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# Preparation and characterization of crosslinked polyimide–poly(dimethylsiloxane)s

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## Abstract

Crosslinked polyimide–poly(dimethylsiloxane)s with theoretical content of the siloxane phase up to 60 wt% were prepared. The starting materials were *p*-aminophenyltrimethoxysilane terminated polyamic acids with number average molecular weight of 10,000 g mol$^{-1}$, based on 4,4′-oxydiphthalic anhydride and 4,4′-oxydianiline and dimethoxydimethylsilane. The structure of the prepared polymeric materials was analyzed using $^{29}$Si and $^{13}$C NMR solid-state spectroscopy. Their thermal and mechanical properties, chemical resistance and density were evaluated. The influence of the basic catalysts employed (ammonium hydroxide) on the course of the reaction and properties of the materials was also studied. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Crosslinked polyimide–poly(dimethyl)siloxanes; $^{29}$Si and $^{13}$C solid state NMR spectroscopy; Siloxane phase

## 1. Introduction

Aromatic polyimides (PI) exhibit very good chemical, mechanical and dielectric stability at temperatures up to 200–250°C. They are mostly used in (micro)electronics, aviation industry, aerospace investigation and as polymeric separation membranes [1].

The range of PI application can be broadened by combining them with another polymer (e.g. by blending or copolymerization) [1]. Considerable attention in both theoretical and application fields has been devoted to polyimide–polysiloxane copolymers, especially to linear polyimide–poly(dimethylsiloxane)s (PI–PDMS) [2]. By incorporation of terminated siloxane oligomers into polyimide chains, random or block copolymers are formed. The final properties depend on both, the type of copolymer and/or its weight compopsition and the molecular weight of the components used. PI–PDMS show many properties of PI and, also, inter alia, higher solubility and impact strength, lower moisture absorption and lower dielectric constant. However, incorporation of PDMS reduces the thermal stability and modulus of the copolymers [2,3].

The overall stability of linear polymers can be improved by crosslinking. Furukawa [4] prepared block PI–PDMS with a low content of vinyl groups in the siloxane moieties, and 1,1,3,3-tetramethyldisiloxane or poly(hydroxymethylsiloxane) were used as crosslinking agents. The final products were insoluble and exhibited a higher thermal stability and a lower coefficient of thermal expansion in comparison with linear copolymers.

Preparation of PI crosslinked with short –Si–O–Si– chains is based on a polyimide precursor (polyamic acid (PAA)) terminated with *p*-aminophenyltrimethoxysilane (APTMS) [5]. During thermal exposition, the PAA is transformed to PI and hydrolyzed methoxy groups react mutually to form –Si–O–Si– crosslinks. To prepare polyimide–silica hybrid materials with covalently bound phases via a sol–gel process we previously used PAA of controlled molecular weight terminated with APTMS [6]. Tetramethoxysilane served as the silica precursor.

In the present work *p*-aminophenyltrimethoxysilane terminated PAA of controlled molecular weight and dimethoxydimethylsilane (precursor of poly(dimethylsiloxane) chains) are used to prepare crosslinked PI–PDMS. The final crosslinked products are formed as a result of thermal exposition of a thin layer of a mixture of polyimide and poly(dimethylsiloxane) precursors on a glass or Teflon substrate.

## 2. Experimental

4,4′-Oxydiphthalic anhydride (ODPA) (Chriskev),

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pyromellitic dianhydride (PMDA) and 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (both Aldrich) were heated to 180°C overnight in a vacuum before use. 4,4′-Oxydianiline (ODA) (Aldrich), *p*-aminophenyltrimethoxysilane (APTMS) and dimethoxydimethylsilane (DMDMS) (both ABCR) were used as received. *N*-Methyl-2-pyrrolidone (NMP) (Merck) was distilled under vacuum over phosphorus pentoxide and stored in an inert atmosphere.

