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Preparation of poly(amideimide siloxane) from trimellitic anhydride chloride, oxylene diamine and oligo(dimethylsiloxane) diamine

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A novel poly(amideimide siloxane) block copolymer was prepared from oligo(dimethylsiloxane), trimellitic anhydride chloride and oxylene diamine using trimethylsilyl chloride as the reaction activator. Trimethylsilyl chloride enhanced the reactivity of oligo(dimethylsiloxane), resulting in a higher yield and viscosity of the product. The high reactivity of *N*-trimethylsilylated siloxane diamine stems from the silicon σ–π effect, and a nucleophilic addition–elimination reaction is proposed. The addition of a small amount of *N*-methylpyrrolidone in tetrahydrofuran led to a higher yield. The temperature of 10% weight loss for the product exceeded 355°C according to thermogravimetric analysis data. A transient change in the contact angle of water on the sample surface was observed, suggesting surface segregation of the hydrophobic component in the polymer.

(Keywords: poly(amideimide siloxane); block copolymer; addition–elimination)

INTRODUCTION

The advantages of siloxane-containing polymers include oxidative resistance, good biocompatibility, flexibility of the main chain and low surface energy[1]. The desired properties of siloxanes can be achieved *via* the controlled synthesis of block copolymers where the soft component is oligo(dimethylsiloxane) (ODMS). This approach has been widely used to produce siloxane-containing polystyrene[2], polyimide[3,4], polyamide[5,6], polysulfone[1,7], polyurethane[8] and so on. However, one of the difficulties in synthesizing these materials is the low reactivity of siloxane diamine compared to the aromatic diamines, resulting in a product of low yield and low molecular weight or viscosity. To overcome this problem, Oishi and coworkers[9,10] reported on the addition of trimethylsilyl chloride (TMSCl) to ODMS to activate the preparation of the aromatic polyamide. Later they reported on the preparation of polyamide multiblock copolymers composed of poly(dimethylsiloxane) (PDMS), aromatic acids and diamines[11].

Polyamideimide (PAI)[12] represents a family of compounds that are soluble in many organic solvents, while polyimide itself is seldom soluble in organic solvents when it is fully imidized unless it possesses a swivel moiety in the backbone[13]. PAI has been used to produce gas separation membranes[14] and several reverse osmosis membranes[15,16] because of its high temperature resistance and water selectivity. The siloxane-containing PAIs (SPAIs) are a family of compounds that possess both a rubbery hydrophobic component and a glassy component. Siloxane-containing polyamideimide is expected to have the solubility of polyamideimide and some of the desirable properties of ODMS such as processability, increased free volume, hydrophobicity, low moisture permeability, biocompatibility and so on. One of the desirable features of the incorporation of siloxane units is the expected increase in the separation capability of the base PAI as a membrane.

Recently, for multicomponent polymers such as siloxane-containing polyamides it was reported that surface segregation occurs as a result of the lower surface tension component being preferentially enriched on the surface[1,17]. For block copolymers of polystyrene with several polymers, Patel *et al.*[1] found via X-ray photoelectron spectroscopy (x.p.s.) that the lower surface tension component was segregated on the surface of a sample in contact with air, whereas dynamic contact angle measurements showed that the hydrophilic component was enriched on the block copolymer in water. The rearrangement of the polymer chain occurs according to the surface tension of the contact material, and the rate of rearrangement depends on the flexibility of the polymer chain. Therefore, when surface segregation and rearrangement of the polymer chain occur, a transient change in the surface structure is expected.

In this paper we report on the procedure for the preparation and characterization of SPAI. The role of TMSCl, the effects of solvents on the reaction system and the surface characteristics are also evaluated and

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Table 1 Effect of ODMS content on the yields and viscosities of the SPAIs

Sample	Molar ratio of monomers ODA : ODMS	ODMS content^a (mol%)	Yield (%) Without TMSCl	 With TMSCl	η_{inh}^{b} (dl g^{-1}) Without TMSCl	 With TMSCl
SPAI-1	9 : 1	13	64.8	86.3	0.19	0.45
SPAI-2	8 : 2	21	63.5	82.5	0.21	0.42
SPAI-3	7 : 3	32	48.5	75.2	0.25	0.41
SPAI-4	6 : 4	44	43.3	71.0	0.27	0.43

