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ORIGINAL ARTICLE

Functionalization of polymeric membranes by impregnation and in situ cross-linking of a PDMS/β-cyclodextrin network

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Abstract In this paper a new method for the functionalization of porous membranes with β-CD is reported. Porous polypropylene (PP) hollow fibres have been impregnated with a mixture composed by a partially cross-linked polydimethylsiloxane (PDMS) and β-cyclodextrin (β-CD). The prepolymerization of the PDMS components was necessary to avoid their inclusion in the β-CD cavity. The firm heterogenization of the β-CD was obtained by in situ cross-linking of the PDMS/β-CD network in the porous membranes.The presence of the PDMS/β-CD network in the membranes was confirmed by FT-IR-ATR (on the outer and inner surfaces) and EDX analyses (on the cross-section).The effect of the impregnation times on membrane morphology, loading and porosity has been investigated.The binding capacity of the heterogenized β-CDs has been tested using the phenolphthalein as guest molecule.

Keywords β-cyclodextrin · Impregnation and cross-linking · Membrane functionalization · Porous membranes · Recognition properties

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Introduction

The aim of this work is the functionalization of porous membranes with β-cyclodextrins (β-CDs). We want to conjugate the recognition properties of the cyclodextrins with the selective transport properties of artificial membranes.

Cyclodextrins have been extensively used in separation processes because they can discriminate between many molecules with similar properties (positional isomers, enantiomers, etc.). Cyclodextrins are cyclic oligomers composed of α-1,4-linked-D-glucopyranose units (6 for α-CD, 7 for β-CD and 8 for γ-CD, but the existence of some larger CDs was observed) which form hydrophobic cavities able to accommodate, by total or partial encapsulation, numerous molecules containing hydrophobic groups [1]. The guest molecules interact with the CD and form inclusion complexes by weak interactions such as hydrogen bonds, electrostatic interactions and Van der Waals forces. Most frequently the host:guest ratio is 1:1, but different order of association are also possible. The molecular encapsulation by CDs has been used in pharmaceutical field to improve the bioavailability of drugs with low water solubility; to control the release of drugs, fragrances and flavour; to reduce the volatility of substance; to stabilize reactive guest; to modify the spectroscopic properties and reactivity of molecules; to remove unwanted compounds [2]. Among the different types of cyclodextrins, the β-CDs are the cheaper and they have the most numerous industrial application [1].

Cyclodextrins, because of the presence of asymmetric centers in their structure (the C-1 of each unit, called the anomeric carbon), can also be used as chiral selector in separation processes or in enantioselective

synthesis. Regioselective reaction can be also obtained using the CD as reaction media [3]. Stereoselective and regioselective recognition during complex formation depends on the guest molecule ability to fit the cavity and interact with specific group of the CD, in analogy with enzyme supramolecular chemistry [4]. For example α-CD induces a significant substrate specificity in the hydrolysis of phenyl esters, and the reaction rate of the *meta* isomer is more than 100 times compared to the similar reaction of *para* and *ortho* isomers [5].

The typical truncated cone shaped cavity of the CDs exists both in solution and in solid state; for this reason it is possible to use these systems in heterogeneous form without loss of their recognition properties. CDs have been used in chiral stationary phase for enantioselective chromatography [6–10], in solid-phase microextraction [11] and in molecular imprinted polymers [12, 13].

In our opinion, the integration of membrane technology with the supramolecular chemistry of the cyclodextrins has enormous potentiality for the solid state recognition. The functionalization of membranes with specific molecular selectors is an interesting route for the preparation of synthetic tailor-made receptors. Because of the intrinsic properties of the membranes (modular, easy to scale-up, etc. [14]) these systems can be applied in the continuous processes required in the industry. A remarkable potential for a more rational utilization of the CDs can also be anticipated because the membranes are generally characterized by a more easy recycle compared to other heterogeneous systems such as functionalized silica [15]. Moreover when the selector is heterogenized in the membrane bulk, the selective transport properties of the membranes, can be used to modulate the access of the substrates to the recognition and/or reaction sites [15, 16]. The membrane can also improve the stability of the molecules heterogenized and, similarly to biological membranes, it can actively participate to the recognition process with its functional groups.

