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Synthesis and Properties of Hyperbranched Polyimides Combined with Silica

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Summary: The novel hyperbranched polyimide - silica hybrid materials containing theoretically 16 wt% of an inorganic phase were prepared via a sol-gel process. An amine terminated polyimide precursor (hyperbranched polyamic acid) was prepared from commercially available monomers 4,4′,4″-triaminotriphenylmethane and 4,4′-oxydiphthalic anhydride in molar ratio 1:1. Tetramethoxysilane and/or 3-glycidoxypropyltrimethoxysilane (also used as a coupling agent) were used as silica precursors. During thermal exposition the polyimide precursor was transformed to hyperbranched polyimide and hydrolyzed alkoxy groups reacted mutually to form silica. The final products were self-standing films, whose structure was characterized by using IR and ^{13}C and ^{29}Si solid state NMR spectroscopy. The influence of the amount of silica and/or coupling agent on their structure and thermal properties was described.

Keywords: ^{13}C and ^{29}Si solid state NMR spectroscopy; hyperbranched polyimides; silica; sol-gel process; thermal properties

Introduction

Linear aromatic polyimides have become one of the most important class of high-performance polymers. Due to their excellent thermal, mechanical and dielectric properties, they have found many applications in (micro)electronics, aircraft industry and as membranes for separation technologies.[1] Hyperbranched polyimides (HBPI), having highly branched structure and large number of terminal groups, have attracted an increasing attention in recent years because they are expected to have unique pro-perties when compared to their linear analogues.[2] The range of polyimide properties and also applications can be broadened by their combining with another material. Of special interest are polyimide – silica hybrid materials prepared via a sol-gel process for their overall stability and a low coefficient of thermal expansion and water sorption.[3,4]

In this work, the preparation, structure and some properties of the series of HBPI - silica hybrid materials, whose polyimide moieties are based on the commercially available 4,4′,4″-triaminotriphenylmethane and 4,4′-oxydiphthalic anhydride, are studied.

Experimental Part

An amine terminated hyperbranched polyimide precursor (hyperbranched polyamic acid (HBPAA)) was prepared from 4,4′,4″-triaminotriphenylmethane (MTA) (Dayang Chemicals, China) and 4,4′-oxydiphthalic anhydride (ODPA) (Aldrich, Czech Republic) in molar ratio of monomer molecules 1:1 at room temperature. The concentration of solids in 1-methyl-2-pyrrolidone (NMP) (Merck, Czech Republic), used as a solvent, was 4 wt%.[5] A portion of this precursor was end-capped with 3-glycidoxypropyltrimethoxysilane (GPTMS) (Aldrich). A desired amount of GPTMS was added directly to a 4 wt%

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solution of HBPAA in NMP and the reaction was allowed to proceed at room temperature for 24 h.

A mixture of the HBPAA (modified or unmodified with GPTMS) with a calculated amount of the silica precursor (tetramethoxysilane (TMOS) (Aldrich)) and water (1 mol per 1 mol of methoxy groups) was stirred for 24 h at room temperature. Then it was spread onto a substrate and heat at gradually increased temperature, finally at 250 °C for 1 h. The thickness of the self-standing films obtained was about 50 μm.

IR spectra were recorded on a Nicolet 740 spectrometer. Solid-state NMR spectra were measured using Bruker AVANCE 500 US/WBNMR spectrometer at 99 and 125 MHz for ^{29}Si and ^{13}C, respectively. Dynamic thermogravimetric measurements were performed in air using a Du Pont 990 Thermal Analyzer, module 951 (heating rate 10 °C min^{-1}) . Dynamic mechanical analysis (DMA) was performed using a DMA DX 04T (RMI, Bohdanec, Czech Republic) at 1 Hz in the temperature interval from 25 to 450 °C and with temperature gradient of 3 °C min^{-1}.

Results and Discussion

Three hyperbranched polyimides – silica hybrid materials varying in their composition were prepared in this work and their properties were compared with those for the pure HBPI.

