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Effects of ionic liquid doping on gas transport properties of thermally rearranged poly(hydroxyimide)s

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Outline

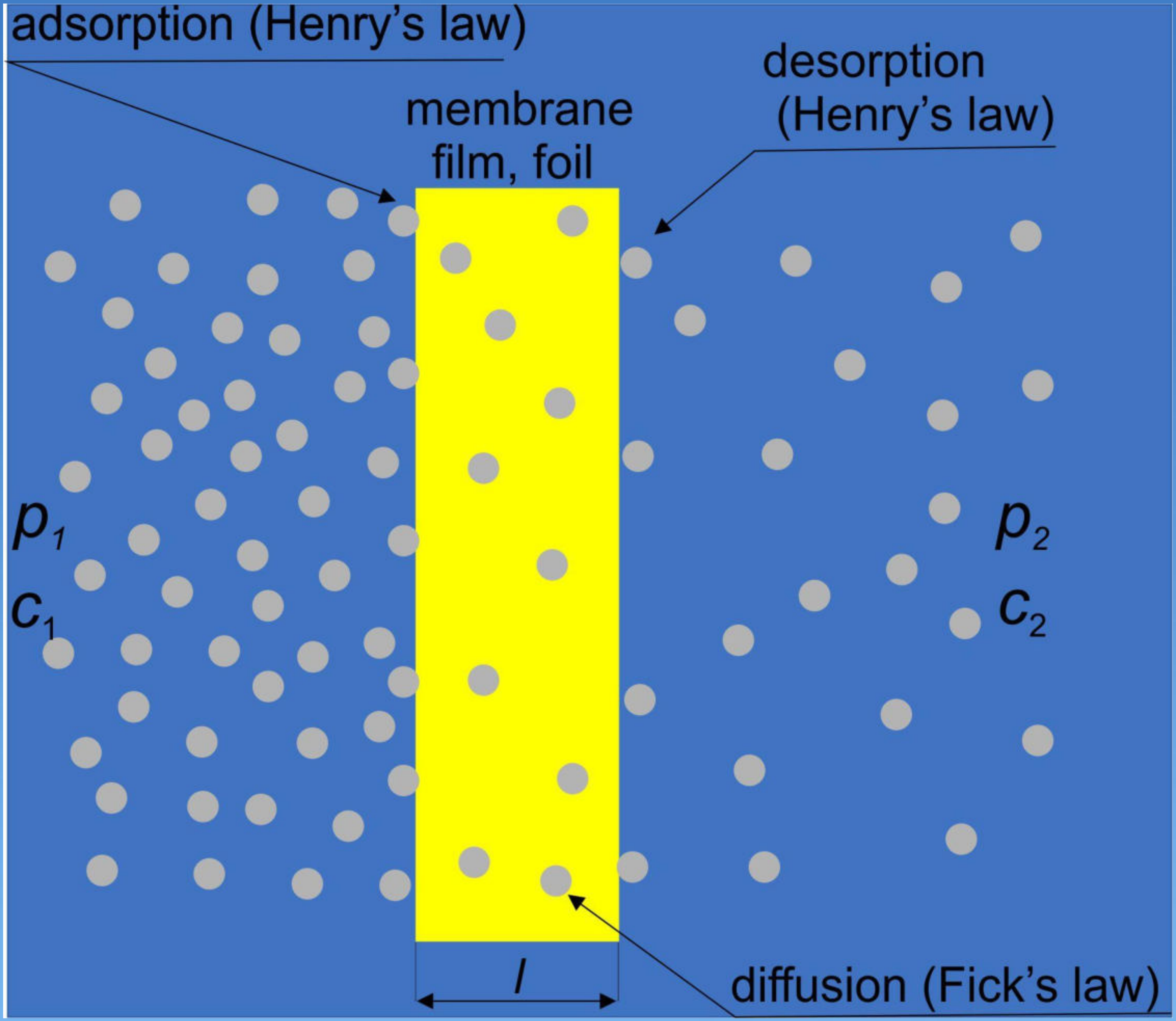
- What is permeability
- Studied polyamides
- Cohen-Turnbull model for gaz molcules transport
- PALS and permeability results
- Conclusions

A lot of polymers present on the market are used in the packaging field, in direct contact or not with the food:
polyolefins, copolymers of ethylene, substituted olefins, like polystyrene (PS), polyesters, polycarbonates (PC); polyamide (PA); acrylonitriles, regenerated cellulose. polylactic acid (PLA)

Polymer materials, in contrast to glass or metal packaging, are permeable at different degrees to small molecules like gases, water vapour, and organic vapour and to other low molecular weight compounds like aromas, flavour, and additives present into food.

Permeability, as reported in the literature, is defined as
the quantification of permeate transmission, gas or vapour,
through a resisting material.

The gas permeation into semicrystalline polymers is then confined into the amorphous regions.



adsorption (Henry's law)

membrane film, foil

desorption (Henry's law)

p_1 c_1

p_2 c_2

l

diffusion (Fick's law)

Henry’s law for gases

Henry's law states that: at a **constant** temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid.

$$C_{equil} = K_H \cdot p_{gas}$$

Fick’s First Law

$$J = -D \cdot \Delta c$$

For one-dimensional diffusion through a polymer membrane and in stationary conditions, can be written as

$$J = -D \cdot \left(\frac{\Delta c}{l} \right)$$

J - the diffusion flux,
D - the diffusion coefficient or diffusivity
Δc the concentration difference across the membrane thickness *l* .

When the diffusion mechanism is in its steady state, the equilibrium of the gas concentration c at the surface and the gas partial pressure p obey to Henry’s law then:

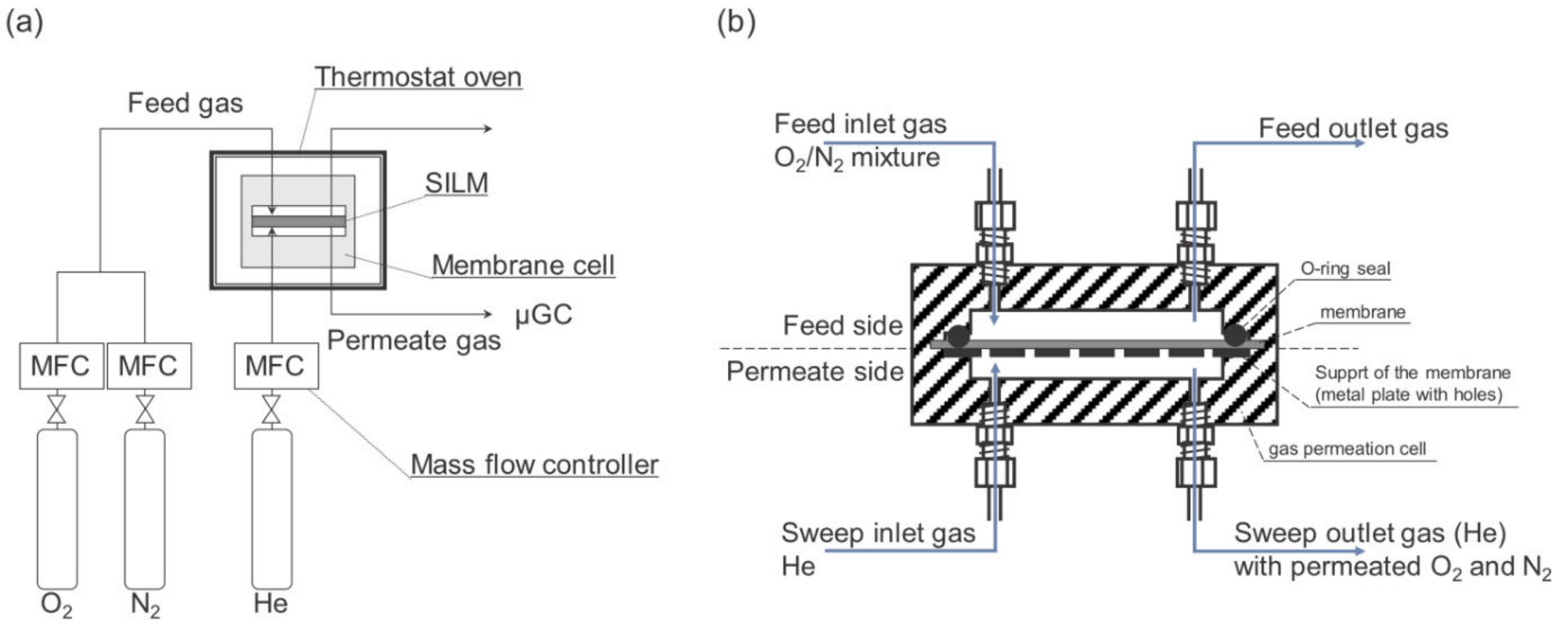
$$J = -D \cdot \left(\frac{K_H \Delta p}{l} \right) = -P \cdot \frac{\Delta p}{l}$$

permeability

The permeability of a polymer to a gas, *P* , is defined as follows:

$$P \equiv \frac{N \cdot l}{f_2 - f_1}$$

N – is the steady-state gas flux through the film
l - is the film thickness,
f_2 and f_1 are the upstream (i.e., high) and downstream (i.e., low) fugacities of gas, respectively



Schematic image of (a) the apparatus and (b) the membrane cell used for the gas permeation test.

