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Generation of a selective layer on polyacrylonitrile membrane supports for separation of aromatic/non-aromatic hydrocarbon mixtures by pervaporation

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SUMMARY: An application of the "pore filling" concept yielded high-performance composite membranes for the selective pervaporation (PV) separation of aromatic/non-aromatic hydrocarbon mixtures. Asymmetric polyacrylonitrile (PAN) membranes (average pore size of about 12 nm) were used as support for polymeric PV separation phases which were prepared in situ by heterogeneous photo-initiated graft copolymerization. The impact of chain length of methyl polyoxyethylene (meth)acrylates and preparation parameters (UV irradiation time and degree of grafting) were analysed using PV with toluene/heptane (20/80 wt-ratio; 80 °C) as model feed. High selectivity and high permeate fluxes were achieved. Major reasons for the excellent performance were the small effective PV barrier thickness (< 5μm) and the covalent anchoring of the coated polymer.

INTRODUCTION

Membrane separation processes have been considered as a promising way to separate organic-liquid mixtures [1]. A suitable membrane can separate organic-liquid mixtures very efficiently, making membrane processes competitive to conventional separation processes such as distillation and extraction [2]. Therefore it is very important to develop new membranes which show high permselectivity.

In applying polymeric membranes to separate organic-liquid mixtures, there is a problem of membrane swelling, which reduces selectivity due to its plasticization effect. Therefore, suppressing membrane swelling is important to obtain good permselectivity. In recent years, numerous investigations about PV were reported and various kinds of membranes were prepared which show high permselectivity. In these membranes, membrane swelling is controlled by their structure [3,4]. We have proposed the "pore filling" concept to prevent membrane swelling [5,6]. Pores of a porous support that is inert to organic liquids were filled with graft polymer by heterogeneous photo-initiated graft copolymerization technique. The

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unlimited swelling of the covalently anchored copolymer is suppresed by the matrix of the support. The resulting composite membranes show high permeabilities and high permselectivities in PV of organic-liquid mixtures.

The subject of the present work is the design of high-performance ”pore filling” composite membranes for selective separation of aromatic/non-aromatic hydrocarbon mixtures. We prepared various composite membranes with thin, defect-free layers of methyl (polyoxyethylene) (meth)acrylates (MePEOMA´s) on/in PAN ultrafiltration (UF) membranes by heterogeneous photoinitiated graft copolymerization. The impact of PEO chain length and preparation parameters upon PV performance was analyzed using the system toluene/heptane as model feed. Selectivities $\alpha_{\mathrm{toluene/heptane}}$ up to 8.5 and permeate fluxes up to 1 kg/m^2 h were achieved.

EXPERIMENTAL

PAN support

The PAN UF support was prepared by the phase inversion technique (solvent: DMF; non solvent: water) at the GKSS. A polyester (PETP) fabric was used as reinforcement. The PAN UF support had the following properties - water flux 140 l/m^2 h at 0.1 MPa; nitrogen flux 156 – 182 m^3/m^2 h at 0.1 MPa; an average pore diameter of about 12 nm and an average thickness of about 60 μm.

Membrane coating with benzophenone (BP)

Pre-weighed membranes were immersed in BP solution (100 mM in methanol) for about 18 h at room temperature (RT). Methanol was evaporated from the sample at RT; the membrane was then kept in a vacuum oven for 1 h.

Photo graft polymerization

The experimental set-up and typical modification procedures have already been described in detail [7,8]. A Fusion UV System F300M was used for UV irradiation. Membrane samples (usually 7.5 cm diameter) were always placed in the centre of a reaction chamber, equipped with a special glass window (light filter, $\lambda_{\mathrm{exc}} > 300$ nm) for UV irradiation. Solutions of monomer in water (c_M) containing the BP-coated membranes were irradiated with UV light (distance 25 cm; ~ 122 mW cm^{-2}; various amounts of time, t_B). The samples were then extracted extensively first with water and then with hot acetone, and dried and weighed to determine the degree of graft polymer modification (DG) which was calculated according to

$$DG = m_{spec} \bullet (m_{gr} - m_o)/m_o \ ,$$

where m_o is the initial membrane sample weight, m_{gr} is the weight after modification, and m_{spec} is the specific weight (per outer surface area) of the membrane type. Using identical modification conditions, the reproducibility of DG was always better than ±10 %.

Pervaporation (PV)

PV experiments were carried out with a laboratory scale apparatus using a stainless steel cell P 28 supplied by CELFA AG. If not stated otherwise, downstream pressure and feed temperature kept constant below 1 mbar and 80 °C, respectively. The feed velocity was increased up to 40 l/h in order to minimize influence of concentration polarization. The permeate was collected in a trap cooled with liquid nitrogen. Fittings and valves between the tank, measuring cell and cooling traps were heated in order to avoid condensation. The fluxes were determined gravimetrically. The composition of feed and permeate was determined by gas chromatography. The membranes were characterized with a mixture of toluene/n-heptane (20/80 wt-ratio).