^{a} Calculated from n.m.r. spectra
^{b} Inherent viscosity

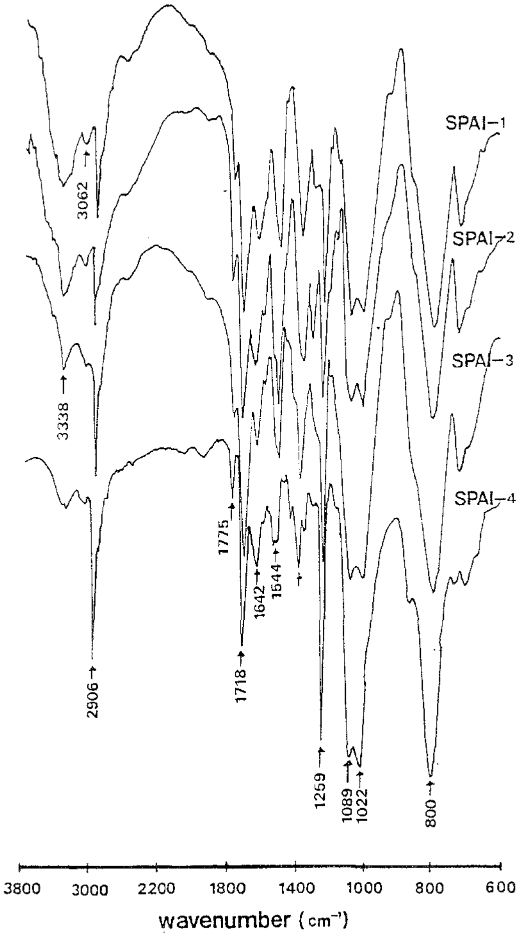


Figure 1 *FT*i.r. spectra of the SPAIs

discussed. Applications of this polymer will be reported shortly.

EXPERIMENTAL

Materials

Trimellitic anhydride chloride (TMAC, Tokyo Kasei) and 4,4′-oxylene diamine (ODA, Aldrich) were used as received. Oligo(dimethylsiloxane) (ODMS, molecular weight 860, ShinEstu) was used after drying at 110°C *in vacuo*. Tetrahydrofuran (THF, Duksan) was treated with molecular sieves several times before use. Trimethylsilyl chloride (TMSCl, Tokyo Kasei) was used as the reaction catalyst. Triethylamine (TEA, Sowha), n-hexane (Duksan) and methanol (Carlo Erba) were also used.

Methods of preparation

For the preparation of SPAI-1 (see *Table 1*), 0.9 g (1 mmol) ODMS, 2.4 g (9 mmol) ODA, 1.4 ml TEA in 15 ml THF, 1.05 g (4 mmol) TMAC and 1 ml TMSCl in 10 ml THF were mixed in a three-necked round-bottomed flask and stirred at room temperature for eight hours under a nitrogen atmosphere. Within an hour, the viscosity of the material in the reaction vessel had increased through the initial reaction between ODA and TMAC (ODA is more reactive than ODMS). At this stage about 5 ml *N*-methylpyrrolidone (NMP, Tedia) was added to facilitate the reaction with ODMS diamine. After the reaction, the mixture was precipitated in a mixture of n-hexane and methanol, and the precipitate was rinsed several times with acetone and methanol and dried at 50°C *in vacuo*.

Table 1 lists the samples we prepared with varying molar ratios of ODA and ODMS. The imidization was performed in steps for one hour each at 150, 200 and 230°C, respectively.

Characterization

The structures of the polymers were confirmed by Fourier transform infra-red (*FT*i.r., Nicolet Magna IR 550) and nuclear magnetic resonance (n.m.r., Varian Gemini 200, 200 MHz) spectroscopy. The solvent used for n.m.r. analysis was 99.5% d_6-dimethyl sulfoxide (d_6-DMSO, Aldrich). Thermogravimetric analysis (t.g.a., Du Pont 951) was used for the thermal decomposition studies with a heating rate of 10°C min^{-1} and a 50 ml min^{-1} nitrogen flow. Contact angle measurements were made using an Erma contact anglemeter (goniometer type G-1). Viscosity measurements were made using a Cannon–Fenske viscometer at 25°C with 0.5 g dl^{-1} polymer solutions in dimethylacetamide (DMAc). At least five measurements were made for each sample and the average value were taken.

RESULTS AND DISCUSSION

The *FT*i.r. spectra in *Figure 1* show the Si–O–Si stretching vibrations at 1089, 1022 and 800 cm^{-1} and a strong peak at 2906 cm^{-1} for the methyl group in ODMS. Characteristic imide peaks appear at 1775 and 1718 cm^{-1}, while the amide peaks appear at 1642 and 1544 cm^{-1}. The intensity of the imide peaks increased as the imidization reaction proceeded.