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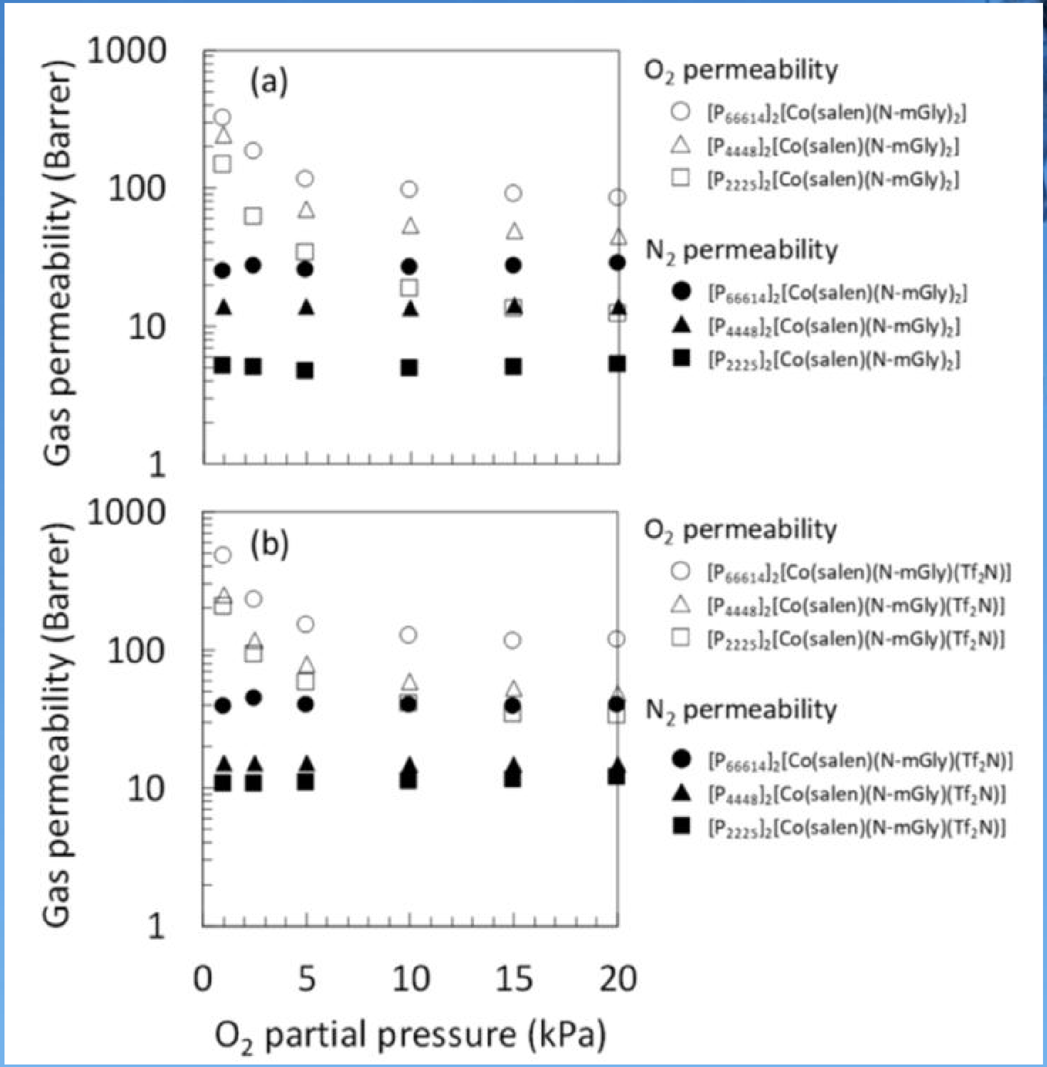
Gas permeate formula

$$P = 10^{-10} \frac{V_d \cdot l}{A \cdot T \cdot R \cdot p_2} \left[\left(\frac{dp_1}{dt} \right)_{ss} - \left(\frac{dp_1}{dt} \right)_{leak} \right]$$

V_d - the downstream volume [cm^3]
A - the effective membrane are [cm^2]
T - the aboslute temperarure [K]
R- the gas constant [cm Hg cm^3 cm^{-2} (STP) K^{-1}]
p_2 - the feed absolute preassure [cm Hg]

$\left(\frac{dp_1}{dt} \right)_{ss}$ - the rate of permeate absolute pressure for steady-state
$\left(\frac{dp_1}{dt} \right)_{leak}$ - the rate of permeate absolute pressure for leak

Permeability coefficients are commonly expressed in Barrers, where 1 Barrer $=10^{-10}$ cm ^{3} (STP) cm/(cm^{2} s cm Hg).



A. Matsuoka et al. Separation and Purification Technology 248 (2020) 117018

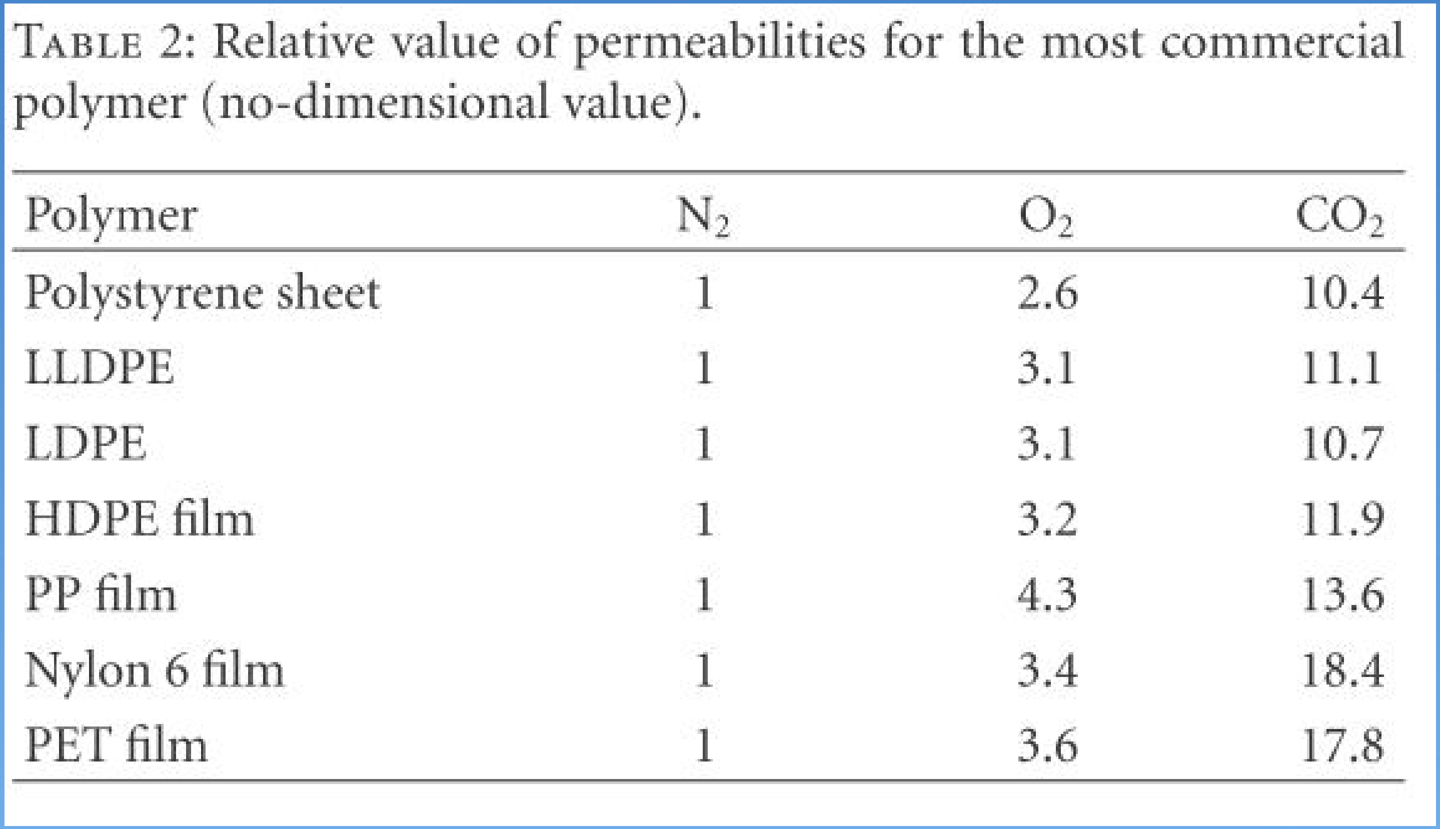


TABLE 2: Relative value of permeabilities for the most commercial polymer (no-dimensional value).

Polymer	N_2	O_2	CO_2
Polystyrene sheet	1	2.6	10.4
LLDPE	1	3.1	11.1
LDPE	1	3.1	10.7
HDPE film	1	3.2	11.9
PP film	1	4.3	13.6
Nylon 6 film	1	3.4	18.4
PET film	1	3.6	17.8

F. Guisheng, et al. Polymer, vol. 36, no. 22, pp. 4345–4346, 1995.

According Cohen –Turnbull model the diffusion coefficient of gases in polymers is as follows:

$$D = A \cdot R \cdot T \exp\left(-\frac{B}{V_f} \right)$$

R - the gas constant,
T - temperature
A and B - empirical constants,
V_f - the average free volume of a polymer,

Average free volume can also be understood as a parameter representing the volume within the polymer, which is unoccupied by polymer chains.

M.H. Cohen, D. Turnbull, J. Chem. Phys. 31 (1959) 1164–1169

$$\ln P = A' - \frac{B'}{V_f}$$

T-E formula:

$$\tau_3[ns] = 0.5\left[1 - \frac{R_f}{R_f + \Delta} + \frac{1}{2\pi}\sin\left(2\pi\frac{R_f}{R_f + \Delta}\right)\right]^{-1}$$

$$V_f = \frac{4\pi}{3}R_f^3$$

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Polymer preparation

The (co)polymers were synthesized from 4,4′-(hexa-fluoroisopropylidene)diphthalic anhydride (6FDA) and a mixture of 3,3′-dihydroxybenzidine (HAB) and 2,3,5,6-tetramethyl-1,4-phenylene diamine (4MPD) in a different molar ratio(HPI-1 – HPI-3), as well as poly(hydroxyimide) derived from 4,4′-bisphenol

A dianhydride (BPADA) and HAB (HPI-5) were chosen as TR membrane precursors to be doped with ionic liquid (IL).

