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Segmented polymer networks based on poly(*N*-isopropyl acrylamide) and poly(tetrahydrofuran) as polymer membranes with thermo-responsive permeability

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Abstract

Segmented polymer networks (SPNs) containing a polymer with a lower critical solution temperature were prepared by free radical copolymerization of poly(tetrahydrofuran) (PTHF) bis-macromonomers with *N*-isopropyl acrylamide (NIPAA). The PTHF bis-macromonomers, which were prepared by living cationic polymerization of tetrahydrofuran, were provided with acrylate or acrylamide end-groups by end-capping the living polymer chains with acrylic acid and 3-acrylaminopropanoic acid, respectively. Differential Scanning Calorimetry (DSC) experiments showed clearly that, for the same fractions of both network components, the phase morphology of the SPNs was highly influenced and adjustable by the nature of the end-groups of the bis-macromonomer as a result of their copolymerization behavior with NIPAA. For the same type of multi-component networks, the morphology changed from a heterogeneous up to a rather homogeneous nature by application of bis-macromonomers with, respectively, acrylate or acrylamide end-groups during their preparation. Swelling and DSC experiments on the swollen SPNs revealed, respectively, that the swelling properties and the cloud point temperature (T_{cp}) could be controlled by the network composition. The thermo-responsive water permeability and the possible application of the SPNs as pervaporation membranes for the separation of a water/isopropanol mixture were investigated as a function of temperature and network composition. The permeability and selectivity of the membranes decrease when the T_{cp} is reached. The permeability increases while the selectivity decreases with decreasing crosslink density or higher overall hydrophilicity of the SPNs.

Keywords: Poly(*N*-isopropyl acrylamide); Segmented polymer networks; Thermo-responsive membranes

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1. Introduction

Stimuli-sensitive polymers, especially temperature-sensitive hydrogels and polymeric membranes, have attracted much scientific interest [1–5]. Temperature-sensitive polymers are characterized by a lower critical solution temperature (LCST) which provides hydrogels the possibility to have high swelling degrees at low temperatures and low swelling at high temperatures in a reversible way. This thermo-shrinking behavior reflects the hydrophilic/hydrophobic balance of the polymer chains. The hydrophobic interactions between polymer chains increase at elevated temperatures due to a decrease in the water structure around the hydrophobic groups in the polymer chains [6,7]. Much interest has been focused on poly(*N*-isopropyl acrylamide) (PNIPAA) which undergoes a phase transition at a temperature close to 32 °C. This behavior is reversible and occurs over a narrow temperature range [6,8].

It has been demonstrated earlier that the use of thermo-sensitive polymers in membrane technology could lead to interesting applications. Liang et al. [9] have shown that the incorporation of PNIPAA in pervaporation membranes makes it possible to control the water permeability as a function of temperature. Pervaporation is a promising membrane process to separate liquid mixtures, which are difficult to separate by other more conventional methods, e.g. azeotropic mixtures. In pervaporation, the liquid mixture to be separated (feed) is placed in contact with one side of a non-porous selective membrane and the permeated product (permeate) is continuously removed in the vapor state at the opposite side by vacuum or gas sweeping [10–12].

Because a single polymer usually does not possess the

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optimum properties for a given separation, different polymers were combined in the form of polymer blends [13], block- or graft copolymers [14,15], copolymer networks [16], interpenetrating polymer networks [17] and segmented polymer networks (SPNs) [18] for the synthesis of polymeric pervaporation membranes. The aim of this work is to extend the applicability of smart polymers in membrane processes. For this purpose the specific properties of SPNs and the thermo-sensitive properties of PNIPAA have been combined.

SPNs are polymer structures in which one polymer is grafted with both chain ends to another polymer [19–24]. The physicochemical properties of these networks are controlled by the ratio of the two components and the molecular weight of the macromolecular crosslinkers. In the case of amphiphilic SPNs, the covalent bonding of the hydrophilic phases to the hydrophobic ones limits the maximal swelling and can prevent the swollen network structures from disintegration. This mechanical stability together with their particular swelling behavior and nano-separated morphology [20,22,25] offers a unique combination of properties to use them for example in medical applications [26] and as matrix for the creation of nano-particles [27]. Earlier studies showed that in SPNs not only the hydrophilic/hydrophobic balance but also the morphology of the material and the thermo-responsive properties can be controlled by the composition and the crosslink density of the network [24, 28,29]. Guan et al. [28] reported about the swelling behavior of SPNs based on PNIPAA and a specific poly(tetrahydrofuran) (PTHF) diacrylate ($M_n = 2300$ g/mol), which was also used as hydrophobic segment in other amphiphilic SPNs [30–33].

