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1 **Controlled grafting of multi-block copolymers for improving membrane properties for CO₂**
2 **separation**

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11 **Keywords:** poly(ethylene oxide); grafted multi-block copolymers; polyimides; CO₂-selective
12 membranes

13

14 **Abstract (202 words):** Linear poly(ether-urea-imide)s (PUIs) are attractive multi-block segmented copolymers
15 well-known for high selectivity for CO₂ separations. Their CO₂ permeability generally increases but their
16 selectivity decreases with their polyether soft content limited to 70 wt% to preserve their mechanical properties.
17 In this work, the grafting of a PUI copolymer with PEO-based soft grafts is reported for strongly increasing the
18 membrane properties. The design of the grafted copolymers involved step-growth polymerization, controlled
19 radical polymerization, and “click” chemistry. This strategy ensured the control of grafting rate, graft molecular
20 weight and soft contents varying from 57 to 85 wt%. The membrane properties for CO₂ and N₂ permeation were
21 correlated to the PUI chemical structure, morphology and soft content. The best membrane properties ($P_{CO_2} =$
22 196 Barrer; $\alpha_{CO_2/N_2} = 39$ at 2 bar and 35°C) were obtained for PUI-g-1PEDEGA5000 corresponding to the
23 highest grafting rate and graft length. Compared to the non-grafted PUI, the best grafted copolymer had much
24 higher CO₂ permeability ($\times 17$) while the ideal separation factor α_{CO_2/N_2} was maintained at high level, thus
25 leading to separation properties very close to the Robeson 2008 upper-bound. By allowing very high contents of
26 amorphous soft phase and specific morphology, the new grafting strategy offered high-performance membranes
27 for CO₂ capture.

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38 **1. Introduction**

39 Carbon dioxide (CO₂) is the widely most produced greenhouse gas in the world from power plants
40 [1,2], syngas production [3,4], natural gas extraction [5–7] and transport field [8]. CO₂ capture and
41 storage are major challenges to limit its environmental effects and global warming [9,10]. Research in
42 this area is very active, with implication of public and private partners, but the large-scale deployment
43 of CO₂ capture and storage processes still requires significant research progress. Between many CO₂
44 capture strategies, such as cryogenic distillation, amine absorption or pressure swing adsorption,
45 membrane separation appears as the most attractive process because of low energy consumption of
46 only 70-75 kWh/ton of recovered CO₂ compared to 330-340 kWh/ton for the mostly used chemical
47 absorption process using amine solvents [11]. Mechanisms of separation in these membranes are based
48 on gas-polymer interactions (sorption) and mobility of gas through the free volume fraction of the
49 material (diffusion).

50 Concerning the treatment of post-combustion gases, CO₂/N₂ is the most widely investigated separation
51 in the literature. According to several reviews [12–20], the most efficient membranes for CO₂
52 separation are high porosity membranes, as polymers of intrinsic microporosity (PIMs) or thermally
53 rearranged polymers (TRPs), ionic liquids-based and poly(ethylene oxide) (PEO)-based materials and
54 related polymer blends and mixed matrix membranes. In particular, the broad variety of PEO-based
55 polymers, such as PEO-based poly(meth)acrylates [21–26] and linear multi-block copolymers
56 (poly(ether-ester)s [27–37], poly(ether-amide)s [19,21,38–49], poly(ether-urethane)s [50–55],
57 poly(ether-siloxane-urethane) [56], poly(ether-urea)s [57], poly(ether-imide)s [58–72], poly(ether-
58 sulfone)s [73,74]) have offered wide diversity of CO₂ separation performances from low
59 permeability/high selectivity to high permeability/low selectivity membranes. These copolymers are
60 particularly attractive for CO₂ post-combustion capture thanks to strong interactions between CO₂ and
61 ethylene oxide (EO) units, providing high solubility contribution for CO₂ mass transport through PEO-
62 based membranes. Moreover, the high mobility (glass transition temperature < room temperature) of
63 amorphous PEO allowed to obtain membranes with high CO₂ diffusion coefficient.

64 Nevertheless, PEO exhibits high ability to crystallize, in particular for high PEO soft phase content,
65 generating impermeable phases decreasing gas separation performances [66,75]. To reduce PEO
66 crystallization, PEO-based multi-block copolymers were developed, alternating hard blocks, ensuring
67 good membrane mechanical properties, with soft PEO-based blocks for CO₂ permeation. In order to
68 further reduce soft block crystallization, other ether monomer units (propylene oxide PO,
69 tetramethylene oxide TMO) were also considered in different soft polyether blocks (PPO, PTMO, or
70 Jeffamines or Pluronics oligomers combining EO and PO units) [38,41,54,66,70,76].

71 Another successful approach for reducing PEO crystallinity in polymeric membranes for CO₂ capture
72 consisted of developing grafted (or comb) copolymers with PEO-based grafts by grafting methods
73 very different from the new grafting strategy described in this work. In the literature, several polymer
74 backbones were considered such as polyvinyl polymers (poly(vinyl chloride) [77], poly((vinyl benzyl)
75 trimethylammonium tetrafluoroborate [78], poly(vinyl trimethyl silane) [79], poly(vinyl imidazole)
76 [80], poly(vinyl alcohol) [81], poly(meth)acrylic polymers (poly(methyl methacrylate) [82–84],
77 poly(glycidyl methacrylate) [85], poly(acrylamide) [86], poly(2-(methacryloyloxy)ethyl-
78 trimethylammonium tetrafluoroborate) [78], poly(sulfobetaine methacrylate) [87], poly(2-(4-benzoyl-
79 3-hydroxy phenoxy) ethyl acrylate) [88]), major industrial rubbers (poly(styrene-block-butylene-
80 block-styrene) SBS [89] and the corresponding hydrogenated rubber [90]), poly(1-trimethylsilyl-1-
81 propyne [91]), polydimethylsiloxane [92], poly(ethylene-alt-maleic anhydride) [93] and
82 polyethersulfone [94]. A few of the former grafted (or comb) copolymers with PEO-based grafts were

83 used as polymer matrices in high performance mixed-matrix membranes with different fillers (ZIF-8,
84 UiO66-NH₂, bh-MgO, FeCl₃ etc.) [85,87,95,96] or facilitated transport membranes [97]. However, to
85 the best of our knowledge, this type of grafting has not been reported for PEO-based multi-block
86 copolymers so far, most likely due to their much more complex chemical structure.

87 Coming back to the literature on PEO-based multi-block copolymers of particular interest in this work,
88 the influence of PEO content on CO₂ permeability does not obey a general rule and depends upon the
89 chemical structure of the hard blocks and soft block crystallization [27,30,41,43,61,66,98,99]. When
90 PEO crystallization was efficiently prevented in poly(ether-imide)s or poly(ether-urea-imide)s multi-
91 block copolymers of particular interest in this new work, CO₂ permeability usually strongly increased
92 with the PEO content while membrane selectivity decreased but still remained high for CO₂/N₂
93 separation in most cases [60,61,65,76]. In this view, it would be interesting to further increase the PEO
94 content in these linear multi-block copolymers. However, in the different works reported so far, the
95 PEO content remained limited to ca. 70 wt% for ensuring good membrane withstanding in operating
96 conditions.

97 This work describes a new grafting strategy of PEO-based poly(urea-imide)s (PUIs) multi-block
98 copolymers with PEO-based soft grafts, allowing to strongly push forward the limit of their soft
99 polyether content while avoiding PEO crystallization for greatly improving their membrane properties.
100 Compared to former literature on grafted/comb copolymers with PEO-based grafts, this new grafting
101 strategy offers an advanced design of the grafted copolymers, by allowing the precise control of their
102 structural parameters and a variation of their membrane properties over a very broad range.
103 Furthermore, the use of PUIs provides specific advantages (better physical cross-linking and improved
104 adhesion on different substrates for composite membranes) compared to related polyurethanes (PUs)
105 or polyimides (PIs) [100,101].

106 The synthesis and physical-chemical characterization of a series of twelve original grafted multi-block
107 PUI copolymers is first described. The grafting strategy involved a multi-step procedure based on
108 step-growth polymerization, controlled radical polymerization (CRP) and Copper (I)-catalyzed Alkyne
109 Azide Cycloaddition (CuAAC) “click” chemistry, providing a good control of grafting rate, graft
110 molecular weight and resulting soft content. The grafting influence on the morphology of these new
111 copolymers is then investigated based on different complementary characterizations. The third part
112 reports their membrane properties for CO₂ sorption and pure permeation of CO₂ and N₂. Their
113 correlation to the PUI chemical structure (grafting rate and graft length), morphology and soft content
114 is then discussed to identify the key features to improve their membrane performance for CO₂ capture.

115 **2. Experimental**

116 **2.1. Chemicals and materials**

117 All chemicals were purchased from Sigma Aldrich unless specified otherwise. Jeffamine JFAED
118 2000, 4,4'-Methylene-bis-phenylisocyanate (MDI, 98%), 4,4'-(hexafluoro-*iso*-propylidene)-bis-
119 (phthalic-anhydride) (6FDA, TCI, >98%), *N,N*-dimethylformamide (DMF, analytical reagent grade,
120 99.5%) and triethylamine (NEt₃, >99%) were purified following our former procedures [76,102].
121 Ethoxy di(ethylene glycol) acrylate monomer (EDEGA, >95%) was purified by vacuum distillation at
122 80 °C over benzoquinone. Tetrahydrofuran (THF, analytical reagent grade, 99.7%), copper (II)
123 bromide (CuBr₂, 99%), copper (I) bromide (CuBr, 98%), tris[2-(diethylamino)amine] (Me₆TREN,
124 97%), and *N,N,N',N'',N'''*-pentamethyldiethylenetriamine (PMDETA, 99%) were used as received. 2-
125 Azidoethyl-2-bromoisobutyrate (AEBiB) (functional initiator with a terminal azido group) [103] and

126 4,4'-bis(hydroxymethyl)-1,6-heptadiyne (bisOHyne) (functional diol with two alkyne groups – Figure
127 1) [104,105] were synthesized according to the literature. For EDEGA controlled radical
128 polymerization by Single Electron Transfer-Living Radical Polymerization (SET-LRP), the copper
129 Cu(0) wire surface (3 cm length, 1.5 mm diameter) was activated using a former procedure [46].