1-Butyl-3-methylimidazolium tetrafluoroborate (IL)

The products are labeled as follows:

HPI-1 (6FDA-HAB),
HPI-2 (6FDA-HAB-4MPD 3:1),
HPI-3 (6FDA-HAB-4MPD 1:1),
HPI-4 (6FDA-4MPD),
HPI-5 (BPADA-HAB)

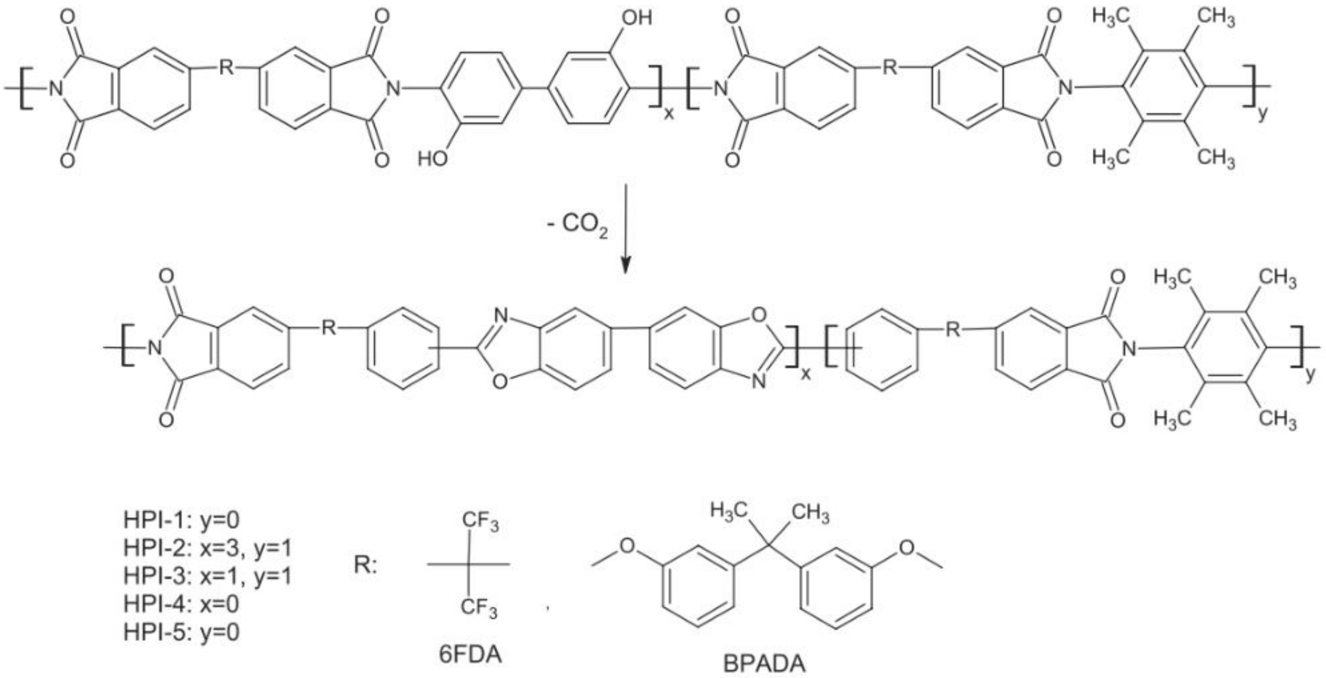
Both, the pure and ionic liquid doped membranes, except for HPI-4 not containing the HAB moiety, were thermally treated to the corresponding polybenzoxazoles (**PBO**s).

The thermal rearrangement was carried out in a tube furnace under an argon atmosphere using a two-step heating program.:

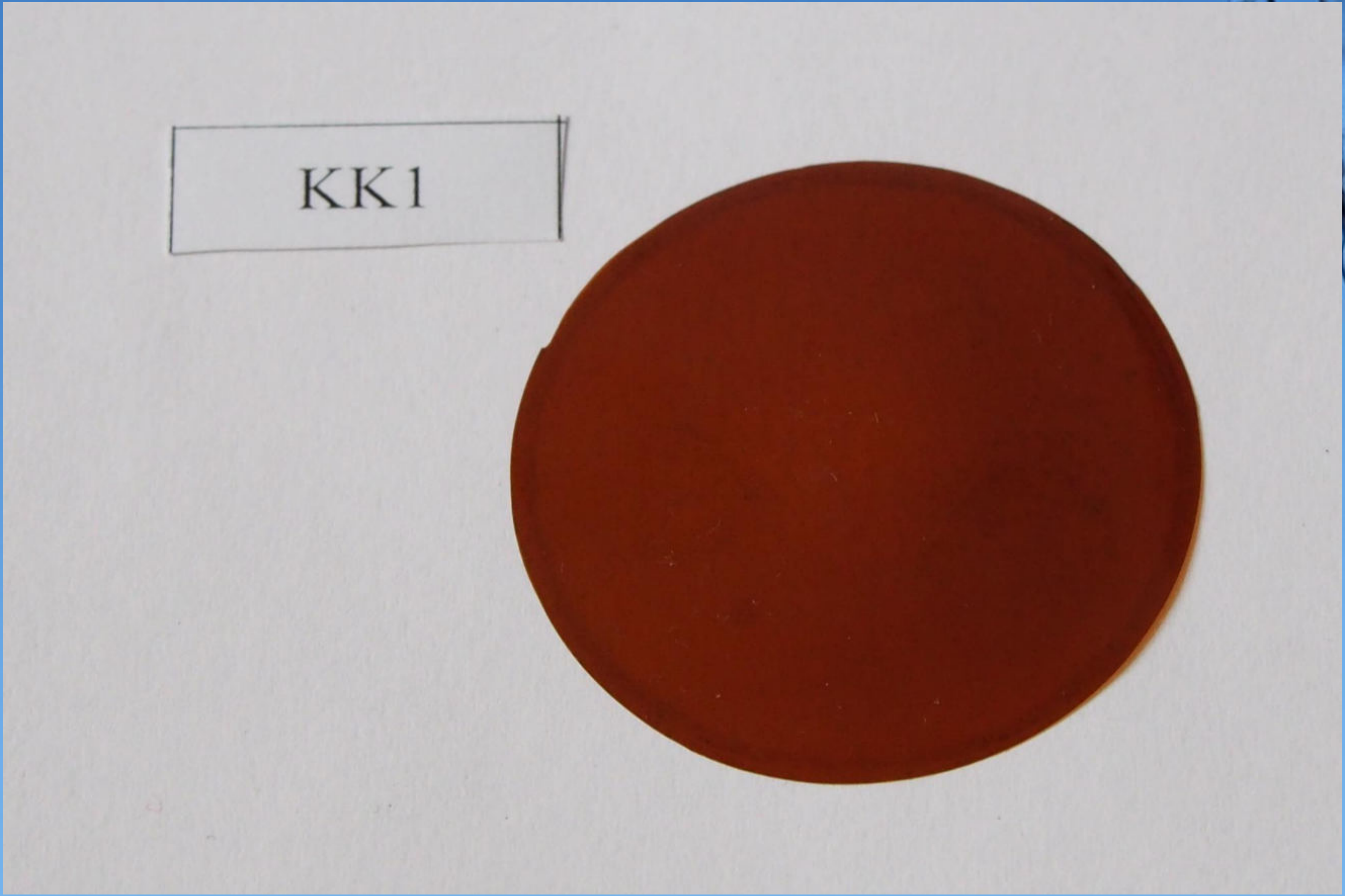
-In the first step, the membrane was gradually heated to 300 °C at a rate of 10 °C min $^{-1}$ and kept at this temperature for an hour.

-In the second step, the tempera ture was raised to 400 °C for the BPADA based membranes or to 440 °C for the 6FDA based ones, at a rate of 5 °C min $^{-1}$.

