Blending PPO-based molecules with Pebax® MH 1657 in membranes for gas separation

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ABSTRACT

This work explores possibilities to blend block copolymers, i.e. Pebax® MH 1657, with a variety of cheap PPO-rich molecules which could potentially play a double role in the resulting membranes as dispersing/stabilizing agents in multi-component casting solutions and as a gas transport medium in the final membrane. These membranes were prepared by solution casting and were characterized by DSC, SEM, AFM, XRD density measurements and FTIR-ATR, while additive incorporation was also studied with theoretical calculations. Gas permeation measurements showed that this approach resulted in increased permeabilities at the expense of mixed-gas selectivity. An interpretation of the blend structure was finally made using gas transport models. The compatibility of these additives with the synthesis of selective gas separation membranes may enable a potential double role in membrane synthesis, i.e. as stabilizing agents in membrane synthesis and as a gas transport medium in the final membrane.

INTRODUCTION

Membrane based processes increasingly meet modern requirements to be environmentally-friendly, energy-efficient and simple in use. Post-combustion CO₂ capture is characterized by low driving forces and streams highly diluted in CO₂, with the consequence that optimum membrane selectivity depends on process and operating conditions, whereas high permeances are always required.¹

Ethylene oxide (EO) based polymers have been the subject of investigation for gas separation membranes owing to the high solubility selectivity for gases, like CO₂ and H₂S, compared to light gases, based on polarizability differences.² More specifically, favorable quadrupole-dipole interactions between CO₂ and the ethers make such materials interesting for both pre- and post-combustion applications.³ Use of EO functional groups in stable membrane structures is not trivial because of the poor film-forming ability of pure PEO.⁴ Additionally, the crystallization behavior of pure PEO with molecular weights (MW) above 1 kDa appears detrimental for gas transport.⁵

Block copolymers are an excellent option towards commercial application of EO functional groups in membranes. PEO in these materials is directly connected to immobile, hard segments by chemical bonds which results in microphase separation between hard and soft segments.⁶ In the commercially available block copolymer PEBAX[®] MH 1657, the polyamide hard blocks thus merely act as physical crosslinks for mechanical and thermal stability of the resulting microphase separated structure. Its specific microdomain morphology results in a 40-50 CO₂/N₂ selectivity, termed sufficient for post-combustion capture, with rather low permeability as main drawback. Polyactive[®], another commercial block copolymer with polyether soft segments, shows a similar gas transport.⁷ The main difference between Pebax[®] and Polyactive[®] can be found in the hard segments, for which the latter consist of poly(butylene terephthalate) (PBT).⁷

Good phase separation of the hard and soft segments is generally desired in combination with a high PEO content. With its low glass transition temperature, PEO possesses high chain flexibility and low melting temperature, creating an amorphous structure with minimal crystallinity.⁸⁻¹⁰ The

presence of hard segments in the soft phase due to incomplete phase separation and incomplete crystallization of the hard segment hinders gas permeation.^{4,8,11}

As a consequence of altered block copolymer morphology, incorporation of PDMS oligomers with PEG side-chains in block copolymers yielded a factor 5 increase in CO₂ permeability.¹² In another study, PEG-dibutyl ether was added to Polyactive which resulted in a similar permeability increase.⁷ The same group also blended PEG ethers with different end groups into Pebax® MH 1657 where addition of 50 wt% dimethyl ended PEG yielded a CO₂ permeability increase from 78 to 606 Barrer.¹³

Similarly, benefits of poly(propylene oxide) (PPO) as soft segment have been implemented in block copolymer structures. While PEO ensured highly selective interaction with CO₂, PPO introduced amorphisation, higher flexibility and thus a higher total free volume.⁸ One series of additives included a random distribution of PPO within a PEO chain (PEG-ran-PPG) whereas the other featured a block of PPO with PEO segments on both ends (PEG-block-PPG-block-PEG), a molecule from the so-called Pluronics® family. The PEG-ran-PPG additive thereby resulted in higher permeability increases (+705% for random vs +545% for block distribution).¹⁴ Also in mixed matrix membranes (MMMs), addition of PEG-ran-PPG resulted in a strong synergistic effect on permeance and selectivity.¹⁵

Unexplored possibilities for membrane synthesis remain when considering the so-called “Pluronic grid”. This family of molecules indeed displays an interesting variation of MWs, PPO vs PEO ratios and structural variation with surfactant properties. These molecules may have a positive influence on colloidal stability in membrane synthesis which often appears challenging.¹⁶

Based on this PPO-rich additive compatibility, it is hypothesized that combinations of both material families, i.e. EO based block copolymers and Pluronics, would yield interesting opportunities for CO₂ selective membranes. For example, these non-ionic surfactant materials could potentially play a double role in membranes as dispersing/stabilizing agents in multi-component casting solutions and as a gas transport medium in the final membrane. This work presents a study on the compatibility of PPO-rich Pluronics and PPG with the well-known polymer Pebax in gas separation membrane synthesis.

