

Description

The invention relates to a semipermeable composite membrane, with a porous carrier substrate, whereby said carrier substrate is provided with a polymer network, obtained by polycondensation, especially interfacial polymerisation, which is built up of at least one reactive polyfunctional monomer or oligomer or prepolymer or polymer having as functional groups -NHR_4 ($\text{R}_4 = \text{H}$ or alkyl with $\text{C}_1\text{-C}_{20}$), -OH or -SH and at least one acid halide containing polymer is a copolymer of one or more vinyl monomers and a monomer containing an acid halide group as functional groups -COX , $\text{-SO}_2\text{X}$, -POXR_5 or $\text{-NR}_6\text{COX}$, wherein X represents Cl, Br or J, while R_5 and R_6 each represent an alkoxy group or an alkyl group with 1-16 carbon atoms, preferably 1-5 carbon atoms, as well as to a process for the manufacture of such membranes and finally to a method for the separation of components in an organic liquid phase or in the vapour phase.

Such composite membranes suitable for reverse osmosis and obtained by interfacial polymerisation, are already known. The article Evolution of Composite Reverse Osmosis Membranes of J.E. Cadotte, American Chemical Society, 1985, discloses for instance the development of a series of composite membranes, which have resulted in the commercial FT-30 membrane manufactured by interfacial polymerisation of aromatic diamines in the aqueous phase with triacyl chlorides in the organic phase (page 279 and following), with as principal application desalination of aqueous solutions. Further, still reference may be made to the U.S. patent specification 4,721,568. For another good review it is referred to the U.S. patent specification 4,360,434 (Kawaguchi et al.). This patent describes amphoteric ion-permeable composite membranes and shows at page 32 which types of monomeric diacid chlorides may be applied therefore.

With the above described FT-30 membranes reverse osmosis tests have been carried out in non-aqueous systems, whereby the separation results obtained in a methanolic environment are listed in Table A.

- From reverse osmosis test on the above FT-30 membrane in a non-aqueous system follows that:
- a. no n-hexane flux (1%, by weight, of n-docosane in n-hexane at room temperature and at 40 bar) is observable
 - b. there is no toluene flux (the same in toluene)
 - c. in a 1%, by weight, solution of PEG 300 in methanol a good retention for PEG 300 (93%) is found but a moderate methanol flux of 30 $\text{kg}/(\text{m}^2\cdot\text{hour})$.

From these data the following conclusions may be drawn.

Applicant prepared composite membranes from aromatic diacid chlorides + aliphatic polyfunctional amines.

Such membranes have been submitted to reverse osmosis tests with the following result:

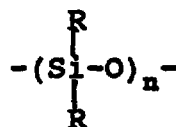
- a. no n-hexane and no n-toluene flux
- b. in methanol moderate to bad methanol fluxes 4-13 $\text{kg}/(\text{m}^2\cdot\text{hour})$ and moderate retentions for PEG 300 (53-68%).

Subsequently membranes have been prepared from aliphatic diacid chlorides + aliphatic polyfunctional amines, with the following result:

- a. no n-hexane and toluene flux; not even when large hydrophobic moieties are introduced, while using $\text{ClOC}(\text{CH}_2)_8\text{COCl}$
- b. in some cases in methanol results may be obtained, which are comparable as in case of a FT-30 membrane (good retention/moderate flux); in some cases better flux values, but somewhat worse retentions (the latter is not desirable).

From the above may be concluded that this type of membrane built up of aromatic and/or aliphatic diacid chlorides + polyfunctional (aromatic or) aliphatic amines is unsuitable for application in n-hexane ($\text{C}_5\text{-C}_8$ aliphatic) or toluene (aromatic) systems. On the other hand, in methanol good retentions may be obtained for PEG 300, but at low fluxes.

The known membranes with monomeric or oligomeric polyacid halides have further in general the disadvantage that they do not show a swelling, have a small mesh size, are rigid, and have a high polarity. Further, there are known composite membranes, which are built up of polymeric diacid chlorides + polyfunctional amine. In this respect mention is made of EP 0 254 556 (Bend Research Inc.). The polymeric diacid chloride comprises terminal acid chlorides with a polymeric middle part



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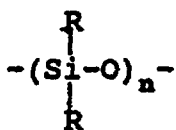
It is known that this middle part has a high affinity to n-hexane and toluene, and is therefore suitable for application in R.O. (reverse osmosis) composite membranes in this type of solvents. However, the used prepolymers based on siloxanes comprise as terminal groups -NCO.

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The membranes described according to this European patent application are suitable for the separation of gases. Not a word is mentioned in the European patent application EP 0 254 556 about the application of such membranes for the separation of components in an organic liquid phase or in the vapour phase.

It is observed that the middle part

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is responsible for the affinity of the top layer for RO separations in an organic environment. Beside the terminal acid chloride groups this is an essential limitation to tune the affinity of the top layer (and thus the flux and retention behaviour) to the solvent stream wherein the separation takes place.

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Now the invention intends to provide semipermeable composite membranes, which eliminate the disadvantages inherent to the known membranes and which are suitable for the separation of components in an organic liquid medium at a good flux and a good retention.

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To this end the invention provides a semipermeable composite membrane, with a porous carrier substrate, whereby said carrier substrate is provided with a polymer network obtained by polymerisation, especially by interfacial polymerisation, which network is built up of at least one reactive polyfunctional monomer or oligomer or prepolymer or polymer with as functional groups -NHR₄ (R₄ = H or alkyl with C₁-C₂₀), -OH or -SH and at least one acid halide containing polymer with as functional groups -COX, -SO₂X, -POXR₅ or -NR₆COX, wherein X represents Cl, Br or J, while R₅ and R₆ each represent an alkoxy group or an alkyl group with 1-16 carbon atoms, preferably 1-5 carbon atoms, characterized in that the acid halide containing polymer is a copolymer if one or more vinyl monomer and a monomer containing an acid halide group.