Chemical structures of studied polymers



Scheme 1. Chemical structures of the studied (co)polyimides (HPI) and schematic representation of thermal rearrangement of HAB based HPIs to PBOs.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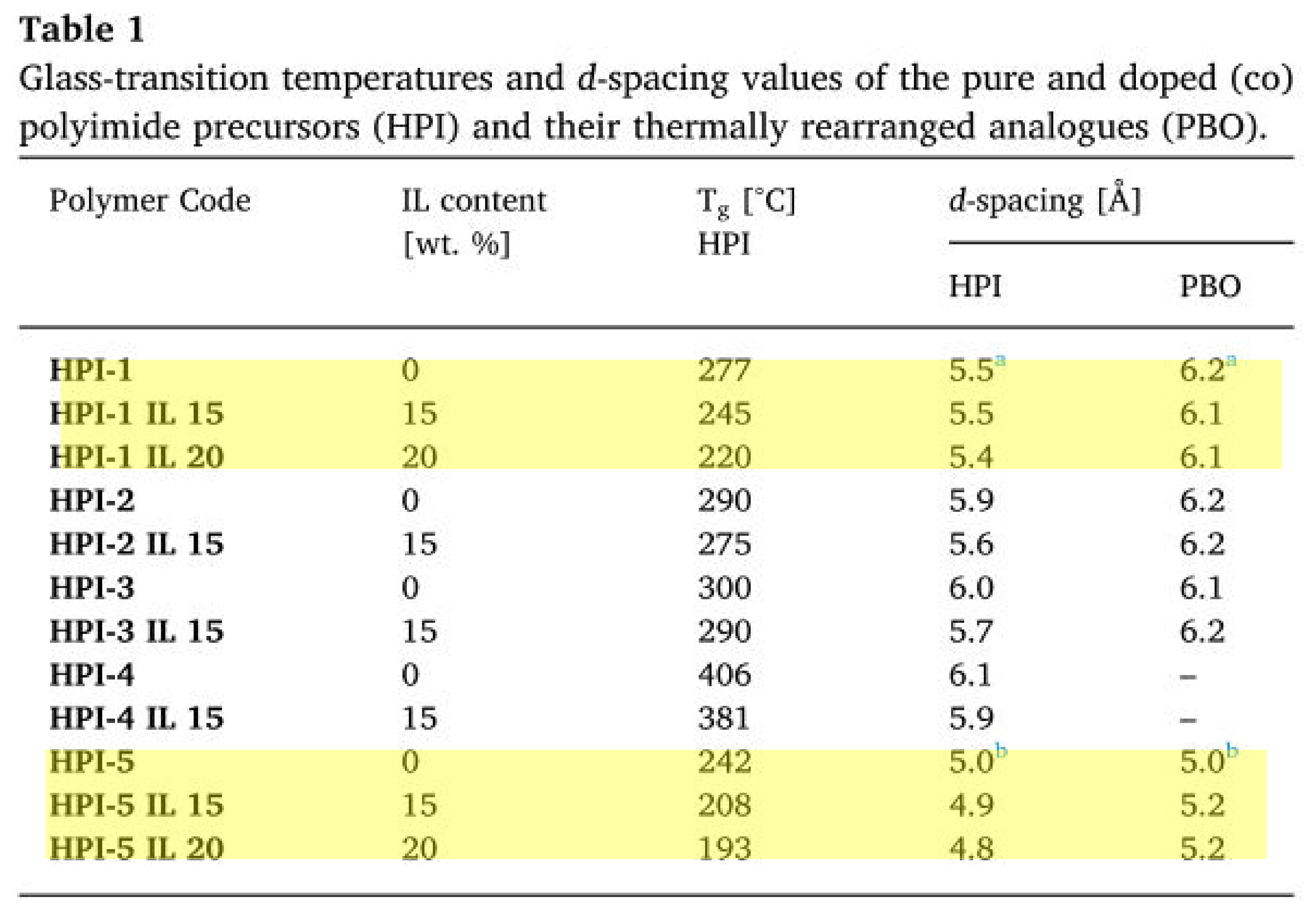
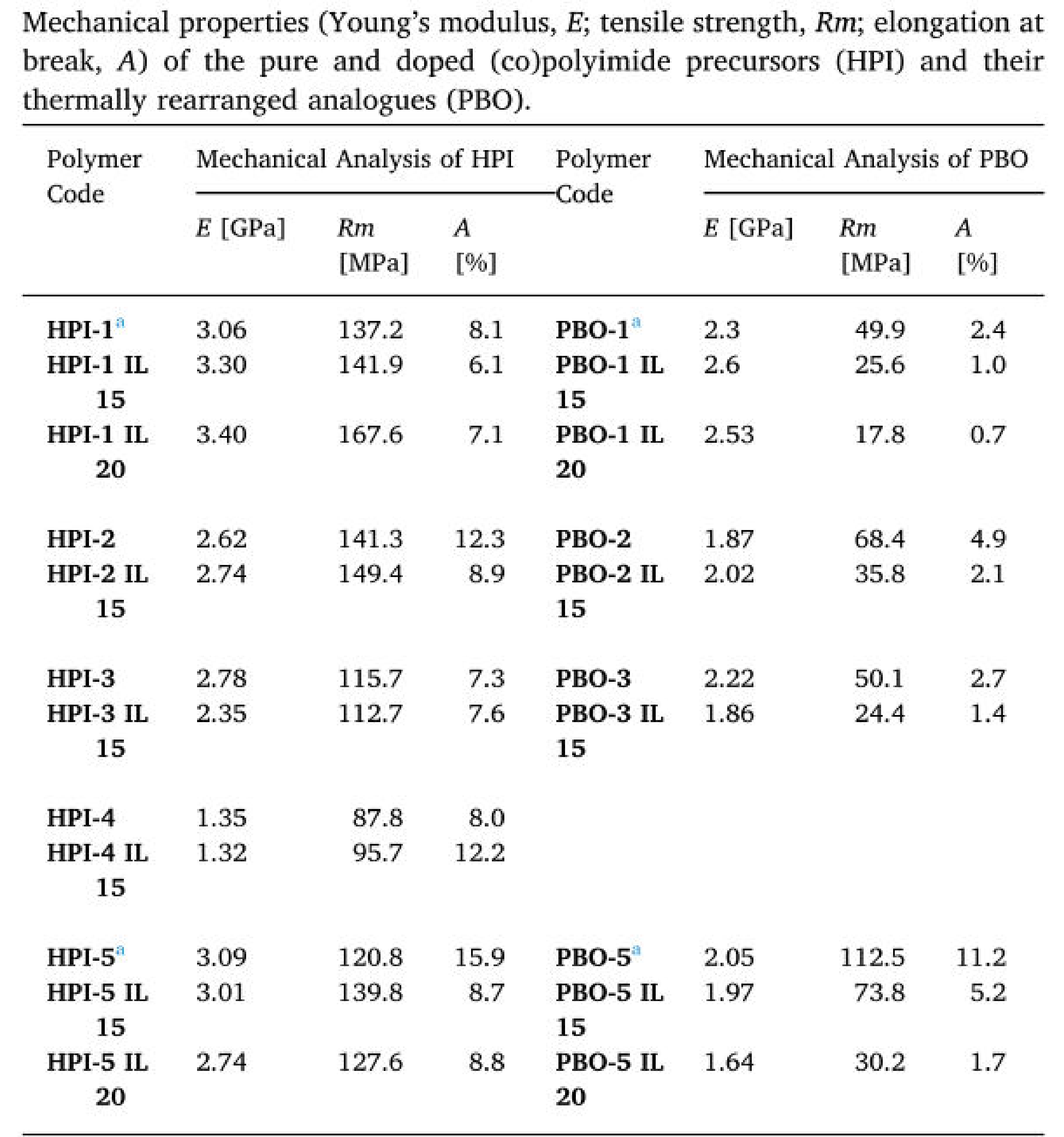


Table 1

Glass-transition temperatures and *d*-spacing values of the pure and doped (co) polyimide precursors (HPI) and their thermally rearranged analogues (PBO).

Polymer Code	IL content [wt. %]	T_g [°C] HPI	*d*-spacing [Å] HPI	*d*-spacing [Å] PBO
HPI-1	0	277	5.5[a]	6.2[a]
HPI-1 IL 15	15	245	5.5	6.1
HPI-1 IL 20	20	220	5.4	6.1
HPI-2	0	290	5.9	6.2
HPI-2 IL 15	15	275	5.6	6.2
HPI-3	0	300	6.0	6.1
HPI-3 IL 15	15	290	5.7	6.2
HPI-4	0	406	6.1	–
HPI-4 IL 15	15	381	5.9	–
HPI-5	0	242	5.0[b]	5.0[b]
HPI-5 IL 15	15	208	4.9	5.2
HPI-5 IL 20	20	193	4.8	5.2



Mechanical properties (Young's modulus, *E*; tensile strength, *Rm*; elongation at break, *A*) of the pure and doped (co)polyimide precursors (HPI) and their thermally rearranged analogues (PBO).

Polymer Code	Mechanical Analysis of HPI			Polymer Code	Mechanical Analysis of PBO		
	E [GPa]	*Rm* [MPa]	*A* [%]		*E* [GPa]	*Rm* [MPa]	*A* [%]
HPI-1[a]	3.06	137.2	8.1	**PBO-1**[a]	2.3	49.9	2.4
HPI-1 IL 15	3.30	141.9	6.1	**PBO-1 IL 15**	2.6	25.6	1.0
HPI-1 IL 20	3.40	167.6	7.1	**PBO-1 IL 20**	2.53	17.8	0.7
HPI-2	2.62	141.3	12.3	**PBO-2**	1.87	68.4	4.9
HPI-2 IL 15	2.74	149.4	8.9	**PBO-2 IL 15**	2.02	35.8	2.1
HPI-3	2.78	115.7	7.3	**PBO-3**	2.22	50.1	2.7
HPI-3 IL 15	2.35	112.7	7.6	**PBO-3 IL 15**	1.86	24.4	1.4
HPI-4	1.35	87.8	8.0				
HPI-4 IL 15	1.32	95.7	12.2				
HPI-5[a]	3.09	120.8	15.9	**PBO-5**[a]	2.05	112.5	11.2
HPI-5 IL 15	3.01	139.8	8.7	**PBO-5 IL 15**	1.97	73.8	5.2
HPI-5 IL 20	2.74	127.6	8.8	**PBO-5 IL 20**	1.64	30.2	1.7