Polyamic acids terminated with APTMS were prepared in a 250 ml two-necked flask equipped with a magnetic stirrer and a nitrogen inlet/outlet. A typical example of the synthesis of terminated PAA of this type (with theoretical number average molecular weight $M_n = 10,000\ \mathrm{g\ mol^{-1}}$) is as follows:

Five grams (0.01612 mol) ODPA was dissolved in 27 ml of NMP and 0.3677 g (0.00173 mol) of the terminating agent (APTMS) was added (the weighing dish + funnel was rinsed with 10 ml NMP) to the reaction mixture and allowed to react with ODPA for 2 h. 3.0566 g (0.01526 mol) ODA (10 ml NMP used for rinsing) was then added and the reaction was allowed to proceed at room temperature for 24 h.

The amount of the crosslinking agent (DMDMS) (calculated to reach the desired siloxane content) and the stoichiometric amount of water per methoxy groups were added directly to a 15 wt% solution of PAA in NMP under stirring. The heterogeneous mixtures became clear after mixing for tenths of minutes. The solutions were mixed for additional 24 h. In case of basic catalysts, pH of reaction mixtures was set to 8–9 by adding ammonium hydroxide.

The reaction mixture was spread onto a substrate and the resulting thin layer (tenths of millimetre thick) was kept at 60°C/24 h, 90°C/5 h, 150°C/2 h, 200°C/2 h and, finally, 240°C/2 h. The thickness of the resulting opaque films ranged from 30 to 50 μm.

NMR spectra were measured using Bruker DSX 200 NMR spectrometer at 39.75 and 50.33 MHz for $^{29}$Si and $^{13}$C, respectively. Samples were placed in a 4 mm $ZrO_2$ rotor. The number of data points was 6 K, magic angle spinning (MAS) frequency was 10–4 kHz, strength of the $B_1$ field ($^{29}$Si and $^{13}$C) was 62.5 KHz. The number of scans for accumulation of NMR spectra was 5000–30,000 to achieve a good signal-to-noise ratio. Ramped/cross-polarization/magic angle spinning (RAMP/CP/MAS) ($^{29}$Si) and Single pulse/magic angle spinning (SP/MAS) ($^{13}$C) experiments were used with relaxation delays of 4 and 20 s, respectively. The CP contact pulse was 2 ms. $^{29}$Si scale was calibrated by the external standard $M_8Q_8$ (−109.8 ppm; the highest field signal). $^{13}$C NMR spectra were externally referenced to glycine carbonyl signal at 176.03 ppm. Temperature of inlet air carrier was set to 30°C. The actual temperature of the sample due to the rotor friction was higher by about 14°C at 10 kHz MAS frequency [7].

Dynamic thermogravimetric measurements were performed in air with a DuPont 990 Thermal Analyzer, module 951 (heating rate 10°C). Dynamic mechanical analysis (DMA) was performed with a DMA DX04T (RMI, Bohdanec, Czech Republic) at 1 Hz, in temperature intervals from −120 to −80 and from 200 to 300°C with temperature gradient of 3°C min$^{-1}$ and in the interval from −80 to 200°C with gradient of 10°C min$^{-1}$. Tensile properties were measured with Instron 1122 at room temperature. The density of the prepared films was determined pycnometrically.

The chemical resistance of PI–PDMS in benzene, toluene, ethanol, methanol and NMP was tested as follows: a film was dried at 100°C for 3 h, weighed, and immersed into the appropriate solvent. After 30 days the relative weight change was determined.