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Surprisingly it appeared that the semipermeable membranes according to the invention, which are novel, are especially suitable for the separation of components in an organic liquid phase or in the vapour phase, for instance polyethylene glycol in methanol, n-docosane in n-hexane, etc. Moreover the membranes according to the invention do not appear to show practically any swelling, they have a substantial mesh size, they are flexible, they have a larger affinity for organic liquids owing to a lower polarity.

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In general the mole fraction of the acid halide containing monomer in the polymer amounts to 1-20 and preferably 5-11% in case of the semipermeable composite membranes according to the invention.

It has appeared that it may be favourable when the polymer network moreover comprises a reactive polyfunctional monomer or oligomer with as reactive groups -COX, -SO₂X, -POXR₅, -NR₆COX or NCO, wherein X represents Cl, Br or J, while R₅ and R₆ each represent an alkoxy group or an alkyl group with 1-16 carbon atoms, preferably 1-5 carbon atoms.

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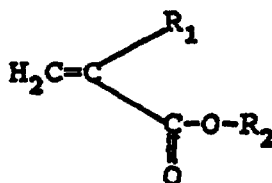
An example of an often used reactive polyfunctional monomer is isophthaloyl chloride.

According to the invention it is preferable when the acid halide containing polymer is a copolymer of acryloyl chloride H₂C=CHCOCl or methacryloyl chloride H₂C=C(CH₃)COCl with one or more vinyl containing monomers.

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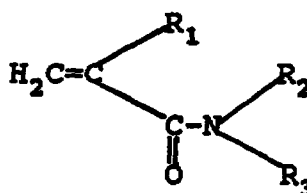
Especially favourable are those semipermeable composite membranes according to the invention, whereby the vinyl containing monomer is an acrylate with the formula

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wherein R_1 and R_2 , whether or not equal to each other, represent H, a C_1 - C_{20} alkyl, an aryl like phenyl, naphthyl, etc., while R_2 is whether or not substituted by an OH, halogen, siloxane, OR, wherein R is a whether or not substituted C_1 - C_{10} alkyl.

Moreover the semipermeable composite membranes according to the invention appear to satisfy properly when the vinyl containing monomer is an acryl amide with the formula



wherein R_1 , R_2 and R_3 , whether or not equal to each other, represent H, a C_1 - C_{20} alkyl, whether or not substituted by OH, halogen, etc., an aryl like phenyl, naphthyl.

Satisfactory separation results are obtained with membranes, wherein the vinyl containing monomer is isobutyl methacrylate, a mixture of isobutyl methacrylate and trifluorethyl acrylate, a mixture of isobutyl methacrylate and ethyl acrylate, a mixture of isobutyl methacrylate and N-vinyl-pyrrolidone, a mixture of isobutyl methacrylate and N-vinyl-N-methylacetamide, a mixture of isobutyl methacrylate and acrylic acid, methyl methacrylate, ethyl acrylate or 2-ethyl-hexyl acrylate.

Examples of other suitable vinyl containing monomers are N-vinyl pyrrolidone, vinyl acetate, butadiene, styrene, vinyl ethers like $\text{C}=\text{C}-\text{O}-\text{R}$, vinyl chloride, vinylidene chloride, isobutylene, acrylonitrile, vinyl pyridine.

Further the invention comprises a process for the manufacture of a semipermeable composite membrane by coating a porous substrate with a polymer network obtained by polycondensation, especially interfacial polymerisation, characterized in that the porous substrate is treated with a solution of at least one reactive polyfunctional monomer or oligomer of prepolymer or polymer with as reactive groups $-\text{NHR}_4$ ($\text{R}_4 = \text{H}$ or alkyl with $\text{C}_1 - \text{C}_{20}$), $-\text{OH}$ or $-\text{SH}$ and possibly a surface active compound in water, after which the substrate treated in this manner is further treated with a solution of at least one acid halide containing polymer with as reactive groups $-\text{COX}$, $-\text{SO}_2\text{X}$, $-\text{POXR}_5$, $-\text{NR}_6\text{COX}$ or $-\text{NCO}$, wherein X represents Cl, Br or J, while R_5 and R_6 each represent an alkoxy group or alkyl group with 1 to 16 carbon atoms, preferably 1 to 5 carbon atoms, in a suitable organic solvent, after which the substrate treated in this manner is dried and subsequently optionally subjected to a heat treatment.

Finally the invention extends to a method for the separation of components in an organic liquid phase or in a vapour phase using the above described semipermeable composite membranes according to the invention.

The invention is now further elucidated by the following non-limitative examples.

Example I

A wet flat support membrane of polyimide (0.30 x 0.18 m), prepared from a 16%, by weight, solution of a polyimide-type (Lenzing, p84) in DMF, was applied to a cylindrical body manufactured of polyethylene. This support membrane was dipped for 15 minutes in an aqueous phase with 1.0%, by weight, $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ (N4) as polyfunctional monomer and 0.04%, by weight, of sodium dodecyl sulphate as surface active compound. Then the membrane was taken out of the aqueous phase, after which the excess of aqueous solution was removed with a rubber roller press. After about 1 minute the membrane was transported to an organic phase, consisting of toluene/chloroform (96/4 g/g) with dissolved therein 0.05%, by weight, of isotaloyl chloride (IPC) and 0.6%, by weight, of poly(isobutyl methacrylate-co-acryloyl chloride) (molar proportion 95/5; η intrinsic viscosity 0.53 dl/g in acetone, $c=0.5$),

obtained after complete conversion during solution polymerisation of a solution of 53.7%, by weight, of the corresponding monomers in chloroform in the presence of 0.5 mol.% 2,2'-azobis (2-ethyl propionitrile) (AIBN) as a radical initiator. The membrane was for about 1 minute in the organic phase. Further the membrane was dried for about 3 minutes at room temperature, transferred to a flat glass plate and thereafter dried for 15 minutes in an air circulation oven at 90 °C.

