

## **Poly(butylene terephthalate-co-5-*tert*-butyl isophthalate) copolyesters. Synthesis, characterization and properties**

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### **Abstract**

A series of poly(butylene terephthalate) copolyesters containing 5-*tert*-butyl isophthalate units up to 50%-mole, as well as the homopolyester entirely made of these units, were prepared by polycondensation from the melt. The microstructure of the copolymers was determined by NMR to be at random for the whole range of compositions. The effect exerted by the 5-*tert*-butyl isophthalate units on thermal, tensile and gas transport properties was evaluated. Both  $T_m$  and crystallinity as well as the mechanical moduli were found to decrease steadily with copolymerization whereas  $T_g$  increased and the polyesters became more brittle. Permeability and solubility slightly increased also with the content in substituted units whereas the diffusion coefficient remained practically constant. For the homopolyester poly(5-*tert*-butyl isophthalate), all these properties were found to deviate significantly from the general trend displayed by copolyesters suggesting that a different chain mode of packing in the amorphous phase is likely adopted in this case.

## Introduction

Poly(butylene terephthalate) (PBT) is a semicrystalline thermoplastic widely used in the manufacturing of durable goods formed by injection-molding. The specific advantages that make PBT the plastic of choice over poly(ethylene terephthalate) (PET) and nylons are its high crystallization rate and crystallinity, and its low affinity for water. Fast crystallization allows injection-molding with short cycle times with production of pieces with high dimensional stability. Since PBT absorbs less than 0.1% of water, its thermal and mechanical properties are essentially unaffected by moisture. These characteristics justify the commercial success of PBT in spite of being made of a more expensive raw material (1,4-butanediol vs. ethylene glycol) and to exhibit lower melting point and slightly poorer mechanical properties than PET.<sup>1</sup>

Most of PBT is mainly used in blends to give a balance of properties for different injection-molding applications. PET, polycarbonate and styrenic copolymers are extensively used for this end. In most cases, the second ingredient is added in minor amounts, so PBT invariably constitutes the continuous phase of the blended material.<sup>2</sup> A variety of optical, mechanical and surface properties can be improved by blending. In some cases, transesterification reactions take place upon blending which leads to copolymers with high phase compatibility and stability.<sup>3</sup>

Copolymerization is becoming more and more attractive, both for industrial and academic interests, as a convenient way to develop new materials with improved properties and processability. Copolymerization addressed to the modification of the technical properties is a sustained research activity in the PBT field,<sup>4,5</sup> in which the realization of the present work should be framed. Recently we have reported on PET copolymers containing 5-*tert*-butyl isophthalate units.<sup>6</sup> In these copolymers, the presence of the asymmetrical isophthalic structure combined with the bulkiness of the *tert*-butyl group introduced significant changes in the crystallizability, mechanical behavior and gas transport properties of PET. It was there observed that the inserted substituted isophthalate units are unable to enter in the poly(ethylene terephthalate) crystal lattice.

In this contribution, we want to report on the synthesis and characterization of the copolymers resulting from the polycondensation of 1,4-butanediol with mixtures of dimethyl terephthalate and 5-*tert*-butyl isophthalate acid. The thermal, mechanical and transport to gasses properties of the new copolymers are examined in order to evaluate the influence of the copolymerization in the behavior pattern of PBT. A

detailed study of the crystal structure and crystallization kinetics of these copolymers will be reported in a soon coming paper.

## Experimental section

1,4-Dimethyl terephthalate (DMT) (99+%) and 5-*tert*-butyl isophthalic acid (<sup>t</sup>BIA) (99+%) were purchased from Sigma-Aldrich Co. Both comonomers were used without further purification. 1,4-butanediol (BD) (99+%, Sigma-Aldrich Co.) was reagent grade and used as received. Tetrabutyl titanate (TBT) catalyst (Merck-Schuchardt) was used without further purification. Solvents used for purification and characterization, e.g. trifluoroacetic acid (TFA), chloroform, diethyl ether, dichloroacetic acid, and other solvents used in solubility experiments were all of either technical or high purity grade, and used as received.

## Synthesis

For the synthesis of PBT homopolyester, DMT and BD in a molar ratio 1:2.2, and TBT were introduced into a three-necked 100 mL round-bottom flask equipped with a mechanical stirrer, a nitrogen inlet, and a vacuum distillation outlet. The temperature was raised to 190 °C and the mixture was stirred for 5 h under a steady nitrogen flow. Approximately 0.6 mmol of TBT catalyst per mole of monomer was used. Polycondensation was then performed at 260 °C under a pressure of 0.3-0.5 mbar. The polymerization was allowed to proceed at this temperature for 2 h, after which, a high viscous liquid was obtained. The reaction mixture was then cooled down to room temperature and atmospheric pressure was recovered with nitrogen flow to prevent degradation. The solid mass was dissolved in chloroform/TFA 8/1(v/v) and the polymer precipitated with cold diethyl ether, collected by filtration and extensively washed with cold methanol and diethyl ether.

