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REVIEWS

Modification of Polymer Membranes for Use in Organic Solvents

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Abstract—The chemical stability of polymer membranes, i.e., their ability to preserve the size, shape, and pore structure in contact with aggressive organic solvents, largely determines their separation characteristics in filtration of organic media. Methods for enhancing the stability of porous membranes based on commercial polymers (polysulfone, polyphenylsulfone, polyacrylonitrile) by chemical and/or physical modification are considered. Chemical modification consists in covalent cross-linking of matrix polymer chains; in some cases, cross-linking of macromolecules requires their preliminary functionalization. Physical modification involves blending of a matrix polymer with another polymer. A promising way to stabilize various membranes is combining a matrix polymer with a chemically cross-linked additional polymer, i.e., forming a semi-interpenetrating network.

Keywords: polymer membranes, organic solvents, stability, modification, cross-linking

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INTRODUCTION

Membrane separation of gas and liquid media consists in selective transport of one or several mixture components through a membrane [1, 2]. In filtration of liquids, the membrane transport of substances occurs under the action of hydrostatic (transmembrane) pressure. Depending on the membrane pore size and/or size of retained impurities, the following baromembrane processes are distinguished: micro-, ultra-, nanofiltration, and reverse osmosis. In nanofiltration, the pore size does not exceed 2 nm (“micropores”); in ultrafiltration, the pore size is in the range 2–50 nm (“mesopores”); and in microfiltration, it is in the range 50–500 nm (“macropores”) [3].

Modern commercial membrane processes for liquid separation in most cases involve filtration of aqueous media. Polymer membranes are used for this purpose most frequently. However, the volume of basic and applied research in the field of separation of organic media tends to increase. Lively and Shoil [4] note that, with the development of chemically durable materials, the membrane filtration can successfully compete with traditional commercial separation methods, as earlier nanofiltration and reverse osmosis as water desalination methods displaced distillation. The membrane filtration of liquids differs from distillation, pervaporation, and crystallization in that it occurs without phase transition, allowing the specific power consumption to be reduced. Organic solvent nanofiltration undergoes the most active development. It is considered as an alternative to distillation in such fields as petroleum chemistry and food and pharmaceutical industries [5–10]. On the other hand, commercial implementation of this process is restricted by narrow range of the existing nanofiltration membranes stable in organic media.

Along with the required separation characteristics (permeability, selectivity), filtration membranes should exhibit structural stability, i.e., preserve the size and the formed pore structure under the conditions of prolonged operation in organic solvents. Jansen [11] formulated five criteria determining the choice of the polymer membrane material: (1) stability of size or structure in solvents, (2) mechanical strength, (3) high glass transition temperature or heat resistance, (4) availability of the material, and (5) cost. The first two criteria are critical in the development of membranes to be used in organic solvents. Swelling of a polymer membrane, i.e., an increase in its weight and volume and the change in its structure due to interaction with the solvent, is the factor determining the chemical stability. The lower is the polymer swelling in the solvent, the higher is its structural stability. Ample experimental data on swelling of typical membrane polymers are presented in recent paper [12].

There are two directions of research aimed at enhancing the stability of polymer membranes in organic media: (1) search for, and synthesis of new materials and (2) modification (physical or chemical) of the existing commercial polymers. The first direction is more fundamental, whereas the second direction is of mainly applied significance, because it does not require the synthesis of new monomers and polymers.

This review deals with the existing methods for modification of membrane materials with the aim of preparing filtration membranes stable in organic media, including aprotic solvents. Three commercial polymers (polysulfone, polyphenylsulfone, polyacrylonitrile) are taken as examples.

WAYS TO ENHANCE THE MEMBRANE STABILITY

The structural stability of polymer membranes in organic solvents can be enhanced by their chemical or physical modification. By chemical modification, a matrix polymer can be transformed into a three-dimensional network. This is achieved by introducing special cross-linking agents forming covalent bond between macromolecules into a polymer matrix. To form such bonds, the polymer should contain reactive functional groups in the chain. If a polymer initially contains such groups, the cross-linking can be performed directly. If there are no such active groups, the cross-linking should be preceded by chemical grafting of reactive groups.