In this work, new types of PTHF-based SPNs have been prepared and investigated for their temperature dependent water permeability and pervaporation properties. The hydrophobic PTHF was chosen to avoid an extensive swelling of the pervaporation membranes in the aqueous feed mixture, which has a negative effect on membrane selectivity [34,35]. Moreover, PTHF-chains are quite mobile in the amorphous state and provide the SPNs more flexibility and rubbery properties. One of the goals of this study was to vary the molecular weight and end-groups of the macromolecular PTHF crosslinker in order to look for a relationship between the chemical structure of the networks and their membrane properties. Acrylate or acrylamide end-groups are introduced by end-capping living PTHF chains, respectively, with acrylic acid and 3-acrylaminopropanoic acid. The bis-macromonomers are copolymerized with NIPAA to prepare thermo-sensitive SPNs. The influence of the end-group on the phase morphology of the SPNs is examined by DSC. The dependence of the swelling, permeability and pervaporation behavior of the SPNs on the temperature and network composition will be described.

2. Experimental

2.1. Materials

Acryloyl chloride (Aldrich 96%) and 2,2,6,6-tetramethylpiperidine (TMP, Acros 98%) were purified by distillation. Tetrahydrofuran (THF, Acros 99 + %) was purified by distillation over CaH_2 and dried on sodium wire under reflux in the presence of traces of benzophenone until a blue color persisted; it was used directly after distillation. Acrylic acid (Aldrich 99%) was purified by vacuum distillation. Trifluoromethanesulfonic anhydride (Tf_2O, Acros 98%) was purified by distillation right before use. *N*-Isopropyl acrylamide (NIPAA, Aldrich 97%) was purified by recrystallization from hexane followed by drying under vacuum and was stored at 4 °C under nitrogen. 3-Aminopropionic acid (Fluka BioChemika) and dicumyl peroxide (Aldrich 98%) were used as received.

2.2. Synthesis of 3-acrylaminopropanoic acid

3-Acrylaminopropanoic acid was synthesized according to a literature procedure [36]. 33.85 g (0.38 mol) of 3-aminopropionic acid and 65.0 g (0.88 mol) of calcium hydroxide were added to 580 ml of water, and the mixture was cooled to 0 °C. 38.99 g (0.43 mol) of acryloyl chloride was added dropwise. After 3 h the suspension was filtrated and the filtrate was acidified to pH equal to 1 by dropwise addition of concentrated hydrochloric acid at 0 °C. The solution was saturated with sodium chloride and extracted with ethyl acetate. The product was purified by repeated recrystallization from ethyl acetate. A yield of 39.3 g (72%) was obtained.

2.3. Synthesis of the PTHF bis-macromonomers

The synthesis of α,ω-acrylate terminated poly(tetrahydrofuran) (PTHFAC) is illustrated for $M_n = 3800$ g/mol. 0.81 ml (4.8 mmol) of Tf_2O was added to 100 ml of dry THF at 25 °C in a two-necked flask provided with a magnetic stirring rod, an inlet for argon and a rubber septum. 0.987 ml (14.4 mmol) of acrylic acid was added to the reaction mixture after 8 min, immediately followed by 2.43 ml (14.4 mmol) TMP. The polymer was precipitated in a 0.1 M NaOH solution at 0 °C, filtered on a cooled glass filter, washed three times with ice water and dried by lyophilization. A yield of 14.8 g (79%) PTHFAC was obtained.

α,ω-Acrylamide terminated poly(tetrahydrofuran) (PTHFAAM) is prepared using a similar method and is illustrated for $M_n = 2400$ g/mol. In this case 6.9 g (48 mmol) of 3-acrylaminopropanoic acid dissolved in dry THF is added to the reaction mixture after 5 min, immediately followed by 8.1 ml (48 mmol) TMP. A yield of 8.2 g (71%) PTHFAAM was obtained.

2.4. Synthesis of the segmented polymer networks

Chosen amounts of bis-macromonomer and NIPAA were mixed in the desired ratio at 65 °C and 1 mol% dicumyl peroxide (relative to NIPAA) was added to start the bulk polymerization in the melt. The mixture was degassed for 30 s under vacuum, injected between two hot glass plates (80 °C) separated by 0.1 mm teflon spacer and kept in an oven for 7 h at 80 °C, 5 h at 90 °C, 5 h at 100 °C and 15 h at 125 °C. Before use, the glass plates were treated with H_2SO_4 (95%) and a solution of chloro-trimethylsilane (10%) in toluene for easier removal of the networks after preparation. After removal of the networks from the glass plates, all soluble fractions were extracted with $CHCl_3$, in a soxhlet apparatus.