The reverse osmosis properties of this membrane were evaluated at room temperature at 40 bar in a solution of 1.0%, by weight, of polyethylene glycol (PEG 300, Fluka) in methanol with as a result a methanol flux of 89 kg/(m².hour) and a retention PEG 300 of 86%.

10 Comparative example Ia

The procedure of example I was repeated on the understanding that the organic phase contained, beside IPC, the non-reactive polymer poly(isobutyl methacrylate). In a reverse osmosis experiment as described in example I this membrane showed a methanol flux of 35 kg/(m².hour) and a retention PEG 300 of 81%. From the above the favourable effect of the acid chloride groups built into the polymer on the methanol flux and retention PEG 300 shows clearly.

Example II

20 In an analogous manner as described in example I a composite membrane was prepared. The organic phase, however, comprised toluene-hexane (14/86 g/g) with dissolved therein a copolymer built up of isobutyl methacrylate (i-BMA) and acryloyl chloride. As a control, example IIa, a composite membrane was made with as barrier layer poly(isobutyl methacrylate).

The results of the flux and retention tests of a reverse osmosis experiment in a 1.0%, by weight, solution of n-docosane in n-hexane, executed at room temperature and at 40 bar, are mentioned in Table B.

Example III

30 The procedure of example I was repeated on the understanding that the organic phase contained, beside 0.05%, by weight, IPC, 0.6%, by weight, of poly(isobutyl methacrylate-co-acryloyl chloride) (molar ratio 89/11; η intrinsic 0.56 dl/g in acetone, $c=0.5$), obtained after complete conversion during solution polymerisation of a 57%, by weight, solution of the corresponding monomers in chloroform in the presence of 0.5 mol.% AIBN as a radical initiator.

The results of the flux and retention tests showed a methanol flux of 99 kg/m².hour and a retention PEG 300 of 87%.

Example IV

40 In the manner described in example I a composite membrane was prepared. The organic phase consisted of freon, toluene, toluene/hexane (10/90 g/g), or toluene/chloroform

The results of the flux and retention tests of 1.0%, by weight, solutions of n-docosane in n-hexane and in toluene and of a 1.0%, by weight, solution of PEG 300 in methanol, evaluated at room temperature and a pressure of 40 bars, are mentioned in Table C.

45 Example V

In the manner described in example I a composite membrane was prepared. The organic phase consisted of freon with dissolved therein 0.61%, by weight, of poly(isobutyl methacrylate-co-acryloyl chloride) (molar ratio 95/5; intrinsic 1.96 dl/g in acetone $c=0.5$), obtained after 65% conversion during solution polymerisation of a 41.7%, by weight, solution of the corresponding monomers in chloroform in the presence of 0.03 mol.% of AIBN as a radical initiator. The aqueous phase comprised 1.0%, by weight, of one of the following polyfunctional amines, to wit H₂N-(CH₂-CH₂-NH)_n-CH₂-CH₂-NH₂ [$n=0(2N)$, $n=2(4N)$, $n=4(6N)$].

55 The results of the flux and retention tests, executed in a corresponding manner as described in example IV, are mentioned in table D.

Example VI

In the manner described in example V a composite membrane was prepared. The aqueous phase contained 1.0%, by weight, of the polyfunctional amine N4, as well as 1.0%, by weight, of triethyl amine as an acid binding agent. As a control a composite membrane was made without the addition of triethyl amine, comparative example Va. The flux and retention tests of a 1.0%, by weight, solution of n-docosane in n-hexane are mentioned in Table E.

From example VI and VIa follows that the addition of an acid scavenger to the aqueous phase has a considerable influence on both the retention n-docosane and the flux.

Comparison of the results of example IVa and VIa shows the influence of the molecular weight of the applied copolymer in the organic phase on both the n-hexane flux and the retention n-docosane.

Example VII

One acts in the manner described in example I in the preparation of a composite membrane. However, the organic phase consisted of toluene/n-hexane with dissolved therein a copolymer, built up of isobutyl methacrylate (i-BMA), 1,1,1-trifluor ethyl acrylate (TFEA) and acryloyl chloride (AC), obtained after a substantially quantitative conversion during solution polymerisation of a 30.7-31.5%, by weight, solution of the corresponding monomers in chloroform in the presence of 0.5 mol.% AIBN as a radical initiator.

The flux and retention tests of a 1.0%, by weight, solution of n-docosane in n-hexane and in toluene are mentioned in Table F.

Example VIII

One acts in the manner described in example I in the preparation of a composite membrane. However, the organic phase consisted of toluene/n-hexane with dissolved therein a copolymer, built up of isobutyl methacrylate (i-BMA), ethyl acrylate (EA) and acryloyl chloride (AC), obtained after a substantially quantitative conversion during solution polymerisation of a 36.9-49.6%, by weight, solution of the corresponding monomers in chloroform in the presence of 0.5 mol.% AIBN as a radical initiator.

The flux and retention tests, executed in a corresponding manner as in example VII, are mentioned in Table G.

Example IX

One acts in the manner described in example I in the preparation of a composite membrane. The organic phase consisted of toluene/n-hexane (42/58 g/g) with dissolved therein poly(isobutyl methacrylate-co-vinyl pyrrolidone-co-acryloyl chloride) (molar ratio 90/5/5, η intrinsic 0.44 dl/g in acetone, $c=0.5$), obtained after 85% conversion during solution polymerisation of a 36.3%, by weight, solution of the corresponding monomers in chloroform in the presence of 0.5 mol.% HIBN as the radical initiator.

The flux and retention tests, executed in a corresponding manner as in example VII, give as a result in n-hexane a n-hexane flux of 49 kg/(m².hour) and a retention n-docosane of 52% and in toluene a toluene flux of 190 kg/(m².hour) and a retention n-docosane of 36%.