Physical modification consists in blending of the matrix polymer with a small amount of another polymer, which can be introduced into the polymer matrix directly or in the form of monomers with their subsequent polymerization initiated by UV or electron-beam irradiation. In the case of multifunctional monomers, the polymerization will yield a network polymer. As a result, the membrane will have the structure of a so-called semi-interpenetrating polymer network (SIPN) in which linear macromolecules of the main polymer are combined with network molecules of the polymer-modifier. Noncovalent interaction of the main polymer and polymer-modifier, e.g., via formation of ionic bonds, is intermediate between physical and chemical modification.

Let us consider the chemical and physical modification of membranes used in nanofiltration of organic solvents with three membrane materials as examples: polyacrylonitrile $[–CH_2–CH(CN)–]_n$ and two sulfone polymers: polysulfone $[–Ph–SO_2–Ph–O–Ph–C(Me_2)–Ph–O–]_n$ and polyphenylsulfone $[–Ph–SO_2–Ph–O–Ph–Ph–O–]_n$, where Ph is *p*-phenylene. The physicochemical properties of these polymers are given in handbook [13].

Modification of Polysulfone-Based Membranes

Chemical modification. Polysulfone membranes cannot be cross-linked directly. Their cross-linking requires preliminary functionalization. Sangermano et al. [14] first synthesized polysulfone oligomers with terminal –OH groups and then converted these groups to methacryloyl groups by esterification. After that, the modified oligomers were subjected to photochemical cross-linking under the action of UV radiation in the presence of special photoinitiator molecules (cross-linking time 1 min). The cross-linking was performed either before or after the membrane casting by phase inversion. In both cases, a network polymer insoluble in organic solvents (dimethylformamide, dimethyl sulfoxide) and in boiling water was obtained. Relatively low degrees of conversion of acrylic double bonds (62 and 41% in cross-linking before and after the membrane casting, respectively) were reached. In accordance with the measured water permeability (from 2.5 to 9.5 L m^{-2} h^{-1} bar^{-1}), Sangermano et al. [14] classed the membranes obtained with ultrafiltration membranes. However, the membrane pore size (from 0.8 to 2 μm) measured by scanning electron microscopy is typical of microfiltration rather than ultrafiltration membranes.

One of the most widely used methods for functionalization of sulfone polymers is chloromethylation, i.e., replacement of hydrogen atoms in the aromatic ring by $–CH_2Cl$ groups. The chloromethylated sulfone was considered as a precursor for preparing new functional polymers [15]. Lee et al. [16] first prepared chloromethylated polysulfone (degree of substitution 0.06–0.36 per monomeric unit, reaction time up to 24 h) and then replaced the $–CH_2Cl$ groups with the methacrylic groups by treatment with methacrylic acid. This led to the formation of a photosensitive polymer, because methacrylic groups are capable of UV-initiated chemical cross-linking. From the modified polymer, Lee et al. cast continuous membranes ~80 μm thick, in which the macromolecules underwent cross-linking under the action of UV radiation. The films obtained were insoluble in aprotic solvents (dimethyl sulfoxide, dimethylacetamide, dimethylformamide, tetrahydrofuran, N-methylpyrrolidone) and in chloroform. Chen et al. [17] also performed polysulfone chloromethylation followed by membrane casting. The ready membrane was immersed in an aqueous imidazole solution for 30 h. The reaction of imidazole with $–CH_2Cl$ groups led to the formation of cross-links between polymer chains; i.e., a polymer network was formed. The membranes obtained were tested for the permeability to a solvent (acetone) and retention of Rose Bengal dye (MM = 1017 g mol^{-1}). Chen et al. found that the membrane became denser with increasing cross-linking time. As a consequence, the membrane permeability to acetone decreased, whereas the dye retention increased. Chen et al. [17] showed that, in contrast to the initial membranes soluble in acetone, dimethylformamide, and dimethylacetamide, the cross-linked membranes are stable in these solvents. Chen et al. conclude that the cross-linked chloromethylated polysulfone membranes show promise for nanofiltration of organic media.

Physical modification. The main studies on physical modification of polysulfone membranes were associated with the development of the above-mentioned SIPN-type structures. For example, Vankelecom et al. published a series of papers [18–21] on introduction of reactive monomers (acrylates) into a polysulfone matrix, followed by their UV-initiated polymerization [18–21].