In our previous work, we reported the heterogenization of a modified β-CD (*O*-octyloxycarbonyl-β-CD) in flat sheet membranes made of an amorphous polyetheretherketone known as PEEK-WC [17]. The membranes were prepared from an homogeneous solution of the polymer and of the modified β-CD, by phase inversion technique induced by a non-solvent [17]. It was found that the β-CD derivative entrapped in membranes is able to recognize and form an inclusion complex with naringin, a bitter component present in grapefruits. Washing with an alkaline solution allows an easy regeneration of the membranes and permits their reuse [17].

Table 1 Codes used to indicate each PP membrane functionalized with β-CD at different impregnation times

Membrane code	Impregnation time (min)
PP0	0
PP1	1
PP5	5
PP10	10
PP20	20
PP5.5H	330
PP6.2H	370
PP17H	1020

In this work a new method was developed for the heterogenization of β-CD in porous membranes by impregnation and successive in-situ cross-linking of polydimethylsiloxane (PDMS) precursors/β-CDs network.

PDMS is very well suited polymer for the heterogenization of specific molecules (e.g. catalysts) in membranes [18]. This hydrophobic highly permeable elastomer characterized by a low glass transition temperatures (Tg = –123 °C), combines an high thermal and mechanical stability with an elevated chemical resistance; it is a low cost material, non-toxic and it exhibits high flexibility and elasticity [19]. PDMS can be easily synthesized from a two component system composed by a vinyl terminated prepolimer and a cross-linker by a Pt catalysed hydrosilylation reaction to form a densely cross-linked polymer network [20].

Porous polypropylene (PP) hollow fibres membrane were impregnated with a mixture formed by the two PDMS components (partially reticulated) and native β-CD. PP is an hydrophobic and economic material, non toxic, with an high resistance to organic solvents. Membrane made of PP, both in flat and tubular

Fig. 1 Photo of the dense PDMS/βCD (on the left) and PDMS (on the right) membranes

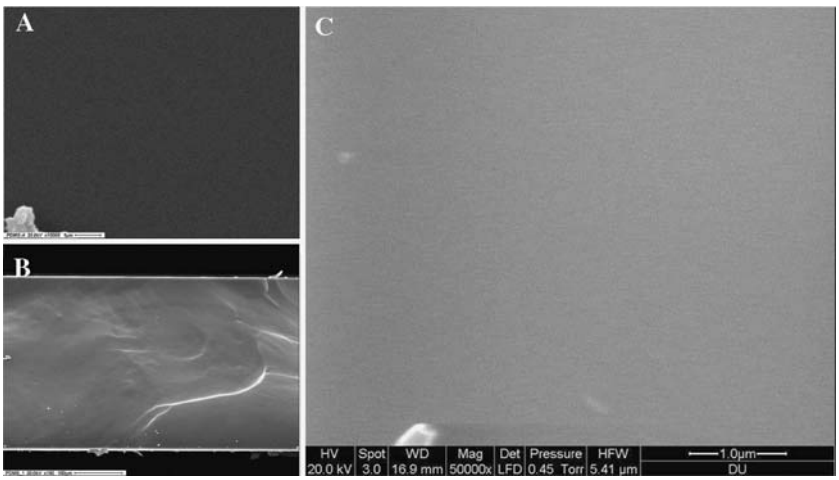

Fig. 2 SEM images of the PDMS flat sheet dense membrane: surface (**A**; 10000×) and cross section (**B**; 195×), and surface of the PDMS/β-CD membrane (**C**; 50000×)