Example X

One acts in the manner described in example I in the preparation of a composite membrane. However, the organic phase consisted of toluene/n-hexane (77/23 g/g) with dissolved therein 0.64%, by weight, of poly(isobutyl methacrylate-co-N-vinyl-N-methyl acetamide-co-acryloyl chloride) (molar ratio 80/15/5, η intrinsic 0.83 dl/g in acetone, $c=0.5$), obtained after 74% conversion during solution polymerisation of a 71.6%, by weight, solution of the corresponding monomers in chloroform in the presence of 0.5 mol.% AIBN as the radical initiator.

The reverse osmosis properties of this membrane were evaluated in a corresponding manner as in example VII, in n-hexane with as a result a n-hexane flux of 37 kg/(m².hour) and a retention n-docosane of 71% and in toluene a toluene flux of 231 kg/(m².hour) and a retention n-docosane of 63%.

Example XI

One acts in the manner described in example I in the preparation of a composite membrane. The organic phase consisted of toluene with dissolved therein a copolymer built up of isobutyl methacrylate (i-BMA), acrylic acid (AZ) and acryloyl chloride (AC), obtained after 89% conversion during solution polymerisation of a 39.3%, by weight, solution of the corresponding monomers in chloroform in the presence of 0.5 mol.% AIBN as the radical initiator. As a control a composite membrane was made starting from poly-isobutyl methacrylate-co-acryloyl chloride) (molar ratio 95/5).

The flux and retention tests, executed in a corresponding manner as in example IV, are mentioned in Table H.

Example XII

One acts in the manner described in example I in the preparation of a composite membrane. The organic phase consisted of toluene with dissolved therein 1.57%, by weight, of poly(methyl methacrylate-co-acryloyl chloride); molar ratio 95/5; η intrinsic (0.84 dl/g in acetone, $c=0.5$), obtained by solution polymerisation of a 51.5%, by weight, solution of the corresponding monomers in chloroform in the presence of 0.5 mol.% AIBN as the radical initiator.

The flux and retention tests were executed in a corresponding manner as in example IV, with as a result a hexane flux of 0 kg/(m².hour), a toluene flux of 34 kg/(m².hour) and a retention n-docosane of 69%, and a methanol flux of 26 kg/(m².hour) and a retention PEG 300 of 68%.

Example XIII

One acts in the manner described in example I in the preparation of a composite membrane. The organic phase consisted of toluene with dissolved therein 1.94%, by weight, poly(2-ethylhexyl acrylate-co-acryloyl chloride); molar ratio 95/5; obtained after 91% conversion during solution polymerisation of a 53.2%, by weight, solution of the corresponding polymers in chloroform in the presence of 0.5 mol.% AIBN as the radical initiator.

The flux and retention tests were executed in a corresponding manner as in example IV, with as a result a hexane flux of 0 kg/(m².hour), a toluene flux of 180 kg/(m².hour) and a retention n-docosane of 34%.

TABLE A

Acid chloride in organic phase ¹ (perc., by weight,)	Amine in aqueous phase (perc., by weight,)	R.O. test data ³	
		Retention Methanol flux	PEG 300 (%) kg/(m ² .hour)
Trimesoyl chloride ²	m-phenylene diamine	93	30
Trimesoyl chloride			
Isophthaloyl chloride	PEI/N4	53	4
Isophthaloyl chloride	idem	68	12
Isophthaloyl chloride	idem	68	13
Trimesoyl chloride			
CLOC(CH ₂) ₂ COCl	idem	74	77
CLOC(CH ₂) ₂ COCl	idem	51	116
CLOC(CH ₂) ₂ COCl	PEI/6N	83	28
CLOC(CH ₂) ₂ COCl	N4	69	60

1 = 1,1,2-trifluor trichlorethane

2 = Commercially obtainable FT-30 membrane (Film Tech)

3 = Composite membranes showed no n-hexane flux and no
toluene flux in solutions containing 1 perc., by weight,
of n-docosane

Table B

Example	Copolymer i-BMA/AC			n-hexane	
	molar ratio	intr.* (dl/g)	perc., by weight,	retention n-docosane (%)	flux kg/m ² .hour
IIa	100/-	0.48	0.54	38	22
IIb	98/2	0.44	0.62	67	21
IIc	95/5	0.53	0.65	73	18

* Evaluated in acetone, $\alpha = 0,5$

From this example follows clearly the favourable effect of the building-in of acid chloride groups in the polymer on the hexane flux and the retention n-docosane.

TABLE C

Vb	Organic phase	n-hexane		toluene		methanol	
		retention n-docosane	flux kg/(m ² .hour)	retention n-docosane	flux kg/(m ² .hour)	retention PEG 300	flux kg/(m ² .hour)
		(%)		(%)		(%)	
IVa	freon		0		nil		0
IVb	toluene	36	137	54	197		high
IVc	toluene/ chloroform (96/4 g/g)	46	106	47	192		high
IVd	toluene/ n-hexane (10/90 g/g)		0	77	87	82	71

This example clearly demonstrates the large influence of the used organic phase on the organic solvent flux and the retention behaviour.

TABLE D

Example	Amine	n-hexane	toluene	methanol
		retention flux n-docosane kg/(m ² .hour)	retention flux n-docosane kg/m ² .hour	retention flux kg/(m ² .hour)
		%	%	%
Va	2N	66	181	27
Vb	4N	73	99	24
Vc	6N	78	82	21
				216
				291
				262
				81
				74
				58
				148
				100
				169

TABLE 2

Example	triethyl amine perc., by weight,	n-hexane	retention n-docosane flux (kg/m ² .hour)
VI	1,0	77	65
VIa	-	56	147

TABLE F

Vb	Organic phase solvent ratio (g/g)	toluene/n-hexane		n-hexane		toluene	
		copolymer i-BMA/TFEA/AC		retention flux		retention flux	
		molar ratio		n-docosane kg/(m ² .h.)		n-docosane kg/(m ² .h.)	
		intr.* perc., (dl/g)	by weight, (%)				
VIIa	16/84	95/-/5	0.53	0.53	74	35	54
VIIb	20/80	70/25/5	0.52	0.62	85	10	77
VIIc	43/47	47/48/5	0.57	0.59		0	85
							57