EXPERIMENTAL

Materials

Pebax[®] MH 1657, hereafter referred to as Pebax, in pellet form was kindly provided by Arkema. This poly(ether-b-amide-6) contains 60 wt% PEG and 40 wt% aliphatic polyamide PA6. It was reported elsewhere that the repeating units consist of approximately 35 ethylene oxide units followed by approximately 9 nylon-6 units.¹² Poly(propylene glycol) ($M_n \sim 425$ g/mol), Pluronic[®] L-81 ($M_n \sim 2800$ g/mol) and Pluronic[®] L-61 ($M_n \sim 2000$ g/mol) were purchased from Sigma-Aldrich. According to the supplier 10 wt% of both Pluronics is constituted by PEG chain ends from equal length.

Membrane synthesis

Pebax was dissolved in a mixture of ethanol/water in 70/30 (v/v) to prepare a 4 wt% polymer solution. Continuous stirring for about 2 h was carried out to ensure complete dissolution. After cooling to room temperature, a homogenous solution was obtained without gelation. Additives were then added in amounts according to the following expression:

$$\text{Additive wt. \%} = \left(\frac{m_{\text{additive}}}{m_{\text{additive}} + m_{\text{Polymer}}} \right) \times 100\% \quad (1)$$

After the addition, the solution was stirred overnight. Membrane films were obtained by solution casting in Teflon petri dishes and subsequent solvent evaporation at room temperature for 2 days. Membrane films were further dried in a vacuum oven at 60°C for 24 h.

Membrane characterization

The ideal and mixed-gas permeabilities and selectivities of membranes were measured in a custom-built high-throughput gas separation (HTGS) set-up (HTML, Belgium). The design of the original set-up is described elsewhere¹⁷, however, its analysis loop was modified to avoid sample carryover and ensure faster measurements compared to the original configuration.

The modification entails maintaining a vacuum in the analysis loop parallel to the GC injection loop and is shown in Fig 1. The flow rate and composition of feed gas mixtures are adjusted by Mass Flow Controllers (MFCs), provided by Bronkhorst (Netherlands) for each gas. A compact gas chromatograph (CGC, Interscience) and a constant volume auxiliary cylinder connected to a MKS Baratron® pressure transducer having a higher limit of 10 mbar, were used to measure the permeate gas composition and permeabilities, respectively.

FIGURE 1 Set-up modification to avoid sample carryover and ensure faster measurements compared to the original configuration

The upstream pressure was adjusted by a back-pressure regulator on the purge line. The desired permeate gas stream was selected via the 16 way valve (V1). The selected permeate was fed to the CGS to analyze the permeate composition. The gas permeability was measured by allowing the gas to expand in an auxiliary cylinder. The rate of pressure increase (dp/dt) in the auxiliary cylinder was measured to calculate gas permeabilities (P_i) via the following equation:

$$P_i = 10^{10} \frac{y_i V L}{x_i p_{up} A R T} \frac{dp}{dt} \quad (2)$$

where P_i is the permeability (Barrers) of component i , x_i and y_i the mole fraction of the components in, respectively, feed and retentate. V is the downstream volume, A the effective

membrane area (1.91 cm²), L is the membrane thickness (cm), T refers to the operating temperature (K), p_{up} is the upstream pressure (cm Hg), R is the gas constant 0.278 cm³ cm Hg/(cm³ (STP) K), dp/dt corresponds to the slope of pressure increase (in cm Hg/s).

The mixed-gas selectivity was calculated by the ratio of the downstream (y) and upstream (x) mole fraction of the two gases by the following equation:

$$\alpha_{ij} = \frac{y_i/y_j}{x_i/x_j} \quad (3)$$

where y_i and y_j are the mole fractions of components i and j, respectively, in the downstream, x_i and x_j are the mole fractions of components i and j, respectively, in the upstream. In GC analysis, y_i/y_j is determined with peak areas corresponding to mole fractions. Careful control of flow rate by MFCs thereby determines x_i/x_j .

Electron microscopy

The cross-section morphology was analyzed with scanning electron microscopy (SEM, JEOL JFC-1300, Tokyo, Japan). Samples were broken in liquid nitrogen and coated with a thin (1.5 - 2 nm) gold layer using a high resolution sputter coater (JEOL JSM-6010LV Scanning Electron Microscope, Tokyo, Japan)

Attenuated Total Reflectance Infra-Red (ATR-FTIR) Spectroscopy

The chemical composition of the membrane surface was analyzed by ATR-FTIR. Spectra were collected from dried membranes using a Varian 670 FTIR Imaging microscope (Agilent technologies) with a Single Point MCT detector and a diamond ATR crystal. Thirty-two scans were collected at a resolution of 4 cm⁻¹.

Density measurements

The buoyancy method was used for determination of experimental density values of membrane samples with the Sartorius YDK 01 Density Determination Kit. Silicon oil was selected as the auxiliary liquid. Density was calculated by filling in the buoyancy G the following formula:

$$\rho = \frac{W(a)}{0.99983} \left[\frac{\rho(fl) - 0.0012 \text{ g/cm}^3}{W(a) - W(fl)} \right] + 0.0012 \text{ g/cm}^3$$

where $G = W(a) - W(fl)$, with $W(a)$ and $W(fl)$, the weight in air and the weight in silicone oil, respectively, and $\rho(fl)$ the density of silicone oil, here equal to 0.972 g cm^{-3} .