Asymmetric porous membranes were prepared by phase inversion using water as a precipitant. Acrylates of various functionalities (5 wt %), from di- to hexafunctional, and the photoinitiator (3 wt %) were introduced into the casting solution. After the casting, the membranes were UV-irradiated in air. The photoinitiator molecules absorbed light and generated free radicals. These radicals reacted with acrylates and launched a chain reaction transforming the multifunctional acrylic monomers into a cross-linked macromolecule. Because the reaction occurred in a polymer matrix, the formation of an SIPN-type structure can be assumed. The reaction yield (degree of conversion of C=C bonds in the monomers) depends on the kind of the monomers and photoinitiator. The highest reaction yield (98%) in 50–200-μm-thick membranes was reached when using pentaacrylates as monomers and acylphosphine oxide as a photoinitiator [18]. The membranes synthesized, in contrast to the initial membranes, appeared to be insoluble in acetone and ethyl acetate but showed certain swelling in tetrahydrofuran. The membrane modification led to a certain decrease in the solvent permeability (for example, the permeability of the membranes to isopropanol decreased from 0.32 to 0.22 L m^{-2} h^{-1} bar^{-1}). The formation of an SIPN-type structure was confirmed by differential scanning calorimetry and thermal gravimetric analysis. It was found, in particular, that the degradation temperature of the modified membranes (428°C) was close to that of the membrane made of cross-linked polypentaacrylate (424°C) [19]. Significant influence on the morphology and transport properties of membranes is exerted by the membrane casting conditions, e.g., time of solvent evaporation prior to loading the solution into the coagulation bath, kind and concentration of the cosolvent, etc. For example, with an increase in the evaporation time from 0 to 100 s, the membrane permeability to isopropanol decreases by more than an order of magnitude [21]. Data on the stability of polysulfone membranes in organic solvents both before and after the modification are given in Table 1. The extent of dissolution was evaluated visually after immersing the membranes in each of the solvents for 72 h.

Strużyńska-Piron et al. [20], along with the above-described procedure involving UV irradiation of the membrane after its formation, examined another sequence of modification, in which the cross-linking of acrylic monomers in the casting solution was performed first and was followed by the membrane formation proper. The sequence of operations was found to influence the membrane morphology. The membrane prepared by UV irradiation of the polymer solution, followed by casting, contained no finger-like macrovoids. This is caused by an increase in the casting solution viscosity due to polymerization of acrylic monomers. An increase in the viscosity decelerates the phase segregation and leads to the formation of spongy rather than finger-like membrane morphology. The UV-initiated cross-linking of the ready membrane led to high retention coefficient (R = 96% for Rose Bengal dye) but low permeability (0.07 L m^{-2} h^{-1} bar^{-1}). At inverse sequence

Solubility[a] in organic solvents of polysulfone membranes and the same membranes after photochemical modification (polysulfone-UV) [19–21]

Solvent	Polysulfone	Polysulfone-UV
Acetone	x	0
Butyl acetate	x	0
Ethyl acetate	1	0
Toluene	1	0
Mixture of xylenes	1	0
Chlorobenzene	1	x
Cyclohexanone	1	x
N-Methylpyrrolidone	1	x
Tetrahydrofuran	1	x
Triethyl phosphate	1	x
Dimethylformamide	1	x

[a] (0) The membrane is insoluble, (x) the membrane swells, and (1) the membrane is soluble.

of modification (UV-initiated cross-linking in solution), the membranes obtained were more permeable (by more than an order of magnitude for methanol) with only a slight decrease in the retention coefficient. As for the chemical stability of the membranes, it was virtually independent of the modification sequence.

