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COMMUNICATION

Systems membranes – combining the supramolecular and dynamic covalent polymers for gas-selective dynameric membranes[†]

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The adequate selection of components makes possible the generation of double dynameric membranes, allowing the fine constitutional modulation of the gas transport performances.

Modular strategies for the fabrication of ultradense macroscopic systems of addressable functional domains¹ have been described for molecular,² hybrid³ or polymeric⁴ systems. Of special interest is the generation of systems in which the diffusional solutes (ions, water molecules or gas molecules) mutually interact within directional transporting pathways. This offers the possibility to use "Systems Membranes",³ the collection of objects (molecules, polymers, nanoplatforms etc.), in order to generate the "fittest"⁵ transporting systems *via* constitutional recognition.⁶ One may conjecture that further development of such systems is related to the molecular control of the transport functions. Low molecular weight additives⁷ and free volume molecular polymers⁸ can be used or tailored to prepare high-flux selective membranes. The combination of permeable with hard segmented components results in formation of segregated, well controlled micro-domains with improved mass transfer functions.^{7c,9} The dynamic polymers or dynamers,¹⁰ combining molecular and supramolecular features, may give the possibility to achieve the molecular limit for the construction of membranes of high diffusional behaviours.¹¹ Metallodynameric^{11b} and dynameric^{11a} membranes can be used to push the limit toward the molecular control of gas or ion selective membranes. A further step consists of implementing this strategy by using directional supramolecular and permeable dynamic covalent polymers. We report in this communication such association between bisureido-dialdehyde supramolecular polymers and dynamic covalent macromonomers, incorporating both non-covalent H-bonds and reversible imino-covalent connections (Fig. 1). The dialdehyde supramolecular connector A and di(tri)amino-terminated macromonomeric building blocks (*i.e.* bis(3-aminopropyl)-polytetrahydrofuran ($M_n \sim 1100 \text{ g mol}^{-1}$), polyTHF 1, bis(3-aminopropyl)-polyethyleneglycol ($M_n \sim$ 1500 g mol⁻¹), polyPEG **2**, bis(3-aminopropyl)-polydimethyl-siloxane ($M_n \sim 2500 \text{ g mol}^{-1}$), polyPDMS 3, and



Fig. 1 (a) Synthesis of double dynameric membranes P1–P4 combining supramolecular self-assembly *via* H-bonding of bisureido-dialdehyde, A, and dynamic covalent imino-bonding with polyTHF, 1, polyPEG, 2, polyPDMS, 3, and polyMePEG, 4, macromonomers.

tris[poly(propyleneglycol), amine-terminated] ether $(M_n \sim 3000 \text{ g mol}^{-1})$, polyMePEG **4**) have been used to conceive double dynameric membranes for gas separation. The dynameric networks might be considered to contain linear (**P1–P3**) or cross-linked star-type (**P4**) soft permeable domains combined with hard supramolecular segments based on five structural features:

(1) The bisureido-compound **A** forms supramolecular ribbons in which the neighbouring ureas lie in the same plane with respect to one another.⁶ Accordingly, arrays of layered stacks of **A** can be generated, such that the bis-aldehyde moieties are disposed at the extremities of each ribbon. Of particular interest is their potential

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ability to generate hard uniform segments as directional fillers in the membranes.¹²

(2) The hydrophobic polyTHF and the hydrophilic poly-PEG linear macromonomers have been used to generate the soft phases considered as permeables for the CO_2 transport.

(3) The polyPDMS is among the most permeable polymers known and present high permeability for gases.⁹

(4) The polyMe(PEG) star-type macromonomers allow a high CO₂ solubility and contribute to the cross-linking behaviour, controlling the free volume of the dynameric network.¹³

(5) The polymeric environment might have a stabilizing effect on the hydrolysis of the imine bond and the amine exchanges during the membrane preparation.¹⁰

The ¹H and ¹³C NMR, ESI-MS spectra of A are in agreement with the proposed formulas.[†] The formation of the imine bonds in P1-P4 is supported by the presence in the FTIR spectra of the imine vibration shift at $\nu_{C=N} = 1605 \text{ cm}^{-1}$ inside the aldehyde vibration shift at $\nu_{C=0} = 1710 \text{ cm}^{-1}$ initially observed for A. The urea vibration band $\nu_{C=0} = 1700 \text{ cm}^{-1}$ was downshifted to 1690 cm^{-1} in **P1–P4** indicating the ureido ribbons formation. Further insight into structural behaviours of P1-P4 is obtained from the X-ray powder diffraction (XPRD). The XRPD patterns of the polyTHF 1 and polyPEG 2, precursors and related materials P1 and P2 present well-resolved peaks at 2θ = $20-25^{\circ}$ (d = 4.0-4.8 Å), indicative of the close packing of the crystallized PEG and THF chains with an ordered lamellar morphology of periodic layers (Fig. S1, ESI[†]). Moreover, the **P2** dynamer displays a broad Bragg diffraction peak at 2θ = 1.10° (d = 60 Å), corresponding to the signature of long-range crystalline architectures of 2. These domains appear only after reaction with A. exhibiting dominant self-organization behaviour and fixing the directional order over nanoscopic distances. Then, supported thin-layer films were obtained by coating solutions of P1 to P4 onto a planar polyacrylonitrile (PAN) support by using the tape casting method. Scanning electron microscopy (SEM) confirmed that the active layers (thickness of about 400 nm-2 µm) were dense without micropinholes with a homogeneous structure at the nanometric scale (Fig. S2, ESI[†]).