Contact angle and surface tension measurements

Interfacial tension of the additives and its polar and dispersive components were determined according to the Owens-Wendt-Rable-Kaeble (WORK) or Fowkes method. A CAM 200 device (KSV) was used for contact angle and surface tension measurements. This device captures images with a CCD firewire camera (512x480) with telecentric zoom optics combined with LED based background lighting and drop profile analysis is done through an algorithm using the Young-Laplace method.

Differential scanning calorimetry (DSC)

DSC was used to study the effect of additive blending upon thermal transition in the range from -70°C to 250°C . A TA instruments DSC Q2000 calorimeter was used to measure membrane samples with heating and cooling rates of $10^{\circ}\text{C min}^{-1}$ under nitrogen purge gas stream (190 mL/min). A first thermal cycle was performed for erasing thermal history of the given samples

with cooling towards -70°C and reheating towards 250°C. Then the actual measurement comprised cooling from 250°C towards -70°C and reheating towards 250°C. The data considered here correspond to this second cycle. Data was analyzed with Universal Analysis software.

Atomic Force Microscopy (AFM)

AFM measurements were performed using a Bruker Dimension 3100D scanning probe microscope. The height and phase images of membrane cross-sections were recorded simultaneously while operating the instrument in tapping mode under ambient conditions. We used commercial silicon tapping mode cantilevers (SSS-NCHR probes from NANOSENSORS™) with an integrated pyramidal tip having a radius of curvature lower than 2 nm, nominal spring constant ~ 42 N/m and nominal fundamental resonance frequency ~ 256 kHz. The phase shifts were measured with respect to the phase of the free cantilever vibrating at the resonance frequency. It should be noted that “phase” here refers to a technical parameter of tapping mode AFM to avoid confusion with descriptions of microdomain morphology in block copolymers. A more detailed explanation on tapping mode AFM for polymer imaging can be found in supporting information. Membrane cross-sections were characterized to limit surface-related effects.

XRD

Powder X-ray diffraction (XRD) patterns were recorded on a STOE STADI P COMBI diffractometer with an image plate position sensitive detector (IP PSD) in the 2θ region from 5° to 60°, with internal resolution of 0.03° and counting time of 1200 s. The measurements were performed in transmission mode at room temperature using CuK α 1 radiation ($\lambda=1.54056$ Å) selected by means of a Ge (111) monochromator.

RESULTS AND DISCUSSION

Introduction

The membranes, synthesized with Pluronic additives, showed no visible signs of phase separation. Fig 2 gives a visual representation of the structural features that might be affected upon additive incorporation. A short discussion on the potential of Pluronics for stabilization of casting solutions can be found in supporting information.

Figure 2: Visual representation of structural features of Pebax MH 1657 possibly affected upon additive incorporation

Theoretical calculation on thermodynamic partitioning

The dispersion of additives blent in block copolymers consisting of different microphases can be theoretically considered with Sumita's approximation method.¹⁸ This method has been used for predicting the selective localization of filler materials in immiscible polymer blends¹⁹ and vinyl

acetate-based polymers in Pebax. In this method, a so-called wetting coefficient, w_{additive} , is calculated as follows:

$$w_{\text{additive}} = (\gamma_{\text{PEO-additive}} - \gamma_{\text{PA6-additive}}) / (\gamma_{\text{PA6-PEO}}) \quad (4)$$

where $\gamma_{\text{PEO-additive}}$, $\gamma_{\text{PA6-additive}}$ and $\gamma_{\text{PA6-PEO}}$ stand for the interfacial energy between, respectively, the polyether phase and the additive, the polyamide phase and the additive, and the polyether phase and the polyamide phase. The surface free energy is thereby approached with a two-component theory considering two contributions to the overall surface free energy, i.e. dispersive interactions (γ^d) and polar interactions (γ^p):

$$\gamma = \gamma^d + \gamma^p \quad (5)$$

A harmonic-mean equation is then used to calculate the interfacial energy for the different material combinations:

$$\gamma_{ij} = \gamma_i + \gamma_j - 4 \left(\frac{\gamma_i^d \gamma_j^d}{\gamma_i^d + \gamma_j^d} + \frac{\gamma_i^p \gamma_j^p}{\gamma_i^p + \gamma_j^p} \right) \quad (6)$$

The resulting wetting coefficient then expresses one of three possible situations about the thermodynamic tendency for dispersion of the additive in

1. the polyamide domain, if $w_{\text{PA6-PEO}} > 1$
2. the polyether domain, if $w_{\text{PA6-PEO}} < -1$
3. in neither domain, but rather at their interphases if $-1 < w_{\text{PA6-PEO}} < 1$

Values about interfacial properties for pure polymers are well known in literature. However, incorporation in block copolymers influences conformational restriction which is well related to interfacial properties.²⁰ Literature values from a similar calculation regarding selective dispersion in Pebax were therefore used¹⁸, values for the PPG, L-61 and L-81 additives were measured and are shown in Table 1. The used values of interfacial properties and calculations for thermodynamic wetting coefficient are shown in Table 2.