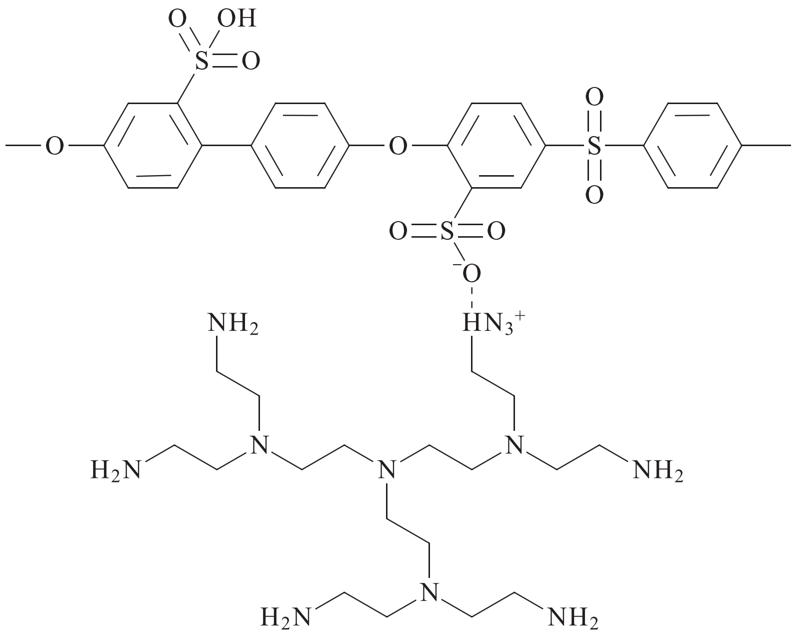
Mian Farrukh et al. [22] modified a porous polysulfone membrane (water permeability ~340 L m^{-2} h^{-1} bar^{-1}) by photochemical polymerization of diacrylates added into the polymer solution jointly with a small amount of a photoinitiator. The UV irradiation was performed in a casting solution (under nitrogen for 1 min). Acrylic monomers were introduced in a large amount (10–30 wt %) comparable to, or even exceeding the polysulfone concentration in the solution (15 wt %). The higher is the concentration of acrylic monomers, the denser are the membranes formed and, correspondingly, the lower is their permeability: Introduction of 10 and 20 wt % monomers led to a decrease in the hydraulic permeability by 30 and by more than 50%, respectively. On introducing 30 wt % acrylates, the membrane became water-impermeable; i.e., at such a high concentration of the monomers the network formed by their polymerization completely blocked the pores of the polymer matrix. The modified membranes consisted of a blend of linear polysulfone macromolecules with a polyacrylate polymer network; i.e., they had the SIPN structure. According to [22], this blend was heterogeneous and had a two-phase structure, as indicated by the presence of two glass transition points. The phase-segregated structure of the modified membranes is apparently due to high concentration of the introduced acrylates. The resistance to solvents was evaluated visually after keeping the films in solvents for no less than 120 h. The modified polysulfone membranes are insoluble in dimethylformamide, tetrahydrofuran, acetone, dimethyl sulfoxide, and toluene; i.e., these membranes can be used in filtration of aggressive organic media.

It should be noted in conclusion that cross-linking of reactive monomers in the polysulfone matrix can be initiated not only by UV but also by electron-beam irradiation [23]. This method is less power-consuming and is environmentally safe, because on photoinitiators are used. Membranes stable in many solvents can be obtained by properly choosing the ionizing radiation dose and the monomer concentration. However, the required equipment is very expensive, so that photochemical initiation is yet preferable.

Modification of Polyphenylsulfone-Based Membranes

Polyphenylsulfone is more stable than polysulfone in organic solvents. Therefore, Darvishmanesh et al. [24] examined the possibility of using it for preparing asymmetric porous membranes for filtration of organic media. They measured the permeation of solvents and retention of Rose Bengal dye both for freshly prepared

Scheme 1. Ionic cross-linking of sulfonated polyphenylsulfone and hyperbranched polyethylenimine.



The ionic cross-links are formed by the proton transfer from the sulfo group of polysulfone to the amine group of polyethylenimine.

membranes (pore size 15–40 nm) and for membranes kept in organic solvents (ethyl acetate, n-hexane, toluene, diethyl ether, acetone, isopropanol) for 48 h. They found that the methanol flux did not change in time only after keeping the membranes in n-hexane. After keeping in acetone and toluene, the membranes lost integrity and became unsuitable for further use. After keeping in isopropanol, diethyl ether, and ethyl acetate, the methanol flux appreciably decreased: by a factor of 2, 4, and 8, respectively. This decrease was accompanied by deterioration of the membrane selectivity. In particular, after keeping in ethyl acetate, the dye retention coefficient decreased almost by half. It was concluded that swelling of the membranes in isopropanol, diethyl ether, and ethyl acetate led to irreversible changes in the pore size and in the pore size distribution and, as a result, to deterioration of the transport properties of the membranes. In another study [25], Darvishmanesh et al. used polyphenylsulfone for preparing hollow-fiber nanofiltration membranes. Experiments on keeping the hollow fibers in solvents for 10 days have shown that they are chemically stable in alcohols and alkanes, undergo appreciable shrinkage in acetone and toluene, and degrade in methyl ethyl ketones. The membranes obtained exhibited the permeability to alcohols and alkanes in the interval 0.2–3 L m^{-2} h^{-1} bar^{-1}. However, in filtration of acetone and toluene, the hollow fibers underwent break.