* Evaluated in acetone, c=0,5

TABLE G

Vb	Organic phase	toluene/n-hexane		n-hexane		toluene	
		solvent ratio (g/g)		copolymer i-BMA/TFEA/AC		retention flux n-docosane kg/(m ² .h.)	
		molar ratio		intr.* perc., (dl/g) by weight,		retention flux n-docosane kg/(m ² .h.)	
VIIa	16/84	95/-/5	0.53	0.53	74	35	54
VIIIa	23/76	72/23/5	0.47	0.59		nil	81
VIIIb	70/30	-/95/5	0.84	0.59		0	60
							138

* Evaluated in acetone, c=0,5

TABLE II

Vb	Copolymer i-BMA/AZ/AC	toluene	methanol
Molar ratio	intr.*	perc., by weight,	retention flux n-docosane kg/(m ² .h.)
XIa 95/ -/5	0,53	1,84	nil
XIb 95/ -/5	1,96	1,89	nil
XIc 93/ 2/5		1,79	77
			64
			27

* Evaluated in acetone, c=0,5

55 Claims

1. Semipermeable composite membrane, with a porous carrier substrate, whereby said carrier substrate is provided with a polymer network, obtained by polycondensation, especially interfacial polymerisation,

TABLE I

Vb	Copolymer i-BMA/AZ/AC	intr.*	perc., by weight,	retention flux n-docosane kg/(m ² .h.)	toluene	retention flux n-docosane kg/(m ² .h.)	methanol
	Molar ratio			(%)		(%)	
XIa	95/-/5	0,53	1,84	nil			
XIb	95/-/5	1,96	1,89	nil			0
XIc	93/2/5		1,79	77	42	64	27

* Evaluated in acetone, c=0,5

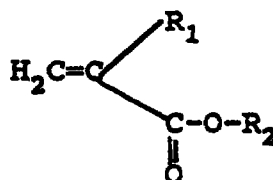
55 Claims

1. Semipermeable composite membrane, with a porous carrier substrate, whereby said carrier substrate is provided with a polymer network, obtained by polycondensation, especially interfacial polymerisation,



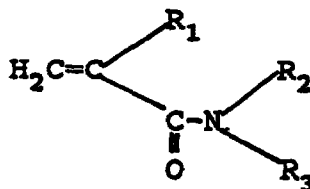
which is built up of at least one reactive polyfunctional monomer or oligomer or prepolymer or polymer having as functional groups -NHR_4 ($\text{R}_4 = \text{H}$ or alkyl with $\text{C}_1\text{-C}_{20}$), -OH or -SH and at least one acid halide containing polymer with as functional groups -COX , $\text{-SO}_2\text{X}$, -POXR_5 or $\text{-NR}_6\text{COX}$, wherein X represents Cl , Br or J , while R_5 and R_6 each represent an alkoxy group or an alkyl group with 1-16 carbon atoms, preferably 1-5 carbon atoms, characterized in that the acid halide containing polymer is a copolymer of one or more vinyl monomers and a monomer containing an acid halide group.

2. Semipermeable composite membrane according to claim 1, characterized in that the mol fraction of the acid halide containing monomer in the polymer is 1-20%.
3. Semipermeable composite membrane according to claim 2, characterized in that the mol fraction of the acid halide containing monomer in the polymer is 5-11%.
4. Semipermeable composite membrane according to claims 1-3, characterized in that the polymer network comprises moreover a reactive polyfunctional monomer or oligomer with as reactive groups -COX , $\text{-SO}_2\text{X}$, -POXR_5 , $\text{-NR}_6\text{COX}$ or NCO , wherein X represents Cl , Br or J , while R_5 and R_6 each represent an alkoxy group or an alkyl group with 1-16 carbon atoms.
5. Semipermeable composite membrane according to claim 4, characterized in that R_5 and R_6 each represent an alkoxy group or an alkyl group with 1-5 carbon atoms.
6. Semipermeable composite membrane according to claim 4 or 5, characterized in that the reactive polyfunctional monomer is isophthaloyl chloride.
7. Semipermeable composite membrane according to claims 1-6, characterized in that the acid halide containing polymer is a copolymer of acryloyl chloride $\text{H}_2\text{C}=\text{CHCOCl}$ or methacryloyl chloride $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{COCl}$ with one or more vinyl containing monomers.
8. Semipermeable composite membrane according to claims 1-7, characterized in that the vinyl monomer is an acrylate with the formula



wherein R_1 and R_2 are identical or different, represent H , an $\text{C}_1\text{-C}_{20}$ alkyl, an aryl, phenyl or naphthyl, while R_2 is unsubstituted or substituted by an OH , halogen, siloxane, OR , wherein R is a substituted or unsubstituted $\text{C}_1\text{-C}_{10}$ alkyl.

9. Semipermeable composite membrane according to claims 1-7, characterized in that the vinyl containing monomer is an acryl amide with the formula



wherein R_1 , R_2 and R_3 , are identical or different, representing H , a $\text{C}_1\text{-C}_{20}$ alkyl, unsubstituted or substituted by OH , halogen, an aryl, phenyl or naphthyl.