N.m.r. spectra (in d_6-DMSO) confirmed the incorporation of the siloxane block, as can be seen in *Figure 2*. The methyl group in the siloxane unit appears at 0.2–0.4 ppm and the peak intensity increases with the

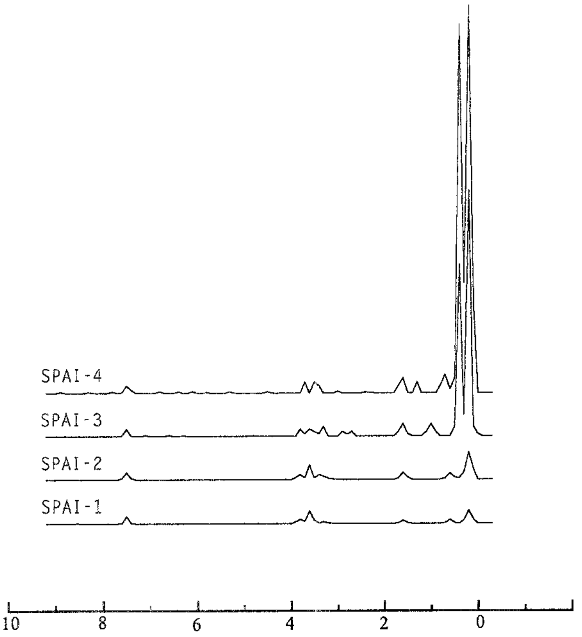


Figure 2 ^{1}H n.m.r. spectra of the SPAIs

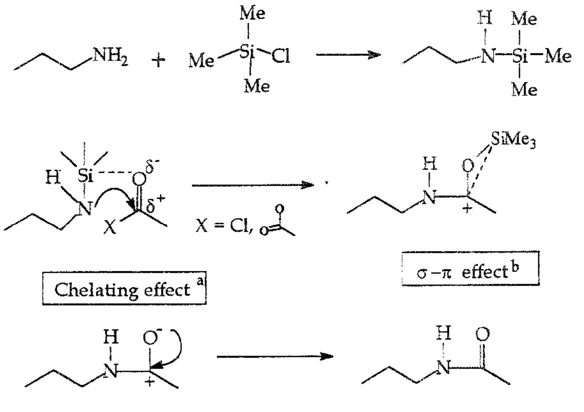
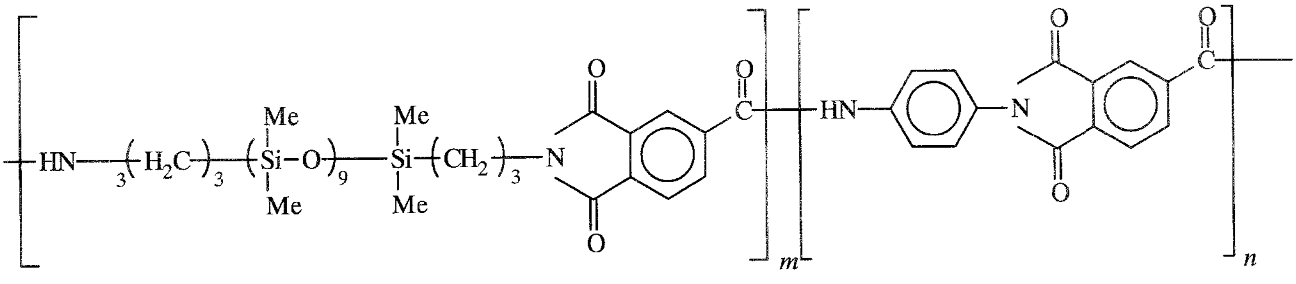


Figure 3 Effects of TMSCl on the formation of the amide linkage: (a) the silicon atom stabilizes the intermediate by bonding to the oxygen atom; (b) the *p*-orbitals of silicon stabilize the carbocation (σ–π effect)

ODMS content. We did not observe any prominent peaks relating to compounds resulting from possible side reactions.