Chemical modification. As in the case of polysulfone, direct cross-linking of polyphenylsulfone chains is impossible, which makes it necessary to introduce functional groups as potential cross-linking points into the polymer chains. Tashvigh et al. [26, 27] preliminary sulfonated polyphenylsulfone macromolecules with introduction of $-SO_3H$ groups into aromatic rings. Then, a small amount of hyperbranched polyethylenimine was introduced into the solution of the resulting polymer, hereinafter denoted as S-polyphenylsulfone. Ionic bonds can be formed between the sulfo groups of the first polymer and $-NH_2$ groups of the second polymer (Scheme 1), leading to the formation of a three-dimensional network of S-polyphenylsulfone chains linked to each other by flexible polyethylenimine bridges.

The transport properties of the membranes (ethanol permeability and dye retention) formed from the above polymer blend depend on the polyethylenimine concentration [26]. The highest permeability ($L_p \approx 8$ L m^{-2} h^{-1} bar^{-1}) was reached at 0.3 wt % polyethylenimine in the casting solution. However, the

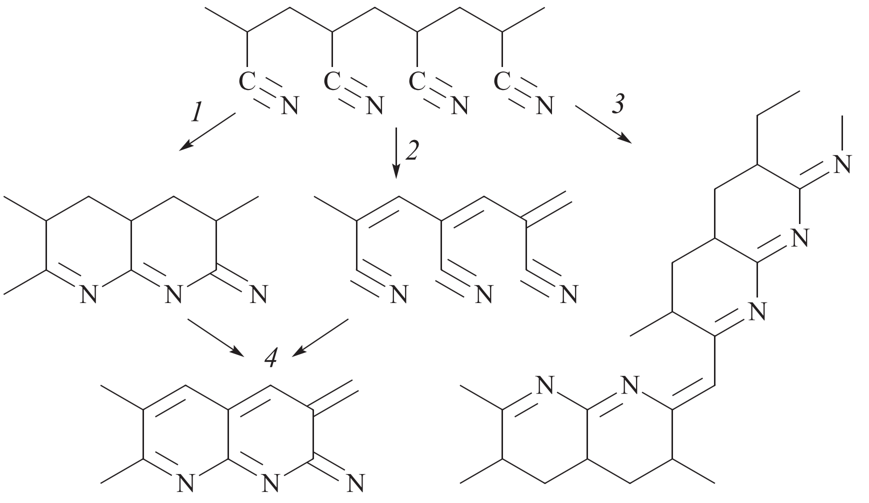
Rose Bengal retention coefficient appeared to be very low ($R = 51\%$). The selectivity was improved by post-treatment involving treatment of the membrane surface with a polyethylenimine solution in water or ethanol under pressure. This treatment intensified the cross-linking, and high selectivity was reached ($R = 99.9\%$ for Rose Bengal dye), although the membrane permeability to ethanol decreased ($L_p \approx 1.5$ L m^{-2} h^{-1} bar^{-1}). This is an example of the known antagonism between the parameter L_p and R: The higher is one of them, the lower is the other parameter. In contrast to membranes containing no polyethylenimine, the "ionically cross-linked" membranes showed stable transport parameters during 2-week testing. The ionic cross-linking of S-polyphenylsulfone is simple in implementation and opens an interesting possibility for preparing chemically durable membranes. Because ionic cross-linking is weaker than covalent cross-linking, this method is efficient for membranes contacting with nonaggressive solvents, e.g., with aliphatic alcohols. To expand the spectrum of the solvents used, Tashvigh et al. suggested a more complex modification method consisting of three steps [27]: (1) preparation of asymmetric membranes from a blend of S-polyphenylsulfone and polybenzimidazole, (2) covalent cross-linking of polybenzimidazole chains with dibromo-p-xylene, and (3) ionic cross-linking of S-polyphenylsulfone with hyperbranched polyethylenimine. As a result, they obtained so-called double cross-linked S-polyphenylsulfone/polybenzimidazole membranes with equal gravimetric content of the polymers. These membranes have the structure of interpenetrating networks in which one of the network polymers is cross-linked by covalent bonds, and the other, by ionic bonds. Along with double cross-linked membranes, Tashvigh et al. studied membranes prepared without adding polyethylenimine, i.e., without performing the third step. In this case, one can speak of an SIPN structure consisting of linear S-polyphenylsulfone chains and cross-linked polybenzimidazole. For the double cross-linked S-polyphenylsulfone/polybenzimidazole (50/50) membranes, Tashvigh et al. measured the permeability to water and organic solvents (methanol, ethanol, acetone, dimethylformamide, tetrahydrofuran, toluene) and the retention of tetracycline (MM = 444 g mol^{-1}) as a model solute. Depending on the solvent, its permeability through the membrane varied in the range 2–11.8 L m^{-2} h^{-1} bar^{-1}, and the tetracycline retention coefficient, from 67 to 97%. These parameters exceed the level reached previously for membranes made of cross-linked polybenzimidazole and even the results of the previous study by the same authors [26]. The stability of the transport properties of double cross-linked membranes was tested in the course of filtration of tetracycline solutions in ethanol and tetrahydrofuran, performed at a transmembrane pressure of 5 bar for 48 h. In the course of the test, the permeability to ethanol and tetrahydrofuran decreased by 20 and 32%, respectively, whereas the tetracycline retention slightly increased, probably owing to the membrane contraction.