The HBPI and the polyimide moieties of the hybrids were based on the trifunctional amine MTA and bifunctional anhydride ODPA (Figure 1). The formation of the three-dimensional structure during the preparation of polyimide precursor (HBPAA) was suppressed by the slow dropwise addition of a dilute solution of one monomer to a solution of the other. The intrinsic viscosity of this HBPAA was 16 ml g^{-1}. [5] The molar amount of the tri- and bifunctional monomers used in the preparation of HBPAA influences the kind and ratio of terminal groups. The monomer ratio 1:1 (i.e. amino:anhydride groups = 3:2) was used in this work and so the amine end-capped HBPAA was formed.

TMOS and GPTMS were used as the silica precursors. Due to the existence of two types of functional groups (epoxy and alkoxy) in its molecule GPTMS also served

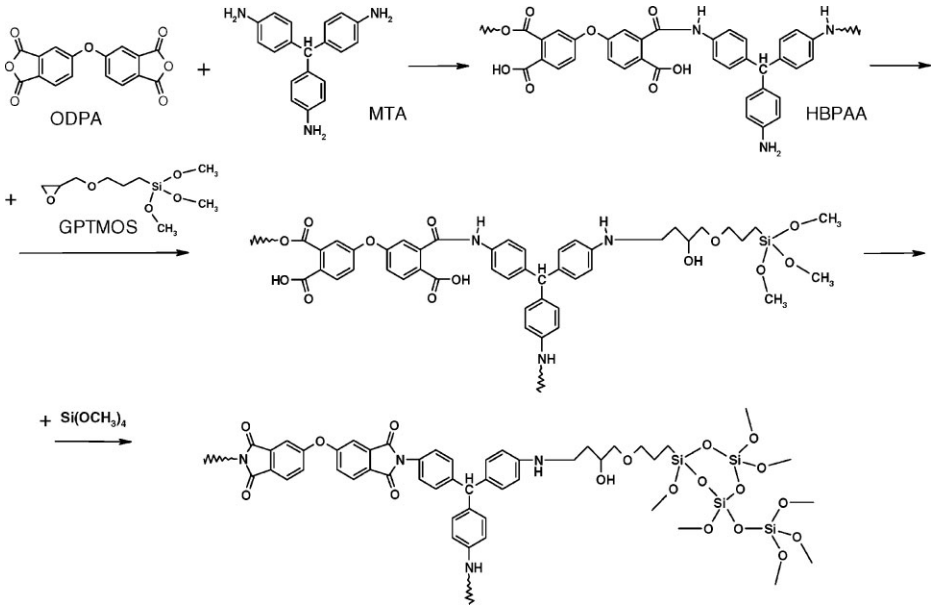

Figure 1.
Synthesis of the hyperbranched polyimide-silica hybrid material.

as a coupling agent linking up polyimide and silica phases of the final hybrid materials (Figure 1). By using a defined amount of GPTMS, the number of the active hydrogen atoms of terminating amino groups taken into the reaction with epoxy groups of GPTMS is controlled.

The first hyperbranched polyimide – silica hybrid material was based on the above specified HBPAA whose all hydrogen atoms of amino groups were reacted with GPTMS. The theoretical content of silica in this final hybrid was 16 wt% (designation: HBPI(GPTMS)). To compare the properties of all materials, other samples also contained the same amount of silica (i.e. 16 wt%). The main difference was in the source of silica phase. The inorganic portion of the second sample was equivalently created from the GPTMS and TMOS (HBPI(GPTMS/TMOS)) and of the third one from the TMOS (HBPI(TMOS)) only. During thermal exposition the polyimide precursor was transformed to hyperbranched polyimide and hydrolyzed alkoxy groups react mutually to form silica (Figure 1).

The obtained materials were analyzed by IR spectroscopy. The IR spectra of the hyperbranched polyimide precursor, pure HBPI and three hybrid materials are shown in Figure 2.