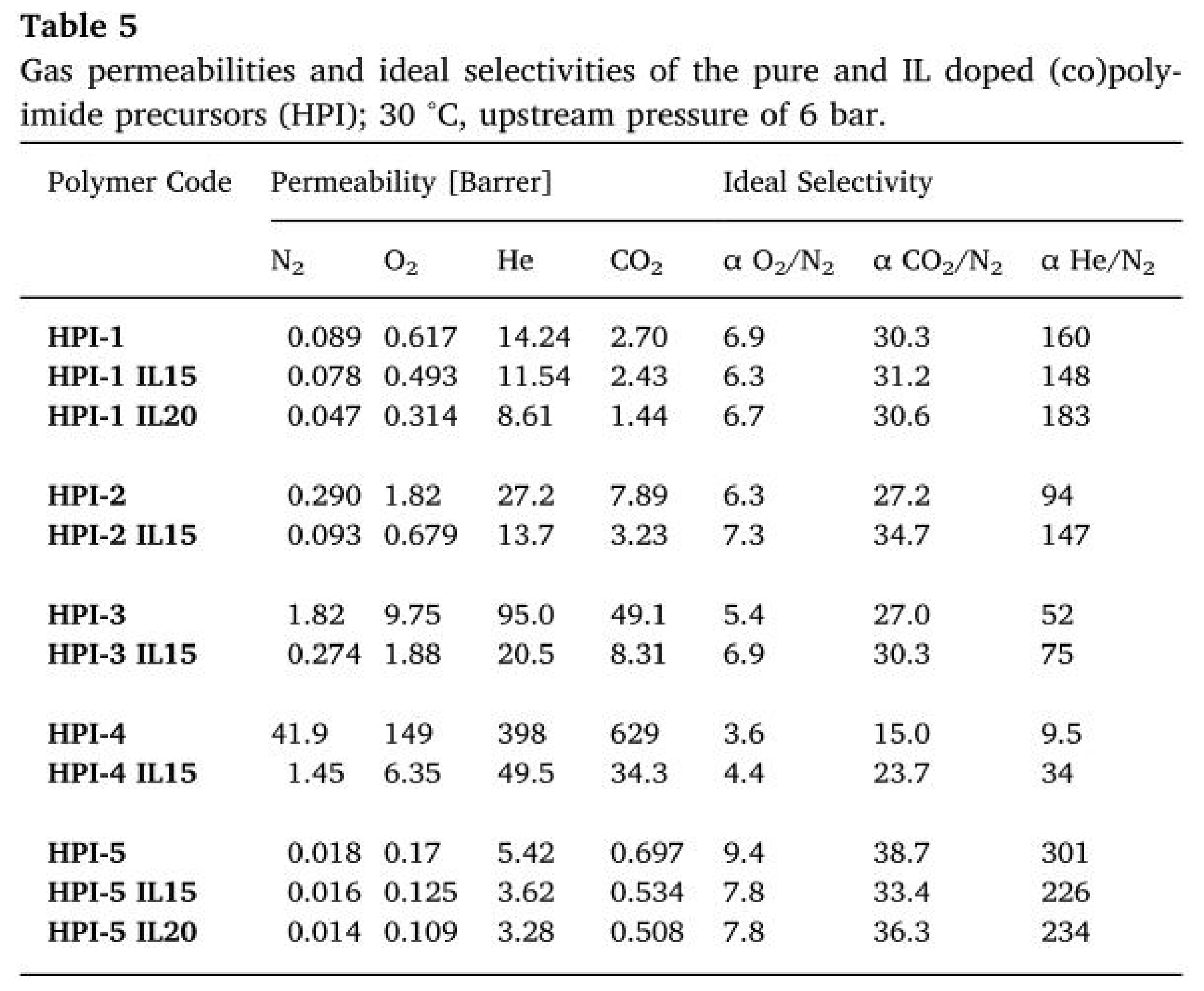


Table 5

Gas permeabilities and ideal selectivities of the pure and IL doped (co)polyimide precursors (HPI); 30 °C, upstream pressure of 6 bar.

Polymer Code	Permeability [Barrer]				Ideal Selectivity		
	N_2	O_2	He	CO_2	α O_2/N_2	α CO_2/N_2	α He/N_2
HPI-1	0.089	0.617	14.24	2.70	6.9	30.3	160
HPI-1 IL15	0.078	0.493	11.54	2.43	6.3	31.2	148
HPI-1 IL20	0.047	0.314	8.61	1.44	6.7	30.6	183
HPI-2	0.290	1.82	27.2	7.89	6.3	27.2	94
HPI-2 IL15	0.093	0.679	13.7	3.23	7.3	34.7	147
HPI-3	1.82	9.75	95.0	49.1	5.4	27.0	52
HPI-3 IL15	0.274	1.88	20.5	8.31	6.9	30.3	75
HPI-4	41.9	149	398	629	3.6	15.0	9.5
HPI-4 IL15	1.45	6.35	49.5	34.3	4.4	23.7	34
HPI-5	0.018	0.17	5.42	0.697	9.4	38.7	301
HPI-5 IL15	0.016	0.125	3.62	0.534	7.8	33.4	226
HPI-5 IL20	0.014	0.109	3.28	0.508	7.8	36.3	234

P N_2 (3.64 Å) < P O_2 (3.46 Å) < P CO_2 (3.3 Å) < P He (2.6 Å)

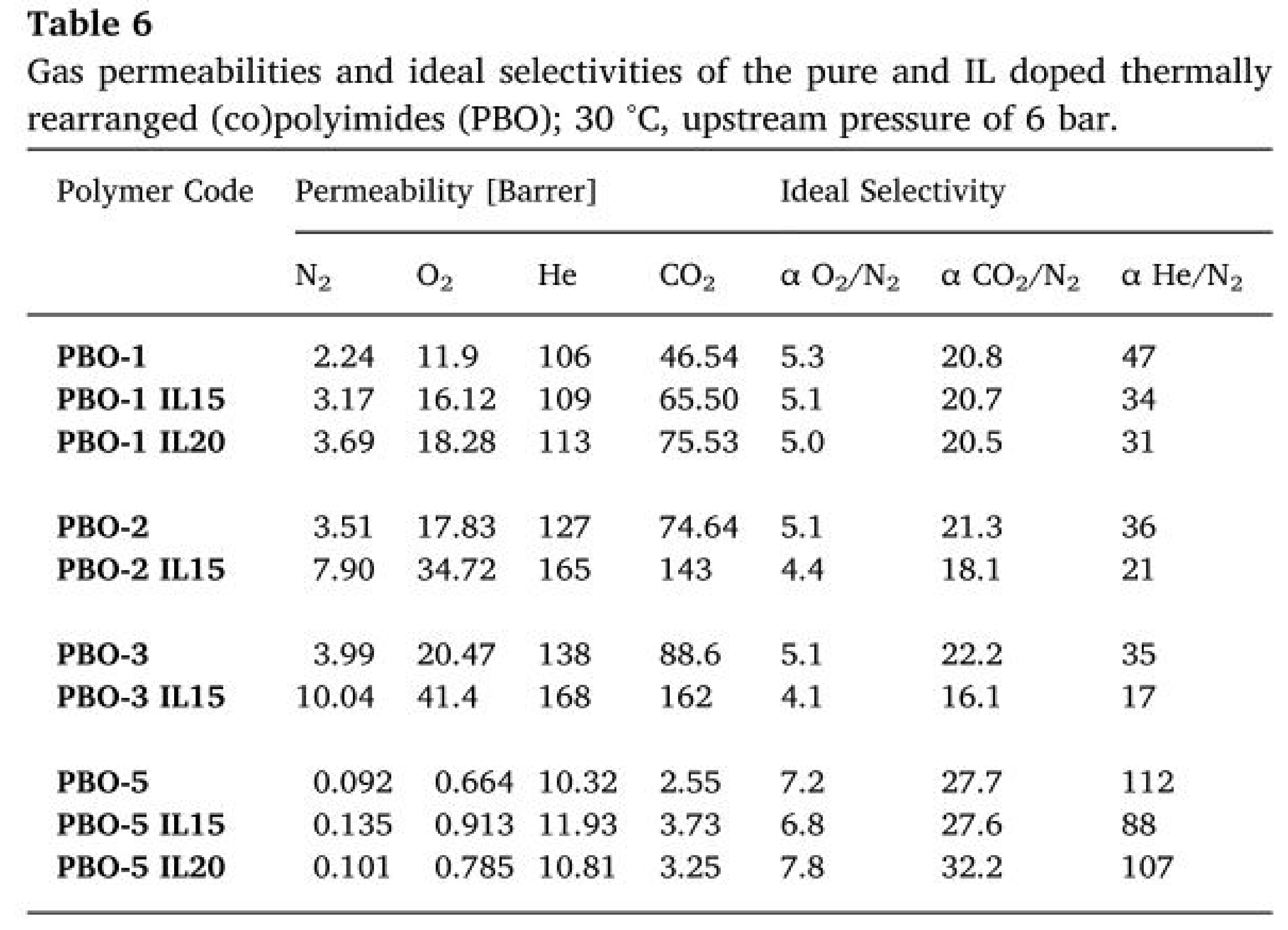


Table 6

Gas permeabilities and ideal selectivities of the pure and IL doped thermally rearranged (co)polyimides (PBO); 30 °C, upstream pressure of 6 bar.

Polymer Code	Permeability [Barrer]				Ideal Selectivity		
	N_2	O_2	He	CO_2	α O_2/N_2	α CO_2/N_2	α He/N_2
PBO-1	2.24	11.9	106	46.54	5.3	20.8	47
PBO-1 IL15	3.17	16.12	109	65.50	5.1	20.7	34
PBO-1 IL20	3.69	18.28	113	75.53	5.0	20.5	31
PBO-2	3.51	17.83	127	74.64	5.1	21.3	36
PBO-2 IL15	7.90	34.72	165	143	4.4	18.1	21
PBO-3	3.99	20.47	138	88.6	5.1	22.2	35
PBO-3 IL15	10.04	41.4	168	162	4.1	16.1	17
PBO-5	0.092	0.664	10.32	2.55	7.2	27.7	112
PBO-5 IL15	0.135	0.913	11.93	3.73	6.8	27.6	88
PBO-5 IL20	0.101	0.785	10.81	3.25	7.8	32.2	107

N_2 (3.64 Å) < O_2 (3.46 Å) < CO_2 (3.3 Å) < He (2.6 Å)