2.5. Permeability experiments

Water permeation and pervaporation experiments were performed with a home-made laboratory pervaporation apparatus. The membrane was placed in a permeation cell with controlled temperature on a porous inox support and the feed was introduced in the upstream part of the cell. The liquid feed (pure water or a 10 wt% isopropanol in water mixture) was in direct contact with the non-porous membrane and the effective membrane area was 10 cm^2. The downstream part of the cell was kept at reduced pressure with an oil pump and the permeate was condensed with liquid nitrogen in one of the cooled traps. The permeation rate (J) was determined by measuring the weight of the permeate:

$$J = \frac{m_p}{A\Delta t} \quad (\mathrm{gm^{-2}\,h^{-1}})$$

where m_p represents the weight of the permeate, A the effective membrane surface and Δt the permeation time.

When a 10 wt% isopropanol in water solution was used as feed mixture, the compositions of the feed and the permeate were measured by a Karl Fisher coulometer (Mitsubishi CA-06). The separation factor α was calculated from:

$$\alpha = \frac{m(1-m_0)}{m_0(1-m)}$$

where m_0 is the water weight fraction in the feed and m the water weight fraction in the permeate.

Upstream sorption experiments were done by swelling the networks to equilibrium in a 10 wt% isopropanol in water mixture. The swollen networks were dried in vacuum and the sorbate was condensed with liquid nitrogen in a cooled trap. The composition of the sorbate was determined with a Karl Fisher coulometer.

2.6. Methods of analysis

^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AM500 spectrometer at 500 MHz. The molecular weights of the bis-macromonomers were measured by gel permeation chromatography (GPC) using a refractometer as detector, and a 60 cm PL Mix C column, with THF as eluent (1 ml min^{-1}). The system was calibrated with polystyrene standards.

Thermogravimetric analysis (TGA) was performed with a PL-TGA (type PL-TG 1000, Polymer Laboratories) under nitrogen atmosphere at a heating rate of 10 °C min^{-1}.

Differential Scanning Calorimetry (DSC) was used to examine the crystallization behavior of the dry networks. A Perkin Elmer DSC7 apparatus with thermal analysis controller TAC7/DX was used. The samples were heated from − 100 to 200 °C at a scanning rate of 10 °C min^{-1}. The degree of swelling of the SPNs was determined gravimetrically. A dried and weighed piece of network was immersed in a solvent at a desired temperature. Periodically, the samples were removed from the solvent, tapped with filter paper to remove excess solvent on the sample surface and weighed until constant weight was reached. The degree of swelling S was defined as:

$$S = 100\frac{W_e - W_0}{W_0\rho}$$

where W_0 is the weight of the dry sample, W_e the weight of the swollen sample and ρ the density of the solvent.

For cloud point (T_{cp}) measurements, networks were placed in water at 5 °C for 24 h. The T_{cp} was determined visually by immersing the test tubes in a water bath, the temperature of which is increased stepwise by 1 °C every 15 min. The temperature, where the networks turned white was taken as the T_{cp}. The T_{cp} was also measured with DSC. The swollen samples were kept into a hermetically closed sample pan at 5 °C for 24 h, then quenched to − 100 °C and heated to 70 °C at a scanning rate of 5 °C min^{-1}. The onset of the endothermal signal between 26 and 32 °C corresponds well with the temperatures obtained from visual measurements.

3. Results and discussion

3.1. Synthesis of the bis-macromonomer

As outlined in the introduction, bis-macromonomers are used as starting materials for the synthesis of SPNs. In order to obtain polymer networks with controllable molecular weight between the crosslinks and to investigate the influence of the network composition on the properties, a control of molecular weight, dispersity and functionality of the macromolecular crosslinkers is required. Trifluoromethanesulfonic anhydride (Tf_2O) has been described earlier as a bifunctional initiator for the living cationic polymerization of THF [37]. In this work, PTHF bis-macromonomers have been obtained by initiation with Tf_2O and end-capping of the living chains, respectively, with acrylic acid (PTHFAC) or 3-acrylaminopropanoic acid (PTHFAAM) in the presence of TMP (Fig. 1). While acrylate terminated polymer chains have been applied earlier for the synthesis of SPNs [28], acrylamide terminated PTHF has been developed in this work with respect to the copolymerization reaction with the acrylamide containing monomer NIPAA.

The molecular weight (M_n) and polydispersity (M_w/M_n) of the bis-macromonomers were measured with GPC. The degree of functionality (F) was calculated from ^{1}H NMR by making use of the integral ratio of the signals of protons of the end-groups and the protons of the main chain (Table 1).

As shown in Table 1, it was possible to synthesize well-defined PTHF bis-macromonomers with acrylate and acrylamide end-groups. The synthesized macromolecular crosslinkers had narrow dispersities (<1.2) and functionalities close to two. In this way, they could be used as building blocks for the synthesis of SPNs.