130 2.2. Copolymers synthesis and characterization

131

132 2.2.1. Synthesis of PUI with alkyne side groups

133 This synthesis was carried out under dry inert atmosphere. In flask number **1**, MDI (1.2 eq/ 1.668
134 g/6.67 mmol) was added to a solution of JFAED 2000 (0.6 eq/ 6.668 g/3.33 mmol) in 27 mL of
135 dry DMF and reacted for 3 h at ambient temperature. In another flask (flask number **2**), MDI (0.8 eq/
136 1.112 g/4.44 mmol) and bisOHyne (0.4 eq/ 0.338 g/2.22 mmol) in 30 mL of dry DMF were
137 reacted for 2h 30min at the same temperature. The content of flask number **2** was then transferred to
138 flask number **1** and 20 mL of dry DMF were added for dilution before polycondensation with 6FDA
139 (1 eq/ 2.468 g/5.55 mmol). NEt_3 (2 eq/ 1.56 mL/11.1 mmol) was used as catalyst for the chemical
140 cyclization of imide groups with progressive rise in temperature (1 h 30 min at 60 °C and 8 h at 80 °C)
141 for preventing side reactions of the alkyne groups. The purification of this new PUI (named PUI-g for
142 PUI ready for grafting) was carried out according to the procedure we formerly reported for a related
143 PUI, which did not contain alkyne side groups [76]. The final drying was operated under vacuum at
144 30°C for 24 h (yield of 85%). $^1\text{H NMR}$ ($\text{DMSO}-d_6$, 300 MHz) : δ : 1.02-1.23 ppm (q, 9.6 H, CH_3);
145 2.39 ppm (s, 1.6 H, CH_2); 2.96 ppm (s, 0.8 H, CH); 3.34-3.49 ppm (m, 52.3 H, CH_2); 3.7-4.1 ppm (m,
146 8.6 H, CH_2 , CH); 5.9 ppm (d, 1.2 H, NH), 7-7.5 ppm (m, 16 H, CH); 7.6-8.2 ppm (d, 6 H, CH); 8.2-8.4
147 ppm (s, 1.2 H, NH); 9.5 ppm (d, 0.8 H, NH). SEC-MALLS (DMF + 2% w/v of LiCl): dn/dc = 0.12
148 mL/g; \overline{M}_n = 94 380 g/mol, \overline{M}_w = 266 400 g/mol, dispersity \mathcal{D} = 2.8.

149 2.2.2. Synthesis of PEDEGA oligomers with an azido terminal group by SET-LRP

150 PEDEGA oligomers with an azido group for “click” chemistry were obtained by adapting our former
151 procedure on the CRP of EDEGA acrylate monomer by SET-LRP [106]. In this work, the three
152 different molecular weights (2000, 3600 and 5000 g/mol) targeted for the PEDEGA grafts were
153 obtained by varying the ratios initiator/monomer/moderator/ligand AEBiB/EDEGA/CuBr₂/Me₆TREN
154 as following: PEDEGA 2000: 1/9.5/0.05/0.2; PEDEGA 3600: 1/18/0.05/0.2 and PEDEGA 5000:
155 1/25/0.05/0.2. The N₃-PEDEGA oligomers were dried under vacuum at 60 °C. $^1\text{H NMR}$ (CDCl_3 , 300
156 MHz) PEDEGA 2000: δ : 1.15-1.20 (m, 36 H, CH_3); 1.3-2.5 (m, 29.7 H, CH_2 and CH); 3.5-3.7 (m, 81
157 H, CH_2); 4.1-4.4 (m, 19.8 H, CH_2); PEDEGA 3600 : δ : 1.15-1.20 (m, 56.3 H, CH_3); 1.3-2.5 (m, 50.4
158 H, CH_2 and CH); 3.5-3.7 (m, 136.4 H, CH_2); 4.1-4.4 (m, 35.6 H, CH_2); PEDEGA 5000: δ : 1.15-1.20
159 (m, 81 H, CH_3); 1.3-2.5 (m, 75 H, CH_2 and CH); 3.5-3.7 (m, 204 H, CH_2); 4.1-4.4 (m, 50 H, CH_2).
160 SEC-MALLS (THF): dn/dc = 0.068 mL/g; PEDEGA 2000 : \overline{M}_n = 2004 g/mol, \overline{M}_w = 2110 g/mol,
161 dispersity \mathcal{D} = 1.053 ; PEDEGA 3600 : \overline{M}_n = 3444 g/mol, \overline{M}_w = 4126 g/mol, dispersity \mathcal{D} =
162 1.198 ; PEDEGA 5000 : \overline{M}_n = 4780 g/mol, \overline{M}_w = 4914 g/mol, dispersity \mathcal{D} = 1.028

163 2.2.3. PUI grafting by “click” chemistry

164 PUI grafting was achieved by CuAAC “click” chemistry between alkyne-functionalized PUI and α -
165 azido-functionalized PEDEGA oligomers, allowing different target grafting rates. In the following, we
166 report the synthesis corresponding to the highest grafting rate (100%) and the longest grafts
167 (PEDEGA5000). Azido-functionalized PEDEGA5000 (1.68 g; corresponding to 1 equivalent with
168 respect to the alkyne side groups of PUI-g) and 4 mL of the PMDETA ligand were added to a solution

169 of 1g of PUI-g (containing 0.378 mmol of alkyne side groups) in 15 mL of distilled DMF. After three
170 freeze-thaw cycles, the catalyst Cu(I)Br (54 mg; 1eq/alkyne group) was introduced under argon flow.
171 After 48 h at 80 °C, the reaction medium was concentrated under vacuum and the crude grafted
172 copolymer was precipitated in water in presence of the PMDETA ligand. The purification was carried
173 out by three washings in water/PMDETA solutions. The soft elastomer copolymer PUI-g-
174 1PEDEGA5000 was finally dried under vacuum at 40 °C overnight (yield: 78%). For ¹H NMR
175 (DMSO-*d*₆, 300 MHz) see Results and Discussion.

176 2.3. Copolymer characterization

177 A Bruker Advance 300 spectrometer was used to obtain ¹H NMR spectra at 300.15 MHz for samples
178 in DMSO-*d*₆ or CDCl₃ with TMS as a reference for the chemical shifts. Size exclusion
179 chromatography with multi-angle laser light scattering (MALLS Wyatt Technology TREOS) was
180 performed to determine the average molecular weights \overline{M}_n , \overline{M}_w and dispersity \overline{D} using our formerly
181 reported procedure [76]. For characterizing PUI-g, 2 % w/v of LiCl was added to the DMF eluent for
182 limiting polymer chain aggregation. The solvent used for SEC-MALLS characterization of the
183 different PEDEGA oligomers was THF.

184 Differential scanning calorimetry (DSC) thermograms were recorded under nitrogen flow with a TA
185 Instruments DSC Q2000 using a standard procedure formerly developed in our laboratory for
186 characterizing other PUI copolymers [76]. The experimental error for the glass transition temperature
187 (*T*_g) at midpoint was ca. 1°C. Polymer films of ca. 200 μm thickness were used for small-angle X-ray
188 scattering (SAXS) characterization at the European Synchrotron Radiation Facility (ESRF) on the
189 BM2D2AM beamline using the procedure formerly used for characterizing the corresponding linear
190 multi-block PUI copolymers [76]. Membrane surface and cross-section images were obtained with a
191 JEOL JSM-6490LV scanning electron microscope (SEM) at an accelerating voltage of 5 kV with
192 magnification of 1.500 and 500, respectively. The membrane cross-sections were prepared by freeze-
193 fracture by immersion in liquid nitrogen and then coated by gold-palladium. Transmission electron
194 microscopy (TEM) was performed on a PHILIPS CM120 instrument at 80 kV. The different elastomer
195 samples for TEM experiments were obtained by cryo-microtomy (80 nm thickness) and stained with
196 Ruthenium tetroxide vapors for 30 minutes.

197 2.4. Membrane casting

198 For each of the new polymer materials, 0.5 g of copolymer was dissolved in 20 mL of distilled DMF.
199 Before casting on a Teflon mold, the copolymer solution was filtered on glass fibers. Most of the DMF
200 was removed at 40 °C. The final membrane drying was achieved for 12h at 60 °C under vacuum. The
201 membrane average thickness measured with an ElcometerTM was ca. 90 μm with a maximum standard
202 deviation of 5 μm.

203 2.5. Sorption experiments

204 The magnetic suspension microbalance Rubotherm 2720 was used to perform the sorption
205 experiments with high purity CO₂ gas (Messer, 99.995%) at different pressures at 35 °C. The CO₂
206 sorption was calculated from the constant mass (with a measurement error of ± 0.02 mg) obtained at
207 sorption equilibrium by equation (1).

$$208 \quad CO_2 \text{ sorbed (wt \%)} = \frac{w_{eq} - w_{t0}}{w_{t0}} \times 100 \quad (1)$$

209 where *w*_{eq} and *w*_{t0} are the sample weights after and before CO₂ sorption, respectively.

210 2.6. Gas permeability measurements

211 Time-lag experiments were carried out at 35 °C and an upstream pressure of 2 bar, after drying the
212 membranes under vacuum overnight in the time-lag cell. Pure gases CO₂ (Messer, 99.995%) and N₂
213 (Messer, 99.995%) were used for the gas permeation experiments. The equipment and procedure have
214 already been described for characterizing the corresponding linear multi-block copolymers [76]. The
215 membrane performance was characterized by gas permeability P and ideal separation factor α_{CO_2/N_2}
216 based on five experiments for each membrane sample (equations (2) and (3)):

$$217 \quad P = \frac{J_{st} * l}{P_{upstream}} \quad (2)$$

218 where l is the average thickness of the active membrane area and J_{st} is the gas obtained for the steady
219 state of gas permeation. In equation 2, the unit of the steady-state flux J_{st} is cm³ (STP).cm⁻².s⁻¹ for
220 allowing a calculation of gas permeability in Barrer.

