH poly(amic ethyl ester) oligomers indicate fairly good molecular weight control. As expected, the inherent viscosity values increased with increasing molecular weight.

Films from the poly(amic ethyl ester) oligomers were thermally cyclized to the corresponding polyimides. The *FT*i.r. spectra of the PI-Si(OCH$_3$)$_3$ and PI-COOH poly(amic ethyl ester) oligomers and the resulting cured polyimide films are shown in *Figure 3*. The amide C = O stretch at 1660 cm$^{-1}$ and the N–H stretch at 3240–3320 cm$^{-1}$ of the poly(amide ester) in *Figures 3a* and *c* are absent in the corresponding cured polyimides (*Figures 3b* and *d*). The asymmetric carbonyl stretch at 1778 cm$^{-1}$ and the C – N stretch at 1380 cm$^{-1}$ which are characteristic of the polyimide[13,14] are apparent in *Figures 3b* and *d*. These peaks are absent in *Figures 3a* and *c*. This confirms the cyclization of the poly(amic ethyl ester) oligomers to the corresponding polyimide under these conditions.

Swelling studies on the cured polyimide films were carried out in NMP for 72 h. As noted in *Table 1*, the cured polyimide films obtained from the PI-COOH poly(amic ethyl ester) oligomers dissolved completely. This was expected since the trifluoromethyl group is known to impart improved solubility even to thermally imidized films of high molecular weight PMDA-3FDA oligomers[15,16]. The imidized films obtained from the PI-Si(OCH$_3$)$_3$ oligomers, however, formed swollen gels in

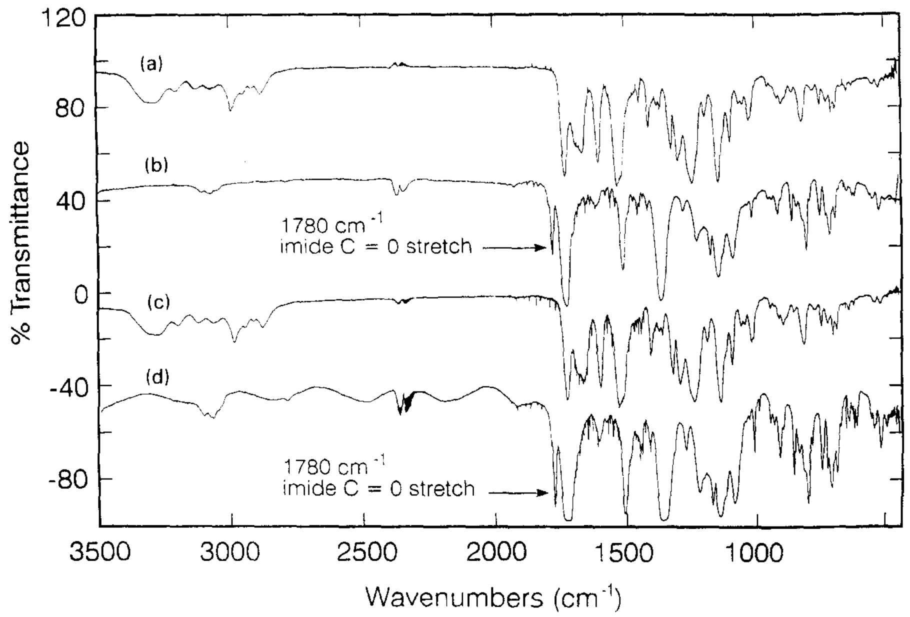

**Figure 3** *FT*i.r. spectra showing % transmittance as a function of wavenumber (cm$^{-1}$) of (a) PI-Si(OCH$_3$)$_3$ oligomer and (b) the cured polyimide; (c) PI-COOH oligomer and (d) the cured polyimide