3.2. Synthesis and solid state properties of the segmented polymer networks

The PTHF bis-macromonomers were radically copolymerized with NIPAA to prepare temperature-sensitive SPNs (Fig. 2). The nomenclature of the networks is illustrated in the following example: PNIPAA(60)-PTHFAC 2200(40) is a network synthesized with 60 wt% NIPAA and 40 wt% PTHFAC 2200 in the reaction mixture.

The soluble fractions of the networks, which only consist of NIPAA monomer and linear PNIPAA, as demonstrated by NMR-analysis, were below 10 wt% when PTHFAC was used while even less than 5 wt% when PTHFAAM was used as macromolecular crosslinker (Table 2). This is a first indication that the nature of the end-group of the bis-macromonomers has a direct influence on the copolymerization behavior between the crosslinkers and the NIPAA monomer. The low soluble fractions indicate an almost complete copolymerization between the bis-macromonomers and NIPAA. The soluble fraction increases with increasing PNIPAA content and molecular weight of the PTHF bis-macromonomer as a result of the decreasing amount of polymerizable end-groups in the reaction mixture which promotes the homopolymerization of PNIPAA.

The composition of the networks could be determined by TGA because the difference in degradation temperature of PTHF and PNIPAA is large enough to observe the degradation of both polymers separately. This is demonstrated in Fig. 3 for TGA-analysis of network PNIPAA(80)-PTHFAAM 4500(20). The composition of the networks was also determined with elemental analysis (EA). The absolute values determined by both methods (TGA and EA) correspond quite well for all the investigated SPNs. From Table 2, it can also be concluded that there was a good agreement between the composition of the SPN and the

Table 1

Nomenclature, molecular weight (M_n), polydispersity (M_w/M_n) and functionality (F) of the PTHF bis-macromonomers

Sample code	M_n[a] (g/mol)	M_w/M_n[a]	F[b]
PTHFAC 2200	2200	1.15	1.9
PTHFAC 3800	3800	1.10	2.0
PTHFAC 5300	5300	1.10	1.9
PTHFAAM 1600	1600	1.15	2.0
PTHFAAM 2400	2400	1.10	1.9
PTHFAAM 4500	4500	1.05	2.0

[a] Measured with GPC, THF as eluent, calibration on polystyrene standards (correction factor 0.56).

[b] Calculated with ^{1}H NMR.

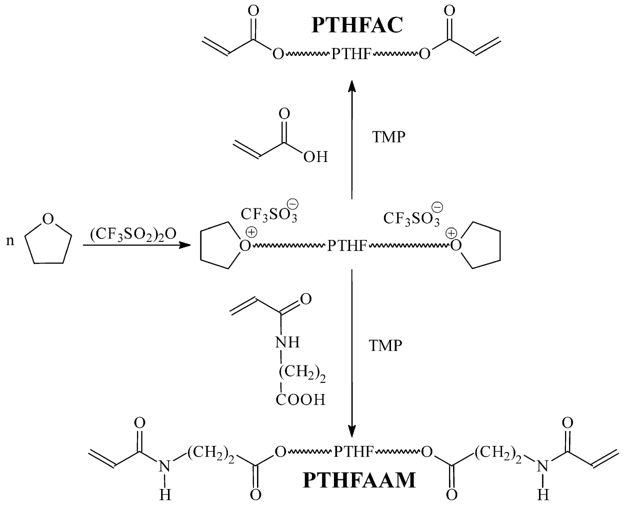

Fig. 1. Synthesis of the PTHF bis-macromonomers with acrylate and acrylamide end-groups.

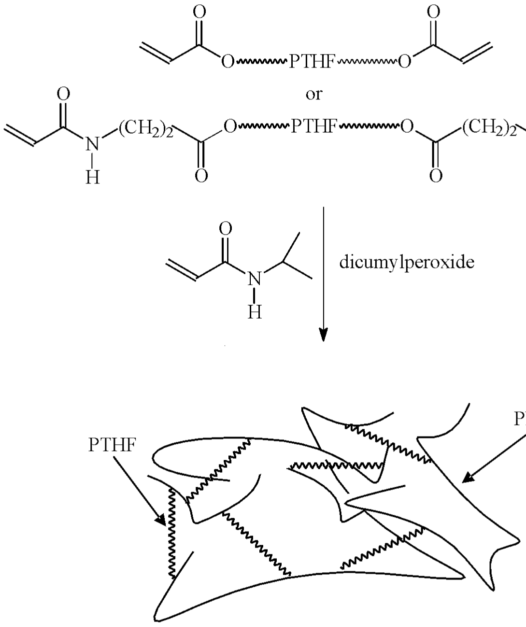

Fig. 2. Schematic presentation of the synthesis of segmented polymer networks.