The characteristic absorption bands of the imide group are observed at about 1780 and 1720 cm^{-1} (symmetric and asymmetric stretching of the ring carbonyl groups) and

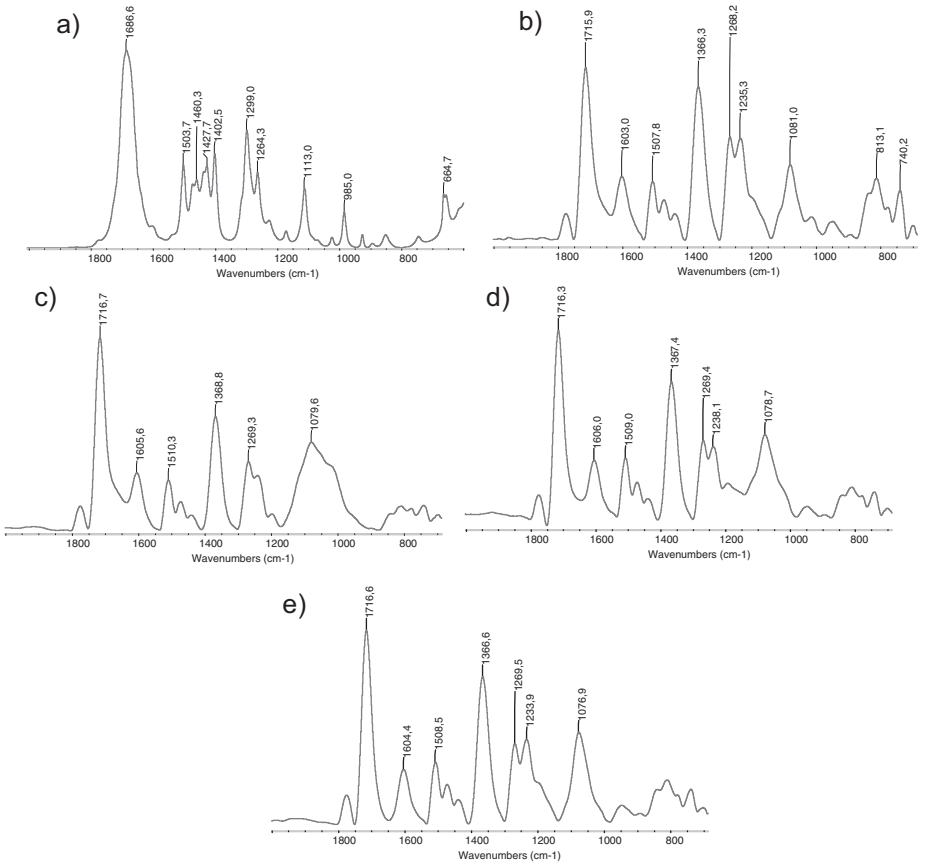

Figure 2.
IR spectra of (a) HBPAA based on MTA and ODPA, (b) HBPI, (c) HBPI(GPTMS), (d) HBPI(GPTMS/TMOS), (e) HBPI(TMOS).

1370 cm^{-1} (stretching of the ring C–N bond). The absorption band at about 1670 cm^{-1} corresponding to the amide bond of the polyamic acid completely disappeared in the spectra of the polyimide and hybrid materials, which indicate the nearly full imidization. The major difference between the spectra of hybrids and HBPI is the existence of the broad absorption band with the maximum at about 1100 cm^{-1} characterizing Si-O-Si linkages.

For the purpose of semiquantitative analysis of the prepared hybrid materials (i.e. HBPI(GPTMS), HBPI(GPTMS/TMOS) and HBPI(TMOS)) ^{13}C and ^{29}Si solid state NMR spectra were measured. In the ^{13}C NMR spectra, the signals with chemical shift between about 100 and 170 ppm correspond to the aromatic and carbonyl carbon atoms in polyimide chains, respectively. In the case where the GPTMS was used, the signals in the region 8-70 ppm appeared in the record belonging to its methylene groups (see the ^{13}C NMR spectrum of the HBPI(GPTMS/TMOS) in Figure 3).

In the ^{29}Si NMR spectra (Figure 4) the signals originating from the GPTMS and/or TMOS are present (Figure 5). The range from −45 to −70 ppm corresponds to signals belonging to GPTMS. The broad signal ranging from −45 to −50 ppm reflects T^1 structure units with two unreacted hydroxyl groups, signal from −50 to −60 ppm T^2 and signal from −60 to −70 ppm T^3 units. The signal range from −85 to −120 ppm corresponds to the signals of the structure units of TMOS. The signal from −85 to −95 ppm indicates Q^2 with two hydroxyl groups condensed, the signal from −95 to −105 ppm Q^3 and from −105 to −115 ppm Q^4 units.[6] From the quantified ^{29}Si NMR spectra (Figure 4), it results the higher degree of silanol groups of GPTMS in their condensation in the TMOS presence (about 77% for HBPI(GPTMS) and 86% for HBPI-(GPTMS/TMOS)). The contribution of TMOS to the inorganic portion of the hybrids is given predominately by the units with three alkoxy groups (Q^3) connected into a partially irregular silica network, i.e. a conversion degree of the TMOS silanol groups is about 75%.