Essentially the same procedure was applied for the synthesis of PB<sup>t</sup>BI using a <sup>t</sup>BIA:BD molar ratio of 1:3. In this case, however, the polycondensation reaction was conducted at 240 °C for 3h and pure chloroform was used for dissolving the crude polymer. Copolyesters PBT<sup>t</sup>BI were prepared using a mixture of DMT and <sup>t</sup>BIA in the selected proportions and the 3:1 molar ratio of diol to diacid being applied now to the sum of the two diacidic comonomers.

## Measurements

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AMX-300 spectrometer at 25.0 °C operating at 300.1 and 75.5 MHz, respectively. Polyesters and copolyesters were dissolved in trifluoroacetic acid (TFA) and spectra were internally referenced to tetramethylsilane (TMS). 10 mg and 50 mg of sample dissolved in 1 mL of deuterated solvent were used for  $^1\text{H}$  and  $^{13}\text{C}$ , respectively. 64 scans were acquired for  $^1\text{H}$  and 1,000 to 10,000 for  $^{13}\text{C}$  with 32 and 64 K data points and relaxation delays of 1 and 2 s, respectively. For quantitative  $^{13}\text{C}$  NMR analysis of the microstructure, signals due to carbonyl carbons of terephthalic and 5-*tert*-butyl isophthalic units were used. Both type of carbons have similar spin-lattice relaxation times ( $T_1$ ) and NOE effects. This fact was corroborated by comparing the composition calculated from  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

Intrinsic viscosities of the polymers dissolved in dichloroacetic acid were measured using an Ubbelohde viscometer thermostated at  $25 \pm 0.1$  °C. Gel permeation chromatography (GPC) was carried out using an *o*-chlorophenol / chloroform mixture (1/9 v/v) as the mobile phase at 35 °C. GPC analysis was performed on a Waters GPC system equipped with a refractive index detector. Two 7.8 mm x 300 mm Styragel columns packed with divinylbenzene cross-linked polystyrene (pore size  $10^3$  and  $10^4$  Å) in series were used for the analysis with the above-mentioned eluent at a flow rate of 0.5 mL min<sup>-1</sup>. Molecular weights and molecular weight distributions were calculated against monodisperse polystyrene standards using the Maxima 820 software.

The thermal behavior of the polyesters was examined by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC Pyris 1 calibrated with indium. DSC data were obtained from 4-6 mg samples under nitrogen circulation. Heating/cooling rates of 10 °C min<sup>-1</sup> were routinely used except for determination of glass temperatures, where the heating rate was 20 °C min<sup>-1</sup>. Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA-6 thermobalance at a heating rate of 10 °C min<sup>-1</sup> under a nitrogen atmosphere.

Tensile tests were performed on rectangular specimens (40 mm x 5 mm) cut from 200 µm-thick films, which were obtained by melt compression. For this the material was sandwiched between two steel platens covered with teflon-coated aluminum foil and appropriate spacers were used to control the thickness of the film. The platens were placed in a press and heated at a temperature 20 °C above the  $T_m$  of the corresponding polymer for 5 min. Successive increasing pressures of 13, 25 and 50 kg cm<sup>-2</sup> were then applied, the platens being held at each pressure for 1 min. Finally the pressure was released and the platens quenched in cold water. DSC thermograms

from these films showed no signs of crystallinity. The probes were stored under vacuum for 48 h before use. The tensile tests were conducted at room temperature on a Zwick BZ2.5/TN1S universal tensile testing apparatus operating at a constant cross-head speed of 10-mm min<sup>-1</sup> using a 0.5 N pre-load and a grip-to-grip separation of 20 mm. All reported tensile data represent an average of at least three independent measurements.

Gas transport properties of amorphous films of PBT<sub>70</sub><sup>t</sup>BI<sub>30</sub>, PBT<sub>50</sub><sup>t</sup>BI<sub>50</sub> copolyesters and PB<sup>t</sup>BI polyester were determined at 25 °C using films prepared also by hot pressing. The thickness of the prepared films ranged between 40 and 80 μm. It was calculated as the arithmetic average of a good number of measurements with a micrometer over the area of the sheet. The transport properties of the polyesters films were tested with nitrogen, oxygen, and carbon dioxide.