## 3. Results and discussion

Polyamic acids of controlled molecular weight $M_n$ terminated with APTMS were used for the preparation of crosslinked PI–PDMS [6,8]. In the polymerization tests ODA was reacted in turn with PMDA [PAA(PMDA–ODA)] (Fig. 1(a)), ODPA [PAA(ODPA–ODA)] (Fig. 1(b)) and 6FDA [PAA(6FDA–ODA)] (Fig. 1(c)). We were not successful in the preparation of self-standing crosslinked PI–PDMS films based on PAA(PMDA–ODA) (probably due to PI(PMDA–ODA) chain rigidity) and PAA(6FDA–ODA) (probably due to incompatability of PI(6FDA–ODA) and PDMS) with $M_n = 5000–10,000\ \mathrm{g\ mol^{-1}}$. On the contrary, films based on PAA(ODPA–ODA) with $M_n = 10,000\ \mathrm{g\ mol^{-1}}$ were self-standing up to 60 wt% PDMS content. Films based on PAA(ODPA–ODA) with $M_n = 5000$ and $7500\ \mathrm{g\ mol^{-1}}$ were also self-standing but their mechanical properties were inferior to those with higher $M_n$. This work, therefore, deals only with crosslinked PI–PDMS based on PAA(ODPA–ODA) with $M_n = 10,000\ \mathrm{g\ mol^{-1}}$.

An amount of DMDMS (calculated to reach the respective final content of 20, 40, 50 and 60 wt% PDMS in the polymeric materials) and an equimolar amount of water per methoxy groups were added to a 15 wt% PAA solution and the mixture was stirred for 12 h. A thin layer (tenths of millimetre thick) was spread from this solution onto a glass or Teflon substrate. After drying at 60°C for 24 h, the film was heated by gradually increasing the temperature to 240°C, then kept at 240°C for 2 h. During thermal exposition PAA is transformed to PI (Fig. 2) and hydrolyzed alkoxy groups react mutually to form poly(dimethylsiloxane) chains

$$(CH_3)_2Si(OCH_3)_2 + 2H_2O = (CH_3)_2Si(OH)_2 + 2CH_3OH$$

$$(CH_3)_2Si(OH)_2 = H[-Si(CH_3)_2-O]_n-OH + (n-1)H_2O$$

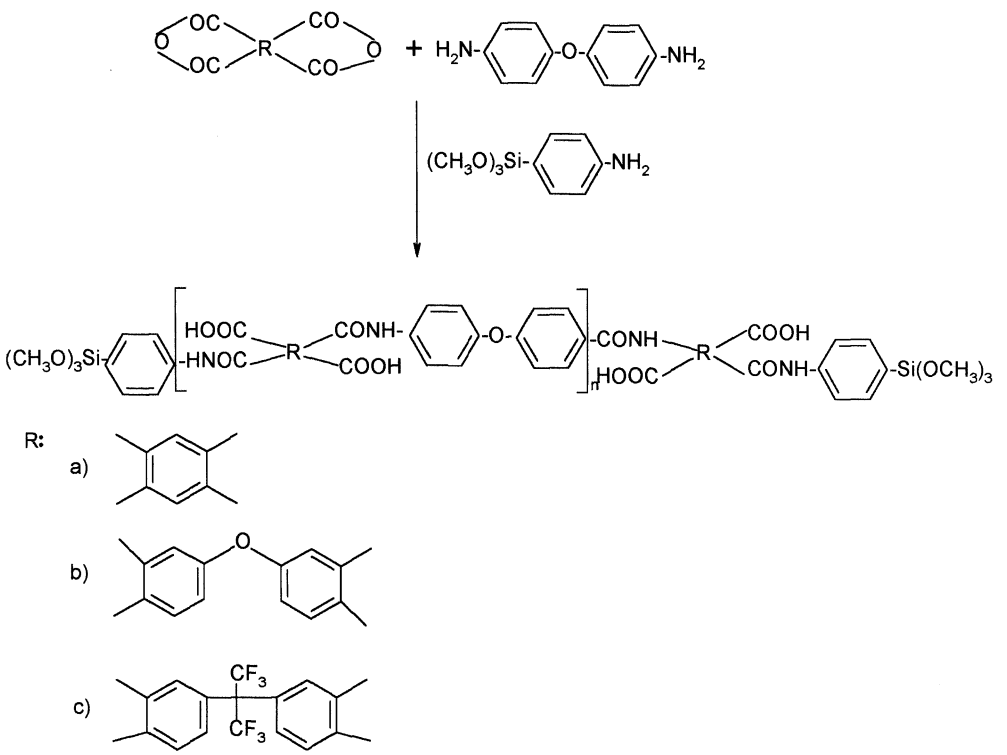

Fig. 1. Synthesis of *p*-aminophenyltrimethoxysilane terminated PAA based on: (a) PMDA and ODA, (b) ODPA and ODA, (c) 6FDA and ODA of controlled molecular weight.