The glass transition temperatures of the pure HBPI, HBPI(GPTMS), HBPI-(GPTMS/TMOS) and HBPI(TMOS) are 377, 350, 372 and 377 °C, respectively.

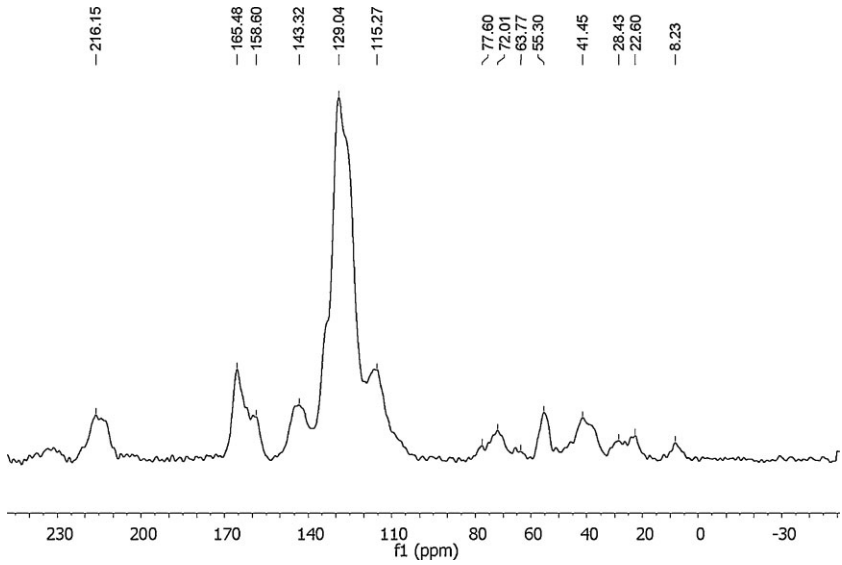

Figure 3.
^{13}C NMR spectrum of HBPI(GPTMS/TMOS).