RESULTS AND DISCUSSION

A PAN UF membrane was used and activated by coating with the photoinitiator benzophenone (BP). (Meth)acrylates with methyl protected polyoxyethylene (PEO) side groups of various sizes (the average molecular weight of the PEO chain was Mw = 103, 200, 400 and 1000 g/mol) were simultaneously graft-copolymerized from water solutions onto the membrane. Quantitative extraction of the side products as homopolymer and unreacted BP followed. UV irradiation time is the mainparameter. The results of the photo-initiated graft copolymerization with four monomers, which differ in the molecular weight of their PEO substituent, are shown in figure 1.

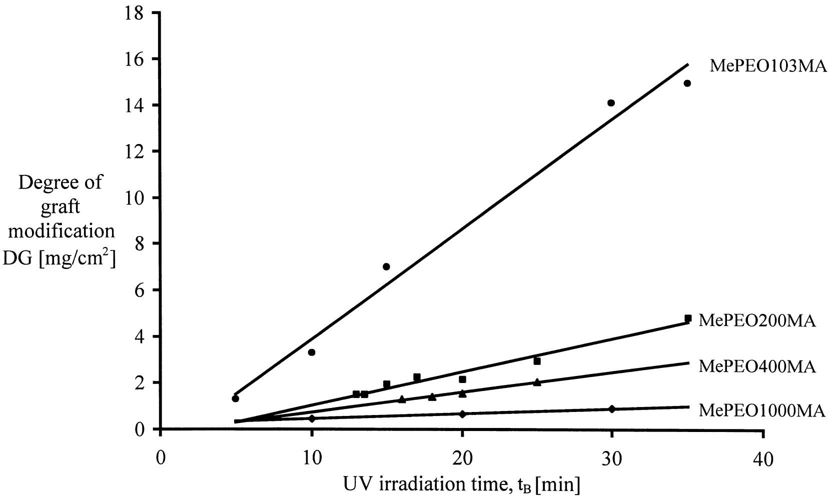

Figure 1: Results of the benzophenone initiated graft copolymerization with different MePEOMA´s; the number shows the M_w of the PEO chain.

The degree of graft modification always varies linearly with the irradiation time; the conditions were selected to prevent polymer precipitation during the polymerization. This is necessary to avoid macroscopic layer inhomogenities.

For a PV application, a dense membrane is needed. To test the usability, we measured the water flux through the membrane. For all grafted monomers, the solvent permeabilities decreased systematically with increasing degree of graft modification. For the used UF membranes at DG beyond 1 mg/cm^2 the UF water flux became negligible (table 1); those ”critical” DG were referred to as DG_{crit}.

Table 1: Water flux through unmodified and modified composite membranes

Sample	DG [μg cm^{-2}]	Water flux [l m^{-2} h^{-1} bar^{-1}]
PAN	unmodified	140
PAN + MePEO200MA	380	2.8
PAN + MePEO200MA	940	0[a]
PAN + MePEO400MA	321	4.9
PAN + MePEO400MA	642	2.7
PAN + MePEO400MA	980	0[a]

[a] No water flux was measureable up to 5 bar.

In ATR-IR spectra of the outer surface of modified membranes, PAN was also detected beside the new poly(meth)acrylate structures; this confirmed additionally, that the membranes have a "pore filling" structure. This means the pores of the UF membrane should be blocked completely with grafted functional copolymers.

In order to evaluate the impact of composite membrane structure on the performance, PV experiments were performed with toluene/heptane mixtures. Differences in membrane PV performance should arise from the variation of the chain length of the graft copolymer side groups. However due to the composite structure (pore filling) only qualitative interpretations were possible. All composite membranes were selective for toluene (table 2). The small (MePEO103MA) and the large size monomers (MePEO400MA) seemed to form less effective barriers; fluxes were high and selectivities low. The MePEO103MA gave a selectivity $\alpha_{\text{toluene/heptane}}$ of 4.7 and a permeate flux of 1.58 kg m^{-2} h^{-1}, and the MePEO400MA gave a selectivity $\alpha_{\text{toluene/heptane}}$ of 4.3 at a permeate flux of 5.20 kg m^{-2} h^{-1}. The best results for the separation of toluene from the feed could be achieved with MePEO200MA. The concentration of toluene after PV increases from 20 up to 68 wt-%. The resulting selectivity was 8.5 at a permeate flux of 0.3 kg m^{-2} h^{-1}. A DG $\geq$ DG$_{\text{crit}}$ was necessary for useful composite membranes. a further increase of the DG over that critical value reduced the total permeate flux and increased the selectivity (figure 2).

