e-Polymers **2009**, no. 081

http://www.e-polymers.org

ISSN 1618-7229

Preparation and characterization of hyperbranched polyimides based on 4,4',4''-triaminotriphenyl-methane

Petr Sysel,[*] *Evgenia Minko, Radana Čechová*

[*]Department of Polymers, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic; fax: +420220443175; e-mail: Petr.Sysel@vscht.cz

(Received: 19 September, 2008; published: 21 June, 2009)

Abstract: This work focuses on the preparation and characterization of novel hyperbranched polyimides based on commercially available 4,4,'4''-triaminotriphenylmethane and pyromellitic dianhydride or 4,4'-oxydiphthalic anhydride. The bi- and trifunctional monomers were reacted in a molar ratio of 1:1 or 2:1 to prepare polyimide precursors (hyperbranched polyamic acids) end-capped with either amino or anhydride groups. The precursors were then transformed into hyperbranched polyimides using thermal imidization. The final products were self-standing films, whose thermal behaviour was characterized by having no weight loss up to 250 ºC and by having glass transition temperatures above 200 ºC. We monitored the permeability of carbon dioxide, organic vapours and water vapour through these membranes. We also compared the properties of these materials with linear polyimides based on 4,4'-methylenedianiline combined with either pyromellitic dianhydride or 4,4'-oxydiphthalic anhydride.
Key Words: hyperbranched polyimides, 4,4,'4''-triaminotriphenylmethane

Introduction

Aromatic polyimides are an important class of high performance polymers. Linear and crosslinked aromatic polyimides exhibit excellent chemical, mechanical and dielectric stability, even at elevated temperatures up to 250 ºC. They are mostly used in the (micro) electronics and aircraft industries, as well as in space exploration and polymeric separation technologies [1]. In the last decade various authors have considered how hyperbranched polyimides (HBPI) might be used to extend the application of this type of polymeric material [2-6].

In the field of synthetic polymers dendritic topology has become recognized as a new class of macromolecular architecture alongside the traditional linear, branch and crosslinked structures. Dendritic polymers can be organized as highly symmetrical dendrimers or as irregular hyperbranched polymers. The main disadvantage of dendrimers is that their preparation requires use of a multistep procedure, whereas hyperbranched polymers can be prepared by the direct one-step polymerization of multifunctional monomers. Consequently, such polymers show great potential for use in a wide range of industrial applications (e.g. drug delivery, coatings) [7].

Because polyimides are insoluble in most common solvents and generally have high glass transition temperatures (approximately 200 ºC and above), they are mostly processed in the form of their precursor – polyamic acid (PAA) [1]. The synthesis of a linear polyamic acid (LPAA) consists of the reaction of an aromatic diamine with an aromatic dianhydride in an aprotic polar solvent (e.g. N-methyl-2-pyrrolidone (NMP)).

The final product, linear polyimide (LPI), is often prepared by thermal solid-state imidization of the LPAA (Fig. 1).

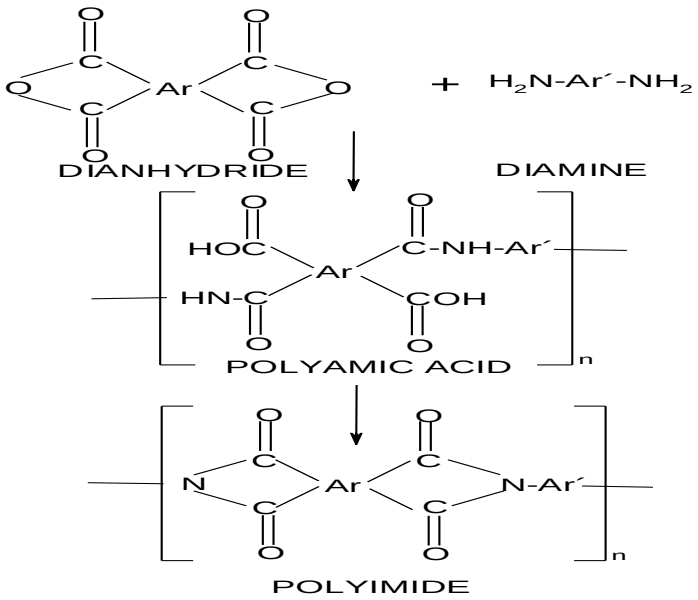

Fig. 1. Two-step preparation of polyimides.