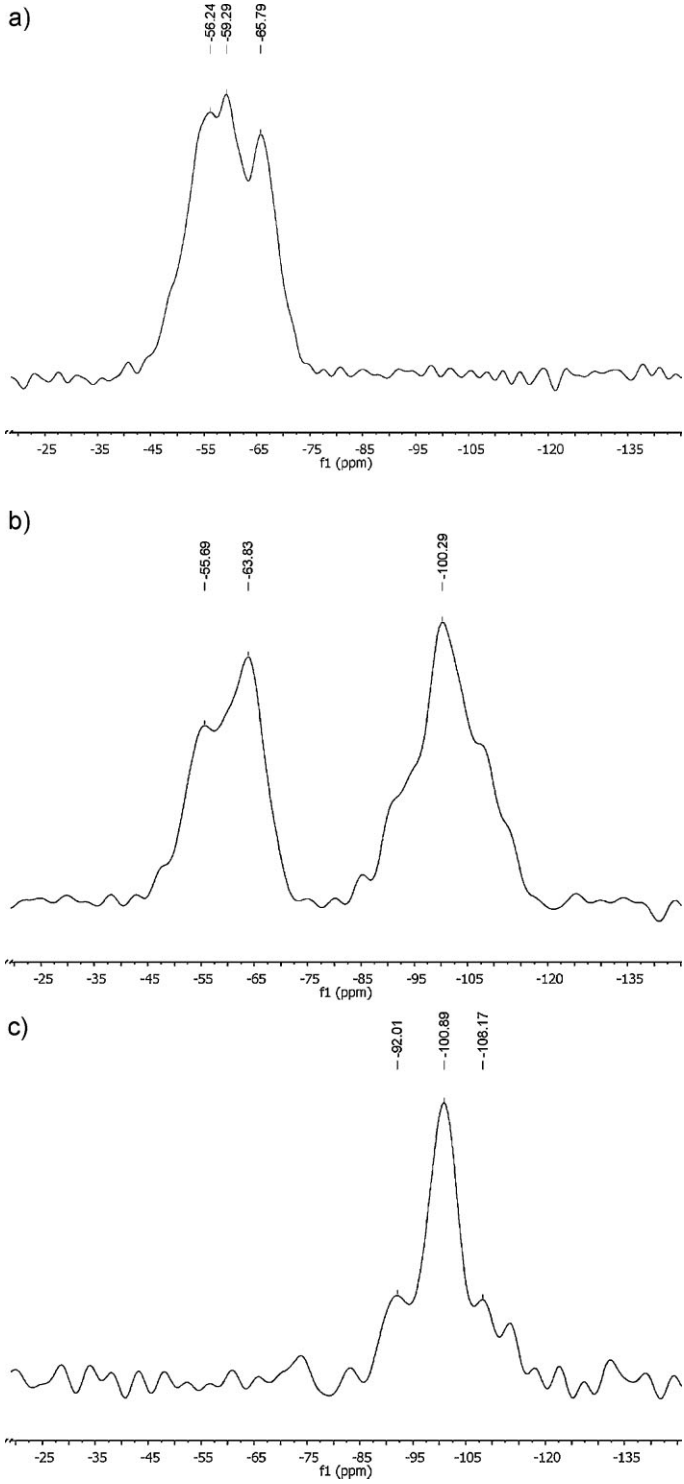

Figure 4.
^{29}Si NMR spectra of (a) HBPI(GPTMS), (b) HBPI(GPTMS/TMOS), (c) HBPI(TMOS).

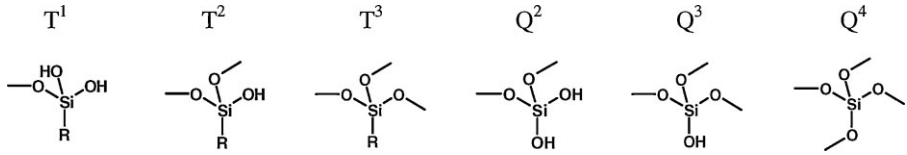

Figure 5.
Basic structure units of the inorganic phase.

The presence of GPTMS moieties also influences a thermooxidative stability of the hybrids. This property was evaluated as the temperature corresponding to the 10 wt% weight loss during a thermooxidative attack (564, 440, 568 and 590 °C for the pure HBPI, HBPI(GPTMS), HBPI(GPTMS/TMOS) and HBPI(TMOS), respectively). From this analysis it follows that the average amount of silica in the final hybrid materials is about of 12 wt%. These lower and comparable values (levels) for the hybrids in comparison with those for the pure HBPI can have a reason in the flexible aliphatic moiety of GPTMS and/or loosening of the molecular packing of HBPI chains at this rather low silica level (16 wt%). GPTMS bound onto HBPI probably makes the growth and compact arrangement of silica in the hybrids more difficult. In harmony with this, the silica particles are not distinct sufficiently in the HBPI(GPTMS) scanning electron microscopy (SEM) photograph. On the contrary, the spherical silica particles with a diameter of 0.2–0.6 μm are obvious in the HBPI(GPTMS/TMOS) and HBPI(TMOS) photographs. It was also shown that the type of end-groups and the course of imidization procedure can influence both T_g and thermooxidative stability of HBPI.[5]

Conclusion

The HBPI(ODPA-MTA) – silica hybrid materials with the theoretical inorganic phase content of 16 wt% were prepared via a sol-gel process. The irregular silica network is formed (a condensation degree of the silanol groups about 75–85%) probably due to the use of an unsufficiently high temperature of thermal exposition (finally 250 °C for 1 h with respect for the HBPI thermal stability). The presence of the GPTMS moieties in the hybrids makes the growth of compact silica particles more difficult and decreases their thermal properties (T_g and thermooxidative stability) in comparison with the hybrids whose silica phase is based on TMOS only.

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