Physical modification. In the above-mentioned studies [24, 25], polyphenylsulfone was used as a membrane material for preparing planar and hollow-fiber membranes. The membranes showed high chemical stability in alcohols and alkanes, but appeared to be unstable in acetone, methyl ethyl ketone, and toluene. Jansen et al. [11] used a known method of physical modification, blending of two polymers with the aim of obtaining a material with improved characteristics. They prepared asymmetric membranes from blends of polyphenylsulfone with Matrimid-type polyimide in 75/25, 50/50, and 25/75 wt % ratios. Matrimid is a mechanically strong and chemically durable polymer used as a porous support of composite membranes for nanofiltration of organic media [28]; it is, however, considerably more expensive than sulfone polymers. Jansen et al. found that the solvent flux through the polyphenylsulfone/Matrimid membrane depended both on the solvent type and on the polymer blend composition. For alcohols and alkanes, the highest flux was observed for the 50/50 blend, and for alkyl acetates, for the 75/25 blend. Visually the membranes preserved the size and shape after keeping them in acetone and methyl ethyl ketone for 48 h. Keeping in these solvents affected the transport properties of the membranes insignificantly: The methanol flux and the retention coefficient of Sudan II dye (MM = 276 g mol^{-1}) remained on the level of the values for the freshly prepared membranes. It should be noted, however, that more aggressive solvents such as tetrahydrofuran and dimethylformamide were not tested in [11].

Modification of Polyacrylonitrile-Based Membranes

Polyacrylonitrile is stable in many organic solvents (alcohols, alkanes, acetone, etc.), and also in mineral acids and weakly alkaline solutions. This stability is associated with the intermolecular dipole–dipole interaction of the

Scheme 2. Chemical transformations of polyacrylonitrile in the course of heat treatment.



(*1*) Cyclization, (*2*) dehydrogenation, (*3*) cyclization + cross-linking, and (*4*) cyclization + dehydrogenation (adapted from [31]).

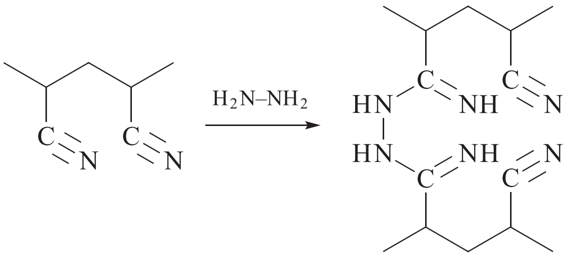
C≡N groups [29]. This polymer has an amorphous-crystalline structure, so that the crystalline domains play the role of physical cross-links supporting the structure of the polymer matrix [30]. However, in aprotic solvents such as dimethyl sulfoxide, dimethylacetamide, dimethylformamide, and N-methylpyrrolidone this polymer dissolves. To enhance the structural stability of polyacrylonitrile membranes in these solvents, their chemical modification is required. Two procedures for such modification can be distinguished: heat treatment of membranes and cross-linking of polyacrylonitrile chains using special chemical agents.