Crosslinked PI–PDMS are formed due to the presence of alkoxy groups at the polymer chain ends (Fig. 3).

It is known from the literature [9] that hydrolysis of alkoxysilanes and subsequent condensation reactions as well as the structure of the final product can be influenced by catalysts (acidic, basic or organometallic compounds). We employed ammonium hydroxide that has the advantage of escaping from the materials during thermal exposition.

The structure of the prepared polymeric materials was studied using $^{29}$Si and $^{13}$C solid-state NMR spectroscopy. $^{29}$Si RAMP/CP/MAS and single pulse NMR spectra of samples PI–PDMS 80/20 (theoretically containing 80 and 20 wt% of PI and PDMS, respectively), PI–PDMS 50/50, $(\text{PI–PDMS})_{\text{cat}}$ 80/20 (i.e. PI–PDMS 80/20, prepared in the presence of a catalyst) and $(\text{PI–PDMS})_{\text{cat}}$ 50/50 are shown in Fig. 4(a)–(d). Two main regions of signals can be distinguished in the NMR spectra [10]. Weaker signals ranging from −70 to −90 ppm ($T^n$) correspond to the terminal structural units of polyimide chains originating from the terminating agent (APTMS). Stronger signals ranging from −5 to −30 ppm indicate and characterize the two-functional $D^n$ structure units of poly(dimethylsiloxane) chains.

The terminal structural units of PI, which are three-functional with respect to condensation reactions, give rise to two signals. The more intensive signal at about −80 ppm

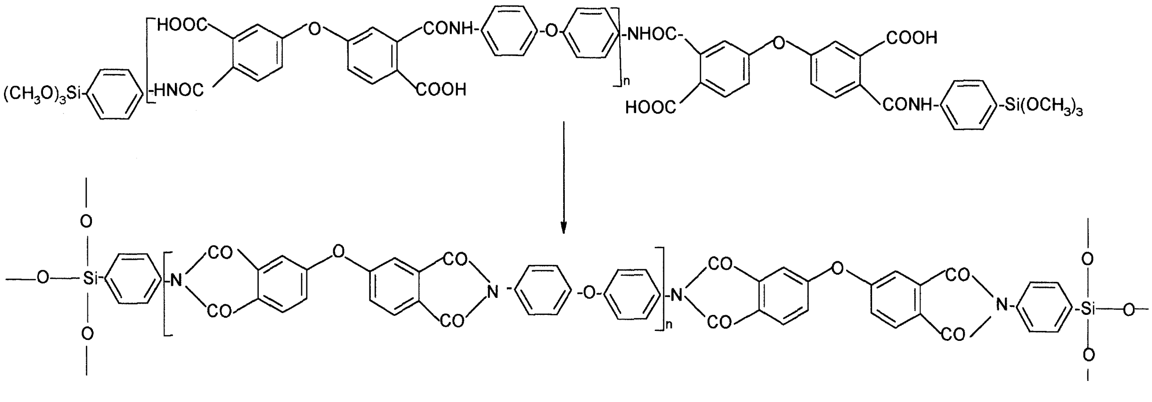

Fig. 2. Thermal transformation of *p*-aminophenyltrimethoxysilane terminated PAA(ODPA–ODA) to PI.