Table 1 shows the effect of the ODMS content on the yields and inherent viscosities of the SPAIs. To evaluate the ODMS contents in the polymers, proton n.m.r. spectra were used. It was assumed that the ratio of the intensities of the proton peaks relating to the siloxane units and aromatic rings could be correlated with the molar ratio of these moieties. Therefore, the ODMS contents in the polymers according to the proton n.m.r. spectra could be obtained from the equation $Am/(Bm + Cn) = x/y$, where A, B and C denote the numbers of protons in the siloxane segment, the aromatic ring in repeat unit I and the aromatic ring in repeat unit II, respectively; m and n denote the molar percentages of repeat units I and II, respectively; and x and y represent the proton peak areas for the siloxane segments at 0.2–0.4 ppm and the aromatic rings at 7–8 ppm in the n.m.r. spectra, respectively. It was found that the calculated values from this equation are similar to the theoretical values from the feed monomer molar percentages.



repeat unit I

repeat unit II

As can be seen from *Table 1*, the reaction yield was about 43–65% without TMSCl in the reaction medium. However, when we used TMSCl as a reaction catalyst, the yield increased to 71–86%. The viscosity of SPAI without TMSCl ranged between 0.19 and 0.27 dl g^{-1}, while the addition of TMSCl to the preparation of SPAI increased the sample viscosity to 0.41–0.45 dl g^{-1}. This clearly proves the role of TMSCl in enhancing the reactivity of ODMS.

The high reactivity of *N*-trimethylsilylated ODMS diamine comes from the fact that the silicon in TMSCl has a strong affinity for oxygen; in addition, the carbocation on the β-position to the silicon can be stabilized through the silicon σ–π effect[18]. Considering these features, an addition–elimination mechanism is proposed for the nucleophilic acyl substitution of an acid chloride or anhydride with *N*-trimethylsilylated ODMS diamine, as illustrated in *Figure 3*.

In our previous study on the poly(dimethylsiloxane)–hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride) (PDMS–6FDA) system[19], the viscosities of the polymers were in the range 0.34–0.48 dl g^{-1}. These values and the viscosities of the present SPAIs are somewhat lower than the viscosities of typical polymers. The reason might be the substantial difference in the solubility parameters of ODA and ODMS segments.

Since the siloxane-segmented copolymer is formed using these monomers, it was advantageous to use THF as the solvent to dissolve ODMS. As the reaction proceeded further, the ODMS segments showed good solubility in THF, while the ODA segments did not, resulting in a rapid increase in the viscosity of the material and a translucent solution. This phenomenon has also been reported by Ikender *et al.*[20]. At this stage, the addition of a small amount of NMP led to an increase in the yield. NMP is thought to dissolve the

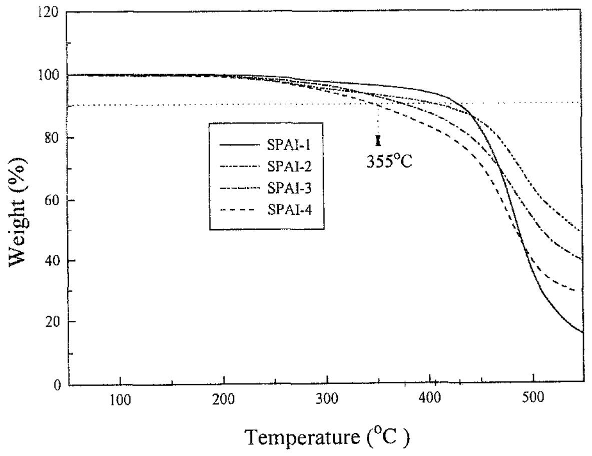


Figure 4 T.g.a. thermograms of the SPAIs

Table 2 Thermal decomposition temperatures of siloxane polyimides and polyamideimide

Sample	T_d[a] (°C)	Ref.
6FDA–PDMS/860[b]	467	20
PMDA–PDMS/860[c]	487	20
BTDA–PDMS/860[d]	479	20
SPAI-1	415	This study
SPAI-2	403	This study
SPAI-3	376	This study
SPAI-4	355	This study
Polyamideimide[e]	490	21
PMDA–SiDA[f]	265	22
BTDA–SiDA	338	22

[a] Temperature of 10% weight loss measured by t.g.a. in nitrogen
[b] 6FDA = hexafluoroisopropylidene-2,2-bis(phthalic acid anhydride), PDMS/860 = poly(dimethylsiloxane) (M_n = 860)
[c] PMDA = pyromellitic dianhydride
[d] BTDA = 3,3′,4,4′-benzophenonetetracarboxylic dianhydride
[e] Polyamideimide = oxydianiline–trimellitic acid anhydride (Torlon)
[f] SiDA = siloxane diamine