The heat treatment of membranes consists in heating them to 200–300°C and keeping at the final temperature for several hours. Depending on the annealing temperature and time and on the kind of the medium (inert or atmospheric), polyacrylonitrile undergoes physical and chemical transformations. The intermolecular interaction of nitrile groups becomes weaker with increasing temperature, and at ~180–200°C intramolecular cyclization with partial conversion of nitrile (C≡N) groups to C=N groups starts. With the progress of the reaction, polyconjugated sequences of C=N bonds are formed (up to five units in a sequence). As a result of cyclization, polyacrylonitrile acquires the so-called ladder structure. On heating to higher temperatures (200–300°C) in the presence of oxygen, C=C bonds are formed by dehydrogenation; also, intermolecular cross-linking is possible [30–32] (Scheme 2). Heat treatment of hollow-fiber polyacrylonitrile membranes at 250°C for 6 h made them more hydrophobic and considerably enhanced their heat resistance and chemical stability [31]. After such heat treatment, the membranes preserved their structure after refluxing in dimethylacetamide (T_b = 166.1°C) for 24 h, whereas the initial membranes dissolved under these conditions within several minutes.

Heat treatment is a power- and time-consuming method; therefore, various ways of its optimization were suggested. One of the procedures consists in preliminary hydrolysis of polyacrylonitrile fibers in an NaOH solution [33]. In the course of hydrolysis, nitrile groups of polyacrylonitrile partially transform into amide ($CONH_2$) and carboxy (COOH) groups and initiate the cyclization of macromolecules by the ionic mechanism (in addition to the cyclization occurring by the radical mechanism on heating nonhydrolyzed polyacrylonitrile). As a result, shorter time and lower temperature of the heat treatment become sufficient. Another procedure consists in introducing a small amount of comonomers, e.g., 1.5 mol % itaconic acid, in polyacrylonitrile synthesis, as it was done in [34]. The presence of such comonomer also induces the cyclization by the ionic mechanism and decreases the activation energy of this reaction, which allows the heat treatment to be performed at reduced temperature. Unfortunately, the modified polyacrylonitrile was not tested in [33, 34] for the resistance to organic solvents. An interesting alternative to the standard heat treatment consists in heating of a polyacrylonitrile sample under the action of IR radiation. The IR radiation influences the energy of the bond vibrations in polyacrylonitrile chains; as a result, the chemical transformation of macromolecules occurs considerably faster (within minutes instead of hours) and at a low temperature [35]. In [36], porous asymmetric polyacrylonitrile membranes were subjected to IR radiation heating and were annealed for 5 min at temperatures from 120 to 180°C. It was found that the intramolecular cyclization started already at 100°C, which is approximately 100°C higher compared to the common heat treatment. Notably, the membranes annealed at 120°C or higher temperatures appeared to be stable in a wide range of solvents, including aprotic solvents (dimethylformamide, N-methylpyrrolidone, dimethylacetamide, dimethyl sulfoxide), for at least 7 days at room temperature. Also, it was found that the flux of alcohols, acetone, and chloroform through the membranes did not noticeably change after their modification but significantly depended on the polymer concentration in the casting solution (in particular, the ethanol permeability decreased from 27 to 2.6 L m^{-2} h^{-1} bar^{-1} with an increase in the polyacrylonitrile concentration in the solution from 5 to 8 wt %). Thus, the membranes obtained in [36] can be used for both ultra- and nanofiltration of organic solvents.

Along with the heat treatment, polyacrylonitrile membranes can be stabilized by the traditional procedure, namely, by cross-linking of polymer chains using special chemical agents. This method was actively used by Peinemann et al. [37–39], who performed cross-linking of polyacrylonitrile chains in an aqueous hydrazine hydrate solution (20 vol %) at 85°C for 6 h (Scheme 3). The membranes obtained after the cross-linking had the mean pore size of 30–50 nm, were stable in organic solvents, including dimethylformamide and N-methylpyrrolidone, and were used as porous supports for preparing composite membranes. The same method for enhancing the stability with somewhat different cross-linking conditions [hydrazine hydrate was dissolved in ethanol (25 vol %) at 70°C, the reaction time was varied from 8 to 18 h] was used in [40] for preparing hollow-fiber polyacrylonitrile membranes. With an increase in the cross-linking time to 18 h, the membranes became denser, their pore size decreased, and the ethanol permeability decreased by an order of magnitude (from 32 to 2 L m^{-2} h^{-1} bar^{-1}). Estimation of the selectivity of the hollow-fiber membrane cross-linked for 18 h showed that Remazol Brilliant Blue R dye (MM = 627 g mol^{-1}) was retained to almost 100%, whereas the lighter Methylene Blue dye (MM = 320 g mol^{-1}) was retained to only 16%. It is important that cross-linking of polyacrylonitrile membranes made them insoluble in aprotic solvents N-methylpyrrolidone and dimethylformamide, in which they were kept for 2 months.