10. Semipermeable composite membrane according to claim 8, **characterized in that** the vinyl monomer is isobutyl methacrylate.
- 5 11. Semipermeable composite membrane according to claim 8, **characterized in that** the vinyl monomer is a mixture of isobutyl methacrylate and trifluorethyl acrylate.
12. Semipermeable composite membrane according to claim 8, **characterized in that** the vinyl monomer is a mixture of isobutyl methacrylate and ethyl acrylate.
- 10 13. Semipermeable composite membrane according to claim 8, **characterized in that** the vinyl monomer is a mixture of isobutyl methacrylate and N-vinyl pyrrolidone.
14. Semipermeable composite membrane according to claim 8, **characterized in that** the vinyl monomer is a mixture of isobutyl methacrylate and N-vinyl-N-methyl acetamide.
- 15 15. Semipermeable composite membrane according to claim 8, **characterized in that** the vinyl monomer is a mixture of isobutyl methacrylate and acrylate acid.
16. Semipermeable composite membrane according to claim 8, **characterized in that** the vinyl monomer is methyl methacrylate.
- 20 17. Semipermeable composite membrane according to claim 8, **characterized in that** the vinyl monomer is ethyl acrylate.
- 25 18. Semipermeable composite membrane according to claim 8, **characterized in that** the vinyl monomer is 2-ethylhexyl acrylate.
19. Process for the manufacture of a semipermeable composite membrane by coating a porous substrate with a polymer network obtained by poly-condensation, especially interfacial polymerisation, whereby the porous substrate is treated with a solution of at least one reactive polyfunctional monomer or oligomer of prepolymer or polymer having as reactive groups -NHR_4 ($\text{R}_4 = \text{H}$ or alkyl with $\text{C}_1 - \text{C}_{20}$), -OH or -SH and a surface active compound in water, after which the substrate treated in this manner is further treated with a solution of at least one acid halide containing polymer which is a copolymer of one or more vinyl monomers and a monomer containing an acid halide group and having as reactive groups -COX , $\text{-SO}_2\text{X}$, -POXR_5 , $\text{-NR}_6\text{COX}$ or -NCO , wherein X represents Cl, Br or J, while R_5 and R_6 each represent an alkoxy group or alkyl group with 1-16 carbon atoms, preferably 1-5 carbon atoms, in a suitable organic solvent, after which the substrate treated in this manner is dried and subsequently optionally subjected to a heat treatment.
- 30 20. The process according to claim 19, characterized in that R_5 and R_6 each represent an alkoxy group or alkyl group with 1 to 5 carbon atoms.
21. Method for the separation of components in an organic liquid phase or in the vapour phase using a semipermeable composite membrane with a porous carrier substrate, on which a polymer network is applied which is obtained by polycondensation, especially interfacial polymerisation, **characterized in that** the organic liquid phase or vapour phase is contacted with a semipermeable composite membrane according to claims 1-18.
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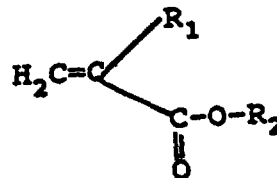
Patentansprüche

- 50 1. Semipermeable Verbundmembran mit einem porösen Trägersubstrat, wobei das genannte Trägersubstrat mit einem durch Polykondensation, insbesondere durch Grenzflächenpolymerisation erhaltenen Polymernetzwerk versehen ist, das aus mindestens einem reaktiven polyfunktionellen Monomer oder Oligomer oder Prepolymer oder Polymer, die als funktionelle Gruppen -NHR_4 ($\text{R}_4 = \text{H}$ oder Alkyl mit $\text{C}_1 - \text{C}_{20}$), -OH oder -SH aufweisen und mindestens einem säurehalogenidhaltigen Polymer aufgebaut ist, das als funktionelle Gruppen -COX , $\text{-SO}_2\text{X}$, -POXR_5 oder $\text{-NR}_6\text{COX}$ enthält, wobei X, Cl, Br oder J bedeutet, während R_5 und R_6 jeweils eine Alkoxygruppe oder eine Alkylgruppe mit 1-16 Kohlenstoffatomen, vorzugsweise 1-5 Kohlenstoffatomen darstellen, dadurch gekennzeichnet, daß das säurehalogen-
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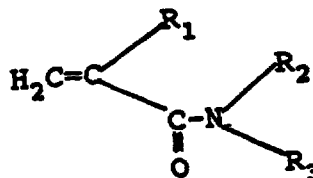
idhaltige Polymer ein Copolymer von einem oder mehreren Vinylmonomeren und einem eine Säurehalogenidgruppe enthaltenden Monomer ist.

2. Semipermeable Verbundmembran nach Anspruch 1, dadurch gekennzeichnet, daß der Molenbruch des säurehalogenidhaltigen Monomers in dem Polymer 1-20% beträgt.
3. Semipermeable Verbundmembran nach Anspruch 2, dadurch gekennzeichnet, daß der Molenbruch des säurehalogenidhaltigen Monomers in dem Polymer 5-11% beträgt.
4. Semipermeable Verbundmembran nach Ansprüchen 1-3, dadurch gekennzeichnet, daß das polymere Netzwerk außerdem ein reaktives, polyfunktionelles Monomer oder Oligomer enthält, das als reaktive Gruppen $-COX$, $-SO_2X$, $-POXR_5$, $-NR_6COX$ oder NCO enthält, wobei X , Cl , Br oder J darstellt, während R_5 und R_6 jeweils eine Alkoxygruppe oder eine Alkylgruppe mit 1-16 Kohlenstoffatomen darstellen.
5. Semipermeable Verbundmembran nach Anspruch 4, dadurch gekennzeichnet, daß R_5 und R_6 jeweils eine Alkoxygruppe oder eine Alkylgruppe mit 1-5 Kohlenstoffatomen darstellen.
6. Semipermeable Verbundmembran nach Anspruch 4 oder 5, dadurch gekennzeichnet, daß das reaktive polyfunktionelle Monomer Isophtaloylchlorid ist.
7. Semipermeable Verbundmembran nach Ansprüchen 1-6, dadurch gekennzeichnet, daß das säurehalogenidhaltige Polymer ein Copolymer von Acryloylchlorid $H_2C=CHCOCl$ oder Methacryloylchlorid $H_2C=C(CH_3)COCl$ mit einem oder mehreren vinylhaltigen Monomeren ist.
8. Semipermeable Verbundmembran nach Ansprüchen 1-7, dadurch gekennzeichnet, daß das Vinylmonomer ein Acrylat mit der Formel



ist, worin R_1 und R_2 gleich oder verschieden sind und H , ein C_1 - C_{20} Alkyl, ein Aryl, Phenyl oder Naphthyl bedeuten, während R_2 unsubstituiert oder mit einem OH , Halogen, Siloxan, OR substituiert ist, worin R ein substituiertes C_1 - C_{10} Alkyl ist.