## Results and discussion

The PBT<sup>t</sup>BI copolyesters described in this work were prepared by a two-step melt-polycondensation as indicated in [Scheme I](#). We have previously used this procedure in the preparation of PET copolymers containing 5-*tert*-butyl isophthalic acid units. Transesterification of DMT and esterification of <sup>t</sup>BIA with 1,4-butanediol to form low-molecular weight hydroxy-capped esters took place in the first stage. This process evolved at 190-220 °C with generation of methanol and water, which were continuously removed from the system to drive the reaction in the desired direction. Copolycondensation of these compounds leading to PBT<sup>t</sup>BI copolyesters took place in the second step at higher temperature and under vacuum conditions to eliminate the excess of BD. The copolymers obtained by this procedure are listed in [Table I](#), where their compositions, viscosities, molecular weights and feed comonomer contents used in each case are given. The homopolyesters PBT and PB<sup>t</sup>BI were prepared by the same procedure for comparison purposes and their data have been also included in [Table I](#).

### [Scheme I](#); [Table I](#)

The chemical structure of the polyesters was ascertained by NMR spectroscopy. Both <sup>1</sup>H and <sup>13</sup>C NMR spectra recorded from TFA solution afforded clear differences in the chemical shifts of the signals arising from BT and B<sup>t</sup>BI, which could

be used to estimate the copolymer composition and to determine the microstructure of the chain. Representative examples of these spectra are depicted in Figure 1. Labeling used to identify these signals are indicated in Scheme II and chemical shifts values for the copolymers and the parent homopolymers PBT and PBT<sup>t</sup>BI are compared in Table II. The compositions of the copolymers in BT and B<sup>t</sup>BI units determined from the data afforded by the <sup>1</sup>H NMR spectra are given in Table I.

Figure 1; Scheme II; Table II

As it is shown in Figure 2, carbonyl signals in <sup>13</sup>C NMR spectra appeared split in three or four peaks corresponding to the triads structures that are feasible to occur in the copolyester. Quantification of the peak areas led to determine the content in terephthalate-centered triads (TTT, *tTt* and *TTt* or *tTT*) and *tert*-butyl isophthalate-centered triads (*TtT*, *ttt* and *Ttt* or *ttT*). The triad compositions were then used to calculate the average sequence lengths and the randomness of each copolymer. Experimental and calculated values for the different copolyesters are collected in Table III. The correspondence between experimental results and the Bernoulli functions for each type of triad is illustrated in Figure 3. We have used previously this methodology in the analysis of PET<sup>t</sup>BI copolyesters.<sup>6b</sup>

Figure 2; Table III; Figure 3

The NMR analysis clearly indicated that a) the composition of the resulting copolymer is essentially the same as that of the feed from which it is generated, and b) the copolymers have a microstructure with the terephthalate and isophthalate units distributed along the chain almost perfectly at random. Such a result could be rather striking since the free 5-*tert*-butyl isophthalic acid had to compete with the terephthalate dimethyl ester. Apparently any preference for the diol existing at the esterification reaction must be then mitigated by extensive transesterification that presumably takes place in the later stage of the process. Similar results were previously observed in the preparation of PET<sup>t</sup>BI copolymers, which were obtained by reaction of the same mixture of diacid and dimethyl ester with ethylene glycol.

The thermal behavior of PBT<sup>t</sup>BI copolyesters was examined by TGA and DSC. Thermograms recorded from PBT<sup>t</sup>BI copolyesters are reproduced in Figure 4 for illustration, and data obtained for the whole set of polyesters are compared in Table IV. PBT is a polyester that distinguishes by its high thermal stability.<sup>8</sup> The TGA analysis showed that the thermal stability of PBT seems to be slightly increased by copolymerization with <sup>t</sup>BIA. As it is shown in Table IV, the whole decomposition process seems to be delayed as the content in <sup>t</sup>BI units increases. This effect must be associated to the mere presence of isophthalic structures in the polyester chain rather than to the *tert*-butyl group since a similar increase in the decomposition temperature is also observed for the homopolymer PBI.