Table 2
Soluble fraction and experimental composition of PNIPAA-PTHF SPNs prepared with two types of bis-macromonomer

Segmented network	Soluble fraction[a] (wt%)	Experimental composition (wt% PNIPAA/wt% PTHF)	
		TGA-analysis	Elemental analysis
PNIPAA(90)-PTHFAAM 4500(10)	4.6	90/10	89/11
PNIPAA(70)-PTHFAAM 4500(30)	3.2	67/33	–[b]
PNIPAA(50)-PTHFAAM 4500(50)	1.8	48/52	49/51
PNIPAA(70)-PTHFAAM 2400(30)	2.8	68/32	–[b]
PNIPAA(70)-PTHFAAM 1600(30)	2.0	70/30	70/30
PNIPAA(90)-PTHFAC 5300(10)	9.2	85/15	84/16
PNIPAA(70)-PTHFAC 5300(30)	6.1	69/31	68/32
PNIPAA(50)-PTHFAC 5300(50)	3.4	49/51	50/50
PNIPAA(70)-PTHFAC 3800(30)	5.8	69/31	–[b]
PNIPAA(70)-PTHFAC 2200(30)	3.7	67/33	66/34

[a] Obtained by soxhlet extraction.

[b] Values have not been determined.

composition of the reaction mixture. The difference between both values never exceeded about 5%, indicating an almost complete copolymerization.

The influence of the nature of the end-groups of the bis-macromonomer on the ultimate phase morphology of the SPNs was examined by DSC (Table 3). DSC analysis on the networks containing PTHFAC showed two glass transitions close to the T_g's of the linear homopolymers (T_g(PTHF) = −84 °C, T_g(PNIPAA) = 130 °C) [38]. For networks with 90 wt% PNIPAA, only one transition is observed at the T_g of the PNIPAA-homopolymer. We suppose that DSC is not sensitive enough to show both T_g-transitions. On the other hand, when low contents of PTHFAAM were used for the synthesis of the SPNs, only one T_g was detected between 105 and 130 °C depending on the network composition. Only for fractions of PTHFAAM higher than 50 wt%, the T_g of PTHF was also found in the DSC analysis. These data on phase morphology strongly indicate that the PTHF chains with acrylamide end-groups are more statistically incorporated in the SPNs because of the chemical resemblance of the reactive groups.

From these data, it could already be concluded that the ultimate phase morphology of SPNs is clearly dependent on the nature of the end-group of the bis-macromonomer used. Therefore, for the same network composition, the nano-separated morphology can be varied over a wide range of domain sizes. To the best of knowledge this has never been shown in the literature on multi-component polymer networks. Solid-state and wide-line NMR studies are now in progress to study these phenomena in more detail and will be reported in a forthcoming paper.

DSC was also used to check the crystallization behavior of the semi-crystalline PTHF segments in the networks. It has been demonstrated earlier that the forced compatibility of the SPNs reduces the crystallinity to a great extent [39]. While the degree of crystallinity of the bis-macromonomers varies between 29 and 36% for molecular weights equal to 1600 and 5300, respectively, no melting peak of PTHF was observed for any of the SPNs investigated.

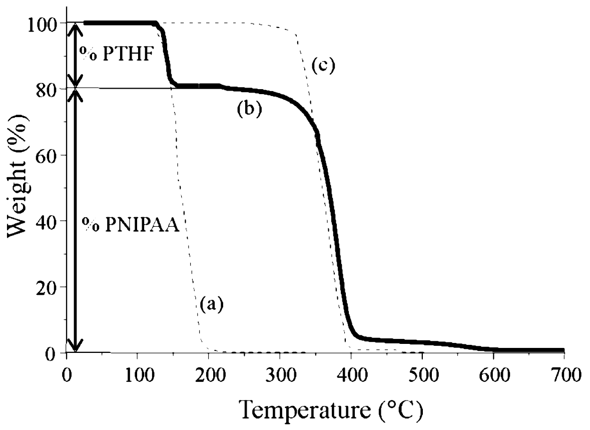

Fig. 3. Determination of the composition of PNIPAA(80)-PTHFAAM 4500(20) with TGA (curve b). The degradation curves of linear PTHF (curve a) and linear PNIPAA (curve c) are also presented (N_2 atmosphere, heating rate 10 °C min^{-1}).

3.3. Swelling behavior of the segmented polymer networks in water below the T_{cp}

The degrees of swelling (S) of the SPNs at 20 °C in water were examined as a function of the network compositions

Table 3
Glass transition temperatures of PNIPAA-PTHF SPNs prepared with two types of bis-macromonomer

Segmented network	T_g's[a] (°C)	
PNIPAA(50)-PTHFAAM 1600(50)	–	105
PNIPAA(70)-PTHFAAM 1600(30)	–	112
PNIPAA(90)-PTHFAAM 1600(10)	–	130
PNIPAA(50)-PTHFAC 2200(50)	−73	134
PNIPAA(70)-PTHFAC 2200(30)	−68	130
PNIPAA(90)-PTHFAC 2200(10)	–	136

[a] Detected with DSC, scanning rate: 10 °C/min.