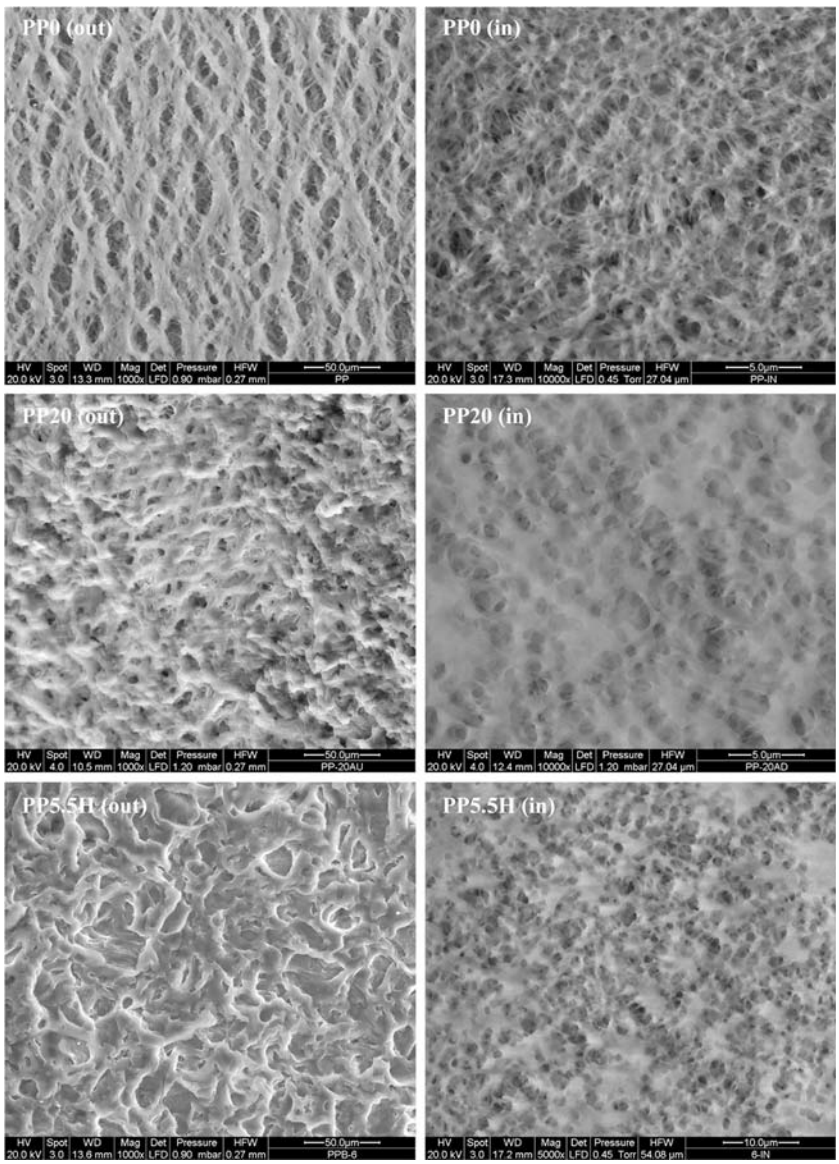

Fig. 3 SEM images of the outer and inner surfaces of the PP native membrane, PP20 and PP5.5H (The magnification of the outer surface is 1000×; the magnification of the inner surface is 10000× with the exception of the PP5.5 membrane for which is 5000×)

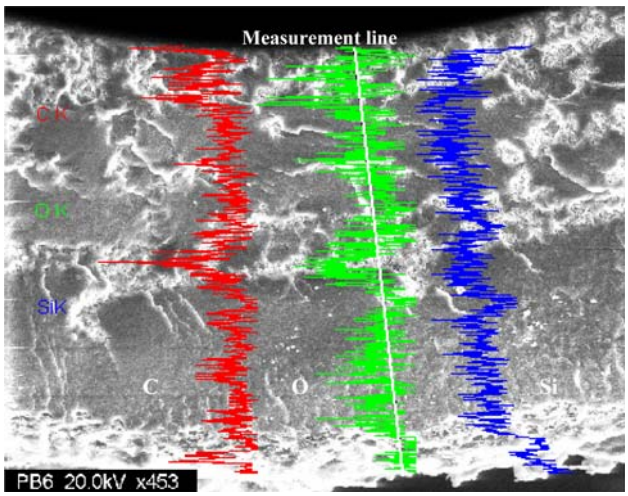

Fig. 4 SEM image of the cross section of the PP5.5H membrane with superimposed EDX analyses for C (red line), O (green) and Si (blue) atoms

