WATER TRANSPORT AND SORPTION IN POLYIMIDE–POLYSILOXANE COPOLYMERS

Petr SYSEL[a], Vladimir HYNEK[b] and Milan SIPEK[b1]

[a] *Department of Polymers, Prague Institute of Chemical Technology, 166 28 Prague 6, Czech Republic; e-mail: petr.sysel@vscht.cz*

[b] *Department of Physical Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6, Czech Republic; e-mail: [1] milan.sipek@vscht.cz*

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Water transport through and sorption in films of polyimide–polysiloxane block copolymers were studied at 25 °C and atmospheric pressure. The permeability and diffusion coefficients and, to a certain extent, also the sorbed amount were found to depend on the content of the polysiloxane blocks.

Key words: Copolymerizations; Block copolymers; Polyimides; Polyimide–polysiloxane copolymers; Polysiloxanes; Water sorption.

Aromatic polyimides (PI) exhibit outstanding dielectric and mechanical properties at elevated temperatures[1] (up to 250 °C). Nevertheless, their high values of water sorption (up to 4 wt.%) impede some (micro)electronic applications[2].

Incorporation of hydrophobic moieties into polyimide chains might supress this drawback. From this point of view, a combination of polyimides with polysiloxanes is very attractive. Polyimide–polysiloxane copolymers (PI–PSX) exhibit most of the properties of polyimides and, in addition, *e.g.*, enhanced solubility and higher toughness and impact resistance[3]. A decreased water uptake of PI–PSX in comparison with homopolyimides has been also tentatively shown[3].

In this work we report on the synthesis of polyimide–polysiloxane block copolymers and the dependence of the transport through and sorption into the films on their composition.

EXPERIMENTAL

Chemicals

5,5′-Oxydiisobenzofurane-1,3-dione (4,4′-oxydiphthalic anhydride, ODPA) (Chriskev) was heated overnight to 160 °C in a vacuum before use. 1,4-Bis(4-amino-1,1-dimethylbenzyl)benzene (Bisaniline P, BIS P) (Mitsui Petrochemical Industries, Ltd.) was used as received. 2-Aminopyridine (2-AP) (Aldrich) was recrystallized from a mixture chloroform–petroleum ether. Octamethylcyclotetrasiloxane (D_4)

(Fluka) was distilled in a vacuum over calcium hydride before use. 1,3-Bis(3-aminopropyl)tetramethyldisiloxane (DSX) (ABCR) was used as received. *N*-Methyl-2-pyrrolidone (NMP), 1,2-dichlorobenzene (DCB) and chlorobenzene (CB) (all Merck) were distilled in a vacuum over phosphorus pentoxide and stored in inert atmosphere.

Synthesis of Polymers

2-Aminopyridine terminated ODPA–BIS P polyimide oligomers with controlled molecular weight were synthesized by solution imidization[4] (first stage in NMP at room temperature for 24 h, second stage in NMP–DCB mixture at 180 °C). The number-average molecular weights M_n of oligoimides were in the range 2 000–18 000 (by ^{1}H NMR spectroscopy).

The α,ω-bis(3-aminopropyl) oligo(dimethylsiloxane) oligomers were prepared by anionic ring-opening equilibrium polymerization of D_4 initiated with potassium siloxanolate in the presence of DSX (ref.[5]). Their molecular weights M_n were in the range 1 000–5 000 (by conductometric titration with HCl).

Polyimide–polysiloxane copolymers were prepared *via* transimidization[4] (in CB at 120 °C for 3 h). Copolymers were characterized by ^{1}H NMR in $CDCl_3$ and by viscometry (intrinsic viscosities in chloroform at 25 °C).

Films (homogeneous foils with thickness 20–30 μm) were prepared from 10 wt.% polymer solutions in chloroform by spreading onto a glass plate with a casting knife.

Apparatus

The differential permeation method was used to determine the permeability coefficient. This method makes it possible to determine also the diffusion coefficient of the permeant in a polymer membrane from an asymptotic solution of the relevant diffusion equations.