Scheme 3. Cross-linking of polyacrylonitrile chains with hydrazine.



As noted above, polyacrylonitrile is used as a porous support for composite membranes. The selective layer materials include, in particular, thermoplastics (polyamides) [37], elastomers [41], and highly permeable polymer glasses [42, 43]. To enhance the structural stability of composite membranes, not only the support polymer, but also the polymer of the thin selective layer is often cross-linked. In [41], the selective layer was made of polyetheramide, a copolymer consisting of hard polyamide blocks and soft polyether segments. This elastomer is known under the name Pebax and has the formula [–CO–PA–CO–O–PE–O–]$_n$ (PA is polyamide, and PE is polyethylene oxide). To reduce swelling in organic solvents, this polymer was subjected to chemical cross-linking using toluene diisocyanate. As expected, with an increase in the cross-linking time and in the cross-linking agent concentration, the layer became denser and the solvent (ethanol) permeability through the membrane decreased. Under the optimum cross-linking conditions (2% cross-linking agent, cross-linking time 30 min), the permeability of the Pebax/polyacrylonitrile composite membrane to ethanol and dimethylformamide was 0.1 and 1 L m^{-2} h^{-1} bar^{-1}, respectively. The retention coefficient of Brilliant Blue dye (MM = 826 g mol^{-1}) was 95% in both cases. These membranes appeared to be chemically resistant to alcohols, acetone, and dimethylformamide. However, in the latter case, the stability was ensured by cross-linking not only of the selective layer polymer, but also of polyacrylonitrile macromolecules (Scheme 3). Highly permeable glassy polymers (polymers with a high fraction of the void volume) include polytrimethylsilylpropyne [$–C(Me)=C(SiMe_3)–$], polymethylpentyne [$–C(Me)=CH(Me_2)–]_n$, and so-called polymers of intrinsic microporosity (PIMs). Fritsch et al. [42] prepared composite membranes with a selective layer from PIM-1 or polytrimethylsilylpropyne. These polymers were blended with polyethylenimine, which was subjected to chemical (with polyethylene glycol diglycidyl ether) or thermal (at 120°C for 16 h) cross-linking. As a result, the selective layer acquired the SIPN structure, which allowed its swelling in n-heptane to be appreciably reduced. Such procedure for modification of the selective polytrimethylsilylpropyne layer was used for preparing CO_2-selective composite membranes [43, 44]. Matson et al. [45] performed similar modification of polymethylpentyne films. Polyethyleneimine was introduced into the polymethylpentyne matrix and was thermally cross-linked at 120°C for several hours. As a result, films with the semi-IPN structure were obtained. At the polyethylenimine concentration in the polymer blend higher than 20 vol %, the films are stable in the organic solvents (cyclohexane, $CHCl_3$, CCl_4) in which the initial polymethylpentyne and polyethylenimine dissolve.

CONCLUSIONS

The considered ways to enhance the structural stability of membranes used for filtration of organic solvents are actually based on two methods: conversion of a linear polymer to a network polymer and blending of the main (matrix) polymer with another (additional) polymer, which can have linear or network structure. The preference of the first or second method is primarily determined by the kind of the membrane material. For example, polyacrylonitrile can be readily cross-linked chemically, whereas polysulfone or polyphenylsulfone cannot be cross-linked directly, and functionalization (i.e., introduction of reactive groups into the chains) is required for this purpose.

The practical performance indicator of modified membranes is their stability in aggressive organic solvents such as dimethylformamide, dimethylacetamide, etc. Stable polysulfone-based membranes can be prepared either by cross-linking of chemically modified chains with the formation of a polymer network or by photopolymerization of acrylic monomers in the polysulfone matrix with the formation of a semi-interpenetrating network. Membranes made of polyphenylsulfone (both virgin and chemically modified) were not tested for the stability in the above solvents, and further studies are required in this field. The stability of polyacrylonitrile membranes in aprotic solvents can be reached either by chemical cross-linking of the chains in a hydrazine solution or by intramolecular cyclization in the course of common or IR-stimulated annealing. A promising route to enhance the chemical stability of membranes is formation of supramolecular structures of the interpenetrating network type; it is efficient not only for polysulfone membranes, but also for membranes based on other materials, including high free volume glassy polymers.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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