One route to the creation of hyperbranched polymers involves the step-growth polymerization of an AB_x monomer; A and B representing two kinds of functional groups that can react with each other, but cannot undergo a self-reaction, $x \geq 2$ [8]. However, it is difficult to obtain some AB_x monomers, e.g. for the preparation of HBPIs [2]. Although the A_2 (bifunctional monomer) + B_3 (trifunctional monomer) methodology can be used to solve this problem [2-8], it is known that direct polymerization of $A_2 + B_x$ ($x \geq 2$) monomers generally results in a three-dimensional end product [9,10]. Besides, suitable trifunctional monomers (anhydrides, amines) are not almost commercially available.

In this study we prepare and characterize novel HBPIs based on commercially available 4,4,'4''-triaminotriphenylmethane combined with either pyromellitic anhydride or 4,4'-oxydiphthalic anhydride. We describe the optimum reaction conditions required to avoid gel formation. We show how the properties of HBPIs are dependent on their composition, and compare them with the properties of LPIs based on 4,4'-methylenedianiline combined with either pyromellitic dianhydride or 4,4'-oxydiphthalic anhydride.

Results and discussion

HBPIs are often prepared using a combination of monomers of the A_2 and B_3 types. Laboratory synthesized triamines and trianhydrides with a relatively complex structure have typically been used for this purpose [2, 5]. However, if the production of HBPIs is to be shifted from the laboratory scale to the industrial scale, monomers will need to be commercially available, and, currently, almost no suitable aromatic trianhydrides and triamines can be found on the market.

In previous studies, in which we used commercially available 2,4,6-triaminopyrimidine as a B_3 monomer [12,13], our results supported the idea that the reactivity of the amino groups of 2,4,6- triaminopyrimidine is different in position 2

compared with either position 4 or 6 [14]. Consequently, it is possible to consider the formation of an irregular hyperbranched polymer structure with a relatively low number of triaminopyrimidine units simultaneously connected in positions 2, 4 and 6.

Therefore, the B_3 monomer used in this study was commercially available 4,4',4''-triaminotriphenylmethane (MTA) (Fig. 2a), whose three amino groups are equivalent. Pyromellitic dianhydride (PMDA) (Fig. 2b) and 4,4'-oxydiphthalic anhydride (ODPA) (Fig. 2c) were used as the A_2 monomers. The polyimides prepared from PMDA and ODPA (together with the same diamine) were found to have quite different glass transition temperatures (T_g) [15]. The flexible ether bridge in the ODPA molecule can favourably influence the preparation of HBPI self-standing films.

The preparation and properties of our HBPIs were compared with those of LPIs based on 4,4'- methylenedianiline (MDA) (Fig. 2d) combined with either PMDA in a molar ratio of 1:1 [LPI(PMDA-MDA)11] or ODPA in a molar ratio of 1:1 [LPI(ODPA-MDA)11].

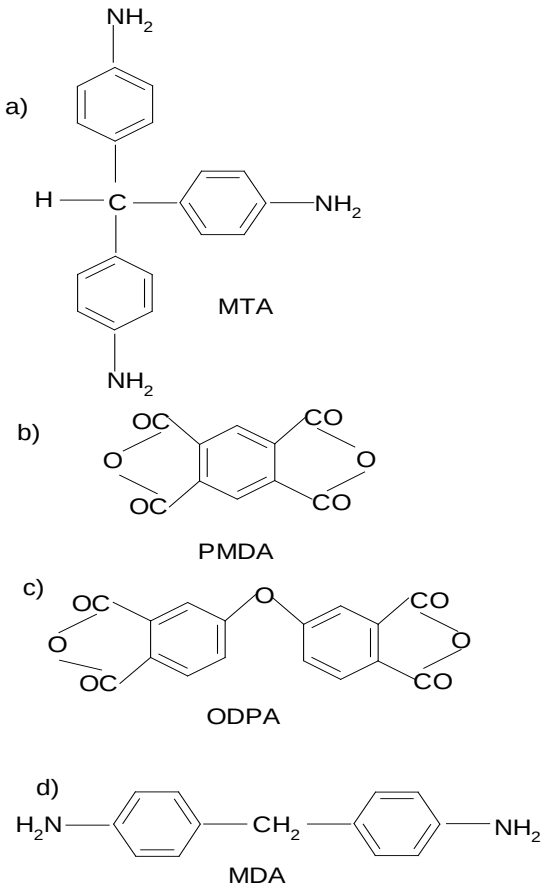

Fig. 2. Chemical structure of a) 4,4',4''-triaminotritriphenylmethane (MTA), b) pyromellitic anhydride (PMDA), c) 4,4'-oxydiphthalic anhydride (ODPA) and d) 4,4'-methylenedianiline (MDA).