Gas transport performances (*i.e.* permeability and selectivity) through membranes are generally controlled by the gas-diffusivity and by solubility-selective behaviours of materials. The pure gas permeabilities for the **P1–P4** membranes are shown in Table 1 and Fig. 2. As a general trend the dynameric membranes allow high permeabilities for the CO₂ and interesting CO₂/light gas selectivities. As expected, the most permeable membrane is **P3**, with permeability and selectivity values in the range of those previously reported for PDMS blends.^{7a} In contrast, for the crystalline polyPEG-based **P2** membranes the CO₂ permeability and the CO₂/N₂ selectivity are strongly much lower than the

Table 1Pure gas permeabilities and selectivities of the P1-P6dynameric membranes

Membrane	$P_{O_{2}}$, Barrer	$P_{N_{2}}$, Barrer	$P_{\rm CO_2}$, Barrer	$S_{\rm CO_2/N_2}$	S_{O_2/N_2}
P1	6.2	2.2	80.2	36.7	2.8
P2	0.33	0.2	3.00	1.7	14.9
P3	474.7	204.8	2685.3	13.1	2.2
P4	3.5	1.6	43.0	28	2.3
P5	3.0	3.0	9.0	3	1
P6	6.0	2.0	25.0	14	3



Fig. 2 (a) Pure gas permeabilities; (b) pure CO_2/N_2 selectivities at 30 °C and 300–400 mbar, as a function of molar ratio %P4 = [P3]/[P4], mol/mol, of macromolecular components.

estimated P = 143 Barrer and $S_{CO_2/N_2} = 48$ performances of amorphous PEG.9a The effect of structuration of the material is clearly not beneficial for the diffusion of gas through the compact low free volume P2 membrane. Despite the very low permeabilities of both gases, the nice $S_{O_2/N_2} = 14.9$ may be retained. In order to compare the effect of self-organization induced via the supramolecular bis-urea motif we prepared the dynameric films P5 and P6 built from the macromonomers 1 and 4 connected via isophthalaldehyde non-structuring cores. The effect of using soft supramolecular fillers $(\mathbf{A})_n$ as directional components in dynameric mixtures is related to the increased CO2 permeabilities and the CO_2/N_2 selectivities (Table 1, compare P1 with P5 and P4 with P6). This emphasizes the major advantage of using such soft segments $(\mathbf{A})_n$ for tuning the diffusive domain morphology with enhanced mass transport functions of gases by increasing the free volume of the matrix, controlled mostly at the molecular scale.

Moreover, there are other opportunities toward this objective and an increased free volume can also be obtained by the incorporation of star-like macromonomers, 4 acting as a separator of linear macromonomers 1-3. Generally, dynameric systems are undergoing exchange, incorporation or decorporation of their macromonomeric subunits linked together by reversible interactions. This might play an important role in the ability to more finely mutate their functional domains.^{10,11} Within this context, we next considered that a combination of the beneficial CO2 diffusive properties of P3 and the cross-linking properties and the CO_2/N_2 selectivity of P4 would be interesting. These experiments confirm that the CO₂ transport through mixed and dynamically exchanged polymeric blends P3/P4⁺ is related to two opposite effects: with increasing concentration of P3, the rivalry between an increasing diffusivity of CO2 over the polar polyPDMS chains of P3 versus the high cross-linking



Fig. 3 Schematic representation of morphology of (a) block-copolymer systems using nanoscopic hard and soft segments and of (b) dynameric systems using self-assembled hard and soft molecular components resulting in the precise control of the size of addressable diffusional domains, toward ultradense macroscopic block co-dynamers.

non-diffusional behaviors of **P4** is related to the strong increase in the initial permeability of **P4** (Fig. 2a), while its selectivity is decreasing (Fig. 2b). This can be mainly attributed to high gas diffusivity through **P3** domains and not to an increase in solubility of **P4** domains of increased CO₂-philic character.

In conclusion, double dynameric membranes taking advantage of both supramolecular hard and macromolecular permeable soft domains can be rationally designed and synthesized for selective separation of the CO₂. The CO₂ permeability and the selectivity strongly increase when supramolecular bisureido-hard segments (A)_n such as reversible ribbon-type connectors are used instead of isophthalaldehyde non-structuring core connectors. These ribbons reinforce and mutually orient the macromonomeric phases in a more significant manner than the polymeric blends. The use of components reversibly connected at the molecular scale would finely control the density and dimensional mutual distribution of soft and hard segments within high density domains of enhanced mass transport properties (Fig. 3).

Finally, adequate selection of macromonomers makes possible important structural variations, beneficial for the modulation of the gas transport properties based on structural behaviours at the molecular level. This is the case of PDMS type membranes reported here pushing the limits rendering possible a CO₂ permeability of 2685 Barrers, while maintaining a good CO₂/N₂ selectivity of 13.1. Within this context the double dynameric membranes reported here show a strong potential for industrial purposes for which high CO₂ permeance (1000 Barrers) and optimal selectivity (*i.e.* $S_{CO_2/N_2} = 20$) are required.¹⁴

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