	γ (N/m)	γ^d (N/m)	γ^p (N/m)
Polyether microphase	48	29	19
Polyamide microphase	38.4	16.65	21.75
PPG additive	31.8	26.5	5.3
L-61 additive	32.5	27	5.5
L-81 additive	32.7	27.8	4.9

Table 1: Interfacial energy values for calculation of the thermodynamic wetting coefficient

Combination	Additive		
	PPG	L-61	L-81
	γ_{ij} (N/m)		
Polyether-Polyamide	3.53	3.53	3.53
Polyether-Additive	7.84	7.51	6.86
Polyamide-Additive	12.25	12.14	11.89
Resulting wetting coefficient	-1.25	-1.31	-1.42

Table 2: Interfacial energy and thermodynamic wetting coefficient for PPG incorporation

The numerical value of the wetting coefficient indicates that PPG will show a thermodynamic preference towards the continuous polyether microphase. However, a critical reflection should be made here. The numerical value of $\gamma_{Nylon\ 6-PEO}$ results in microphase separation between polyamide and polyether groups in practice, while the numerical value of $\gamma_{PEO-PPG}$ suggests

even lower mutual affinity between PPG and the polyether phase as compared to the polyether and polyamide groups. The numerical value of the wetting coefficient should therefore not be regarded as sufficient evidence for a good dispersion of PPG within the polyether microphase. Whereas the dispersive components of the interfacial energy of PPG and the polyether microphase are quite close to each other, the difference between their polar components indeed indicates lower mutual affinity. Next to thermodynamical considerations, the actual location of the additive could also be determined by factors such as e.g. partial irreversible adsorption of the additive²¹ or the relative viscosity of host polymer phases.²² The predictions of this model should thus be treated with care.

Critical reflection can also be made with regard to the values demonstrated in Table 1. Although polypropylene glycol tends to be more hydrophobic than PEG, the polar component for PPG tends to be bigger than for L-81. This can be ascribed to the hydroxyl-terminations of PPG, which tend to strongly influence properties for smaller molecules. The higher polar component of L-61 as compared to L-81 could also be rationalized in that sense. It can also be reflected in this model that a higher fraction of EO units inside the structure will obviously lead to a higher affinity for the continuous polyether phase inside Pebax.

DSC

Table 3 shows the data on thermal behavior with regard to the crystallinity degree, melting temperatures (upon heating) and crystallization temperatures (upon cooling). The degree of crystallinity in the different microphases was calculated as follows:

$$X_{c,i} = \frac{\Delta H_m}{\Delta H_m^0} \times 100 \quad (7)$$

where ΔH_m stands for the melting heat of the corresponding microphase, normalized for its weight percentage in the sample. ΔH_m^0 is the melting heat of the microphase in 100% crystalline state, which corresponds to 166 J g⁻¹ and 230 J g⁻¹ for the PEO and PA6, respectively.²³

The melting temperatures reported in Table 3 show only little variation for the polyether microphase and remain essentially constant for the polyamide phase. Such behavior usually demonstrates immiscibility²⁴ and can be related to the previous section where a thermodynamic preference towards the polyether phase was predicted, however, with a relatively low affinity based on the interfacial tension. The results show that our additives do not act as plasticizers or spacers on the crystalline domains inside the block copolymer. It was shown previously that PEG/PPG copolymer additives, with higher PEO/PPO ratios, did decrease crystallinity in both the polyether and polyamide domains.¹⁴

	X _{c,PEO} (%)	X _{c,PA6} (%)	T _{m,PEO} (° C)	T _{m,PA6} (° C)	T _{c,PEO} (° C)	T _{c,PA6} (° C)
Pebax® MH 1657	20.56	25.57	10.23	204.44	-27.59	153.71
10% L-61	21.21	27.27	9.82	204.56	-26.80	154.90
20% L-61	21.95	26.40	9.96	204.68	-26.46	154.65
30% L-61	20.56	28.17	10.48	204.12	-26.30	156.51
40% L-61	21.80	24.47	10.62	204.69	-26.12	155.18
50% L-61	21.31	22.54	9.76	204.64	-26.25	154.70
10% L-81	22.06	24.54	9.60	204.77	-26.90	153.49
20% L-81	21.43	26.36	9.61	204.74	-26.47	153.94
30% L-81	19.35	26.82	10.54	204.56	-25.31	154.9
40% L-81	20.20	28.01	10.51	204.33	-25.92	153.53
50% L-81	20.05	26.50	11.84	204.62	-25.24	153.39
10% PPG	21.89	25.85	10.78	204.66	-25.78	154.48
20% PPG	22.55	28.00	11.61	204.89	-22.56	157.18
30% PPG	25.28	28.71	12.00	204.99	-20.95	158.85
40% PPG	26.08	30.02	12.83	204.63	-19.06	159.62
50% PPG	24.26	31.91	12.84	204.24	-21.02	158.89

Table 3: DSC analysis of blends with Pebax and additives, i.e. L-61, L-81 and PPG