$$221 \quad \alpha_{CO_2/N_2} = \frac{P_{CO_2}}{P_{N_2}} \quad (3)$$

222 The diffusion coefficient D was estimated from the time-lag θ corresponding to the gas breakthrough
223 time across the membrane (equation (4)). The sorption coefficient S was then deduced from equation
224 (5) corresponding to the solution-diffusion model [107] :

$$225 \quad D = \frac{l^2}{6\theta} \quad (4)$$

$$226 \quad P = D * S \quad (5)$$

227

228 3. Results and discussion

229 3.1. Synthesis and characterization of the grafted PEO-based PUI copolymers

230

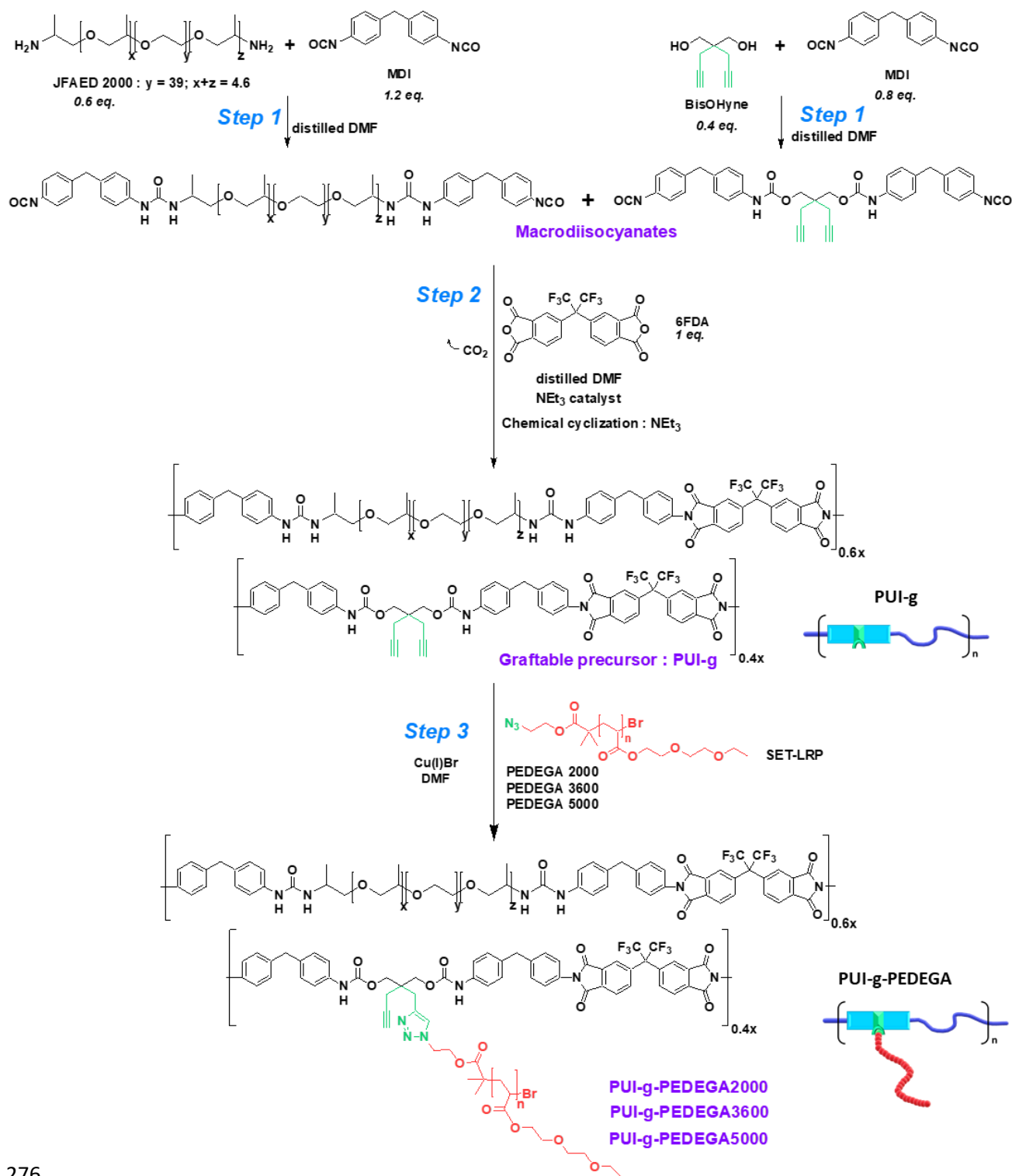
231 3.1.1. Synthesis of the grafted PEO-based PUI copolymers

232 The synthesis of the new grafted copolymers (Fig. 1) started by incorporating alkyne side groups into
233 the best PEO-based PUI multi-block copolymer reported in our former work on CO₂/N₂ separation
234 membranes [76]. The resulting functionalized copolymer (PUI-g) was a PUI “graftable” by CuAAC
235 “click” chemistry. The synthesis of PUI-g involved the reaction of PU macrodiisocyanates with an
236 fluorinated aromatic dianhydride (6FDA) following a fairly uncommon route for polyimide synthesis
237 allowing great structure variability [100,108–115]. In a first step, two different macrodiisocyanates
238 were prepared independently from reactions between a PEO-based diamine (Jeffamine JFAED 2000)
239 and an aromatic diisocyanate (MDI), and a diol containing two alkyne side groups (BisOHyne) and
240 MDI. The use of the Jeffamine for the copolymer synthesis was motivated by the results obtained in
241 our former work on related PEO-based PUI linear multi-block copolymers, having shown the absence
242 of crystallization of the corresponding Jeffamine soft segments in these polymer materials [76].
243 Furthermore, this two-pot strategy was chosen to compensate for the difference in nucleophilicity of
244 the diamine and diol monomers. It avoided using toxic tin-based catalysts and ensured the success of
245 the synthesis. These macrodiisocyanates were then brought together and were reacted with 6FDA by
246 step-growth polymerization. This specific dianhydride was chosen for promoting the copolymer
247 solubility in dipolar aprotic solvents (*e.g.*, DMF) necessary for its grafting.

248 The grafted PUIs were then obtained by CuAAC “click” chemistry (step 3) between PUI-g containing
249 alkyne side groups and PEDEGA CO₂-philic grafts bearing a terminal azido group. These α -azido-

250 functionalized PEDEGA grafts were obtained by SET-LRP controlled radical polymerization using a
251 functional azido initiator to provide the terminal azido group. Relatively low molecular weights of
252 PEDEGA grafts were chosen for ensuring high grafting efficiency. SET-LRP ensured a good control
253 of the graft molecular weight from 2000 to 5000 g/mol as shown by their low molecular weight
254 dispersity. The grafting rate (defined as the percentage of the PUI-g alkyne groups grafted by “click”
255 chemistry) was varied between 25 to 100%, leading to a broad range of soft contents in the grafted
256 copolymers. The name chosen for the grafted copolymers was PUI-g-XPEDEGAY with *X* being the
257 grafting rate (%) / 100 and *Y* the molecular weight (in g/mol) of the PEDEGA grafts. For simplicity, the
258 series of the copolymers grafted with different grafting rates of PEDEGA *Y* was named PUI-g-
259 PEDEGAY.

260 For pervaporation membranes for ETBE biofuel purification [103], we had reported the synthesis of
261 other grafted PUI copolymers from a different precursor PUI and with different grafts, which were
262 polymethacrylate oligomers obtained by ATRP controlled radical polymerization. In this new work,
263 the precursor PUI is original and contains a monomer unit (bisOHyne) with two alkyne side groups
264 allowing the straightforward grafting by “click” chemistry and playing a particular role for the
265 morphology developed by the new grafted copolymers as discussed later in section 3.1.3. The use of
266 this new monomer unit has the great advantage of saving one synthesis step compared to our earlier
267 grafting route. Moreover, in this work, the chemical structure of the grafts has also been changed for
268 PEO-based polyacrylate oligomers to provide much better properties for CO₂ permeation. These
269 polyacrylate oligomers were obtained by another controlled radical polymerization (SET-LRP, which
270 is better adapted to acrylate monomers), by extending the approach we had formerly developed for the
271 synthesis of pseudopeptide bioconjugates for CO₂ capture [106]. In this work, new PEDEGA
272 oligomers with different molecular weights were synthesized to vary the graft length, leading to 3
273 series of twelve original grafted PUI copolymers with different grafting rates and graft lengths (Table
274 1).
275



276

277 **Fig. 1. Synthesis of the graftable precursor PUI-g by step-growth polymerization (steps 1 and 2) and grafting with soft**
 278 **grafts PEDEGA (step 3).**

279 3.1.2. Physical chemical characterization of the grafted PEO-based PUI copolymers

280 Characterization by ¹H NMR enabled to validate the chemical structure of PUI-g and that of the
 281 grafted PUIs and to calculate their experimental grafting rate. As an example, Fig. 2 shows the proton
 282 identification of PUI-g, PEDEGA 5000 grafts and the grafted copolymer PUI-g-1PEDEGA5000.

283 Monomers stoichiometry in PUI-g (JFAED 2000 (0.6) + BisOHyne (0.4)/MDI (2)/6FDA(1)) was

284 checked using protons peak integrations, which also confirmed the expected amount of alkyne side
 285 groups in PUI-g. The spectrum of the grafted multi-block copolymer PUI-g-1PEDEGA5000 exhibited
 286 ¹H NMR signals coming from both PUI-g and PEDEGA 5000. SEC-MALLS was also used to
 287 qualitatively verify the efficiency of the copolymer grafting (see Fig. S1). The grafting rates *GR* were
 288 calculated from integration area *A*₁ of CH₃ protons of JFAED 2000 propylene oxide units and CH₃
 289 protons of PEDEGA grafts (δ: 1.15-1.20 ppm : D, I, m on Fig. 2) and integration area *A*₂
 290 corresponding to CH protons of MDI and CH protons of triazole ring (δ: 7-7.5 ppm : A, a, b, d, e on
 291 Fig. 2) by solving equation 6.

$$292 \quad \frac{A_1}{A_2} = \frac{0.6 \times (3 + 5.16 \times 3) + 0.4 \times 2 \times \left(\frac{GR}{100}\right) \times (6 + 3 \times \overline{X_{nPEDEGA}})}{0.6 \times 2 \times 8 + 0.4 \times 2 \times 8 + 0.4 \times 2 \times \left(\frac{GR}{100}\right)} \quad (6)$$

$$293 \quad \text{with} \quad \overline{M_{nPEDEGA}} = M_{AEBiB \text{ initiator}} + \overline{X_{nPEDEGA}} \times M_{EDEGA} \quad (7)$$

294 In equation 7, $\overline{M_{nPEDEGA}}$ is the number-average molecular weight of the PEDEGA grafts determined
 295 by SEC-MALLS analysis, and $\overline{X_{nPEDEGA}}$ is the corresponding number-average degree of
 296 polymerization. M_{EDEGA} is the molecular weight of the EDEGA monomer unit and $M_{AEBiB \text{ initiator}}$ is
 297 the molecular weight of the AEBiB initiator used for the synthesis of the azido-PEDEGA oligomers.