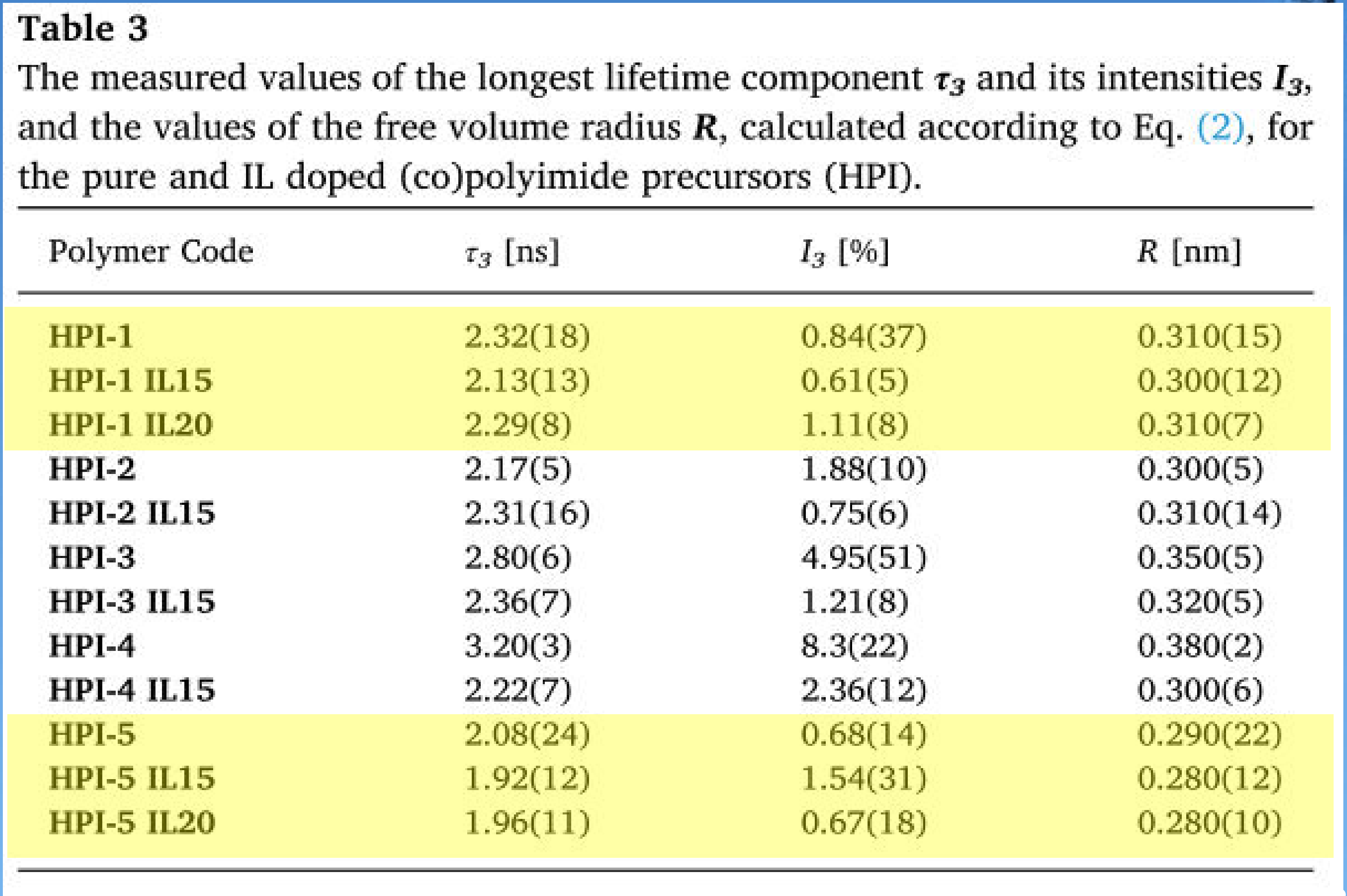


Table 3

The measured values of the longest lifetime component τ_3 and its intensities I_3, and the values of the free volume radius R, calculated according to Eq. (2), for the pure and IL doped (co)polyimide precursors (HPI).

Polymer Code	τ_3 [ns]	I_3 [%]	R [nm]
HPI-1	2.32(18)	0.84(37)	0.310(15)
HPI-1 IL15	2.13(13)	0.61(5)	0.300(12)
HPI-1 IL20	2.29(8)	1.11(8)	0.310(7)
HPI-2	2.17(5)	1.88(10)	0.300(5)
HPI-2 IL15	2.31(16)	0.75(6)	0.310(14)
HPI-3	2.80(6)	4.95(51)	0.350(5)
HPI-3 IL15	2.36(7)	1.21(8)	0.320(5)
HPI-4	3.20(3)	8.3(22)	0.380(2)
HPI-4 IL15	2.22(7)	2.36(12)	0.300(6)
HPI-5	2.08(24)	0.68(14)	0.290(22)
HPI-5 IL15	1.92(12)	1.54(31)	0.280(12)
HPI-5 IL20	1.96(11)	0.67(18)	0.280(10)

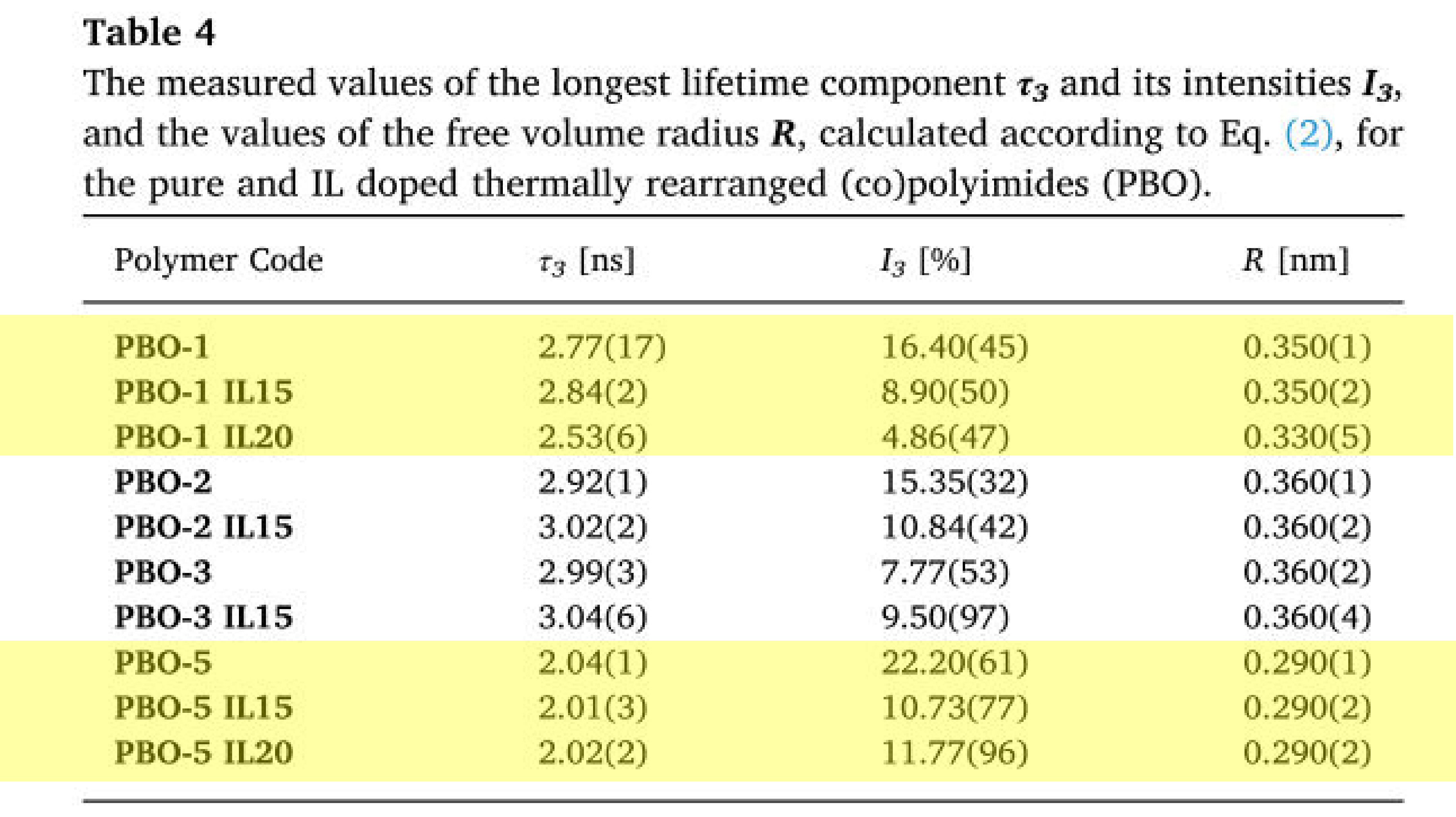


Table 4

The measured values of the longest lifetime component τ_3 and its intensities I_3, and the values of the free volume radius R, calculated according to Eq. (2), for the pure and IL doped thermally rearranged (co)polyimides (PBO).