The polyether melting temperature associated with PPG addition shows a slight upward variation as compared to addition of L-61 or L-81 and pristine Pebax. It is hypothesized that the PEO end-chains of L-61 and L-81 result in a slightly different location relative to the micro-separated domains than the central PPO chain. The slight difference between L-61 and L-81 might similarly be explained by a longer central PPO chain for the latter. Although all additives thus appear immiscible with the polyether crystalline domains, molecular positioning (of parts) of the additives might differ somewhat. This possibly provides precise tuning possibilities with molecules somewhat richer in PEO which show more interaction with microphases or position near their interfaces. It is indeed known that *chain confinement* at domain interfaces in block copolymers influences crystallization.²⁵ This has not been yet specifically described in connection to gas separation membranes. The concept is related to chain mobility effects due to block chains fixed at interfaces between different domains.²⁶

The degree of crystallinity generally increases upon additive incorporation. A more pronounced crystallinity increase can be seen for PPG incorporation as compared to the Pluronics. The hydroxyl terminations (i.e. glycol ends) are more dominant for the shorter PPG molecule, previously reported in terms of a relative increase in the number of end groups.²⁷ This might result in stronger hydrogen bonding interactions, and thus slightly enhanced crystallinity. Similarly, PPG addition also results in a shift towards a higher crystallization temperature of PEO upon cooling. This behavior was reported for incorporation of PEG modified polyoctahedral

oligomeric silsesquioxanes (PEG-POSS) in Pebax as well, which was therefore termed a nucleating agent in the polyether domain.²⁸

Also for the Pluronics, the hydroxyl chain terminations yield hydrogen bonding interactions, which are presumably stronger than interactions between the PPO segments of the additive and Pebax. Elegant approaches for eliminating hydrogen bonding have been demonstrated in the past.¹³ Specifically for high loadings of L-61 it can be seen, however, that crystallinity is reduced in the polyamide Pebax domains.

XRD

The XRD spectra for addition of L-81 to Pebax are shown in Fig 3. Peaks can be observed at 19.9° and 23.85° and compare well with other work.^{11,29} Also here it can be seen that our additives do not act as plasticizers or spacers for crystallinity since the d-spacing does not readily change. The relative intensity of the signals changes and reflects addition of non-crystalline material to the membrane.

Fig 3: XRD spectra for additive addition to Pebax

Calculated and experimental density

The experimental density values obtained with the buoyancy method are shown in Fig 4, together with the values calculated according to the additive model:

$$\rho = \phi_1\rho_1 + (1 - \phi_1)\rho_2$$

An increase in density generally is indicative of intermolecular interactions favoring better packing of the constituents. Measurement of blend density is therefore known as a less sensitive indicator for the transition between compatibility and incompatibility.³⁰

Figure 4: calculated and experimental density for PPG and L-81 incorporation into Pebax

An increase in blend density, compared to the calculated density according to the theoretical model, of about 1% reportedly indicates weak molecular interactions between additive and main polymer.³⁰ It is hypothesized that these interactions take place in the amorphous phases of Pebax, as XRD and DSC showed little influence on crystallinity upon additive incorporation. The discussion of hydrogen bonding in DSC characterization agrees well with these observations.

AFM

Simultaneous topographical and phase detection was applied on membrane cross-sections through tapping-mode AFM. A recent study on gas separation membranes also used this principle

for more detailed characterization of this type of block copolymers.³¹ More generally, the phase change is sensitive to surface properties of polymeric materials, such as viscoelasticity, stiffness, and composition.^{32–34} An aspect that requires careful consideration is that phase detection implies characterization of differential stiffness properties, which means that the scale for hard and soft properties is not absolute and may inverse even for the same sample due to self-adjustment of the system between the working frequencies of different imaging regimes. More extensive information about this can be found elsewhere.³⁵

Local stiffness variations between hard and soft domains can thus be mapped, although typically hidden under a 1 nm thick soft segment overlayer.³⁶ Measurements were done on membrane cross-sections to minimize this effect as much as possible. Fig S2 demonstrates an optical microscopy image of a cross-section in AFM observation. Roughness of our observations is only briefly discussed here, as sample pretreatment may have a severe influence

In Fig 5 (right), it can be seen that nanodomain structures with high phase difference with the AFM tip appear dispersed in a background of lower phase difference. The size of the nanodomains can be more clearly observed in the 2D map of Fig 6, showing that the domain sizes are in the order of a few tens of nanometers. This agrees well with the nanodomain morphology often observed in similar types of block copolymer.³⁷

Figure 5: 3D mapping of topography (left) and phase detection (right) for Pebax cross-section

Figure 6: 2D map of phase difference for Pebax

In Fig 7, it can be seen that nanodomain structures with high phase difference appear to be more interconnected upon 20 wt% additive incorporation. As their size increases, their amount appears to decrease. Roughness appears increased upon additive incorporation, however, one should note that the cross-section of a membrane sample is characterized here instead of the surface.

Figure 7: 3D mapping of topography (left) and phase detection (right) for cross-section of 20 wt% L-81 addition to Pebax

For 50 wt% additive incorporation, shown in Fig 8, care should be taken in interpreting the results. The scale for differential hardness properties was inversed (described above) as compared to the previous characterization and for clarity its color scale was inverted (the original can be found in supporting information). This characterization indicates further modification of nanodomain structures towards a lower number of individual nanodomains with higher individual sizes. This is also shown in the 2D map in Fig 9. Roughness of the cross-section appears to have increased further compared to lower additive loadings.