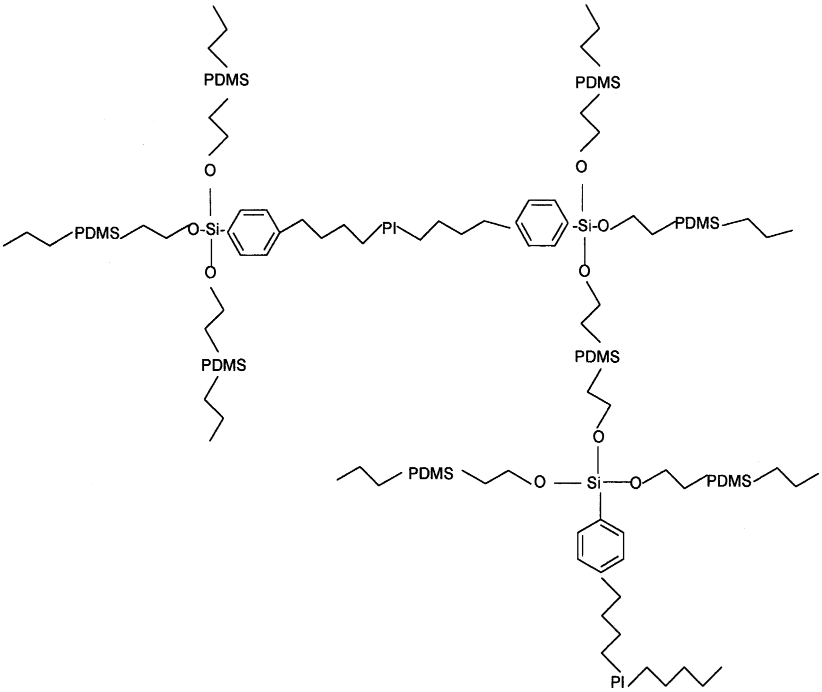

Fig. 3. Crosslinked PI–PDMS.

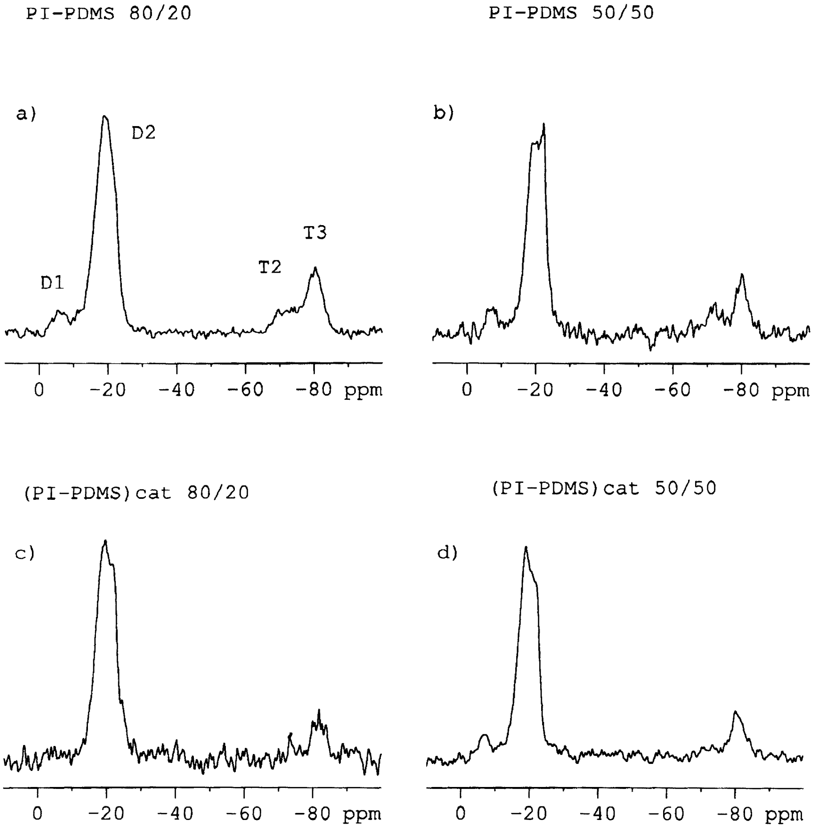

Fig. 4. $^{29}$Si RAMP/CP/MAS NMR spectra of PI–PDMS 80/20 (a), PI–PDMS 50/50 (b), (PI–PDMS)$_{\mathrm{cat}}$ 80/20 (c) and PI–PDMS (50/50)$_{\mathrm{cat}}$ (d).