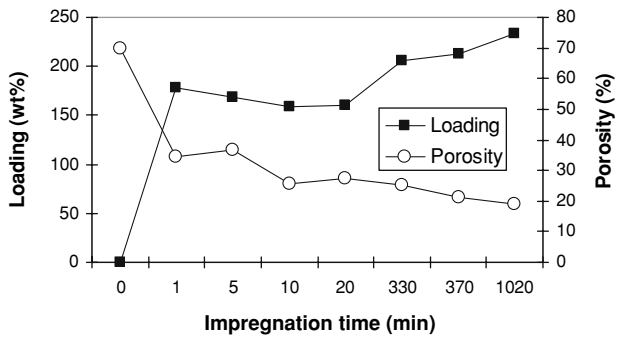

Fig. 5 Loading of the PDMS/βCD network in modified PP membranes and membrane porosity versus impregnation time

configuration, are widely used in membrane separation processes such as membrane contactors [21].

We studied the effect of the impregnation times on the loading in membrane of the PDMS/β-CD network and, consequently, on membranes properties. The results obtained in this preliminary investigation can be extended to other membranes, also in flat configuration, and other CD, also functionalized.

Experimental

β-CD and dichlorometane (DCM) were supplied from Sigma-Aldrich. PDMS was synthesized from a prepolymer (General Electric, RTV 615 A) and a cross-linker (General Electric, RTV 615 B).

Hydrophobic Accurel® PP hollow fibres membranes (nominal pore size diameter 0.22 μm; membrane thickness 530 ± 50 μm; inner diameter 1550 ± 150 μm) were purchased from Membrana GmbH, Germany.

The cross-section and surface morphology of the membranes were examined by a Quanta 200 FEI Philips scanning electron microscopy (SEM). Cross-sections were prepared by fracturing the membrane in liquid nitrogen.

EDX microanalyses were performed with a EDAX-Phoenix instrument (detector Super Ultra Thin Window, Si/Li crystal analyser).

Fourier transform infrared (FT-IR) analysis, also with an attenuated total reflectance method (ATR), were performed using a Perkin Elmer Spectrum One.

The load (L) of the PDMS/β-CD network in the PP modified membranes was defined by the formula:

$$L = \frac{(W_m - W_n)}{W_n} * 100$$

where W_m and W_n are respectively the weight of a modified and a native membrane of the same length.

Membrane porosity (ε) was measured by the gravimetric method, determining the weight of ethanol contained in the membrane pores. The porosity was calculated by the following equation:

$$\varepsilon = \frac{(w_2 - w_1)/D_w}{((w_2 - w_1)/D_w) + (w_1/D_p)} * 100$$

where w_1 is the weight of the dry membrane, w_2 the weight of the wet membrane (membrane immersed in ethanol for 24 h at room temperature and wiped to remove the traces of solvent on the surface), D_w the ethanol density and D_p is the polymer density (0.9 g/cm^3).