Table 4
Degree of swelling, crosslink densities and cloud point temperatures of PNIPAA-PTHF SPNs with two types of bis-macromonomer

Segmented network	S in H_2O at 20 °C (%)	S in H_2O at 60 °C (%)	Crosslink density[a] (10^{-4} mol/g)	T_{cp}[b] (°C)
PNIPAA(90)-PTHFAAM 1600(10)	195	30	1.25	30.5
PNIPAA(90)-PTHFAAM 2400(10)	590	30	0.83	30.0
PNIPAA(90)-PTHFAAM 4500(10)	650	35	0.44	30.0
PNIPAA(80)-PTHFAAM 4500(20)	210	25	0.89	27.5
PNIPAA(70)-PTHFAAM 4500(30)	120	25	1.33	26.5
PNIPAA(60)-PTHFAAM 4500(40)	60	20	1.78	25.1
PNIPAA(50)-PTHFAAM 4500(50)	35	15	2.22	24.0
PNIPAA(80)-PTHFAC 2200(20)	165	20	1.82	27.5
PNIPAA(80)-PTHFAC 3800(20)	195	25	1.05	28.0
PNIPAA(80)-PTHFAC 5300(20)	335	25	0.75	27.5
PNIPAA(90)-PTHFAC 5300(10)	820	40	0.38	29.5
PNIPAA(70)-PTHFAC 5300(30)	220	25	1.13	26.0
PNIPAA(60)-PTHFAC 5300(40)	100	20	1.51	24.0
PNIPAA(50)-PTHFAC 5300(50)	85	15	1.89	24.0

[a] Number of crosslinks per unit weight of network.

[b] Obtained by DSC.

and the molecular weight of the bis-macromonomer (Table 4). The crosslink densities of the networks, calculated according to the method described by Kennedy and Allen [40], are also presented in Table 4. Although the phase morphologies of the SPNs clearly differ in the solid state, their swelling behavior at room temperature shows classical trends. The degree of swelling increases with decreasing crosslink density or higher overall hydrophilicity of the SPNs, i.e. with higher molecular weight of the bis-macromonomer and/or higher PNIPAA-content.

3.4. Thermo-responsive swelling behavior of the segmented polymer networks

The effect of temperature on the swelling behavior of the SPNs was also studied. In Fig. 4, the degree of swelling versus temperature diagrams of swollen SPNs with PTHFAAM are presented. Similar results were found for networks synthesized with PTHFAC as macromolecular crosslinker. The degrees of swelling above the T_{cp} (60 °C) are also presented in Table 4. For a crosslink density up to 3.75×10^{-4} mol/g, an abrupt change in the degree of swelling was observed when the temperature was brought above the T_{cp} (Fig. 4, curves a–d). For higher crosslink densities, a more continuous contraction was observed (Fig. 4, curve e).

The sharp volume transition is ascribed to the thermo-responsiveness of the PNIPAA chains. Below the T_{cp}, the polymer–water interactions of the PNIPAA chains dominate, while above the T_{cp}, the water molecules are rejected out of the swollen network because of the stronger polymer–polymer interactions. For high crosslink densities, the formation of such interactions becomes difficult because of mobility restrictions, which results in a less pronounced gel contraction.

Similar T_{cp}-values were found for the water-swollen networks by DSC and visual observations. The T_{cp} of the networks shifts to lower temperatures with increasing

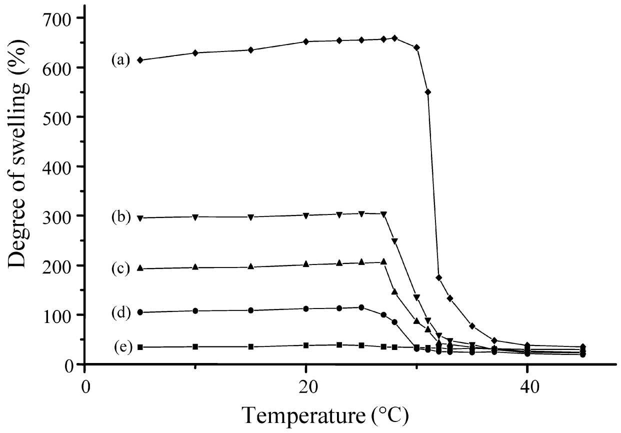

Fig. 4. Degree of swelling in water as a function of temperature for the following SPNs: (a) PNIPAA(90)-PTHFAAM 4500(10); (b) PNIPAA(80)-PTHFAAM 4500(20); (c) PNIPAA(70)-PTHFAAM 4500(30); (d) PNIPAA(60)-PTHFAAM 4500(40); (e) PNIPAA(50)-PTHFAAM 2400(50).