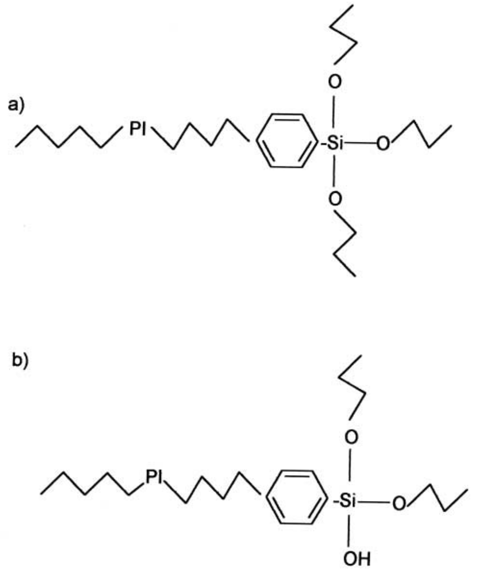

Fig. 5. (a) $T^3$, (b) $T^2$ structure unit.

indicates $T^3$ structure units in which all three hydroxyls take part in the reaction with the precursor of poly(dimethylsiloxane) chains. The other signal at about $-70$ ppm corresponds to the $T^2$ structure units containing one residual hydroxyl group (Fig. 5). The formation of a partially irregular polymer network, especially in products prepared by the uncatalyzed reaction (Fig. 4(a) and (b)), is apparent from the presence of the $T^2$ signal (the resulting network is not completely formed by three polysiloxane chains radiating from both ends of polyimide chain).

The presence of poly(dimethylsiloxane) chains in the products is indicated in $^{29}$Si NMR spectra by signals ranging from $-5$ to $-30$ ppm. The strong signal at about $-20$ ppm consists of several overlapping signals. The shorter poly(dimethylsiloxane) chains, namely those dimethylsiloxane structural units ($D^2$) close to the terminal units of the polyimide chains, give rise to the low-field shifted signal at about $-18$ ppm. Dimethylsiloxane structural units ($D^2$) in longer polysiloxane chains are reflected by signals at about $-22$ ppm [10,11]. The later signal is quite distinct in the spectrum of PI–PDMS 50/50 (Fig. 4(b)), but almost disappears in the spectrum of PI–PDMS 80/20 (Fig. 4(a)). The lower intensity of this signal in the spectrum of (PI–PDMS)$_{cat}$ 50/50 (Fig. 4(d)) indicates that shorter PDMS chains are formed in the reaction catalyzed by $NH_4OH$. The probable reason is that all active sites (terminal hydroxyls at the end of polyimide chains) take part in the base-catalyzed condensation reactions.

The increasing extent of the condensation reaction during the base-catalyzed reaction is also documented by the absence or reduced intensity of the signal at about $-10$ ppm in the spectra of (PI–PDMS)$_{cat}$ 80/20 and (PI–PDMS)$_{cat}$ 50/50 (Fig. 4(c,d)). This signal indicates the presence of terminal $D^1$ structural units of poly(dimethylsiloxane) chains $[-(Si(CH_3)_2-O)_n-R]$, not attached to the polymer network at both ends.

For the purpose of quantitative analysis of the prepared materials $^{13}$C SP/MAS NMR spectra with long repetition delay were measured for PI–PDMS and (PI–PDMS)$_{cat}$. The spectra of PI–PDMS 80/20, PI–PDMS 50/50, (PI–PDMS)$_{cat}$ 80/20 and (PI–PDMS)$_{cat}$ 50/50 are shown in Fig. 6(a)–(d). The signals with chemical shift between100 and 170 ppm correspond to aromatic and carbonyl carbon