Membrane functionalization by β-CD heterogenization

A solution (25.0 wt%) of the PDMS components, prepolymer and cross-linker in a ratio 10:1 was prepared using DCM as solvent and stirred for 2 h at room temperature. This solution, unless otherwise indicated, was partially cured by heating at 80°C for 1 h. The β-CD was then added with a loading of 20.4 wt% relative to PDMS components. The mixture was left under magnetic stirring for additional 24 h then it was used for the impregnation of porous polypropylene (PP) hollow fibres membrane. The PP membranes, before impregnation by vertical immersion in the mixture left under magnetic stirring, were closed at the extremities with a Teflon cup. Different impregnation times were tested: from 1 min to 17 h (Table 1). The impregnated

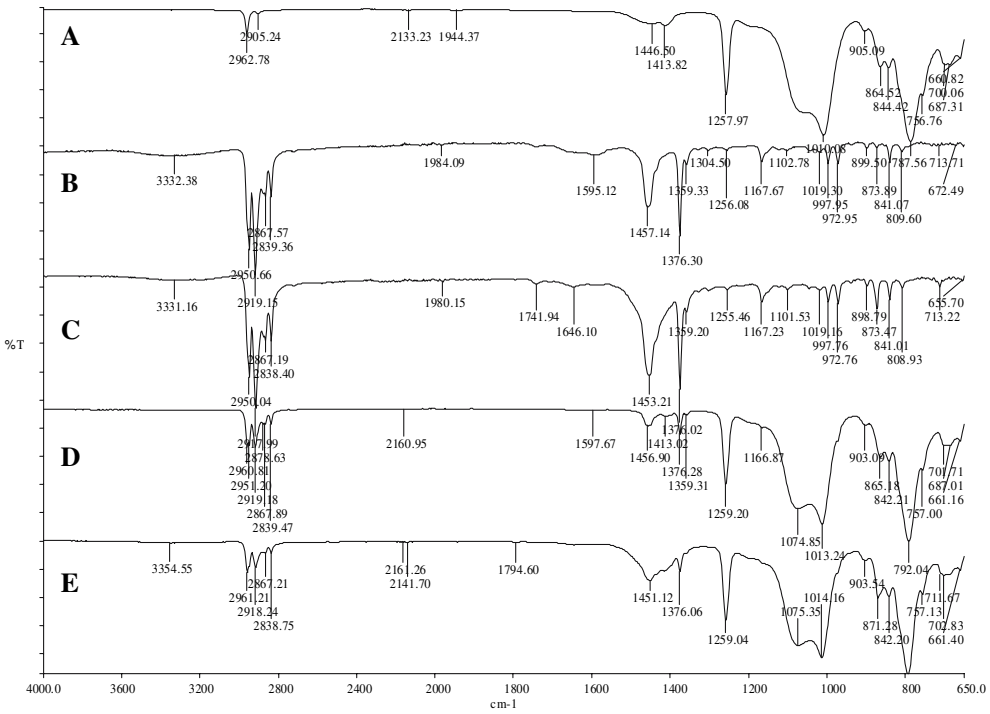

Fig. 6 FT-IR-ATR spectra of the: PDMS/βCD dense membrane (**A**); PP native (**B**, inner side); PP native (**C**, outer side); PP5.5H (**D**, inner side) and PP5.5H (**E**, outer side)

membranes were kept overnight at room temperature to allow the DCM evaporation, after they were cured under vacuum at 150 °C for 1 h. The functionalized membranes were washed many times with water to remove unreacted components and finally air dried.

As reference samples, we also prepared flat sheet dense membranes by phase inversion technique induced by solvent evaporation [22]. The PDMS prepolymerized network or the PDMS/βCD mixture were cast on a petri disk, kept overnight at room tempera-