The molar amount of A_2 and B_3 monomers used in the preparation of HBPIs influences the kind and ratio of terminal groups. If the A_2:B_3 ratio = 1:1 (i.e. anhydride:amino groups = 2:3) amine end-capped HBPIs are formed [HBPI(PMDA-

MTA)11 (Fig. 3) and HBPI(ODPA-MTA)11]; if the ratio is 2:1 (i.e. 4:3) anhydride terminated HBPI [HBPI(PMDA-MTA)21 and HBPI(ODPA-MTA)21] are produced.

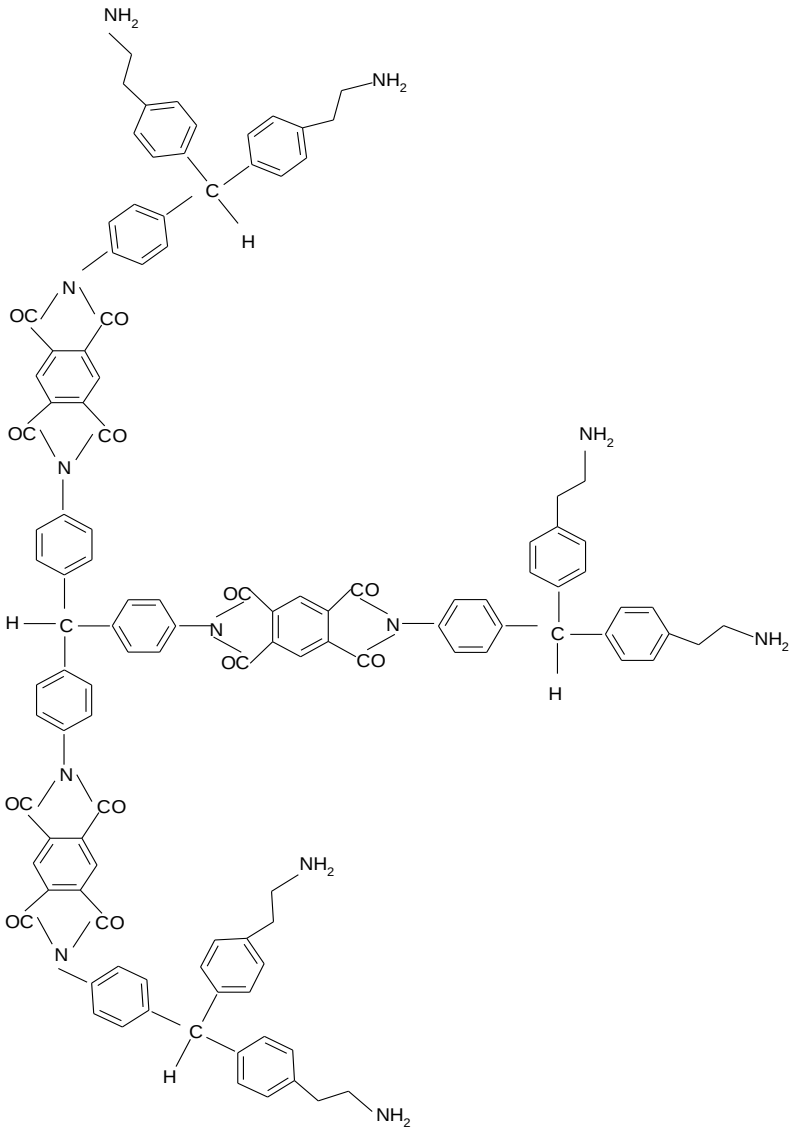

Fig. 3. Chemical structure of HBPI(PMDA-MTA)11.

When A_2 and B_3 monomers are used, a three-dimensional structure forms during the course of polymerization [9, 10]. In our experiments the formation of this structure was suppressed by the slow dropwise addition of a dilute solution of one monomer to a solution of the other (see Experimental part); in both cases, a solution of a dianhydride in NMP being added to an MTA solution. For each polymer type, we recorded the highest concentration of solids found (Tab. 1), with higher concentrations leading to insoluble final products ((micro) gel). The same procedure (with a highest concentration of 6 wt% for PMDA-based LPAA, and 4 wt% for ODPA-based LPAA) was used for the preparation of linear analogues; the formation of three-dimensional product (gel) not being typical in this case. As Tab. 1 shows, a highest concentration of only 1 wt% was found for anhydride end-capped HBPAA. The polyimide precursors could not be separated from such low-concentrated solutions, even though, in addition to traditional distilled water, we used methanol, ethanol and propanol as precipitating agents. Table 1 also displays the kinematic

viscosities of the HBPAA and LPAA solutions, and the intrinsic viscosities (limiting viscosity numbers) of the polymers.