298 Table 1 shows that the experimental grafting rates were very close to the theoretical ones for all the
 299 grafted copolymers. Therefore, very high grafting efficiencies were obtained in this work (Table 1 –
 300 column 4) and the copolymer/graft coupling by CuAAC “click” chemistry was quantitative. Therefore,
 301 all the PEDEGA grafts introduced in the reaction medium were effectively grafted onto PUI-g
 302 ensuring the control over the number of grafts in the grafted copolymers.

303 The very high grafting efficiency also enabled to control the grafting rate very easily from 25% to
 304 100%, resulting in soft contents varying in a very broad range from 57 to 85 wt% (Table 1 - last
 305 column). The soft content for each grafted copolymer was then calculated from the corresponding
 306 grafting rate *GR* and PEDEGA graft number-average molecular weight $\overline{M_{nPEDEGA}}$ according to
 307 equation 8 and reported in Table 1. Consequently, the new grafting strategy enabled to increase the
 308 maximum PUI soft content from 70 wt% in our former work on PUI multi-block copolymers to the
 309 very high content of 85 wt% for the grafted PUI multi-block copolymer PUI-g-1PEDEGA5000
 310 corresponding to the highest grafting rate and the highest PEDEGA graft molecular weight.

$$311 \quad \text{Soft content (wt\%)} = \frac{0.6 \times M_{JFAED2000} + 0.4 \times 2 \times \left(\frac{GR}{100}\right) \times \overline{M_{nPEDEGA}}}{M_{\text{repeating unit of grafted copolymer}}} \times 100 \quad (8)$$

$$312 \quad \text{with } M_{\text{repeating unit of grafted copolymer}} = 0.6 \times M_{JFAED2000} + 0.4 \times M_{bisOHyne} + 0.4 \times 2 \times$$

$$313 \quad \left(\frac{GR}{100}\right) \times \overline{M_{nPEDEGA}} + 2 \times M_{MDI} + M_{6FDA} - 2 M_{CO2} \quad (9)$$

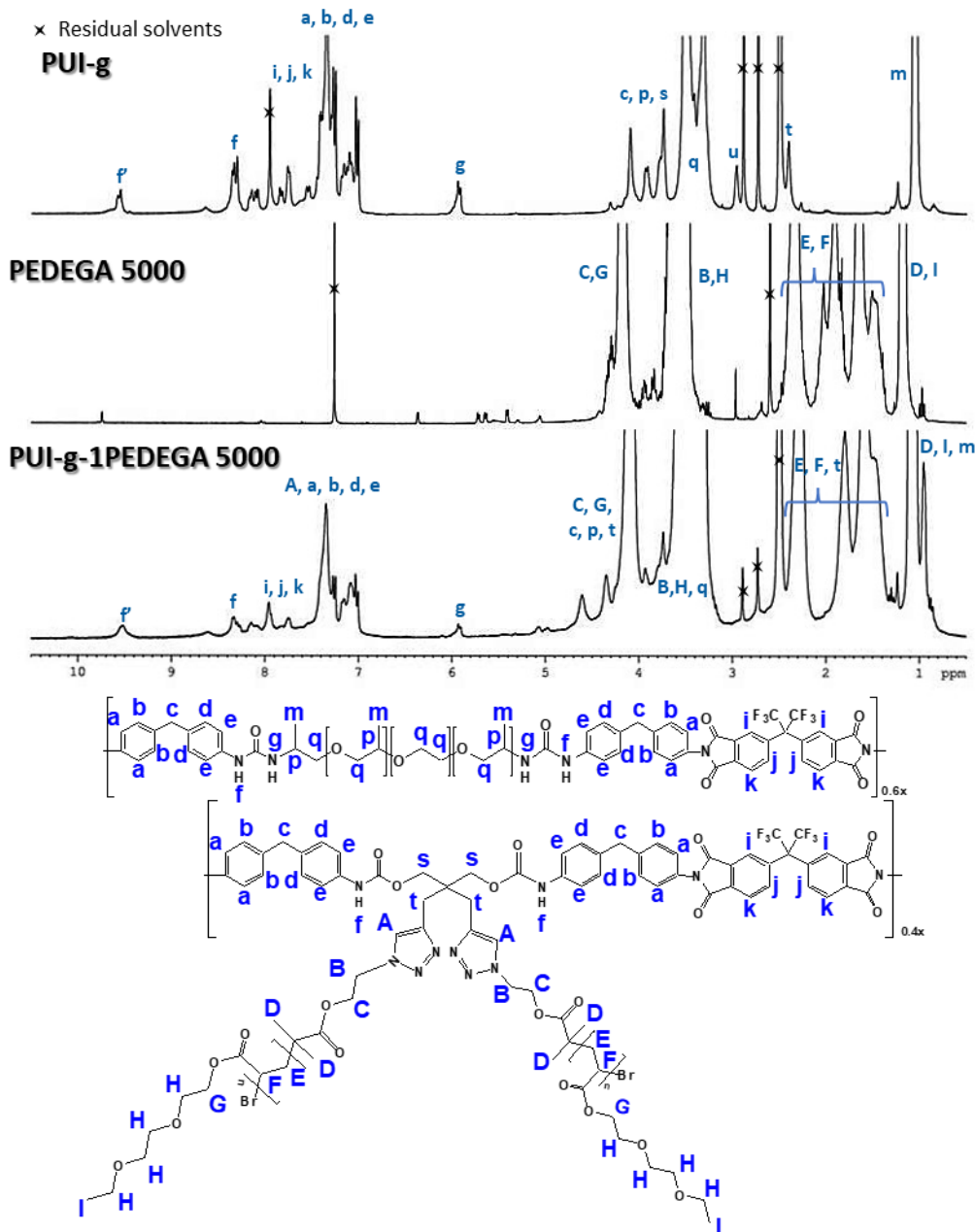
314 In equation 9, $M_{\text{repeating unit of grafted copolymer}}$ is the molecular weight of the repeating unit of the
 315 grafted copolymer and M_i the molecular weight of species *i*.

316 **Table 1. Grafting rate, grafting efficiency and soft content of PUI-g and grafted PUIs, with PUI-g-XPEDEGAY: X the**
 317 **grafting rate/100 and Y the molar mass of PEDEGA grafts.**

Sample	Theoretical grafting rate (%)	Experimental grafting rate (%)	Grafting efficiency (%)	Soft content (wt %) (¹ H NMR)
--------	-------------------------------	--------------------------------	-------------------------	---

		(¹ H NMR)	(¹ H NMR)	
PUI-g	-	-	-	57
PUI-g-0.25PEDEGA2000	25	24	96	64
PUI-g-0.5PEDEGA2000	50	49	98	69
PUI-g-0.75PEDEGA2000	75	76	100	72
PUI-g-1PEDEGA2000	100	101	100	75
PUI-g-0.25PEDEGA3600	25	24	96	68
PUI-g-0.5PEDEGA3600	50	51	100	74
PUI-g-0.75PEDEGA3600	75	75	100	79
PUI-g-1PEDEGA3600	100	100	100	82
PUI-g-0.25PEDEGA5000	25	26	100	71
PUI-g-0.5PEDEGA5000	50	50	100	78
PUI-g-0.75PEDEGA5000	75	75	100	82
PUI-g-1PEDEGA5000	100	100	100	85

318



319

320 Fig. 2. ¹H NMR characterization of PUI-g, soft graft PEDEGA 5000, and PUI-g-1PEDEGA5000 (copolymer with
 321 maximum grafting rate and graft molecular weight taken as way of example).

322 3.1.3. Morphology characterization for the PEO-based grafted PUI multi-block copolymers

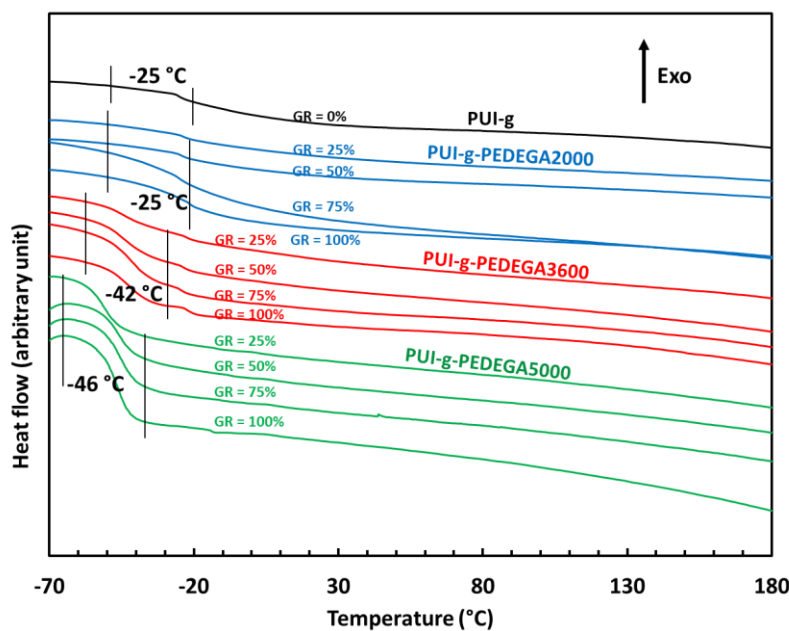
323 Multi-block (segmented) copolymers have complex morphology and this morphology has a great
 324 influence on their permeability and membrane properties [33,38,40,116]. In this context, reducing the
 325 fraction of crystalline phases remains a major challenge for the design of high-performance
 326 membranes [27,33,40,66]. In these copolymers, the soft and hard blocks can be fully mixed, partially
 327 mixed or separated, depending on the chemical structure and molecular weight of these blocks. The
 328 best membrane properties are usually obtained when the quasi-impermeable hard blocks are excluded
 329 from the soft blocks, which corresponds to strong phase separation also ensuring good material
 330 physical cross-linking [27,33,40,66]. In the following, the morphology of the new grafted copolymers
 331 was assessed by complementary techniques in comparison with that of their precursor PUI-g.