Figure 8: 3D mapping of topography (left) and phase detection (right) for cross-section of 50 wt% L-81 addition to Pebax

Figure 9: 2D mapping of phase difference for 50 wt% L-81 addition to Pebax

SEM

SEM pictures from pristine Pebax and blend membranes upon 50wt% additive incorporation are shown in Fig 10. A defect-free structure with no microscopic signs of phase separation is observed, in agreement with other work.^{14,18} Structural features (e.g. little cracks) that can be distinguished were presumably caused by sample pretreatment.

Figure 10: SEM cross-sections of membranes prepared with different additives in Pebax at 50% loadings, a) blank, b) L-81, c) L-61, d) PPG

ATR-FTIR

IR spectra for the reference Pebax membrane and the membranes with 50 wt% additive are shown in Fig 11. Characteristic peaks for pristine Pebax can be found at 3298 cm^{-1} for hydrogen bonded amide groups, 1732 cm^{-1} and 1637 cm^{-1} for hydrogen bonded carbonyl groups and 1099 cm^{-1} for ether groups.³⁸ More detailed analysis demonstrates changes in the peak around 1090 cm^{-1} to lower wavenumbers for incorporation of PPG, to higher wavenumbers for L-61 and little or no difference for L-81 incorporation in comparison to pristine Pebax. Lower wavenumbers indicate stronger hydrogen bonding for PPG, which is in accordance with DSC observations, whereas lower hydrogen bonding for L-61 may similarly reflect the reduced crystallinity observed in the PA domains. A decreased degree of hydrogen bonding has been related to improved gas transport properties.¹⁴ Apart from hydrogen bonding, other weak intermolecular interactions have been suggested as well, even towards hydrophobic interactions between EO groups.³⁹

Despite problems due to overlapping contributions of PEG and PPG, introduction of a peak around 2970 cm^{-1} can be seen for all additives, which indeed can be ascribed to aliphatic CH stretching, e.g. in PPG or PPO parts of L-61 and L-81.⁴⁰ More detailed recording of interactions would be possible through application of a two-dimensional correlation method.⁴¹

Fig 11: IR spectra for the reference Pebax membrane and the membranes with 50 wt% additive

Fig 12: IR spectra in more detail, 3100-2700 cm^{-1} (left), 1200-1000 cm^{-1} (right)

Gas transport

The effect of additive incorporation in Pebax on the gas separation performance of the membranes is demonstrated in Fig 13 and Fig 14 for CO₂/N₂ gas mixtures with 15/85 molar ratio at 5 bar. Additive incorporation gradually lowers the mixed-gas selectivity while increasing the gas permeability, as expected from introduction of PPO-rich additives due to the presence of the extra methyl group as compared to PEO units.⁸

Figure 13: Permeability of the membranes as a function of incorporation of PPG, L-61 or L-81 for CO₂/N₂ gas mixtures with 15/85 molar ratio at 5 bar

Figure 14: Mixed-gas selectivity of the membranes as a function of incorporation of PPG, L-61 or L-81 for CO₂/N₂ gas mixtures with 15/85 molar ratio at 5 bar

FFV calculations have been done in specific cases where the binary interaction principle applies, however, its applicability to our approach could be doubted. A literature reference could be made to reflect on changes in FFV upon PPG-rich additive incorporation. PEG- and PPG-based diacrylate crosslinked networks were prepared in other work and their fractional free volume was estimated as 0.118 and 0.160, respectively.⁴² In our case, we used the specific volume that reflects the openness of a polymer to gas transport.⁴³ As diffusivity was not measured, the relation between CO₂ permeability and specific volume is demonstrated in Fig 15.

Fig 15: Relation between CO₂ permeability and specific volume variation upon additive incorporation

The polyether microphase in Pebax gives highly selective transport of CO₂ with a medium permeability, whereas Pluronic addition lowers selectivity and increases permeability. The gas transport properties do not exclude a potential double role for membrane synthesis through a combination of stabilizing effects and permeability enhancement, however at the expense of selectivity. Our results thereby suggest that its use for stabilizing effects in a multi-component casting mixture does not require limitation to a stoichiometric amounts of Pluronic as no dramatic deterioration of gas transport properties was observed for addition of e.g. 10 wt% of Pluronic.

In the majority of studies concerning additive blending in Pebax, gas transport properties were altered through reducing crystalline effects with strong permeability enhancements.^{13,14,44,45}

Our PPO-rich additives interacted with the amorphous parts, altering gas transport properties

through a higher specific volume. Incorporation of PDMS-PEG on the other hand previously resulted in a heterogeneous blend with a 5-fold increase in CO₂ permeability, the authors assumed no significant change in general microdomain morphology. A comparison of permeabilities for the different approaches is shown in Table 4

	Additive	CO ₂ Permeability (Barrer)
Yave et al.	PEG (200g/mol)	~153
Yave et al.	PEG-DME (500g/mol)	650
Li et al	Calcium lignosulfonate (CaLS)	140
Khosravi et al.	PEG-ran-PPG	677
Reijerkerk et al.	PDMS-PEG (3800 g/mol)	532
Our work	L-61 (2000 g/mol)	304