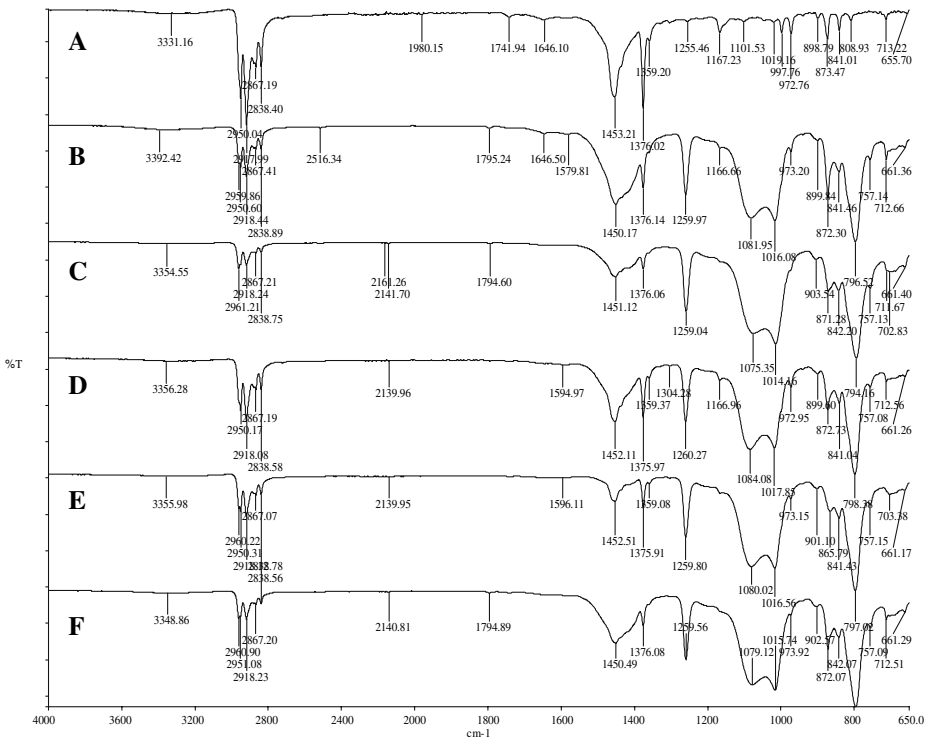

Fig. 7 FT-IR-ATR spectra of the: PP native (**A**); PP17H (**B**); PP5.5H (**C**); PP10 (**D**); PP5 (**E**) and PP1 (**F**). For all the membranes the outer surface was analyzed

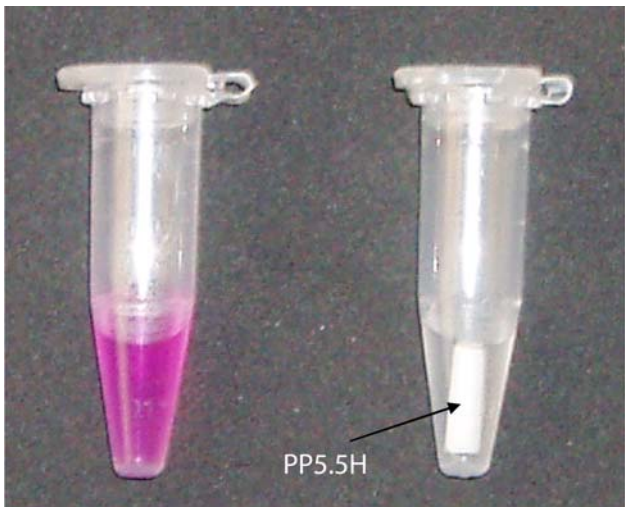

Fig. 8 Decolouration of a phenolphthalein solution (on the left) after immersion of the PP5.5H membrane (on the right) because of the formation of β-CD/phenolphthalein inclusion complexes (colourless)

ture, cured under vacuum at 150 °C for 1 h, washed with water and dried. The two membranes obtained were both dense and in the PDMS/βCD membrane the cylodextrin was uniformly distributed in the polymeric matrix (Figs. 1, 2)

Results and discussion

In addition to the physical entrapment of the β-CD in the PDMS cross-linked network, weak interactions (Van der Waals interactions and hydrogen bonds) between the hydrophobic polymeric network and the cyclodextrin hydrophobic and hydrophilic groups allow the successful heterogenization. Moreover covalent links might be also formed between the unreacted SiH groups with the hydroxyl groups of the β-CD in the presence of the Pt catalyst (contained in the component RTV 615 B).