332 Fig. 3 shows the DSC thermograms for PUI-g and the grafted PUI multi-block copolymers displayed
333 in three series of data corresponding to different graft molecular weights (PEDEGA 2000, 3600 and
334 5000) and grafting rates varying from 25 to 100%. In all of these thermograms, the glass transition
335 temperature T_g of the hard blocks was not observed because the DSC scanning temperature has been
336 limited to prevent the chemical degradation of the PEO-based soft blocks, as also reported in earlier
337 works on other PEO-based polyimides [59,61,66,76]. For PUI-g, the T_g of -25°C was well below
338 ambient temperature, meaning that the JFAED 2000 soft blocks formed a soft rubbery phase.
339 However, this T_g was much higher than that of the JFAED 2000 oligomer ($T_g = -65^\circ\text{C}$) due to the
340 constraints imposed by the hard blocks representing almost half of the copolymer weight. Compared
341 to the corresponding multi-block copolymer JFAED2000/MDI/6FDA ($T_g = -39^\circ\text{C}$) containing only 30
342 wt% of hard blocks reported in our former work [76], the T_g of PUI-g was higher, as expected from its
343 much higher hard block content (43 wt%).

344 For the grafted PUI copolymers, a unique glass transition *for the soft phase* was observed in each
345 thermogram, evidencing the presence of only one soft phase composed by JFAED 2000 soft blocks
346 and PEDEGA grafts (Fig. 3). For the shortest grafts (PEDEGA 2000), the T_g of ca. -25°C remained
347 almost identical to that of PUI-g (Table 2), showing that the soft phases exhibited comparable
348 dynamics in both non-grafted copolymer and multi-block copolymers grafted with the shortest
349 PEDEGA grafts. However, when the length of the PEDEGA grafts was increased (PEDEGA 3600 and
350 5000), the T_g was strongly decreased to -46°C . Therefore, the grafting with longer PEDEGA grafts
351 allowed shifting the T_g towards the T_g of the corresponding PEDEGA oligomers ($T_g = -50^\circ\text{C}$) and
352 strongly improved the mobility of the corresponding soft phase. For any given graft length, the
353 grafting rate (GR) was not found to have significant impact on the polymer glass transition dynamics
354 for GR above 25%. Therefore, for the longest grafts (PEDEGA 3600 and 5000), the grafting of the
355 first grafts induced the spacing of the macromolecular backbone and generated a constant
356 microenvironment for the soft phase. However, as expected, the values of ΔC_p associated to the glass
357 transition of the grafted multi-block copolymers (which is related to the weight of the soft phase
358 undergoing the glass transition) increased with their soft phase content (Table 2 – column 4). The
359 thermograms obtained for PUI-g-PEDEGA3600 showed a secondary glass transition at ca. -25°C (*i.e.*
360 the T_g of PUI-g). However, this glass transition corresponded to a very small ΔC_p compared to the
361 main glass transition, involving that the corresponding soft phase was very limited compared to that
362 developed by the mixing of the soft blocks and grafts.

363 Furthermore, the absence of crystallinity was observed in the thermograms of all the PUI copolymers,
364 with no melting endotherms even for the highest soft contents. Therefore, the Jeffamine soft segments
365 did not crystallize in the new grafted copolymers, as it was also observed for the related linear multi-
366 block copolymers reported in our former work [76]. This was due to the particular structure of the
367 Jeffamine, whose propylene oxide units prevented crystallization. In addition, the PEDEGA grafts did
368 not crystallize either, in good agreement with former works on other grafted (or comb) copolymers
369 with related PEO-based poly(meth)acrylate grafts [77,80,92,95]. In conclusion, DSC experiments
370 showed that the new grafted multi-block architecture allowed to obtain membrane materials with very
371 high PEO-based soft phase content (up to 85 wt%) without crystallinity, which is a strong advantage
372 for gas permeation.

373



374

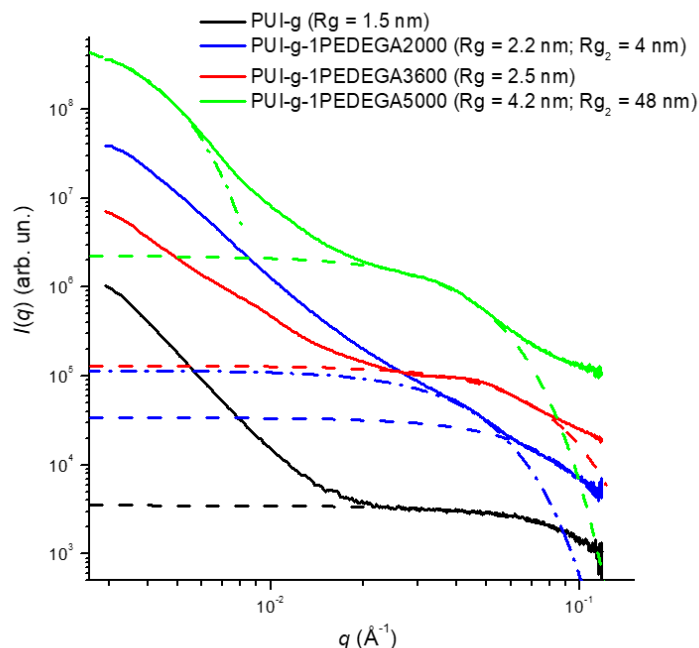
375 Fig. 3 Thermograms of PUI-g and grafted PUI multi-block copolymers with different lengths of grafts (PEDEGA
 376 2000, 3600 and 5000) and different grafting rates (GR) from 25 to 100% (second heating – 10°C/min). Note: The
 377 thermograms have been shifted for improved visualization and correspond to arbitrary heat flow values.

378 Table 2. DSC results of PEDEGA oligomers and grafted PUI multi-block copolymers (second heating – 10°C/min).

Sample	Soft phase content (%)	T _g (°C)	ΔC _p (J/(g·°C))
JFAED 2000 [76]	-	-65	0.20
PEDEGA 2000	-	-50	0.66
PEDEGA 3600	-	-49	0.74
PEDEGA 5000	-	-51	0.75
PUI-g	57%	-25	0.33
PUI-g-0.25PEDEGA2000	64%	-23	0.33
PUI-g-0.5PEDEGA2000	69%	-24	0.35
PUI-g-0.75PEDEGA2000	72%	-25	0.36
PUI-g-1PEDEGA2000	75%	-25	0.45
PUI-g-0.25PEDEGA3600	68%	-45	0.35
PUI-g-0.5PEDEGA3600	74%	-45	0.42
PUI-g-0.75PEDEGA3600	79%	-41	0.44
PUI-g-1PEDEGA3600	82%	-42	0.50
PUI-g-0.25PEDEGA5000	71%	-46	0.40
PUI-g-0.5PEDEGA5000	78%	-47	0.44
PUI-g-0.75PEDEGA5000	82%	-46	0.51
PUI-g-1PEDEGA5000	85%	-46	0.55

379

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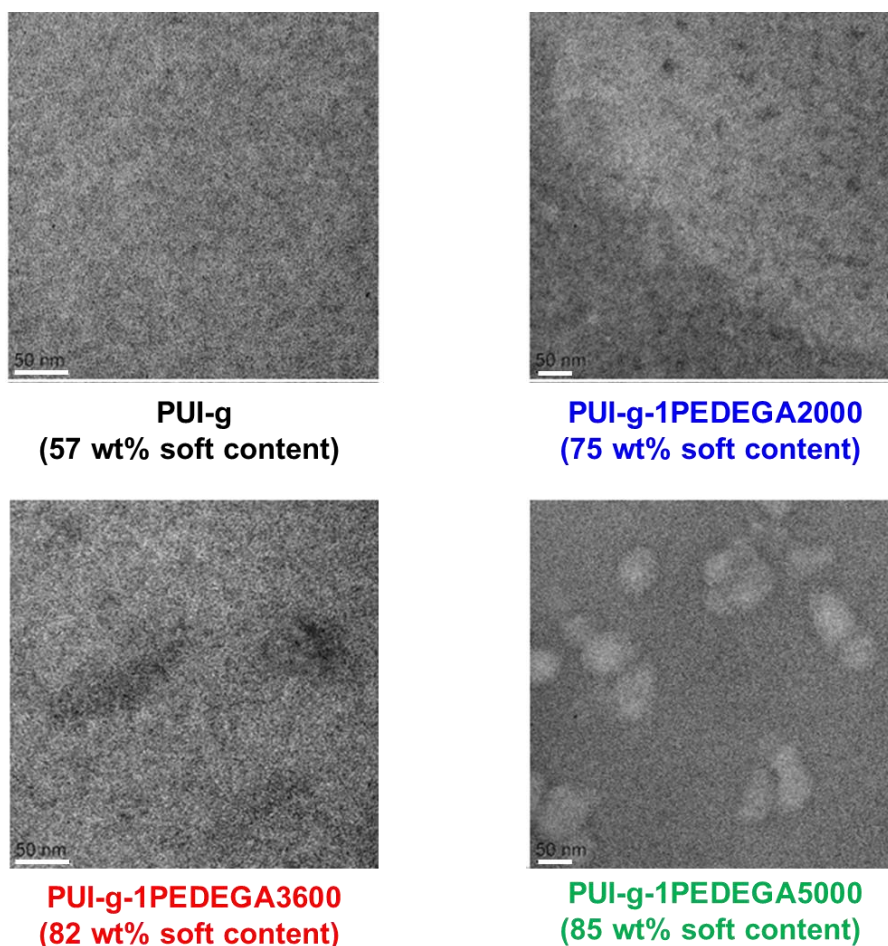


381

382 **Fig. 4 - Influence of soft grafts molecular weight on SAXS experiments for the PUI copolymers grafted with maximum**
 383 **grafting rate (100%) and their precursor PUI-g.**