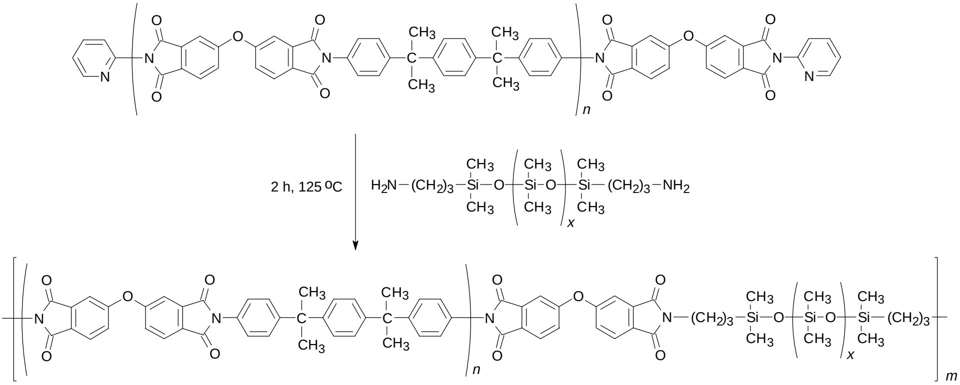
The apparatus employed in the differential permeation method consisted of a cell separated with a flat membrane. One side of the membrane is exposed to the carrier gas (that flows through the cell with a constant rate), the other side to the flowing gas (or vapour) whose permeability through the membrane is measured. The studied gas that penetrated through the membrane is mixed with the carrier gas, and the composition of the gaseous mixture is determined by measuring the change in thermal conductivity using a pair of thermistors connected in a Wheatstone resistance bridge. The time dependence of the resulting voltage signal reflects the permeation flux density of the gas (or vapour) through the membrane which is in turn directly related to the transport parameters of the measured gas. The apparatus was connected to a computer to increase the productivity and reliability of the measurement and enable quick evaluation of experimental data[6].

Gravimetric sorption measurements were carried out at 100% relative humidity (25 °C). Contact angles were measured at room temperature using in-house designed and built instrument (a method of the sloping sheet[7]).

RESULTS AND DISCUSSION

Polyimide–polysiloxane block copolymers differing in the polysiloxane content were prepared by transimidization (Scheme 1) using the polyimide oligomers in excess (theoretical number-average molecular weight, M_n = 40 000). As the glassy character and high glass transition temperatures are desirable for most of polyimide applications, the maximum concentration of the rubbery PSX was limited to 30 wt.%. The studied polymers (including an ODPA–BIS P homopolyimide with theoretical M_n = 40 000) are given in Table I.

Mass transport through isotropic non-porous polymer membranes is mostly driven by chemical potential, pressure or temperature gradients. This transport can be regarded to be a sequence of sorption, dissolution, activated diffusion and desorption steps of the permeant. The mass transport through a polymer membrane is therefore characterized by permeability (*P*) and diffusion (*D*) coefficients and sorption[8]. The obtained values of these parameters are summarized in Table I.



SCHEME 1

An increase in the polysiloxane content from 0 to 20 wt.% resulted in a decrease in the water sorption. A further increase in polysiloxane content to 30 wt.% did not significantly influences this value. Our results are in fair agreement with the data[9] showing that incorporation of 10 wt.% of polysiloxane segments into polyimide reduces specific interaction of water vapour with the polymer surface. No additional drop in this parameter was found when the polysiloxane content was 30 wt.%.

TABLE I
Transport and sorption parameters and contact angles of the studied polymers

Sample code	PSX wt.%	$10^{12} \cdot P^a$ mol m^{-1} Pa^{-1} s^{-1}	$10^{12} \cdot D^b$ m^2 s^{-1}	Sorption g water/1 g polymer	Contact angle, °
PI–PSX 0	0	5.75	1.03	0.0242	90–91
PI–PSX 10	10	5.84	1.18	0.0167	95
PI–PSX 20	20	10.05	4.03	0.0077	100–101
PI–PSX 30	30	15.22	5.25	0.0080	102

[a] Permeability coefficient. [b] Diffusion coefficient.

It is known[9] that the surface concentration of hydrophobic polysiloxane is higher than in the bulk. One can therefore conclude that this relatively low concentration of the polysiloxane blocks is already sufficient for the formation of a hydrophobic surface layer preventing water from entering into the bulk. This was also supported by our measurements of the contact angle of water on the whole surface of the employed polymers (Table I). The values of the contact angle were higher for the copolymers containing 10 and 20 wt.% of PSX, respectively, than for the homopolyimide control, but the increase in the amount of polysiloxane to 30 wt.% did not bring any substantial change of the contact angle.

On the other hand, the permeation and diffusion coefficients increase with the polysiloxane content up to 30 wt.%. This means that values of these coefficients can be controlled by the ratio of the glassy polyimide and rubbery polysiloxane in a broad range.

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