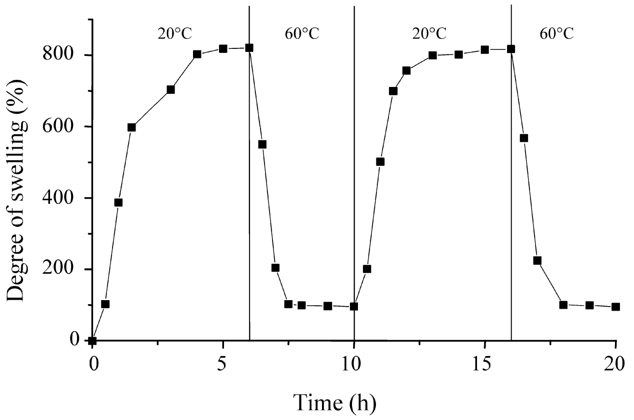

Fig. 5. Thermo-responsive swelling behavior of network PNIPAA(90)-PTHFAC5300(10).

Table 5
Permeability of some segmented networks at 20 and 60 °C

Segmented polymer network	Water permeability at 20 °C (g/m^2 h)	Water permeability at 60 °C (g/m^2 h)
PNIPAA(80)-PTHFAC 2200(20)	420	105
PNIPAA(80)-PTHFAC 3800(20)	440	125
PNIPAA(80)-PTHFAC 5300(20)	460	225
PNIPAA(90)-PTHFAC 2200(10)	600	245
PNIPAA(70)-PTHFAC 2200(30)	300	40

amount of hydrophobic PTHF (Table 4). In this way, the thermo-responsive properties of the networks based on PNIPAA and PTHF could be adjusted as a function of the composition of the networks.

The reversibility of the swelling/deswelling process of the networks was also examined by changing the temperature periodically above and below the T_{cp} as shown for a particular SPN in Fig. 5.

From this figure, it becomes clear that the shrinking is about 3 times faster than the swelling process of the SPNs. As the polymer chains are stretched in a swollen network, the diffusion of the water molecules out of the hydrogel during shrinking is easier than the diffusion in the dense polymer coils during the swelling process.

3.5. Water permeability of the segmented polymer networks

The water permeability of the SPNs was measured as a function of temperature. When the T_{cp} is reached, a sharp decrease in permeability is observed as a result of the decrease in hydrophilicity of the membranes. The water permeability and the corresponding swelling degrees for PNIPAA(80)-PTHFAC 5300(20) are presented in Fig. 6. Similar results were found for all other networks synthesized with PTHFAC or PTHFAAM as macromolecular crosslinker.

As expected, the composition of the SPNs and the molecular weight of the bis-macromonomers influence the water permeability at all temperatures. In Table 5, the water permeability is presented below and above the T_{cp} for different SPNs synthesized with PTHFAC as crosslinker. Similar results are observed for networks based on PTHFAAM. Above and below the T_{cp}, the water permeability follows the same trends as described earlier for the swelling behavior of the SPNs and is thus directly related to the crosslink density and the overall hydrophilicity. Below the T_{cp}, when the SPNs are amphiphilic and highly swollen in water, higher PNIPAA contents result in a higher hydrophilicity and faster water permeation through the networks. Above the T_{cp}, both components in the SPNs are hydrophobic and the water permeability is more dependent on the molecular weight of the bis-macromonomer. Thus, the effect of the crosslink density is more pronounced than below the T_{cp}.

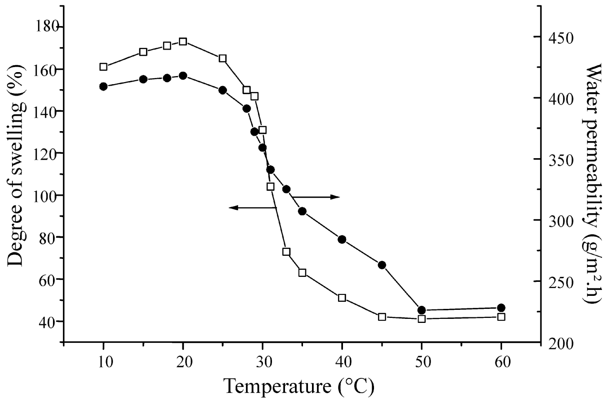

Fig. 6. Degree of swelling in water and water permeability as a function of temperature for PNIPAA(80)-PTHFAC 5300(20).

3.6. Pervaporation experiments with water/isopropanol mixtures

Pervaporation experiments were performed on a water/-isopropanol mixture (90/10 wt%). Isopropanol is a relative hydrophobic molecule that is still soluble with water for all concentrations. At all temperatures the membranes permeate the smaller water molecule faster than isopropanol (Table 6), although sorption experiments indicated that isopropanol was preferentially sorbed at the upstream part of the membrane.