Tab. 1. Characterization of polyimide precursors: hyperbranched (HBPAA) and linear (LPAA) polyamic acids.

Polyamic acid	c[a](wt%)	ν[b](m^2s^{-1})	$[\eta]$[c] (mlg^{-1})
HBPAA(PMDA-MTA)11[d]	6	$3.62x10^{-5}$	47.9
HBPAA(PMDA-MTA)21	1	$3.10x10^{-6}$	---[e]
HBPAA(ODPA-MTA)11	4	$3.17x10^{-5}$	16.0
HBPAA(ODPA-MTA)21	1	$2.23x10^{-6}$	---
LPAA(PMDA-MDA)11[f]	6	$2.98x10^{-5}$	45.5
LPAA(ODPA-MDA)11	4	$2.83x10^{-5}$	35.5

[a]concentration of polyamic acid in NMP, [b]kinematic viscosity of the solution of polyamic acid, [c]limiting viscosity number (intrinsic viscosity), [d]hyperbranched polyamic acid based on PMDA and MTA in a molar ratio of 1:1, [e]unsuccessful isolation of polyamic acid from solution, [f] linear polyamic acid based on PMDA and MDA in a molar ratio of 1:1

In agreement with general assumption, the kinematic viscosities of the 1 wt% solutions of HBPAA were approximately one order lower than the other, more highly concentrated, solutions. Of course, solution viscosities can also be influenced by the molecular weight of dissolved polymers. The higher intrinsic viscosity values $[\eta]$ of PMDA-based HBPAA and PMDA-based LPAA in comparison with those obtained for the ODPA-based polyamic acids can be given by the differences in molecular weights and/or character of polymer coils in solution. However, the value $[\eta]$ of 16 ml g^{-1} obtained for HBPAA(ODPA-MTA)11 was unexpectedly low.

HBPAA and LPAA were transformed into HBPI and LPI, respectively, using thermal exposition up to 230 ºC (see Experimental part). The obtained materials were analyzed by IR spectroscopy (Figs. 4-5). Fig. 4 shows the typical IR spectra obtained for both HBPAA(ODPA-MTA)21 and its corresponding HBPI. The absorption bands at 1777 and 1718 cm^{-1} (symmetric and asymmetric stretching of the ring carbonyl groups), together with the band at 1384 cm^{-1} (stretching of the ring C-N bond), are distinct in the spectrum of HBPI(ODPA-MTA)21 and characterize the formation of imide structures. The absence of the band at 1687 cm^{-1} [amide group of polyamic acid - see the IR spectrum of HBPAA(ODPA-MTA)21] supports our notion that thermal treatment leads to almost complete imidization.

Fig. 5 compares the IR spectra of HBPI(ODPA-MTA)11 and HBPI(ODPA-MTA)21. In addition to the characteristic polyimide absorption bands described above, the distinct band at 1622 cm^{-1} corresponds to terminal amino groups in the spectrum of HBPI(ODPA-MTA)11, and the band at 1851 cm^{-1} corresponds to terminal anhydride groups in the spectrum of HBPI(ODPA-MTA)21.

The resistance of these materials to selected solvents (NMP, heptane, toluene, methanol) was evaluated from their weight change after immersion in the respective media for 35 days. The final materials were insoluble in these media. The highest uptake of HBPI(PMDA-MTA)11 was found in NMP (75 %), while uptake was much lower in methanol and toluene (10 %) and heptane (4 %). The uptake of HBPI(ODPA-MTA)11 in NMP was markedly lower (10 %), and slightly lower in

methanol (7%), toluene (1 %) and heptane (0 %). This may be more a consequence of morphology than of chemical composition, the chemical stability of PMDA-based polyimides theoretically being higher than those based on ODPA [1]. Surprisingly, although HBPIs are known to be more soluble, their resistance to the tested solvents was comparable to that of the analogous LPIs [2,5].