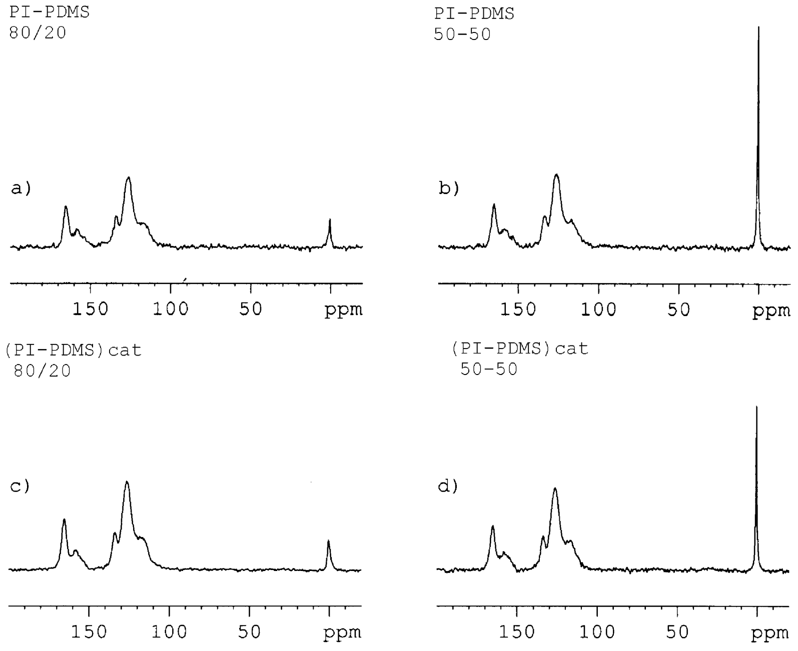

Fig. 6. $^{13}$C SP/MAS NMR spectra of PI–PDMS 80/20 (a), PI–PDMS 50/50 (b), (PI–PDMS)$_{cat}$ 80/20 (c) and PI–PDMS (50/50)$_{cat}$ (d).

Table 1
Content and molecular weight of PDMS in crosslinked PI–PDMS

| | PDMS content (wt%) | | $M_n$ PDMS[a] (g mol$^{-1}$) | |
|---|---|---|---|---|
| | Theor. | Exper.[b] | Theor. | Exper. |
| PI–PDMS 80/20 | 20 | 10 | 830 | 340 |
| PI–PDMS 60/40 | 40 | 22 | 2220 | 950 |
| PI–PDMS 50/50 | 50 | 31 | 3330 | 1500 |
| PI–PDMS 40/60 | 60 | 30 | 5000 | 1480 |
| (PI–PDMS)$_{cat}$ 80/20 | 20 | 10 | 830 | 340 |
| (PI–PDMS)$_{cat}$ 60/40 | 40 | 21 | 2200 | 900 |
| (PI–PDMS)$_{cat}$ 50/50 | 50 | 22 | 3330 | 940 |
| (PI–PDMS)$_{cat}$ 40/60 | 60 | 28 | 5000 | 1330 |

[a] With assumption of equal reactivity and participation of all terminal hydroxy groups.

[b] By $^{13}$C NMR.

atoms in the polyimide chain, while the presence of methyls in PDMS is indicated by the signal at around 0 ppm [12,13]. The theoretical and experimental values of $M_n$ are summarized in Table 1. They were calculated assuming equal reactivity and participation of all terminal hydroxy groups in the resulting polymer network.

A lower content of PDMS in comparison with theoretical predictions may be explained by DMDMS and low-molecular-weight oligomers escaping before the formation of higher-molecular-weight oligomers. Note that the values of $M_n$ of PDMS in materials prepared by the base-catalyzed polymerization are lower compared with $M_n$ of PDMS prepared by the uncatalyzed process. The differences in $M_n$ correspond very well with the reaction mechanism of uncatalyzed and base-catalyzed polycondensation of DMDMS. Although the base-catalyzed condensation reactions are fast, the hydrolysis of alkoxy groups is slow under these conditions [13,14]. This then means that a large portion of monomer remains in the reaction mixture for a long time. During this period a part of the monomer may escape at elevated temperatures. Contrary to the base-catalyzed reaction, a different situation is encountered in the case of uncatalyzed or acid-catalyzed process. Although condensation reactions are slower compared with the base-catalyzed process, hydrolysis and the formation of higher-molecular-weight oligomers is fast [15]. Accordingly, a lower amount of monomer may escape during the latter process.