Table 4: Comparison of gas transport with other approaches

The blend structure of our samples was investigated as well since transport parameters yield information on microphase structure⁴⁶ and miscibility on molecular level.⁴⁷ Generally, the gas permeability in homogenous blends can be described through semi-logarithmic models, whereas a parallel model previously correlated better for describing permeability in heterogenous blends with additives.¹² The former thus shows a better correlation with:

$$\ln(P) = \theta_1 \ln(P_1) + \theta_2 \ln(P_2) \quad (8)$$

where θ_i refers to the volume fraction of the phase with permeability P_i . Heterogenous blends have shown better correlation as follows:

$$P = \theta_1 P_1 + \theta_2 P_2 \quad (9)$$

This correlation was verified with current and other work. Data on the permeability for pure additives are not available, but the correlation was checked by plotting the residuals for

permeability prediction as dependent variable and the volume fraction as independent variable. As such, a good fit requires the residuals to be randomly scattered around zero, i.e. no trends should be visible in the residuals when plotting them as a function of the independent variable. The regression analysis for the two different models was evaluated with this criterium. The residuals plot for PPG incorporation can be found in Fig 16. The homogeneous model seems to be a good fit, for PPG incorporation as its residuals sufficiently satisfy the condition of random scatter around 0. Also, for L-81 incorporation a heterogeneous model can be rejected as demonstrated in Fig 17. For high loadings, however, the homogenous model does not seem to be an optimal fit either. This may reflect a complex situation due to high loading of an additive with surfactant properties inside a block copolymer. For L-61 addition, a homogeneous model clearly also applies as shown in Fig 18. Additives with lower molecular weight appear to yield a more pronounced homogeneous blend structure.

Fig 16: Residuals plot for PPG addition

Fig 17: Residuals plot for L-81 addition

Fig 18: Residuals plot for L-61 addition

CONCLUSIONS

In strong contrast with phase-selective chemistry, addition of PPO-rich Pluronics® and PPG in our approach resulted in interactions with the amorphous parts of Pebax with an increase in permeabilities and decrease in mixed-gas selectivities. The demonstration of additive compatibility with membrane synthesis for gas separation does not exclude a double role for these molecules as dispersing/stabilizing agents in multi-component casting solutions and as a gas transport medium in the final membrane. The structural variation of Pluronics could be further exploited for this purpose and eventually combined with other smart additives. Simultaneous use of different additives may allow targeting different structural features of Pebax.

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REFERENCES AND NOTES

1. Huang, Y.; Merkel, T. C.; Baker, R. W. *J. Memb. Sci.* **2014**, *463*, 33.
2. Kim, J. H.; Ha, S. Y.; Lee, Y. M. *J. Memb. Sci.* **2001**, *190*, 179.
3. Lin, H.; Freeman, B. D. *J. Memb. Sci.* **2004**, *239*, 105.
4. Luo, S.; Stevens, K. A.; Park, J. S.; Moon, J. D.; Liu, Q.; Freeman, B. D.; Guo, R. *ACS Appl. Mater. Interfaces* **2016**, *8*, 2306.
5. Scofield, J. M. P.; Gurr, P. A.; Kim, J.; Fu, Q.; Kentish, S. E.; Qiao, G. G. *Ind. Eng. Chem. Res.* **2016**, *55*, 8364.
6. Lin, H.; Freeman, B. D. *J. Mol. Struct.* **2005**, *739*, 57.
7. Yave, W.; Car, A.; Funari, S. S.; Nunes, S. P.; Peinemann, K.-V. *Macromolecules* **2010**, *43*, 326.
8. Reijerkerk, S. R.; Arun, A.; Gaymans, R. J.; Nijmeijer, K.; Wessling, M. *J. Memb. Sci.* **2010**, *359*, 54.
9. Ilzer, A. C.; Arun, A.; Reijerkerk, S. R.; Nijmeijer, K.; Wessling, M.; Gaymans, R. J. *J. Appl. Polym. Sci.* **2010**, *117*, 1394.
10. Reijerkerk, S. R.; Wessling, M.; Nijmeijer, K. *J. Memb. Sci.* **2011**, *378*, 479.
11. Bondar, V. I.; Freeman, B. D.; Pinnau, I. *J. Polym. Sci. Part B-Polymer Phys.* **2000**, *38*, 2051.
12. Reijerkerk, S. R.; Knoef, M. H.; Nijmeijer, K.; Wessling, M. *J. Memb. Sci.* **2010**, *352*, 126.
13. Yave, W.; Car, A.; Peinemann, K.-V. *J. Memb. Sci.* **2010**, *350*, 124.
14. Khosravi, T.; Omidkhah, M. *RSC Adv.* **2015**, *5*, 12849.
15. Khosravi, T.; Omidkhah, M. *J. Energy Chem.* **2017**, *26*, 530.
16. Mahdi, E. M.; Tan, J.-C. *J. Memb. Sci.* **2016**, *498*, 276.
17. Khan, A. L.; Basu, S.; Cano-Odena, A.; Vankelecom, I. F. J. *J. Memb. Sci.* **2010**, *354*, 32.
18. Abdollahi, M.; Khoshbin, M.; Biazar, H.; Khanbabaei, G. *Polymer (Guildf)*. **2017**, *121*, 274.
19. Roman, C.; García-Morales, M.; Gupta, J.; McNally, T. *Polymer (Guildf)*. **2017**, *118*, 1.
20. Anastasiadis, S. H. Wolf, B. A.; Enders, S., Eds.; Springer Berlin Heidelberg: Berlin, Heidelberg, **2011**; pp 179.
21. Zhao, X.; Zhao, J.; Cao, J.-P.; Wang, D.; Hu, G.-H.; Chen, F.; Dang, Z.-M. *Mater. Des.* **2014**, *56*, 807.
22. Baudouin, A.-C.; Devaux, J.; Bailly, C. *Polymer (Guildf)*. **2010**, *51*, 1341.
23. Rabiee, H.; Soltanieh, M.; Mousavi, S. A.; Ghadimi, A. *J. Memb. Sci.* **2014**, *469*, 43.
24. El-Hadi, A. M. *Polímeros* **2014**, *24*, 9.