The prepolimerization step prevents that the unreacted PDMS chains might sorb in the β-CD cavity rendering the β-CD inaccessible for the guest molecules. The molecular encapsulation of the PDMS precursors might also reduce their reactivity preventing the cross-linking reaction.

As reported in literature [20], the unreacted PDMS components can sorb in pores large from 6 Å onwards (the β-CD cavity diameter is 6.0–6.5 Å [1]). However when the PDMS components are prepolymerized, cavity blocking can be excluded. On the contrary, when the β-CD was added to the PDMS precursors without the preliminary prepolimerization, the mixture became highly viscous and the formation of irregular aggregates was observed on the membrane surfaces impregnated with this system.

The cross section, inner and outer surfaces morphology of the functionalized hollow fibres membranes were examined by scanning electron microscopy and compared with those of the native PP membrane. The outer surface of the functionalized membranes has a lower porosity compared to the native membrane, and the difference increase with the increasing of the impregnation time (Fig. 3). Also the inner surface of the modified membranes shows different morphology compared to the native PP (Fig. 3). The PDMS/β-CD network penetrates the PP hollow fibres from the outer to the inner surface (Fig. 3). The intrusion of the PDMS/β-CD network in the porous membrane was also confirmed with chemical analyses by energy dispersive X-ray spectrometry (EDX) carried out in the cross sections of the PP membranes loaded with the PDMS/β-CD network. The intensity profiles of the characteristic X-ray of Si and O (atoms not present in the native PP) demonstrated that the PDMS/β-CD network is present in the whole membrane thickness (Fig. 4). Increasing the impregnation time of the PP membranes, the loading of the PDMS/β-CD network increased and the membrane porosity decreased (Fig. 5).

FT-IR spectra performed with an attenuated total reflectance method (ATR) on the inner and outer surfaces of the modified PP membranes confirmed the presence of the PDMS/β-CD network in the functionalized membranes.

The strong absorption bands at 1013–1075 cm^{-1} associated with Si–O–Si asymmetric stretching [23] was present in the spectra of the PDMS/β-CD dense membrane and the outer and inner surfaces of the modified PP membranes (Figs. 6, 7). Moreover the signal at 1259–1260 cm^{-1} of the symmetric C–H stretching of the methyl groups and the signal at 787–798 cm^{-1} of the Si–C stretching [23] are also present in the same spectra but clearly absent in the absorption spectrum of native PP (Figs. 6, 7). The absence of the broad band at 3,380 cm^{-1} of the hydroxyl group in the spectrum of the PDMS/β-CD membrane and the modified PP membranes might be the confirmation of the chemical link between the β-CD an the PDMS chain (Figs. 6, 7). Another possible explanation of this observation might be the folding of the β-CDs inside the membrane during the curing step, and the presence of a thin layer of PDMS polymer which cover the surfaces.

The accessibility and binding capacity of the β-CDs cavity in the modified membranes was confirmed using the phenolphthalein as guest molecule [24].

The membranes loaded with the PDMS/β-CD network were immersed in an aqueous solution of phenolphthalein $5 \cdot 10^{-5}$ M at pH 10.5 (violet coloured). The rapid decolouration of the solution was observed because of the transformation of the phenolphthalein into its colourless lactanoid dianion within the cavity of the β-CD [24] (Fig. 8).

The described membrane preparation method can be extended to other modified cyclodextrins for the study of their (stereo) selective recognition properties towards substrates of specific interest.

Conclusions

The possibility to heterogenize cyclodextrins in porous membranes by impregnation and successive in-situ cross-linking of a PDMS precursors/β-CD network was demonstrated. The inclusion of the PDMS components in the β-CD cavity was avoided by the partial cross-linking of the PDMS before the adding of the cyclodextrin.

Different PDMS/β-CD network loading inside the membranes were obtained varying the impregnation time. The increase of the loading in membrane, reduces the membrane porosity. The β-CD heterogenized in the PP membranes, in analogy with the free β-CD, showed binding capacity towards phenolphthalein.

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