Table 3 Solubilities of SPAIs in various solvents

Solvent	SPAI-1	SPAI-2	SPAI-3	SPAI-4
DMF	VS[a]	VS	VS	VS
DMAc	VS	VS	VS	VS
DMSO	VS	VS	VS	VS
NMP	VS	VS	VS	VS
THF	I[b]	I	PS[c]	S[d]
Dioxane	I	I	I	I
Toluene	I	I	I	I
n-Hexane	I	I	I	I

[a] Very soluble
[b] Insoluble
[c] Partially soluble
[d] Soluble

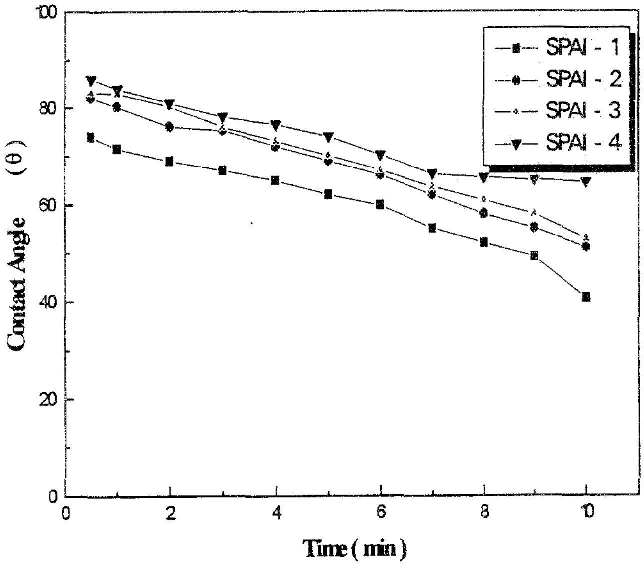


Figure 5 Transient contact angle measurements for the SPAIs

ODA segments during the polymerization stage and enhance the polymerization in a homogeneous medium. However, if typical solvents for the synthesis of aromatic polyamides and polyimides such as DMAc or dimethylformamide (DMF) and NMP were used instead of THF, the incorporation of the ODMS segments was not enhanced, as shown by n.m.r. studies.

SPAIs are thermoplastic segmented copolymers containing siloxane segments and amide groups along a non-processable backbone chain of a polyimide. It is expected that these SPAIs will have the high temperature stability of the polyimide and the processability of the siloxane through its solubility towards some mild solvents such as THF and hydrocarbons.

In *Figure 4*, the t.g.a. curves of the SPAI samples show that the 10% decomposition temperatures of all the samples are above or around 355°C. As the ODMS content increased in the sample, the residue content increased at high temperature because of the presence of silicones. *Table 2* compares the decomposition temperatures of some siloxane polyimides and polyamideimide. The SPAI samples are in the amorphous state according to the X-ray diffraction patterns (not shown here).

Table 3 shows the solubilities of the SPAIs. In general, poly(amideamic acid)s are soluble in polar solvents such as DMF, DMAc, DMSO, THF and methanol, but are only soluble in strongly polar aprotic solvents after imidization. From *Table 3*, the solubilities of SPAI-1 and SPAI-2 are similar to those of general polyamideimides, but SPAI-3 and SPAI-4 show solubility in THF, a mild solvent. In other words, the siloxane segments enhance the solubility of the SPAIs, and the solubility towards THF can be controlled by altering the siloxane content. From *Tables 2* and *3*, it is concluded that the thermal stability and processability can be manipulated by altering the siloxane content in the SPAI.

Recently, Patel *et al.*[1] reported that siloxane-containing polystyrene and polyamide show surface segregation through the preferential surface enrichment of the lower surface tension component. X.p.s. measurements showed the lower surface tension component to be segregated on the surface of a sample in contact with air, whereas dynamic contact angle measurements showed the hydrophilic component to be enriched on the block copolymer in water. The rearrangement of the polymer chain occurs according to the surface tension of the contacting material, and the rate of rearrangement depends on the flexibility of the polymer chain. Siloxane-containing PAIs possess both rubbery and glassy components or both hydrophobic siloxane segments and relatively hydrophilic amideimide bonds. Therefore, when surface segregation and rearrangement of the polymer chain occur, a transient change in the surface structure is expected.