The temperature corresponding to a 10 wt% weight loss in the course of thermooxidative degradation decreased with increasing content of PDMS (Table 2). All materials showed no weight loss up to 350°C. It also means that the final temperature of 240°C is sufficient for the transformation of DMDMS to PDMS. Ioku et al. [12] reported the temperature of 10 wt% loss of 535°C (10°C min$^{-1}$, in air) for PI based on PMDA and ODA with uncontrolled molecular weight containing 30 wt% of unbound poly(dimethylsiloxane) (prepared from dimethyldiethoxysilane).

PI–PDMS with a higher PDMS content exhibit two glass transition temperatures ($T_g$). The glass transition temperature at $-119$ to $-117$°C corresponds to PDMS, the higher $T_g$ at 255–269°C corresponds to PI. The higher $T_g$ is shifted to lower temperatures in comparison with $T_g$ of PI–PDMS 100/0 (prepared from PAA terminated with APTMS without adding DMDMS). The value of $T_g = 265$°C has been reported for PI(ODPA–ODA) without molecular weight control [1].

The tensile strength of the PI–PDMS decreased with increasing PDMS content (Table 2) and the elongation at break increased from 5 to 20%. The density also decreased with increasing PDMS content (Table 2).

Resistance of these materials to selected solvents (NMP, toluene, benzene, ethanol, methanol) was evaluated by the weight change after immersion for 30 days into the respective media. The lowest weight change was found in benzene (max. +1.5 wt%) (regardless of composition) and the highest weight change was found in methanol (+10.8 wt%) and ethanol (+13.2 wt%) for PI–PDMS 40/60 and (PI–PDMS)$_{cat}$ 40/60.

A detailed study of molecular dynamics and morphology of these polymeric materials is to be published.

Table 2
Properties of crosslinked PI–PDMS

| | $T^a$ (°C) | $T_g^b$ (°C) | | Strength (MPa) | Density (g cm$^{-3}$) |
|---|---|---|---|---|---|
| PI–PDMS 100/0 | 582 | – | 290[c] | 127 | – |
| PI–PDMS 80/20 | 578 | – | 269 | 96 | 1,35 |
| PI–PDMS 60/40 | 558 | −117 | 268 | 80 | 1,25 |
| PI–PDMS 50/50 | 486 | −117 | 255 | 67 | 1,23 |
| PI–PDMS 40/60 | 428 | −119 | 260 | – | – |
| (PI–PDMS)$_{cat}$80/20 | 576 | – | 263 | 98 | 1,34 |
| (PI–PDMS)$_{cat}$60/40 | 558 | – | 265 | 86 | 1,30 |
| (PI–PDMS)$_{cat}$50/50 | 522 | −118 | 264 | 84 | 1,26 |
| (PI–PDMS)$_{cat}$ 40/60 | 502 | −117 | 265 | – | 1,23 |

[a] Temperature corresponding to10 wt% loss.

[b] By DMA.

[c] Higher $T_g$.

## 4. Conclusion

The crosslinked PI–PDMS with theoretical content of the siloxane phase of up to 60 wt%, prepared from PAA(ODPA–ODA) of controlled molecular weight ($M_n = 10,000\ \mathrm{g\ mol^{-1}}$) terminated with APTMS and DMDMS, provide opaque self-standing films. PI–PDMS with a higher PDMS content exhibit two $T_g$.

A smaller PDMS weight content in comparison with theoretical expectations was determined in all of the analyzed products. The length of PDMS chains increases with increasing content of the siloxane phase in the resulting materials. In the reaction catalyzed by $NH_4OH$ the more regular network and shorter PDMS chains in comparison with the uncatalyzed reaction are formed.

The thermooxidative stability and tensile strength of the PI–PDMS decrease with increasing content of PDMS.

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