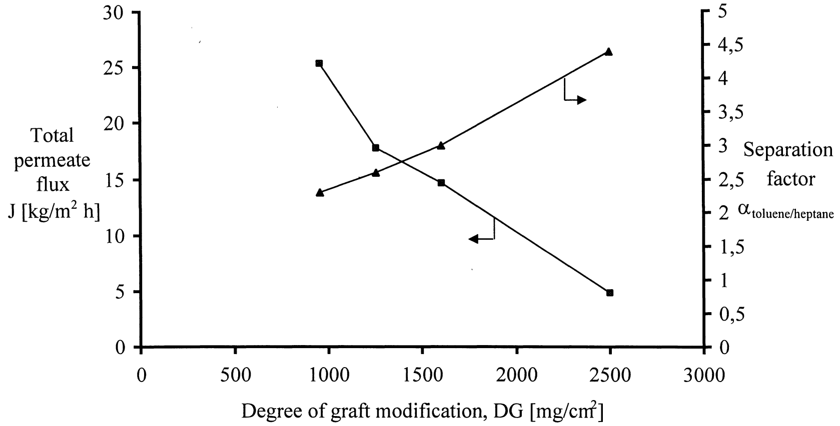

Figure 2: PV result of a composite membrane with MePEO400MA as graft copolymer.

Table 2: Selected photo graft copolymer PAN composite membranes with preparation parameters and representative PV results for toluene/heptane mixtures (20/80 wt-ratio) as feed

Monomer	UV irradiation time t_B [min][a]	Degree of graft modification DG [mg/cm^2]	Total Permeate flux J [kg/m^2 h]	Permeate concentration [wt-%]	Selectivity $\alpha_{toluene/heptane}$
MePEO103MA	9	1.66	11.9	25.2	1.3
MePEO103MA	10	2.86	1.58	55.4	4.7
MePEO200MA	13	1.35	9.78	46.2	3.5
MePEO200MA	17	2.02	2.93	55.1	4.6
MePEO200MA	25	2.67	4.08	48.6	4.1
MePEO200MA	35	4.15	2.68	53.7	5.0
MePEO200MA	60	5.94	0.31	67.8	8.5
MePEO400MA	15	0.96	25.31	36.2	2.3
MePEO400MA	20	1.26	18.73	37.8	2.7
MePEO400MA	22	1.28	16.73	39.4	2.6
MePEO400MA	25	1.78	13.76	40.5	2.9
MePEO400MA	25	2.37	10.87	41.4	3.0
MePEO400MA	30	2.50	5.20	51.2	4.3

[a] The concentration of the monomer (c_M) was always 5 g/l.

All results could be explained by a "pore filling" model for the graft copolymer composite membranes. A modification with DG $\geq$ DG_{crit} is necessary to block all separation layer pores of the UF membrane. This could be realized by graft functional polymer chains attached to the surface of the matrix polymer PAN, but it was effective only if the pores were small enough (average pore diameter $\leq$ 12 nm) [5]. The photo-excitation allowed heterogeneous graft copolymerization initiation also in such small pores. This was not possible with the plasma excitation previously used for pore filling of MF membranes [9].

In all cases, the covalent attachment to the matrix membrane polymer ensured that under PV conditions the graft polymer layer remains stable on/in the membrane. A very thin graft copolymer film on the outer surface ($d < 1$ µm according to ATR-IR, below the SEM detection limit) changed the interface properties [10]. The selective barrier was essentially confined inside the very thin separation layer of the UF matrix membrane, thus also minimizing the barrier thickness. Hence, the total PV selective layer was much thinner than in other homogeneous or composite PV membranes [11,12]. This was the prerequisite of the extraordinarily high fluxes. Moreover, fixation inside the pores prevented the selective polymer from excessive swelling, thus also providing the high selectivities. As a consequence, too much graft polymer ($DG \geq DG_{crit}$) as film on the outer surface did not improve the selectivity. In general, to ensure high fluxes and selectivities, optimization of the permeant/polymer interactions was required. Enhanced graft polymer toluene affinity correlated with improved selectivity but reduced flux.

CONCLUSION

The pore filling heterogeneous graft copolymerization concept has been applied to asymmetric membranes and was quite successful. High PV fluxes along with good selectivities for the removal of toluene from heptane could be achieved. With MePEOMA as graft copolymer selectivities $\alpha_{toluene/heptane}$ between 4 - 8.5 and permeate fluxes between 0.3 - 5 kg m^{-2} h^{-1} could be obtained, if the degree of graft polymerization was over the critical value (DG_{crit}). This was necessary to block all separation layer pores of the UF membrane. Due to the simple functionalization principle, a great variety of PV selective thin layer composite membrane structures could additionally be prepared. This method provides promising possibilities to approach other PV separation problems.

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