9. Semipermeable Verbundmembran nach Ansprüchen 1-7, dadurch gekennzeichnet, daß das vinylhaltige Monomer ein Acrylamid der Formel



ist, worin R_1 , R_2 und R_3 gleich oder verschieden sind und H , ein unsubstituiertes oder durch OH , Halogen, ein Aryl, Phenyl oder Naphthyl substituiertes C_1 - C_{20} Alkyl ist.

10. Semipermeable Verbundmembran nach Anspruch 8, dadurch gekennzeichnet, daß das Vinylmonomer Isobutylmethacrylat ist.



11. Semipermeable Verbundmembran nach Anspruch 8, dadurch gekennzeichnet, daß das Vinylmonomer ein Gemisch von Isobutylmethacrylat und Trifluorethylacrylat ist.
12. Semipermeable Verbundmembran nach Anspruch 8, dadurch gekennzeichnet, daß das Vinylmonomer ein Gemisch von Isobutylmethacrylat und Ethylacrylat ist.
13. Semipermeable Verbundmembran nach Anspruch 8, dadurch gekennzeichnet, daß das Vinylmonomer ein Gemisch von Isobutylmethacrylat und N-Vinylpyrrolidon ist.
14. Semipermeable Verbundmembran nach Anspruch 8, dadurch gekennzeichnet, daß das Vinylmonomer ein Gemisch von Isobutylmethacrylat und N-Vinyl-N-Methylacetamid ist.
15. Semipermeable Verbundmembran nach Anspruch 8, dadurch gekennzeichnet, daß das Vinylmonomer ein Gemisch von Isobutylmethacrylat und Acrylsäure ist.
16. Semipermeable Verbundmembran nach Anspruch 8, dadurch gekennzeichnet, daß das Vinylmonomer Methylmethacrylat ist.
17. Semipermeable Verbundmembran nach Anspruch 8, dadurch gekennzeichnet, daß das Vinylmonomer Ethylacrylat ist.
18. Semipermeable Verbundmembran nach Anspruch 8, dadurch gekennzeichnet, daß das Vinylmonomer 2-Ethylhexylacrylat ist.
19. Verfahren zur Herstellung einer semipermeablen Verbundmembran durch Beschichten eines porösen Substrats mit einem durch Polykondensation, insbesondere Grenzflächenpolymerisation erhaltenen Polymernetzwerk, wobei das poröse Substrat mit einer Lösung von mindestens einem reaktiven, polyfunktionellen Monomer oder Oligomer oder Prepolymer oder Polymer, die als reaktive Gruppen $-NHR_4$ ($R_4 = H$ oder Alkyl mit C_1-C_{20}), $-OH$ oder $-SH$ aufweisen, und einer grenzflächenaktiven Verbindung in Wasser behandelt wird, wonach das so behandelte Substrat in einem geeigneten organischen Lösungsmittel weiter mit einer Lösung von mindestens einem säurehalogenidhaltigen Polymer behandelt wird, das ein Copolymer von einem oder mehreren Vinylmonomeren und einem eine Säurehalogenidgruppe enthaltenden Monomer ist, das als reaktive Gruppen $-COX$, $-SO_2X$, $-POXR_5$, $-NR_5COX$ oder $-NCO$ aufweist, wobei X Cl, Br oder J darstellt, während R_5 und R_6 jeweils eine Alkoxygruppe oder Alkylgruppe mit 1-16 Kohlenstoffatomen, vorzugsweise 1-5 Kohlenstoffatomen darstellen, wonach das so behandelte Substrat getrocknet wird und danach wahlweise einer Wärmebehandlung unterworfen wird.
20. Verfahren nach Anspruch 19, dadurch gekennzeichnet, daß R_5 und R_6 jeweils eine Alkoxygruppe oder eine Alkylgruppe mit 1-5 Kohlenstoffatomen darstellen.
21. Verfahren zur Trennung von Komponenten in einer organischen Flüssigphase oder in der Dampfphase unter Verwendung einer semipermeablen Verbundmembran mit einem porösen Trägersubstrat, auf dem ein Polymernetzwerk aufgebracht ist, das durch Polykondensation, insbesondere Grenzflächenpolymerisation erhalten worden ist, dadurch gekennzeichnet, daß die organische Flüssigphase oder Dampfphase mit einer semipermeablen Verbundmembran nach Ansprüchen 1-18 in Kontakt gebracht wird.

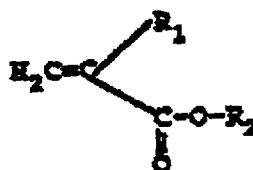
Revendications

1. Membrane composite semiperméable comportant un substrat de support poreux, ce substrat de support comprenant un réseau de polymère obtenu par polycondensation, en particulier par polymérisation interfaciale, constitué d'au moins un monomère, un oligomère, un prépolymère ou un polymère polyfonctionnel réactif, comportant comme groupes fonctionnels, des groupes $-NHR_4$ ($R_4 = H$ ou un groupe alkyle en C_1-C_{20}), $-OH$ ou $-SH$, et d'au moins un polymère à groupe halogénure d'acide comportant comme groupes fonctionnels, des groupes $-COX$, $-SO_2X$, $-POXR_5$ ou $-NR_5COX$, X représentant Cl, Br ou I, tandis que R_5 et R_6 représentent chacun un groupe alkoxy ou un groupe alkyle comportant de 1 à 16 atomes, de préférence de 1 à 5 atomes de carbone, caractérisée en ce que le



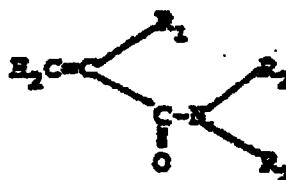
polymère à groupe halogénure d'acide, est un copolymère d'un ou plusieurs monomères vinyliques et d'un monomère contenant un groupe halogénure d'acide.