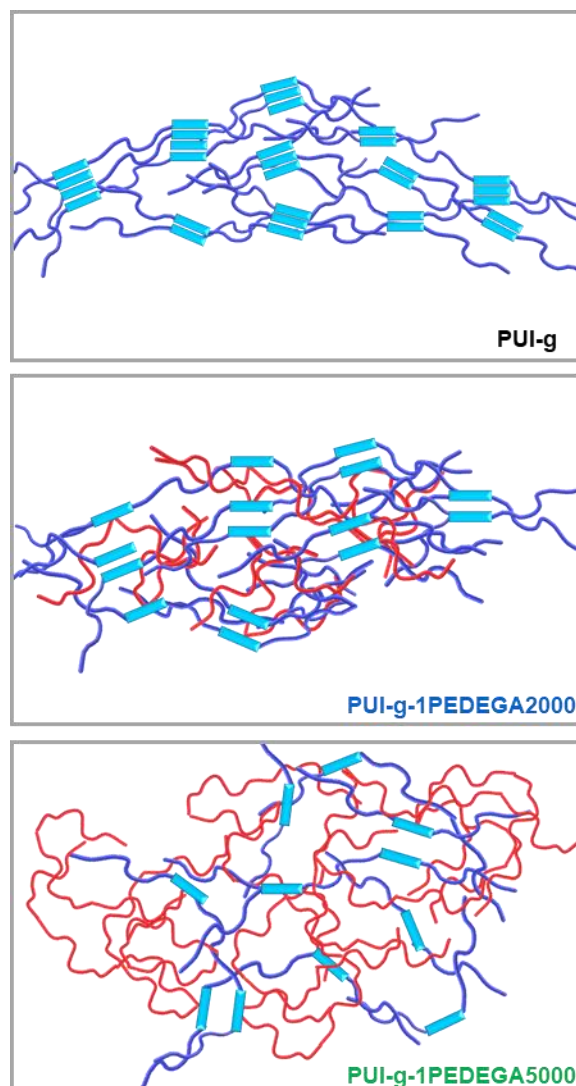
384 The morphology at the nanoscale was investigated by synchrotron SAXS and TEM experiments for
 385 the highest grafting rate (100%) for each graft length (PEDEGA 2000, 3600 and 5000), corresponding
 386 to the best membrane materials of each series of grafted copolymers, and compared with that of the
 387 precursor PUI-g. For PUI-g, the SAXS pattern (Fig. 4) showed the same type of nano-structuration of
 388 the hard blocks as that observed for the corresponding linear PUI based on the same soft blocks
 389 JFAED 2000 in our previous work [76]. The analysis of the SAXS pattern with the Guinier's law for
 390 isometric particles ($I(q)=I_0\exp(-R_0^2q^2/3)$) at high q values led to a gyration radius of 1.5 nm (in
 391 comparison with 2 nm in our former work [76]) for the hard block domains. Fig. 4 shows that the
 392 corresponding shoulder is shifted towards the lower q -range for the grafted copolymers. Accordingly,
 393 the use of Guinier's law led to gyration radius for the hard block domains, with very small sizes
 394 varying from 2.2 nm to 4.2 nm. As the grafting sites were strategically located on the
 395 aromatic/aliphatic hard blocks based on the new monomer unit (bisOHyne) (which correspond to 40
 396 mol% of the hard blocks as shown in Fig. 1), grafting induced the swelling of the hard block
 397 nanodomains as shown by the increase of the corresponding gyration radii compared to that of the
 398 PUI-g precursor. Furthermore, all systems displayed an increase of scattered intensity in the low q
 399 range, indicative of larger scale fluctuations in the repartition of hard and soft phases. In particular, for
 400 PUI-g-1PEDEGA5000 corresponding to the longest grafts and to the extreme soft content of 85 wt%,
 401 the SAXS pattern obtained in the low q -range ($q < 4 \cdot 10^{-3} \text{ \AA}^{-1}$) showed the beginning of another
 402 shoulder resolved in the assessable q -range, corresponding to a gyration radius of the order of 48 nm.
 403 For the corresponding TEM analyses, the preparation of the samples by cryo-ultramicrotomy was
 404 particularly difficult for the grafted copolymers due to their high soft contents and led to some
 405 shadows on the corresponding TEM pictures (Fig. 5). Nevertheless, the TEM images showed fine dark
 406 nanodomains with characteristic sizes of less than 5 nm (in good agreement with the SAXS results)
 407 corresponding to the stained hard blocks. The TEM images also showed that their dispersion in the
 408 soft phase increased with the PEDEGA graft length. This dispersion was related to the dragging of
 409 hard blocks induced by the covalent grafting of the PEDEGA grafts on the aromatic/aliphatic hard

410 blocks. In accordance with the SAXS experiments, the TEM image of PUI-g-1PEDEGA5000 revealed
411 unstained/clear soft nanodomains with characteristic dimensions of the order of 50 nm. Fig. 6
412 schematically illustrates the morphology of PUI-g and the grafted copolymers with the shortest and
413 longest PEDEGA grafts as deduced from the SAXS and TEM experiments. The grafting induced the
414 expansion of the soft content, along with the dragging of some hard blocks in the soft phase (PUI-g-
415 1PEDEGA2000). The longer the grafts, the greater the soft content and dragging of these hard blocks
416 in the soft phase (PUI-g-1PEDEGA5000).



417

418 **Fig. 5. Influence of soft grafts molecular weight on TEM images of the PUI copolymers grafted with maximum**
419 **grafting rate (100%) and their precursor PUI-g. Note: the white scale represents 50 nm.**



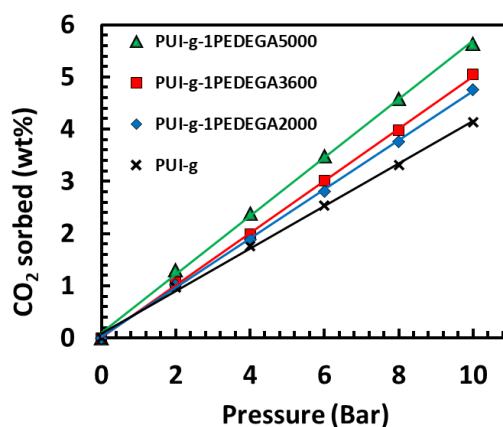
420
421

422 **Fig. 6. Schematic illustration of the influence of soft grafts molecular weight on morphology of the grafted PUI**
423 **copolymers with the maximum grafting rate (100%)**

424 3.1.4. CO₂ sorption properties

425 The CO₂ mass uptake at sorption equilibrium of the different copolymers was assessed at 35 °C with
426 increasing CO₂ pressures between 0 and 10 bar in a microbalance. Fig. 7 shows the influence of
427 PEDEGA soft grafts molecular weight on the CO₂ sorption isotherms of the grafted PUI copolymers
428 with maximum grafting rate (100%) and their precursor PUI-g. The sorption isotherms for all the
429 membrane materials were linear and characteristic for Henry dissolution typical for rubbery polymers.
430 Linear CO₂ isotherms have also been reported for other PEO-based linear multi-block copolymers
431 (Polyactive 3000 and 4000) at high temperatures (50-70°C) ensuring the melting of the PEO
432 crystallites although a deviation from Henry's law was observed at lower temperatures corresponding
433 to semi-crystalline PEO blocks [37]. In this work, the grafted copolymers were non-crystalline due to
434 the use of JFAED 2000 and their particular grafted copolymer structure, and Henry's law was
435 followed even at relatively low temperature (35°C). At the pressure of 2 bar chosen for the gas
436 permeation experiments, a relatively low amount of CO₂ (ca. 1 wt%) was absorbed in the grafted
437 multi-block copolymers and their precursor PUI-g. However, for each CO₂ pressure, the CO₂ mass

438 uptake increased with the graft length and soft phase content up to 5.6 wt% at 10 bar for the best
439 grafted PUI multi-block copolymer (PUI-g-1PEDEGA5000) corresponding to the longest grafts and
440 highest soft content.

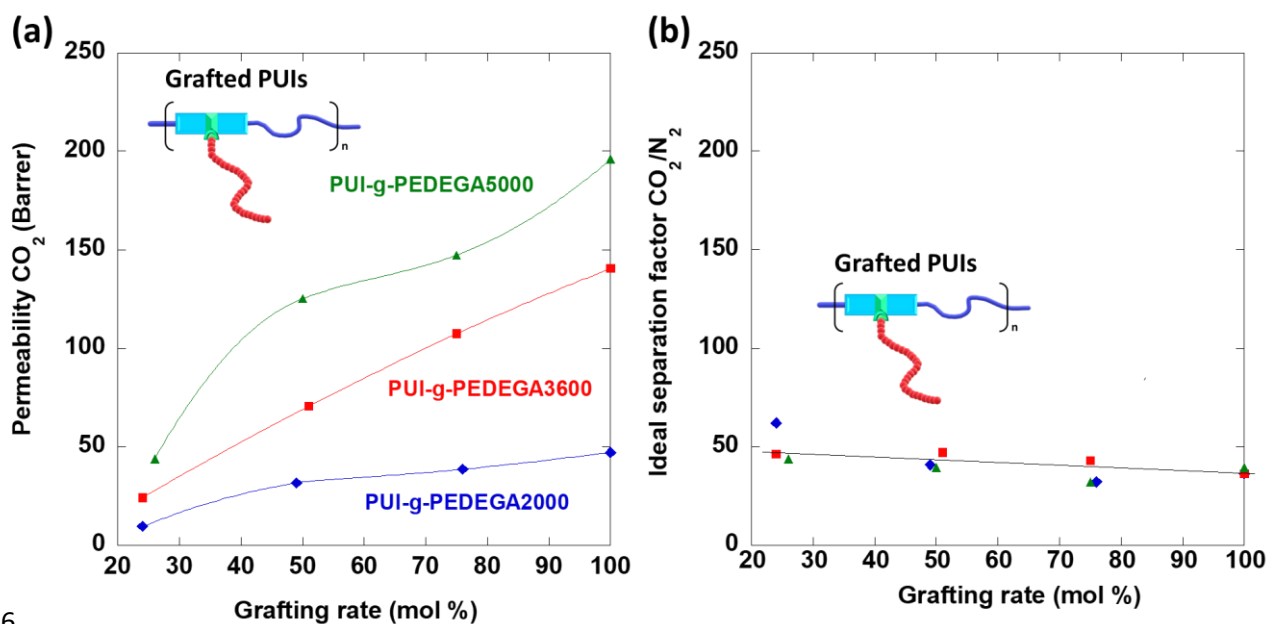


441

442 **Fig. 7. Influence of soft grafts molecular weight on CO₂ sorption isotherms of the PUI copolymers grafted with**
443 **maximum grafting rate (100%) and their precursor PUI-g at 35°C.**

444 3.1.5. CO₂ permeation properties

445 The CO₂ permeation properties of the grafted copolymers and their precursor PUI-g were determined
446 for the pure gases CO₂ and N₂ at 2 bar and 35 °C referring to usual conditions for CO₂ capture [33,99].
447 The membranes were dense (no pores) with thicknesses of ca. 90 μm as shown by SEM experiments
448 (Fig S2). The membrane thicknesses used for gas permeability calculations were measured with an
449 Elcometer micrometer and averaged on the active surface area for each membrane. Pure gas
450 experiments were performed in this study because former works on other PEO-based multi-block
451 copolymers have shown that their permeation properties were almost the same for mixed-gas
452 separation [75,117]. Because of the mild conditions of CO₂ capture from flue gas, with moderate feed
453 pressure and relatively low CO₂ content in feed mixture (5-14%), the CO₂ partial pressure is low.
454 These conditions generally lead to relatively low CO₂ sorption (as also found in this work) and very
455 limited plasticizing of such copolymers [75,117].