Contact angle measurements[17] were conducted for SPAI samples and the results are illustrated in *Figure 5*. A water droplet was dropped onto the surface of a membrane prepared on top of a Teflon plate. Contact angle measurements showed that the initial contact angle immediately after dropping the water was for most samples above 80°, meaning that the surface was more or less hydrophobic. The contact angles were dependent on the ODMS content. However, a transient drop in contact angle was found for all the SPAI samples from around 80° to less than 60° (except SPAI-4) in 10 minutes. These facts suggest that the SPAI polymer is made of a siloxane-segmented copolymer where there is surface segregation of the hydrophobic siloxane components preferentially enriched on the film surface, and the hydrophilic polyamide or polyamideimide units may rearrange when in contact with water.

CONCLUSIONS

Siloxane-containing polyamideimides were prepared by reacting ODMS, TMAC and ODA using TMSCl as the reaction activator. TMSCl enhanced the reactivity of ODMS, resulting in higher yields and viscosities of the SPAI samples. The high reactivity of *N*-trimethylsilylated ODMS diamine comes from the silicon $\sigma-\pi$ effect, and a nucleophilic addition–elimination reaction was proposed. The reaction solvent was THF, and the addition of a small amount of NMP led to a higher yield of the product. The inherent viscosities of SPAIs ranged between 0.41 and 0.45 $\mathrm{dl\,g^{-1}}$. *FT*i.r. and n.m.r. spectra suggest the successful preparation of SPAIs. Thermal analysis of the SPAIs showed that the temperatures of 10% weight loss exceeded 360°C. Transient changes in the contact angles of water on the SPAIs were observed, indicating surface segregation of the segmented copolymer.

REFERENCES

1 Patel, N. M., Dwight, D. W., Hedrick, J. L., Webster, D. C. and McGrath, J. E. *Macromolecules* 1988, **21**, 2689
2 Tesoro, G. C., Rajedran, G. P., Uhlmann, D. R. and Park, C. E. *Ind. Eng. Chem. Rev.* 1987, **26**, 1672
3 Maudgal, S. and St Clair, T. L. *Int. J. Adhes. Adhes.* 1984, **4**, 87
4 Lee, Y. M. and Moon, Y. D. *J. Korean Ind. Eng. Chem. Soc.* 1991, **4**, 340
5 Kiyotsukuri, T., Tsutsumi, N. and Ayama, K. *J. Polym. Sci, Polym. Chem. Edn* 1987, **25**, 1591
6 Kajiyama, M., Kakimoto, M. and Imai, Y. *Macromolecules* 1989, **22**, 4143
7 Matzner, M., Noshay, A., Robinson, L. M., Merriam, C. N., Barclay Jr, R. and McGrath, J. E. *J. Appl. Polym. Symp.* 1973, **22**, 143
8 Kobmehl, G. and Neumann, W. *Makromol. Chem.* 1987, **188**, 93
9 Oishi, Y., Padmanaban, M., Kakimoto, M. and Imai, Y. *J. Polym. Sci., Polym. Chem. Edn* 1987, **25**, 3387
10 Oishi, Y., Kakimoto, M. and Imai, Y. *Macromolecules* 1988, **21**, 547
11 Oishi, Y., Kakimoto, M. and Imai, Y. *Macromolecules* 1988, **22**, 4143
12 Alvino, W. M. and Frost, L. W. *J. Polym. Sci. A-1* 1971, **9**, 2209
13 Becker, K. H. and Schmidt, H. *Macromolecules* 1992, **25**, 6784
14 Tsutsumi, N., Nishikawa, Y., Kiyotsukuri, T. and Nagata, M. *Polymer* 1994, **35**, 1268
15 Kawaguchi, T., Taketani, Y., Sasaki, N., Minematsu, H., Hayashi, Y. and Hara, S. *US Pat. 4 302 336*, 1981
16 McCray, S. B. *Eur. Pat. Appl. 308 153*, 1988
17 Kano, Y. and Akiyama, S. *Polymer* 1993, **34**, 376
18 Mark, J. E. in 'Silicon-Based Polymer Science' (Eds J. M. Ziegler and F. W. G. Fearon), Advances in Chemistry Series 224, American Chemical Society, Washington, DC, 1990, p. 47
19 Moon, Y. D. and Lee, Y. M. *J. Appl. Polym. Sci.* 1993, **50**, 1461
20 Ikender, Y., Ahmad, K. S., Warren Jr, P. S., Dinesh, T., Wilkes, G. L. and McGrath, J. E. *Polymer* 1984, **25**, 1800
21 Bolton, B. A. *Polym. Eng. Sci.* 1966, **6**, 2267
22 Ghadir, M., Zimonyi, E. and Nagy, J. *Angew. Makromol. Chem.* 1994, **214**, 123