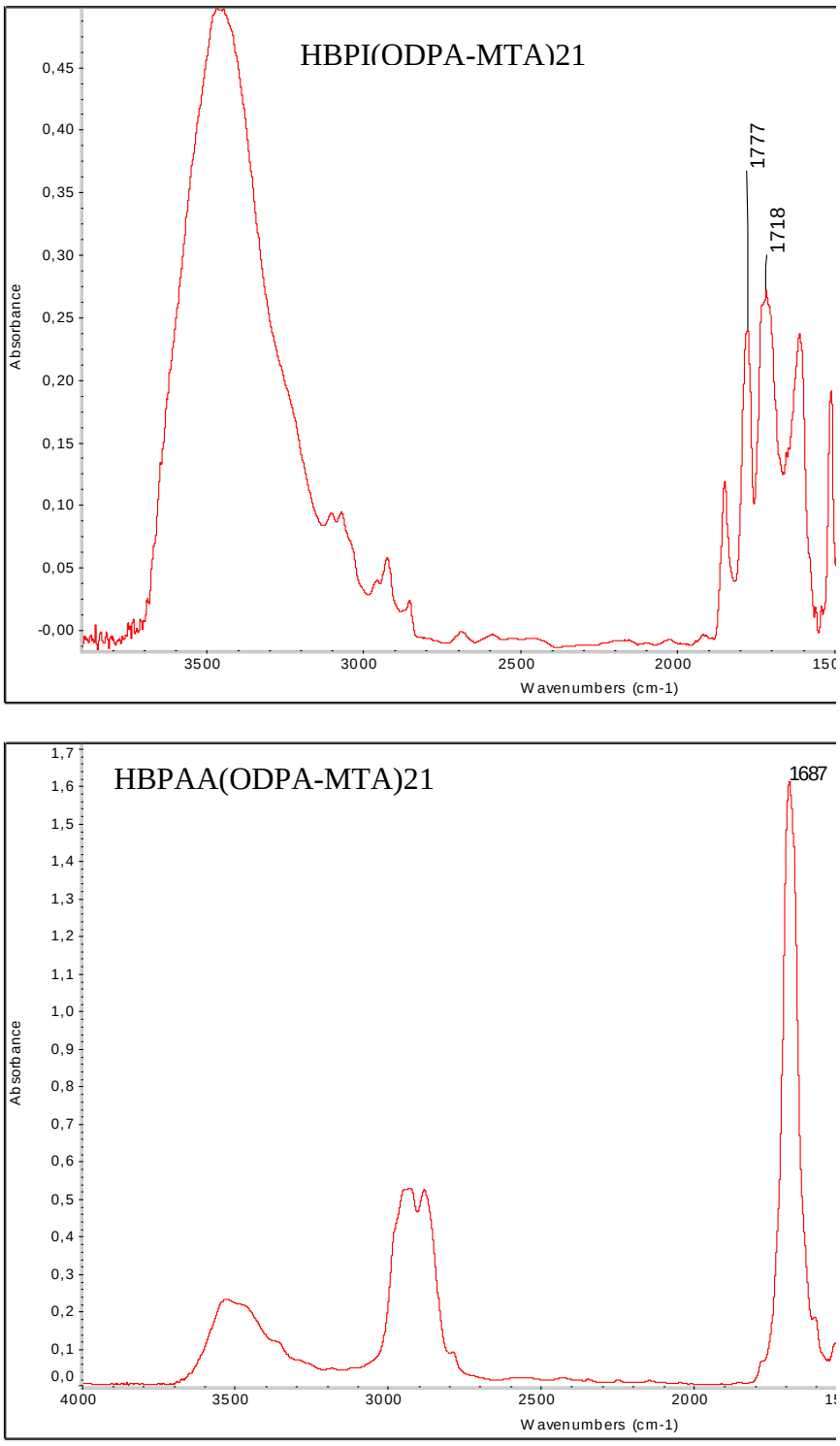

Fig. 4. IR spectra of HBPI(ODPA-MTA)21 (top) and HBPAA (ODPA-MTA)21 (bottom).

For the both amine- and anhydride end-capped HBPIs, their ^{1}H NMR spectra were not obtained due to their insolubility. Therefore, we estimated the degree of branching using ^{1}H NMR analyses of their precursors (HBPAA). The degree of branching is defined as the ratio of the sum of dendritic and terminal units vs. total units (linear, dendritic, and terminal units) [2]. The signals in the region of 5-6 ppm corresponding to the hydrogen of methine group (C-H) were used for this purpose. To make clear the assignment of the signals in this region, three model compounds from phthalic anhydride and MTA were prepared (see Experimental part) and analyzed by ^{1}H NMR spectroscopy. The degree of the amine end-capped HBPAA was evaluated to be slightly higher than 0.6. In the spectrum of the anhydride end-capped HBPAA, one signal was only found in the region of 5-6 ppm. It supports the assumption that the degree of a such type of product should be close to 1.