Polymer Code	τ_3 [ns]	I_3 [%]	R [nm]
PBO-1	2.77(17)	16.40(45)	0.350(1)
PBO-1 IL15	2.84(2)	8.90(50)	0.350(2)
PBO-1 IL20	2.53(6)	4.86(47)	0.330(5)
PBO-2	2.92(1)	15.35(32)	0.360(1)
PBO-2 IL15	3.02(2)	10.84(42)	0.360(2)
PBO-3	2.99(3)	7.77(53)	0.360(2)
PBO-3 IL15	3.04(6)	9.50(97)	0.360(4)
PBO-5	2.04(1)	22.20(61)	0.290(1)
PBO-5 IL15	2.01(3)	10.73(77)	0.290(2)
PBO-5 IL20	2.02(2)	11.77(96)	0.290(2)

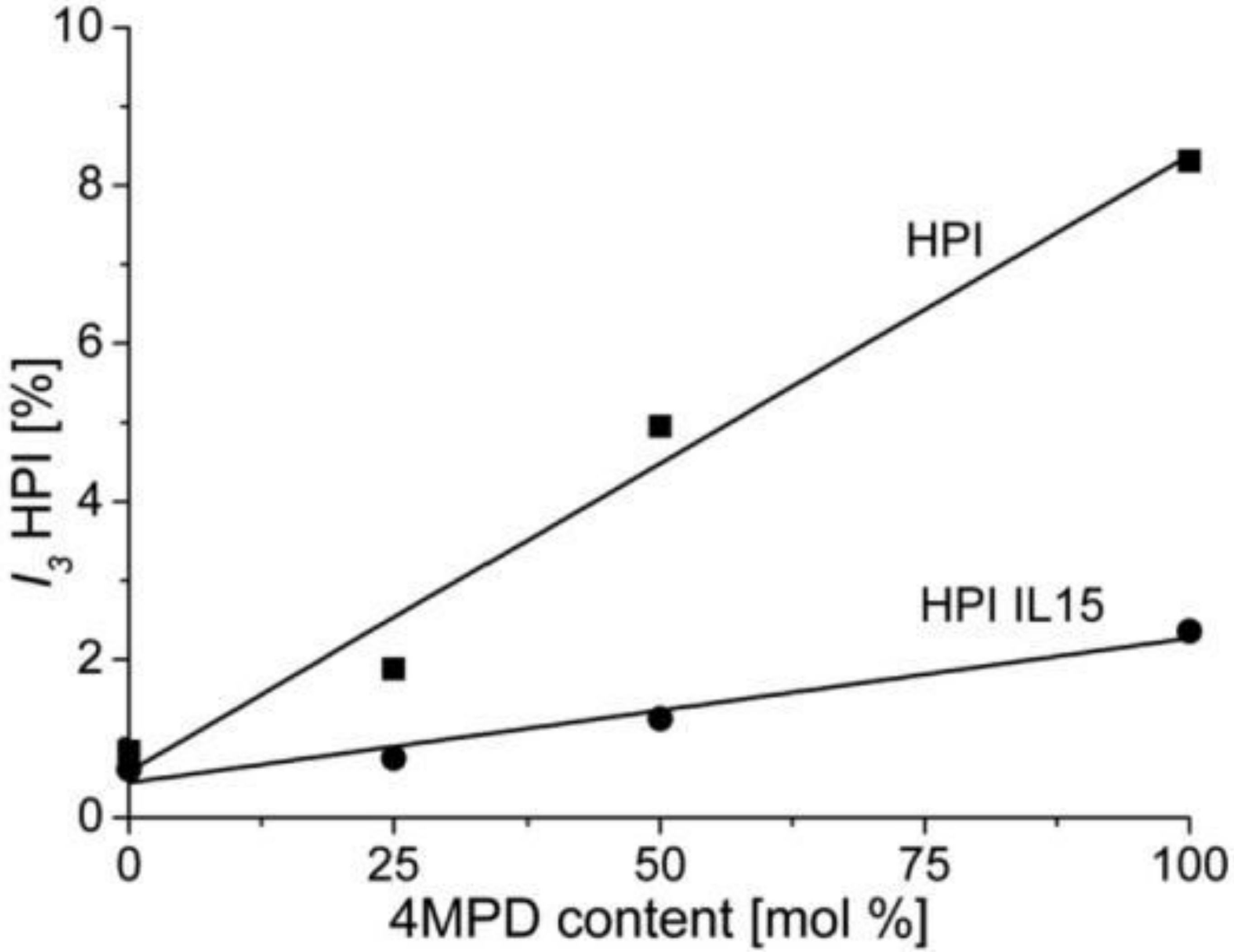
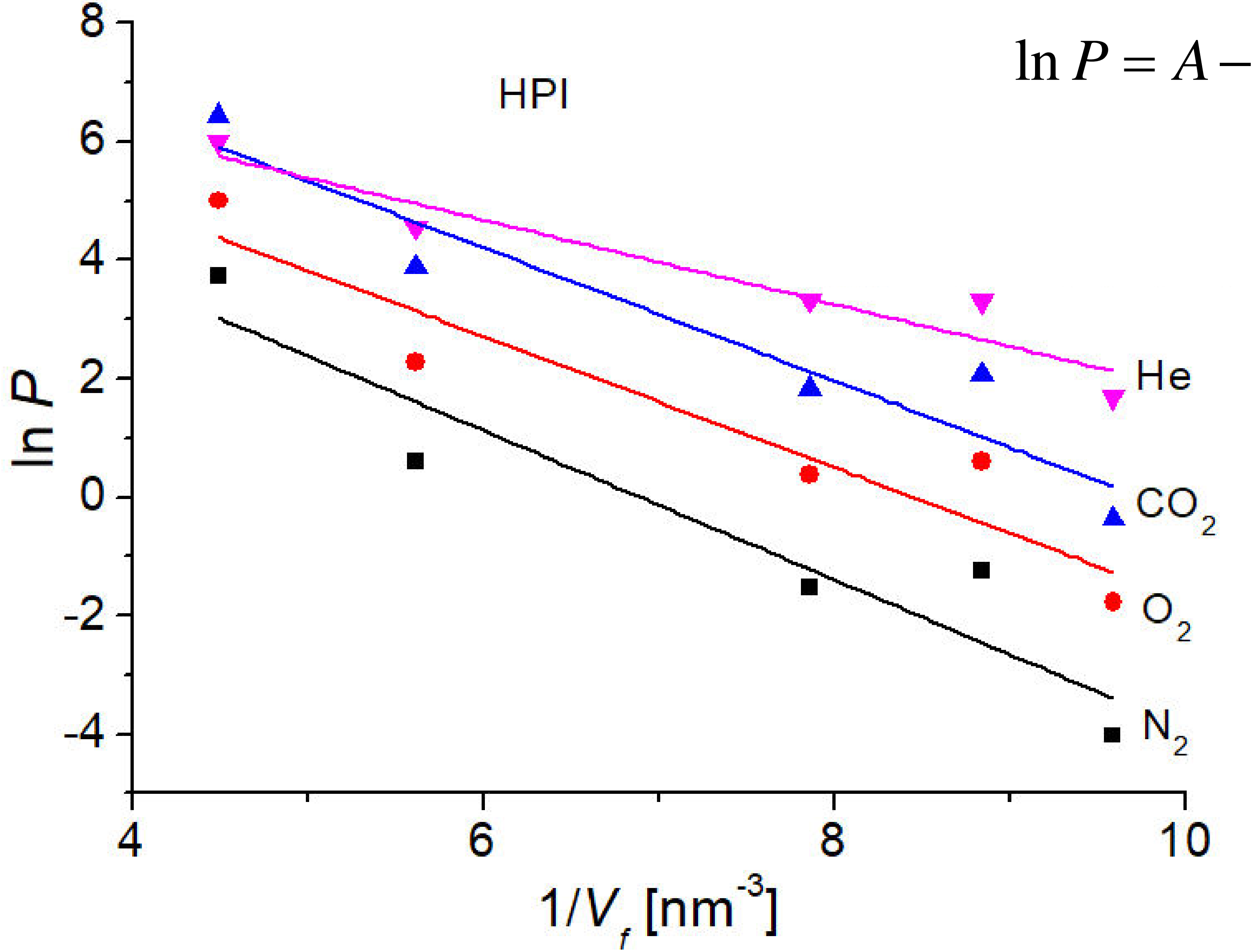
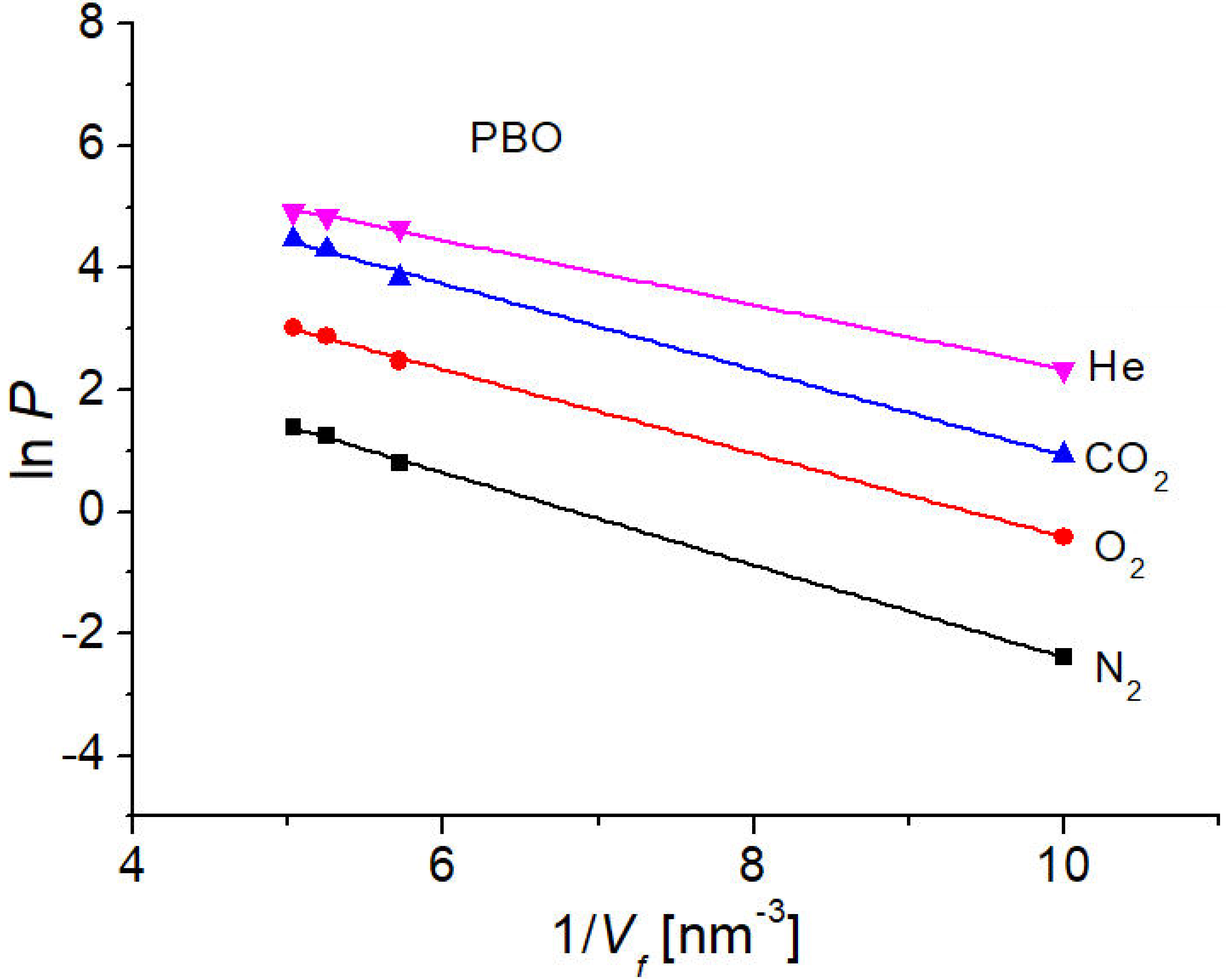
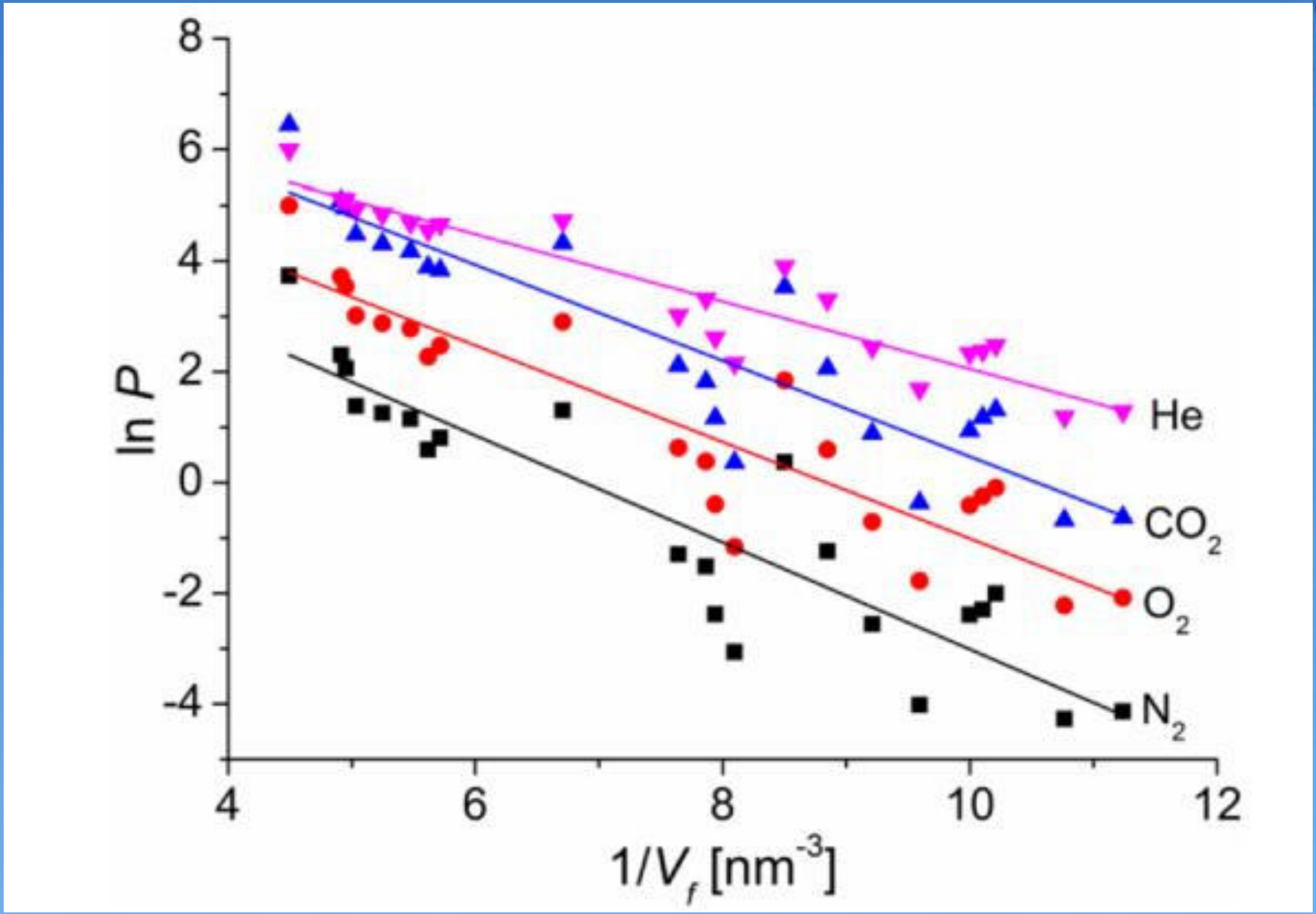