456

457 **Fig. 8. Influence of grafting rate on (a) permeability of CO₂ and (b) ideal separation factor α_{CO_2/N_2} for the grafted**
 458 **PUI copolymers at 2 bar and 35°C.**

459

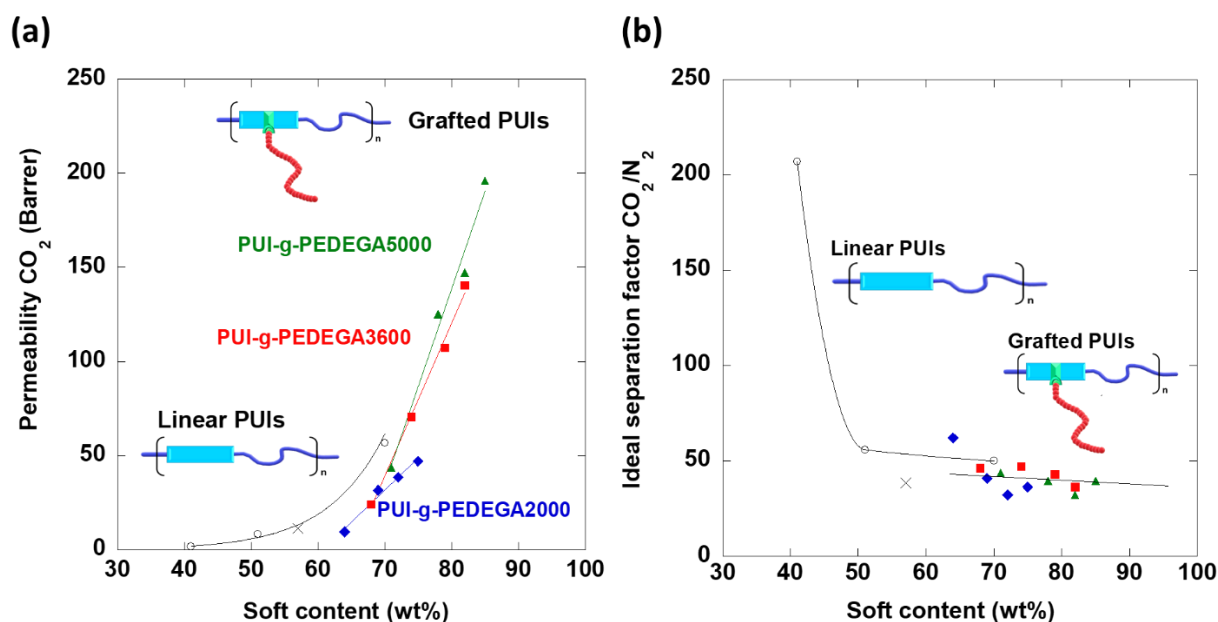
460 Fig. 8 shows the influence of grafting rate on CO₂ permeability and ideal separation factor α_{CO_2/N_2}
 461 for three series of grafted multi-block copolymers with increasing PEDEGA graft molecular weight
 462 from 2000 to 5000 g/mol. The CO₂ permeability increased with the grafting rate for all the grafted
 463 copolymers (Fig. 8a). When the PEDEGA graft molecular weight was increased, the increase of CO₂
 464 permeability was further improved because of the stronger contribution of the longer PEDEGA grafts
 465 to the soft phase content. Globally, the grafting strategy greatly increased CO₂ permeability from 11.5
 466 Barrer for the precursor PUI-g to 196 Barrer for the best grafted multi-block PUI copolymer PUI-g-
 467 1PEDEGA5000, corresponding to the highest grafting rate (100%) and PEDEGA graft molecular
 468 weight (5000).

469 At the same time, the ideal separation factor α_{CO_2/N_2} was maintained at a high level close to 40 for all
 470 the grafted copolymers, whatever their grafting rate and PEDEGA graft molecular weight (Fig. 8b).
 471 The CO₂ sorption coefficients slightly increased with the grafting rate and PEDEGA graft molecular
 472 weight and the N₂ sorption coefficients were extremely low for all these membranes, corresponding to
 473 very high ideal sorption selectivity also reported for other PEO-containing copolymers [15,17,71]
 474 (Table S1 – Supporting information). However, the variation of CO₂ sorption coefficients with the
 475 copolymer structural parameters was much lower than that of the CO₂ diffusion coefficients, which
 476 increased over almost one order of magnitude within the range of study. Therefore, diffusion increase
 477 was mainly governing improvement in gas permeation through these membranes due to the increase in
 478 their soft content. This trend was also in good agreement with former works on other PEO-based
 479 multi-block copolyimide membranes for CO₂ separations [58,63,70,72,98].

480 To highlight the specific interest of the grafting strategy developed in this work, Fig. 9 compares the
 481 membrane properties of the grafted PUI copolymers with those of related linear PUI multi-block
 482 copolymers previously reported in our former work [76]. The linear PUI multi-block copolymers
 483 exhibited a chemical structure comparable to that of the grafted PUI copolymers, with hard blocks
 484 made of MDI/6FDA monomer units, and JFAED soft blocks with increasing molecular weights from

485 600 to 2000 g/mol (corresponding to soft phase contents increasing from 41 to 70 wt%, respectively).
 486 Fig. 9a shows that the CO₂ permeability of the linear PUI copolymers increased exponentially from 2
 487 Barrer to 57 Barrer when their soft content was increased from 41 to 70 wt%, which was the
 488 maximum soft content allowed for the linear PUI copolymers. Such drastic permeability increase was
 489 previously related to the separation of their soft and hard blocks for the highest soft content with
 490 percolation of a soft elastomer phase [76]. At the same time, the ideal separation factor $\alpha_{\text{CO}_2/\text{N}_2}$ of the
 491 linear PUI multi-block copolymers strongly decreased with their soft content from 207 to 50 Barrer.
 492 Therefore, the CO₂ permeability of the linear PUI copolymers was strongly restricted by a
 493 permeability-selectivity trade-off, albeit still displaying high selectivity for CO₂/N₂ separation.

494 The grafting strategy enabled to overcome the soft content limitation of the linear PUI copolymers by
 495 allowing much higher soft contents up to 85 wt%. For each series of grafted copolymers, CO₂
 496 permeability increased linearly with the copolymer soft content. The same type of linear permeability
 497 increase has been reported for different multi-block copolymers and it is generally ascribed to some
 498 intermixing between the soft and hard blocks as reviewed in a former work [118]. In this new work,
 499 the linear permeability increase relates to the special morphology developed by the grafted PUI
 500 copolymers, involving the dragging of the hard blocks bearing the PEDEGA grafts within the soft
 501 phase (as explained in section 3.1.3). In the grafted PUI copolymers, both CO₂ and N₂ diffusivity
 502 increased due to their soft content increase (Table S1 – Supporting information). However, the hard
 503 blocks mixed within the soft phase acted as impermeable obstacles and contributed to limit the
 504 increase in the diffusion coefficients of the gas molecules and, consequently, to limit the decrease in
 505 membrane ideal separation factor, which was maintained at high level even for the highest soft
 506 contents (Fig. 9b). Therefore, the special morphology of the new membranes allowed a CO₂
 507 permeability increase by a factor of 17 with quasi-constant membrane selectivity ($\alpha_{\text{CO}_2/\text{N}_2}$ of ca. 40).



508
 509 **Fig. 9. Influence of copolymer soft content on (a) permeability of CO₂ and (b) ideal separation factor $\alpha_{\text{CO}_2/\text{N}_2}$ for the**
 510 **grafted PUI copolymers (filled symbols), the precursor PUI-g (x) and the corresponding linear PUI copolymers**
 511 **(empty circle symbols, data taken from our former work [76]) at 2 bar and 35°C.**

512

513

515 **Table 3. Membrane separation properties of the grafted PUI copolymers compared with different linear multi-block**
 516 **copolymers with polyether soft blocks and their blends with PEO-based additives reported in the literature.**