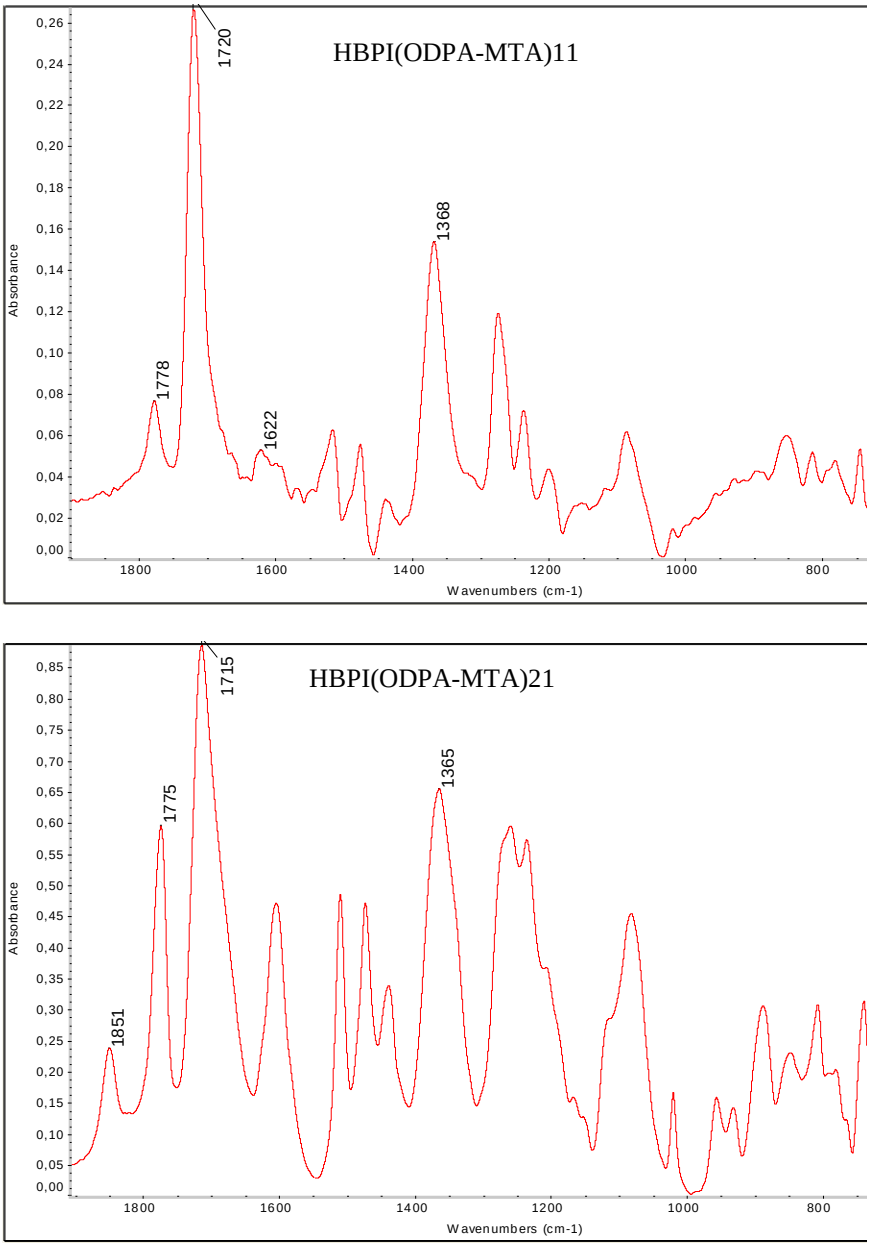

Fig. 5. IR spectra of HBPI(ODPA-MTA)21 (top) and HBPI(ODPA-MTA)11 (bottom).

Tab. 2 presents the glass transition temperatures (T_g), and the temperatures corresponding to 10 wt% weight loss during thermooxidative attack. In both cases, the T_g of the amine end-capped HBPI was higher than that of the LPI based on the same dianhydride. Interactions between the terminal amino groups may be one reason for the higher T_g of the amine-terminated hyperbranched structures. On the other hand, the thermooxidative stabilities (evaluated as the temperatures corresponding to 10 wt% loss during thermogravimetric analysis with a temperature gradient of 10 ºC min^{-1}) of the LPIs were higher than those of the corresponding HBPIs. The lower thermal stability of the HBPIs might be due to deficiencies in their chain entanglements resulting from a lower number of physical crosslinks [2]. The higher thermooxidative stability of amine end-capped HBPIs, compared to anhydride end-capped HBPIs, again could be the result of interactions between the terminal amino groups.