The temperature dependent behavior of the permeability and selectivity is presented for PNIPAA(80)-PTHFAC 3800(20) in Fig. 7. There is a sharp decrease in both

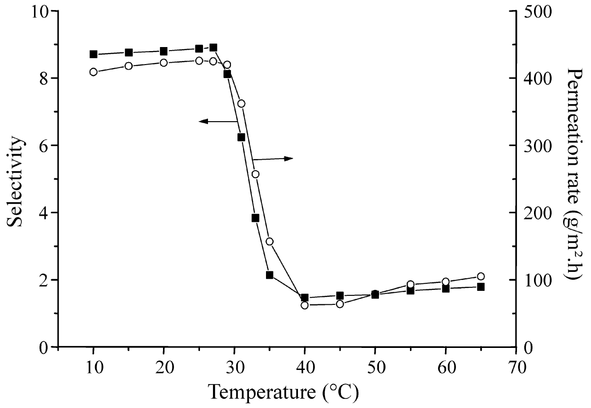

Fig. 7. Permeation rate and selectivity of membrane PNIPAA(80)-PTHFAC 3800(20) as a function of temperature (feed:water/isopropanol 90/10 wt%).

Table 6
Permeation rate and selectivity at 20 and 60 °C for a selection of segmented polymer networks (feed:water/isopropanol 90/10 wt%)

Segmented polymer network	20 °C		60 °C	
	Selectivity α	Permeation rate (g/m^2 h)	Selectivity α	Permeation rate (g/m^2 h)
PNIPAA(80)-PTHFAC 2200(20)	9.0	405	1.9	85
PNIPAA(80)-PTHFAC 3800(20)	8.8	420	1.8	95
PNIPAA(80)-PTHFAC 5300(20)	8.3	445	1.6	130
PNIPAA(90)-PTHFAC 2200(10)	8.1	560	1.8	135
PNIPAA(70)-PTHFAC 2200(30)	9.7	285	2.0	35

permeability and selectivity of the membranes upon raising the temperature above the T_{cp} of the SPN. These results are unexpected, because a decrease in permeability generally leads to an increase in selectivity [10,12]. They can be explained by the considerations of hydrophilic/hydrophobic properties of the networks. Below the T_{cp} the networks are amphiphilic and highly swollen in the aqueous feed mixture, while above the T_{cp} the networks become hydrophobic and less swollen. As the PNIPAA-chains are more stretched and diffusion is easier below the T_{cp}, water, which is the preferentially permeated component, is transported faster through the membrane at these temperatures. On the other hand, above the T_{cp} the hydrophobic and shrunken state of both polymer segments in the membranes hinders the diffusion of the small water molecules and promotes the transport of the preferentially adsorbed more hydrophobic isopropanol. These phenomena result in the observed decreasing membrane permeability and selectivity (Table 6). The lower selectivity at higher temperature could be applied to extract the hydrophobic component from the membranes for a regeneration purpose. More experiments on other solvent mixtures are needed to confirm this hypothesis.

The performance of the membranes depends on the membrane composition and molecular weight of the PTHF bis-macromonomers. Table 6 shows an overview of the selectivity and permeation rates of some segmented networks synthesized with PTHFAC. It can be observed that at all temperatures the membrane performance follows the same trends as those observed for the water permeability, i.e. the permeation rate decreases and the selectivity increases with lower molecular weight and higher fractions of bis-macromonomer. Similar results were obtained for networks synthesized with PTHFAAM, which indicates that the degree of heterogeneity in the dry state does not have a significant influence on the permeability behavior of the SPNs.

4. Conclusions

SPNs based on hydrophobic PTHF and thermo-responsive PNIPAA were synthesized by free radical copolymerization of PTHF bis-macromonomers with NIPAA in the bulk state. Elemental analysis, TGA and detection of soluble fractions all confirmed the almost quantitative copolymerization reaction in these multi-component polymer networks. The hydrophilic/hydrophobic balance and the crosslink density of the networks were varied by changing the ratio of both polymers in the network and the molecular weight of the macromolecular crosslinker. It has been reported for the first time that the phase behavior of the SPNs in the dry state is much influenced and adjustable by the nature of the end-groups of the bis-macromonomers. While acrylate end-groups resulted in SPNs with a clearly two-phase morphology, SPNs synthesized with PTHFAAM had a much more homogeneous morphology. The polymer networks showed a thermo-responsive swelling and pervaporation behavior, which highly depend on the crosslink density and the overall hydrophilicity of the networks. This study has extended the applicability of thermo-sensitive polymers in membrane processes.

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