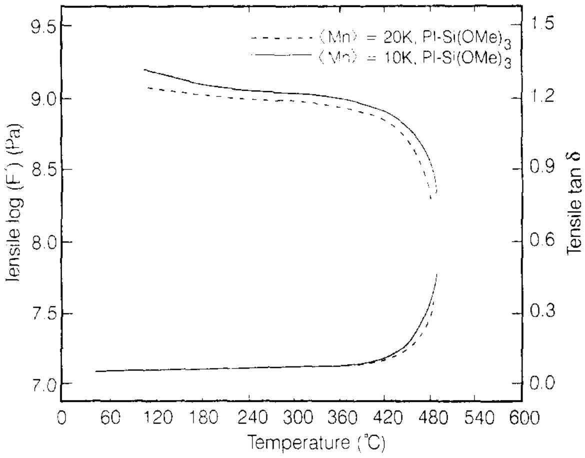

**Figure 4** D.m.t.a. spectra of thermally cured polyimide films obtained from PI-Si(OMe)$_3$ poly(amic ethyl ester) oligomers

NMP. The network from the PI-Si(OCH$_3$)$_3$ [($\langle M_n \rangle = 10\,000\,\mathrm{g\,mol^{-1}}) = 10\,\mathrm{K}$] oligomers was swollen approximately 500% (w/w) while those from the 20 K PI-Si(OCH$_3$)$_3$ oligomers were swollen approximately 1000%. This confirms that crosslinked networks are generated thermally from the PI-Si(OCH$_3$)$_3$ poly(amic ethyl ester) oligomers but not from the PI-COOH oligomers. The crosslinking process presumably occurs via a combination of hydrolysis and condensation. Soluble PMDA-3FDA poly(amic ethyl ester) oligomers show a $T_g$ or softening at $\sim$ 120°C. Subsequent imidization ($>$ 250°C) and crosslinking transform these soluble precursors into an insoluble network.

The d.m.t.a. spectra of the cured polyimide films are shown in *Figure 4*. The crosslinked polyimides exhibit remarkably high glass transition temperatures ($>$ 480°C); values comparable to those of higher molecular weight materials. The thermal stabilities of both the crosslinked and uncrosslinked polyimide films were comparable (*Table 1*), and the 5% weight loss temperature was found to be $>$538°C. Isothermal t.g.a. indicated a negligible weight loss ($<$1%) even after 500 min at 400°C. The tensile properties of the crosslinked polyimide films obtained from the PI-Si(OMe)$_3$ oligomers are reported in *Table 2*. The poor mechanical properties of the PI-COOH oligomer ($\langle M_n \rangle = 10\,\mathrm{K}$) precluded accurate tensile measurements. Trends in the data are consistent with the suggestion that the (PI-Si(OMe)$_3$) precursors are transformed into crosslinked polyimide networks, consistent with a hydrolysis and condensation network forming reaction[17,18], which exhibit excellent mechanical properties.

**Table 2** Tensile properties of cured polyimide films from PI-Si(OMe)$_3$ oligomers

| Theoretical $\langle M_n \rangle$ of precursor (g mol$^{-1}$) | Tensile strength$^a$ (MPa) | Strain$^a$ (%) | Modulus$^a$ (MPa) |
|---|---|---|---|
| 10000 | 110 | 8 | 2100 |
| 20000 | 103 | 14 | 1850 |

[a] Crosshead speed: 5 mm min$^{-1}$

## *Conclusions*

Stable, controlled molecular weight poly(amic ethyl ester) oligomers terminally functionalized with trimethoxysilyl groups have been successfully synthesized and characterized. These oligomers were transformed into insoluble crosslinked networks upon heating. The crosslinked polyimides exhibited thermal and mechanical properties comparable to higher molecular weight linear polyimides. The mechanical properties of the crosslinked samples were far superior to those displayed by oligomers of comparable molecular weight in the absence of Si(OMe)$_3$ end groups. High solids content solutions of moderate viscosity can be prepared from the low molecular weight oligomers. This, coupled with the drop in modulus of the polyamic esters with imidization and crosslinking, suggest that the reactively end-capped oligomers should display improved planarization characteristics. This feature is currently under investigation.

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