Tab. 2. Characterization of hyperbranched (HBPI) and linear (LPI) polyimides.

Polyimide	T_g[a] (ºC)	T[b] (ºC)
HBPI(PMDA-MTA)11[c]	423	523
HBPI(PMDA-MTA)21	---	452
HBPI(ODPA-MTA)11	287	509
HBPI(ODPA-MTA)21	---	375
LPI(PMDA-MDA)11[d]	355	592
LPI(ODPA-MDA)11	276	566

[a]glass transition temperature, [b]temperature corresponding to 10 wt% weight loss, [c]hyperbranched polyimide based on PMDA and MTA in a molar ratio of 1:1, [d]linear polyimide based on PMDA and MDA in a molar ratio of 1:1

We monitored the transport of carbon dioxide (permeability coefficient $0.6x10^{-17}m^2Pa^{-1}s^{-1}$), toluene vapours ($2.96x10^{-17}m^2Pa^{-1}s^{-1}$), heptane vapours ($1.32x10^{-17}$ $m^2Pa^{-1}s^{-1}$) and water vapour ($7.68x10^{-16}$ $m^2Pa^{-1}s^{-1}$) through the HBPI(ODPA-MTA)11 membrane. It seems that this HBPI is more permeable to the vapours of polar liquids (i.e. water). Unfortunately, we found virtually no increase in the permeability coefficient of carbon dioxide (0.4 $x10^{-17}$ $m^2Pa^{-1}s^{-1}$) compared with LPI(ODPA-MDA)11. Thus, our results cannot be used to support the idea that cavities existing in the structure of rigid hyperbranched polymers influence the free volume of a polymer, and, consequently, other properties that depend on its free volume (i.e. permeability) [2,3]. It is, therefore, necessary to conduct further experiments to establish the potential of HBPIs as separation membranes.

Conclusions

Hyperbranched polyimides based on 4,4',4''-triaminotriphenylmethane and pyromellitic dianhydride or 4,4'-oxydiphthalic anhydride were prepared in the form of thin self-standing films. By varying in the concentration of monomers the amine or anhydride terminated products were synthesized. Their hyperbranched structure was supported by finding the high degrees of branching. The amine end-capped hyperbranched polyimide had the higher thermooxidative stability compared to anhydride terminated one. Nevertheless, the thermooxidative stability of both types of hyperbranched polyimides was lower compared to the corresponding linear

analogues. The amine terminated hyperbranched product showed nearly by one order higher permeability coefficient of water than of toluene and heptane.

Experimental part

Materials

Pyromellitic dianhydride (PMDA) and 4,4'-oxydiphthalic anhydride (ODPA) (both Aldrich, Czech Republic) were heated to 170 °C for 5 h in a vacuum before use. 4,4'-Methylenedianiline (MDA) (Aldrich) and 4,4',4''-triaminotriphenylmethane (MTA) (Dayang Chemicals, China) were used as received.

MTA elemental analysis: theor.: C 78.90%, H 6.57%, N 14.53%

found: C 77.35%, H 6.90%, N 14.52%

MTA melting point: m. p. (theor.) 201 °C (ref. [11])

m.p. (exper.) 198-201 °C

1-Methyl-2-pyrrolidone (NMP) (Merck, Czech Republic) was distilled under vacuum over phosphorus pentoxide, and stored in an inert atmosphere.

Preparation

All glassware was dried at 120 °C for 3 h prior to use. Hyperbranched polyamic acids (HBPAA) and LPAA were prepared in a 250 ml two-necked flask equipped with a magnetic stirrer and a nitrogen inlet/outlet. We followed the general procedure for the preparation of amine end-capped HBPAA based on PMDA and MTA [HBPAA(PMDA-MTA)11].

At room temperature, a solution of 3.438 g (0.016 mol) PMDA in 65 ml of NMP was added dropwise to a solution of 4.562 g (0.016 mol) of MTA in 86 ml of NMP for approximately 45 min. This reaction mixture was then stirred at room temperature for 24 h.

A solution of either HBPAA or LPAA in NMP was spread onto a glass substrate. The resulting thin layer (tenths of millimetres thick) was kept at 60 °C/12 h, 100 °C/1 h, 150 °C/1 h, 200 °C/2 h and, finally, at 230 °C/1 h. The thickness of the transparent reddish self-standing films obtained was about 50 μm.