25. Nakagawa, S.; Marubayashi, H.; Nojima, S. *Eur. Polym. J.* **2015**, *70*, 262.
26. Michell, R. M.; Müller, A. J. *Prog. Polym. Sci.* **2016**, *54*, 183.
27. Yoon, S.; MacKnight, W. J.; Hsu, S. L. *J. Appl. Polym. Sci.* **1997**, *64*, 197.
28. Rahman, M. M.; Filiz, V.; Shishatskiy, S.; Abetz, C.; Neumann, S.; Bolmer, S.; Khan, M. M.; Abetz, V. *J. Memb. Sci.* **2013**, *437*, 286.
29. Wang, S.; Liu, Y.; Huang, S.; Wu, H.; Li, Y.; Tian, Z.; Jiang, Z. *J. Memb. Sci.* **2014**, *460*, 62.
30. MacKnight, W. J.; Karasz, F. E.; Fried, J. R. In *Polymer Blends Volume 1*; Academic Press, **1978**; pp 186.
31. Fam, W.; Mansouri, J.; Li, H.; Chen, V. *J. Memb. Sci.* **2017**, *537*, 54.
32. Zhong, Q.; Inniss, D.; Kjoller, K.; Elings, V. B. *Surf. Sci.* **1993**, *290*, L688.
33. Bar, G.; Thomann, Y.; Whangbo, M.-H. *Langmuir* **1998**, *14*, 1219.
34. Magonov, S. N.; Elings, V.; Whangbo, M.-H. *Surf. Sci.* **1997**, *375*, L385.
35. James, P. J.; Antognozzi, M.; Tamayo, J.; McMaster, T. J.; Newton, J. M.; Miles, M. J. *Langmuir* **2001**, *17*, 349.
36. McLean, R. S.; Sauer, B. B. *Macromolecules* **1997**, *30*, 8314.
37. Barbi, V.; Funari, S. S.; Gehrke, R.; Scharnagl, N.; Stribeck, N. *Macromolecules* **2003**, *36*, 749.
38. Murali, R. S.; Sridhar, S.; Sankarshana, T.; Ravikumar, Y. V. L. *Ind. Eng. Chem. Res.* **2010**, *49*, 6530.
39. Israelachvili, J. *Proc. Natl. Acad. Sci. U. S. A.* **1997**, *94*, 8378.
40. Ni, P.-H.; Pan, Q.-S.; Zha, L.-S.; Wang, C.-C.; Elaïssari, A.; Fu, S.-K. *J. Polym. Sci. Part A Polym. Chem.* **2002**, *40*, 624.
41. Shinzawa, H.; Uchimaru, T.; Mizukado, J.; Kazarian, S. G. *Vib. Spectrosc.* **2017**, *88*, 49.
42. Kalakkunnath, S.; Kalika, D. S.; Lin, H.; Raharjo, R. D.; Freeman, B. D. *Macromolecules* **2007**, *40*, 2773.
43. Yampolskii, Y.; Pinnau, I.; Freeman, B. D. *Materials Science of Membranes for Gas and Vapor Separation*; **2006**.
44. Yave, W.; Car, A.; Peinemann, K.-V.; Shaikh, M. Q.; Rätzke, K.; Faupel, F. *J. Memb. Sci.* **2009**, *339*, 177.
45. Li, Y.; Li, X.; Wu, H.; Xin, Q.; Wang, S.; Liu, Y.; Tian, Z.; Zhou, T.; Jiang, Z.; Tian, H.; Cao, X.; Wang, B. *J. Memb. Sci.* **2015**, *493*, 460.
46. Kolařík, J.; Fambri, L.; Pegoretti, A.; Penati, A. *Polym. Eng. Sci.* **2000**, *40*, 127.
47. Senuma, A. *Macromol. Chem. Phys.* **2001**, *202*, 1737.

FIGURE 4 IR spectrum of pristine Pebax and blends with L-61, L-81 or PPG. A) Overall spectrum B) 3100-2700 cm^{-1} C) 1200-1000 cm^{-1}

GRAPHICAL ABSTRACT

GRAPHICAL ABSTRACT FIGURE ((50 mm wide by 50 mm high, 100 dpi resolution)) .tiff or .eps file format.

FIGURE 1 Figure Caption. (Reproduced from [ref. no.], with permission from [Publisher].) ((delete if not applicable))

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