2. Membrane composite semiperméable selon la revendication 1, caractérisée en ce que la fraction molaire du monomère à groupe halogénure d'acide, dans le polymère, est de 1 à 20 %.
3. Membrane composite semiperméable selon la revendication 2, caractérisée en ce que la fraction molaire du monomère à groupe halogénure d'acide, dans la polymère, est de 5 à 11 %.
4. Membrane composite semiperméable selon la revendication 1, caractérisée en ce que le réseau de polymère, comprend en outre un monomère ou un oligomère polyfonctionnel réactif comportant, comme groupes réactifs, des groupes $-COX$, $-SO_2X$, $-POXR_5$, $-NR_6COX$ ou $-NCO$, X représentant Cl , Br ou I , tandis que R_5 et R_6 représentent chacun un groupe alkoxy ou un groupe alkyle comportant de 1 à 16 atomes de carbone.
5. Membrane composite semiperméable selon la revendication 4, caractérisée en ce que R_5 et R_6 représentent chacun un groupe alkoxy ou un groupe alkyle comportant de 1 à 5 atomes de carbone.
6. Membrane composite semiperméable selon la revendication 4 ou 5, caractérisée en ce que le monomère polyfonctionnel réactif est le chlorure d'isophtaloyle.
7. Membrane composite semiperméable selon les revendications 1 à 6, caractérisée en ce que le polymère à groupe halogénure d'acide, est un copolymère de chlorure d'acryloyle $H_2C=CHCOCl$ ou de chlorure de méthacryloyle $H_2C=C(CH_3)COCl$, avec un ou plusieurs monomères vinyliques.
8. Membrane composite semiperméable selon les revendications 1 à 7, caractérisée en ce que le monomère vinylique, est un acrylate de formule :



dans laquelle R_1 et R_2 sont identiques ou différents, et représentent H , un groupe alkyle en C_1-C_{20} , un groupe aryle, un groupe phényle ou un groupe naphthyle, tandis que R_2 est non substitué ou substitué avec un groupe OH , un atome d'halogène, un groupe siloxane, un groupe OR , R représentant un groupe alkyle en C_1-C_{10} substitué ou non substitué.

9. Membrane composite semiperméable selon les revendications 1 à 7, caractérisée en ce que le monomère vinylique, est un acrylamide de formule :



dans laquelle R_1 , R_2 et R_3 sont identiques ou différents et représentent H , un groupe alkyle en C_1-C_{20} non substitué ou substitué avec un groupe OH , un atome d'halogène, un groupe aryle, un groupe phényle ou un groupe naphthyle.



10. Membrane composite semiperméable selon la revendication 8, caractérisée en ce que le monomère vinylique est le méthacrylate d'isobutyle,
- 5 11. Membrane composite semiperméable selon la revendication 8, caractérisée en ce que le monomère vinylique est un mélange de méthacrylate d'isobutyle et d'acrylate de trifluoroéthyle.
12. Membrane composite semiperméable selon la revendication 8, caractérisée en ce que le monomère vinylique est un mélange de méthacrylate d'isobutyle et d'acrylate d'éthyle.
- 10 13. Membrane composite semiperméable selon la revendication 8 caractérisée en ce que le monomère vinylique est un mélange de méthacrylate d'isobutyle et de N-vinylpyrrolidone.
14. Membrane composite semiperméable selon la revendication 8, caractérisée en ce que le monomère vinylique est un mélange de méthacrylate d'isobutyle et de N-vinyl-N-méthylacétamide.
- 15 15. Membrane composite semiperméable selon la revendication 8, caractérisée en ce que le monomère vinylique est un mélange de méthacrylate d'isobutyle et d'acide acrylique.
16. Membrane composite semiperméable selon la revendication 8, caractérisée en ce que le monomère vinylique est le méthacrylate de méthyle.
- 20 17. Membrane composite semiperméable selon la revendication 8, caractérisée en ce que le monomère vinylique est l'acrylate d'éthyle.
- 25 18. Membrane composite semiperméable selon la revendication 8, caractérisée en ce que le monomère vinylique est l'acrylate de 2-éthylhexyle.
19. Procédé de fabrication d'une membrane composite semiperméable en revêtant un substrat poreux avec un réseau de polymère obtenu par polycondensation, en particulier par polymérisation interfaciale, de sorte que le substrat poreux est traité avec une solution d'au moins un monomère, un oligomère, un prépolymère ou un polymère polyfonctionnel réactif comportant, comme groupes réactifs, des groupes -NHR₄ (R₄ = H ou un groupe alkyle de C₁ à C₂₀), -OH ou -SH, et d'un composé tensioactif dans de l'eau, après quoi le substrat traité de cette façon est en outre traité avec une solution du ou de chaque polymère à groupe halogénure d'acide consistant et un copolymère d'un ou plusieurs monomères vinyliques et d'un monomère contenant un groupe halogénure d'acide et comportant, comme groupes réactifs, des groupes -COX, -SO₂X, -POXR₅, NR₆COX ou -NCO, X représentant Cl, Br ou I, tandis que R₅ et R₆ représentent chacun un groupe alkoxy ou un groupe alkyle comportant de 1 à 16 atomes de carbone, de préférence de 1 à 5 atomes de carbone, dans un solvant organique approprié, après quoi le substrat traité de cette façon est séché puis éventuellement soumis à un traitement thermique.
- 30 35 40 20. Procédé selon la revendication 19, caractérisée en ce que R₅ et R₆ représentent chacun un groupe alkoxy ou un groupe alkyle comportant de 1 à 5 atomes de carbone.
- 45 21. Procédé de séparation de composants dans une phase liquide organique ou en phase vapeur, en employant une membrane composite semiperméable comportant un substrat de support poreux sur lequel est appliqué un réseau de polymère obtenu par polycondensation, en particulier par polymérisation interfaciale, caractérisé en ce que la phase liquide organique ou la phase vapeur est mise en contact avec une membrane composite semiperméable selon les revendications 1 à 18.
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