Model compounds were prepared from phthalic anhydride and MTA at the molar ratio 1:1, 2:1 and 3:1, respectively using d_6-DMSO as a solvent. (These precursors were also imidized by heating at 160 °C for 24 h after addition of d_{10}-xylene as an azeotropic agent). The samples were directly analyzed using ^{1}H NMR spectroscopy.

Characterization

^{1}H NMR spectra were taken on **Bruker** Avance DRX 500 at 500 MHz in d_6-dimethylsulfoxide. IR spectra were recorded on a Nicolet 740 spectrometer using either liquid samples (solutions of polyamic acids) or KBr pellets (solid polyimides). Dynamic thermogravimetric measurements were performed in air using a TG-750 Stanton-Redcroft (heating rate 10 °C min^{-1}). Dynamic mechanical analysis (DMA) was performed using a DMA DX 04T (RMI, Bohdaneč, Czech Republic) at 1 Hz as the temperature rose from room temperature to 450 °C; the temperature gradient being 3 °C min^{-1}. We used the following procedure to test the chemical resistance of

the materials in the NMP, as well as in methanol and toluene: each film was dried at 100 °C for 3 h, weighed, and immersed in an appropriate solvent. After 35 days the weight change was determined. The kinematic viscosities of the HBPAA and LPAA solutions were measured using a capillary viscometer at 20 °C, and their intrinsic viscosities measured in NMP at 25 °C.

We measured the permeation of carbon dioxide, organic vapours and water vapour at 25 °C using a specially constructed differential flow permeameter. The membrane was fixed in a permeation cell and put into contact with a mixture of a gas or vapour with hydrogen (carrier gas) at a constant pressure. The penetrating gas (vapour) from the downstream (feed) side of the membrane to upstream side was from upper department of cell carried away by a stream of pure hydrogen. Changes of thermal conductivity of hydrogen (due to gas (vapour) permeation were monitored by a pair of the thermal conductivity detectors built into the Wheatstone resistance bridge. The reference thermistor is in permanent contact with pure carrier gas while the measuring one is in contact with mixture of permeant and hydrogen. A stable voltage signal from resistance bridge was obtained until reaching of steady-state.

Acknowledgements

This work was supported by the Grant Agency of the Czech Republic through grant No. 203/06/1086 and research program MSM 6046137302. A fruitful discussion with professor J. Kralicek is highly acknowledged.

References

[1] Hergenrother, P.M. *High Perform. Polym*. **2003**, *15*, 3.
[2] Fang, J.; Hidetoshi, K.; Okamoto, K. *Macromolecules* **2000**, *33*, 4639.
[3] Fang, J.; Hidetoshi, K.; Okamoto, K. *J. Membr. Sci*. **2001**, *182*, 245.
[4] Hao, J.; Jikei, M.; Kakimoto, M. *Macromolecules* **2003**, *36*, 3519.
[5] Jikei, M.; Kakimoto, M. *J. Polym. Sci., Part A: Polym. Chem*. **2004**, *42*, 1293.
[6] Suzuki, T.; Yamada, Y.; Tsujita, Y. *Polymer* **2004**, *45*, 7167.
[7] Tomalia, D. A. *Aldrichimica ACTA* **2004**, *37*(2), 39.
[8] Gao, C.; Yan, D. *Prog. Polym. Sci*. **2004**, *29*,183.
[9] Flory, P.J. *J. Am. Chem. Soc.* **1952**, *74*, 2718.
[10] Odian, G.; *Principles of polymerization*, 4th ed. New York: John Wiley & Sons, **2004** (chapter 2).
[11] Hellwinkel, D.; Fritsch, H. *Chem. Ber.* **1990**, *123*, 2207.
[12] Bershtein, V.A.; Egorova, L.M.; Yakushev, P.N.; Sysel, P.; Hobzova, R.; Kotek, J.; Pissis, P.; Kripotou, S.; Maroulas, P. *Polymer* **2006**, *47*, 6765.
[13] Maroulas, P.; Kripotou, S.; Sysel, P.; Hobzova, R.; Kotek, J.; Pissis, P. J. *Non-Crystal. Solids* **2006**, *352*, 4800.
[14] Liu, Y.; Chung, T. *J. Polym. Sci.: Part A: Polym. Chem*. **2002**, *40*, 4563.
[15] Chung, T.; Vora, R. H.; Jaffe, M. *J. Polym. Sci. Part A: Polym. Chem.* **1991**, *29*, 1207.