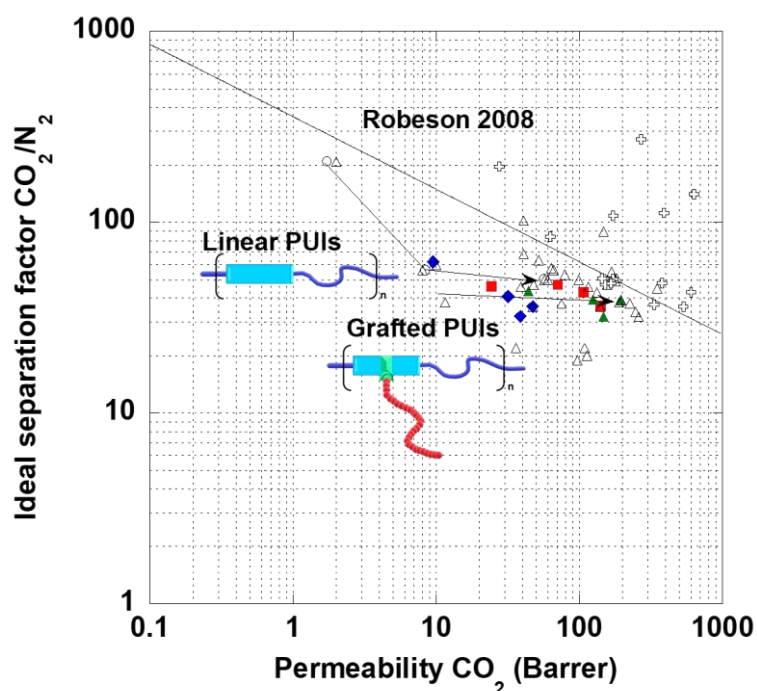
Sample	P_{CO_2} (Barrer)	α_{CO_2/N_2}	CO_2 pressure	T (°C)	Ref.
POLY(ETHER-AMIDE)S (PEBAX)					
Pebax 2533 (PTMO/PA12)	260	32	6.8 atm	25°C	[33]
Pebax 4033 (PTMO/PA12)	113	20	10 bar	35°C	[38]
Pebax 1074 (PEO-PA12)	133	43	2 bar	35°C	[46]
Pebax 1074 (PEO-PA12)	168	55	13.8 bar	35°C	[119]
Pebax 4011 (PEO/PA6)	66	56	10 atm	35°C	[38]
Pebax 1657 (PEO/PA6)	79	53	1 bar	30°C	[35]
Pebax 1657 (PEO/PA6)	157	47	3 bar	45°C	[45]
Pebax 1657 (PEO/PA6)	147	89	13.8 bar	35°C	[119]
POLY(ETHER-ESTER)S					
PEO-PBT	115	46	300 mbar	30°C	[30]
PEO-PTT	183	51	300 mbar	30°C	[31]
PEO ₂₀₀₀ -T6T6T	180	49	4 atm	35°C	[43]
(PEO- <i>ran</i> -PPO) ₂₅₀₀ -T6T6T	348	45	4 bar	35°C	[41]
Polyactive 1500 (PEGT/PBT)	226	37.7	1 bar	40°C	[34]
Polyactive 3000 (PEGT/PBT)	190	38	1 bar	40°C	[34]
Polyactive 4000 (PEGT/PBT)	75	37.5	1 bar	40°C	[34]
POLY(ETHER-URETHANE)S					
PU (PEO ₁₀₀₀ /MDI/BD)	36	22	1 bar	30°C	[120]
PU (PEO ₂₀₀₀ /MDI/BPA)	48	47	2 atm	35°C	[99]
PU (PEO-PU epoxy network)	63.4	57.6	2 bar	35°C	[55]
PU Elastollan	41	68.2	1 bar	25°C	[53]
PU (PTMO/IPDI/BDA)	109	21.9	4 bar	30°C	[54]
PU (PTMO/HDI/Naphtyl-based diamine)	247	33.8	4 bar	30°C	[54]
POLY(ETHER-IMIDE)S					
PI (6FDA/JFAED600/6FpDA)	97	19	2 bar	25°C	[63]
PI (BPDA/JFAED2000/ODA)	60	50	3 bar	30°C	[61]
PI (ODPA/JFAED2003/ODA)	52	63	6 bar	30°C	[70]
PI (PMDA/JAFED2300/m-PD)	99	50	2 atm	35°C	[99]
PI (PMDA/PEO ₂₀₀₀ /ODA)	10	60	3 bar	30°C	[62]
PI (BPDA/PEO ₆₀₀₀ /ODA)	41	102	3 bar	30°C	[69]
PI (pent-PI-PEO ₂₀₀₀)	39	46	3 atm	35°C	[65]
POLY(ETHER-UREA-IMIDE)S					
PUI JFAED600	2	207	2 bar	35°C	[76]
PUI JFAED900	8	56	2 bar	35°C	[76]
PUI JFAED2000	57	50	2 bar	35°C	[76]
Precursor PUI	11.5	38	2 bar	35°C	This work
PUI-g-1PEDEGA2000	47	36	2 bar	35°C	This work
PUI-g-1PEDEGA3600	140	36	2 bar	35°C	This work
PUI-g-1PEDEGA5000	196	39	2 bar	35°C	This work
RELATED MULTI-BLOCK					

COPOLYMER BLENDS WITH PEO-BASED ADDITIVES

Pebax 1657/PEG200 (50wt%)	151	47	600 mbar	30°C	[121]
Pebax 1657/PEG200 (50wt%)	172	50.5	4 bar	35°C	[122]
Pebax 1657/PEG600 (40wt%)	62.9	83.8	3 bar	25°C	[123]
Pebax 1657/PEG-DME (50wt%)	606	43	300 mbar	30°C	[124]
Pebax 1657/PEG-DME (40wt%)	378	48	800 mbar	30°C	[35]
Pebax 1657/PEO-based polysorbate T20 (50 wt%)	144	50.7	1 bar	25°C	[125]
Pebax 1657/PEO-based polysorbate T80 (50 wt%)	167	47.8	1 bar	25°C	[125]
Pebax 1657/PDMS-PEG (50wt%)	532	36.1	4 bar	35°C	[122]
Pebax 1657/Crosslinked PEG-diacrylate	27.5	195.8	3 bar	25°C	[126]
Polyactive 1500/PEG-POSS (30 wt%)	334	37.1	1 bar	40°C	[34]
Pebax 1657/PEG550 (30wt%)/calix[4]arene(0.5 wt%)	632.6	140	10 bar	35°C	[127]
Pebax 1657/PEG200 (20 wt%)/glycerol (15 wt%)/NiFe ₂ O ₄ (3 wt%)	269	273.4	10 bar	35°C	[128]
Pebax 1657/PEG400 (1.5 wt%)/Porous organic polymer (1 wt%)	392	112	1 bar	30°C	[129]
Pebax 1657/PEG600 (20 wt%)/NaY (30 wt%)	172.6	107.9	1.5 bar	30°C	[130]

517

518 Table 3 makes a comparison of the membrane properties of the new grafted multi-block copolymers
519 with other PEO (or PTMO)-based (linear/ungrafted) multi-block copolymers reported in literature for
520 CO₂ capture. For experimental conditions close to those used in this work (feed pressure of 2 bar and
521 temperature of 35°C), the best grafted PUI multi-block copolymer (PUI-g-1PEDEGA5000) offers high
522 permeability (196 Barrer) and high selectivity (39) and ranks among the most permeable PEO-based
523 multi-block copolymers with high selectivity $\alpha_{\text{CO}_2/\text{N}_2}$ such as Pebax 1657 [35,45] and Polyactive
524 1500 [30,34]. However, as expected from the data reported in literature, PUI-g-1PEDEGA5000 does
525 not compete with most of the multi-block copolymer blends with PEO-based additives, most of them
526 having better CO₂ permeability or/and selectivity for CO₂ capture [35,45,121–126]. Nevertheless,
527 PUI-g-1PEDEGA5000 could be an excellent candidate for new polymer blends with PEO-based
528 additives or their combination with porous organic polymers, metal organic frameworks or metal
529 oxides reported for this application [127–130]. The corresponding permeability-selectivity diagram
530 (Fig. 10) refines this comparison and further illustrates the strong differences between the linear and
531 grafted PUI multi-block copolymers. In addition to maintaining high selectivity for CO₂/N₂ separation,
532 the grafted multi-block copolymers enabled a strong increase in CO₂ permeability going very close to
533 the Robeson 2008 upper-bound for the separation of CO₂ from N₂.



535

536 **Fig. 10. Robeson plot showing the CO₂ separation performances of the grafted PUI copolymers (filled symbols), the**
 537 **corresponding linear PUI copolymers (empty circle symbols, data taken from our former work [76]), different other**
 538 **linear polyether-based multi-block copolymers (empty triangles) and their blends with PEO-based additives (empty**
 539 **crosses) reported in the literature.**

540 4. Conclusion

541 A new strategic way of grafting was developed for PEO-based multi-block copolymers to improve
 542 their membrane performance for CO₂ capture. The grafted PUI multi-block copolymers were
 543 synthesized by combining step-growth polycondensation, controlled radical polymerization and
 544 “click” chemistry to provide good control of their structural parameters (grafting rate, number and
 545 length of the grafts, and copolymer soft content). The new grafting strategy allowed to strongly
 546 increase the copolymer soft content up to 85 wt% compared to the maximum soft content (ca. 70 wt%)
 547 obtained for the corresponding linear PUI copolymers reported in our former work [76].

548 The new grafted PUI multi-block copolymers were non-crystalline (amorphous) materials even for the
 549 highest copolymer soft contents. Since crystallinity is one of the most widespread limitations of PEO-
 550 based copolymers for CO₂ separation membranes, the grafted PUI materials were particularly suitable
 551 for this application. The physical cross-linking provided by their UI hard blocks allowed the obtaining
 552 of cohesive membrane materials with exceptionally high soft contents. Furthermore, by a strategic
 553 grafting of the PEO-based grafts onto specific hard blocks, the grafted multi-block copolymers
 554 displayed special nano-structuration and morphology, combining high to very high soft content and
 555 the dragging of the grafted hard blocks within the soft phase.

556 The CO₂ permeability strongly increased up to 17-fold with the grafting rate, graft molecular weight
 557 and copolymer soft content while the ideal separation factor $\alpha_{\text{CO}_2/\text{N}_2}$ remained quasi-constant at a
 558 high level close to 40. The behavior of the grafted PUI copolymers was very different from that
 559 obtained for the corresponding linear PUI copolymers, which were strongly penalized by a
 560 permeability/selectivity trade-off in our former work. The particular behavior of the new grafted

561 copolymers was related to their special morphology involving impermeable obstacles dispersed in the
562 highly permeable phase, allowing maintaining high membrane selectivity even for the highest soft
563 contents.

564 The best membrane properties (196 Barrer and ideal separation factor of 39 at 2 Bar and 35°C) were
565 finally obtained for PUI-g-1PEDEGA5000 combining the highest grafting rate (100%), the highest
566 PEDEGA graft molecular weight (5000) and resulting copolymer soft content (85 wt%). A
567 comparison with literature shows that this grafted copolymer ranks among the best PEO-based
568 copolymers reported for CO₂/N₂ separation. This grafted copolymer shows a good
569 permeability/selectivity compromise associated with a combination of good film-forming and
570 adhesion properties onto different substrates. In the future, it could be used for developing mixed
571 matrix membranes, thin layer composite membranes or blend membranes for CO₂ capture.
572 Furthermore, the new grafting strategy could also be extended for designing a wide range of new high-
573 performance membrane materials for CO₂ separations.

574

575 *Supporting Information* reports a figure showing an example of grafting monitoring by SEC-MALLS,
576 a figure showing SEM pictures for membrane surfaces and cross-sections for precursor PUI-g and a
577 grafted multi-block copolymer and a table reporting the permeability, sorption and diffusion
578 coefficients for pure gases CO₂ and N₂ for the grafted PUI copolymers and their precursor PUI-g.

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Fig. 1. Synthesis of the graftable precursor PUI-g by step-growth polymerization (steps 1 and 2) and grafting with soft grafts PEDEGA (step 3).

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Fig. 8. Influence of grafting rate on (a) permeability of CO_2 and (b) ideal separation factor $\alpha_{\text{CO}_2/\text{N}_2}$ for the grafted PUI copolymers at 2 bar and 35°C .

Fig. 9. Influence of copolymer soft content on (a) permeability of CO_2 and (b) ideal separation factor $\alpha_{\text{CO}_2/\text{N}_2}$ for the grafted PUI copolymers (filled symbols), the precursor PUI-g (\times) and the corresponding linear PUI copolymers (empty circle symbols, data taken from our former work [1]) at 2 bar and 35°C .

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No color should be used for the figures in print.

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