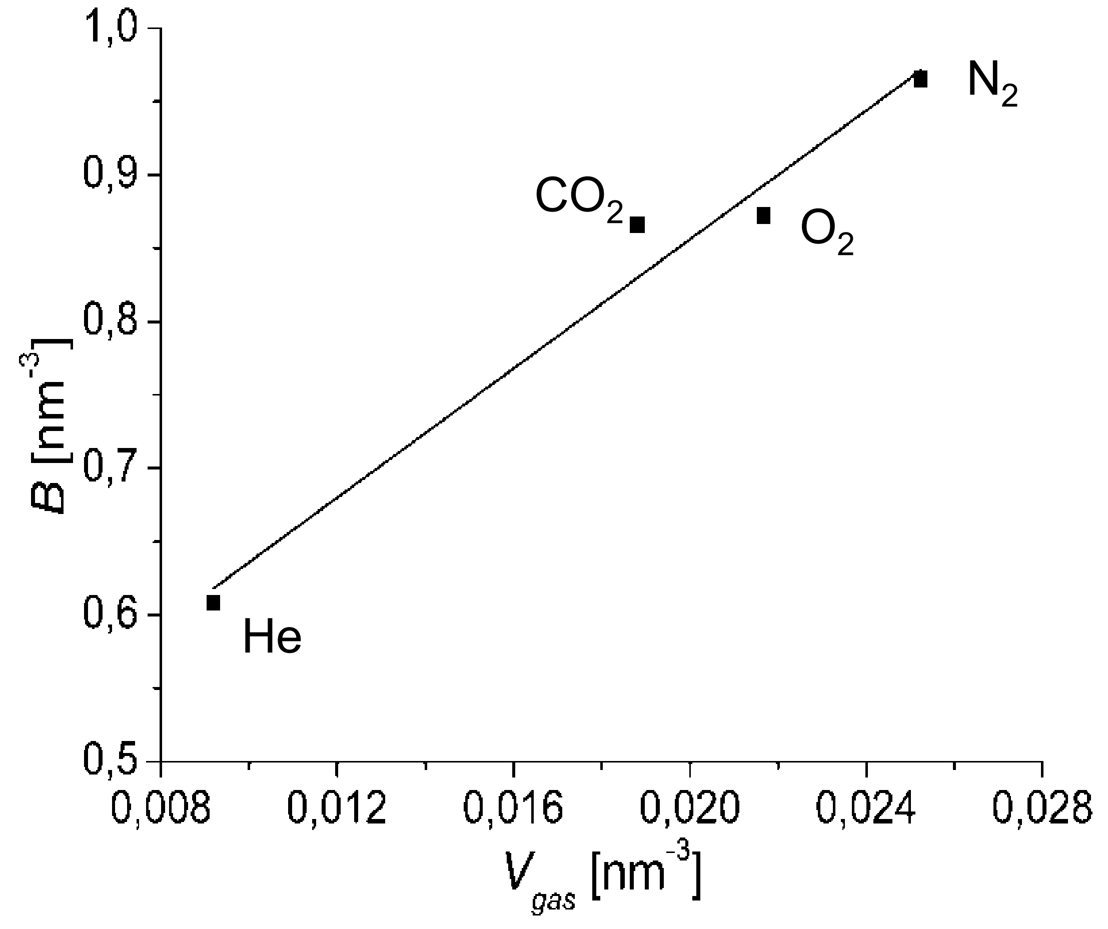
Fig. 3. Intensities, I_3, of *o*-Ps annihilation in the pure and IL doped 6FDA based (co)polyimides. I_3 is taken from Table 3.

$$\ln P = A - \frac{B}{V_f}$$




PBO
ln P
1/V_f [nm^{-3}]
8
6
4
2
0
-2
-4
4
6
8
10
He
CO_2
O_2
N_2


ln P
8
6
4
2
0
-2
-4
4
6
8
10
12
$1/V_f$ [nm^{-3}]
He
CO$_2$
O$_2$
N$_2$



$$\ln P = A - \frac{B}{V_f}$$

The values of the empirical constant *B* from determined from fitting of Eq.(11) to data from figures as the function of volume of the gas molecules calculated using kinetic diameter values. The straight line represents a linear function fitted to the experimental data.

He (2.6Å) < CO_2 (3.3 Å) < O_2 (3.46 Å) < H_2 (3.64 Å)

Summary

The addition of IL was found to have a strong impact on the physical properties, thermal conversion process, as well as gas transport properties of the doped polymers.

The reduced T_g of the precursors (e.g. by 57 °C), and significantly decreased temperature of their conversion to PBO (e.g. by 126 °C) were observed as a result of IL doping.

By fitting the permeability and free volume size data to the Cohen-Turnbull model, it appeared that free volume determined by PALS strongly determines the permeability of gas molecules in these systems,

Separation and Purification Technology 254 (2021) 117664

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Separation and Purification Technology

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