#### Figure 4; Table IV

DSC analysis revealed that  $T_g$  increases steadily along the series with the content in <sup>t</sup>BI units. This effect is exactly the same as that observed for PET copolymers containing the same units and corroborates the strong ability that the *tert*-butyl isophthalate unit has to restrict the chain mobility.<sup>6b</sup> This effect is also reflected in the “crystallizability” of the copolyesters, which appears to diminish with copolymerization. Both crystallinity and melting temperature descend with the content in *tert*-butyl units, and only copolymers containing a maximum of 20% of such units are able to crystallize from the melt in sufficient amount as to be detected by conventional calorimetry. These results together with those previously obtained with PET<sup>t</sup>BI copolyesters, bring into evidence the efficiency of the <sup>t</sup>BI structure to hinder the crystallization process in aromatic polyesters. Nevertheless, it is noteworthy that melting is still observable for PBT<sup>t</sup>BI containing up to 50% of <sup>t</sup>BI units. This is really striking provided that we are dealing with random copolymers with an average sequence length of 2-3 units. Doi et al have reported the presence of crystallinity in PBT copolymers with a content in butylene terephthalate units lower than 50 % and explain their observations by the occurrence of extremely thin lamellae with a thickness of ~2-3 nm.<sup>8</sup> The interpretation of this fact is not straightforward and requires further study to disclose if such narrow lamellae can exist in PB<sup>t</sup>BI copolymers.

A preliminary evaluation of the mechanical properties of the new copolyesters has been carried out. For this, tensile tests were performed for PBT<sub>80</sub><sup>t</sup>BI<sub>20</sub>, PBT<sub>70</sub><sup>t</sup>BI<sub>30</sub>, PBT<sub>60</sub><sup>t</sup>BI<sub>40</sub> and PBT<sub>50</sub><sup>t</sup>BI<sub>50</sub> as well as for the parent homopolymers PBT and PB<sup>t</sup>BI. The

stress-strain curves obtained from these tests are compared in Figure 5 and their respective mechanical parameters are listed in Table IV. It is known that insertion of *tert*-butyl isophthalate groups increases the brittleness of PET. In the present case the opposite effect is rather observed. The mechanical behavior of PB<sup>t</sup>BI appears to be not too far from that displayed by PBT. Both are rigid polymers showing low fluency at room temperature, although the mechanical moduli are slightly higher for the terephthalate polymer. The copolymers present a nearly steady trend consisting of a continuous decreasing in both Young modulus and tensile strength and an increasing in extensibility with the content in <sup>t</sup>BI units. It should be taken into account, however, that comparison with PBT should be made with caution since a semicrystalline sample of this polyester had to be used for testing.

Permeability measurements of PB<sup>t</sup>BI homopolymer and PBT<sup>t</sup>BI copolyesters containing 30 and 50 mol % of <sup>t</sup>BI units were carried out in a pressure-rise constant volume system by the conventional time-lag method. Downstream pressures were plotted against time, and from the extrapolation of the steady-state part of the curve, the intercept with the time axis, the time-lag,  $\theta$ , was obtained. The diffusion coefficient,  $D$ , was calculated as  $D = L^2/6\theta$ ,  $L$  being the thickness of the film. The permeability constant  $P$  is calculated from the slope of the steady-state part of the p-t plot using the following equation:

$$P = \frac{T_{STP}}{p_{STP}} \frac{V \cdot L}{A \cdot T p_{up}} \frac{dp(t)}{dt}$$

where  $V$  is the volume of the system,  $p$  the pressure recorded versus time  $t$ ,  $p_{up}$  is the applied upstream pressure,  $T$  is the absolute temperature,  $A$  is the effective area of the film, and  $T_{STP}$  and  $p_{STP}$  are the temperature and pressure under standard conditions. The solubility coefficient  $S$  is then calculated from the diffusion and the permeability coefficients as  $S = P/D$ .

Diffusion, solubility, and permeability coefficients determined for the transport of  $N_2$ ,  $O_2$ , and  $CO_2$  through PB<sup>t</sup>BI, PBT<sub>70</sub><sup>t</sup>BI<sub>30</sub>, and PBT<sub>50</sub><sup>t</sup>BI<sub>50</sub> amorphous films are compared in Table V. Comparison with homopolymer PBT was neglected since amorphous films of this polyester could not be prepared. As it was expected from the disturbing packing effect of the *tert*-butyl side group, the permeability was observed to increase with the content of <sup>t</sup>BI units for the three gases that were investigated, the effect being less pronounced for the smaller  $N_2$  molecule (Figure 6). Such a straightforward trend is not shared however by either diffusion or solubility coefficients.



In fact, D was found to attain maximum values for the PB<sup>t</sup>BI homopolymer whereas it decreased slightly with copolymerization. On the other side, S appeared to have a rather opposite behavior displaying minimum values for PB<sup>t</sup>BI.

It should be remarked that the same influence of copolymerization on permeability was reported for PET<sup>t</sup>BI copolyesters although the effect was there more pronounced. In spite that the number of aromatic polyesters containing *tert*-butyl isophthalate units that have been examined to date is rather limited, it can be concluded that the effect of the insertion of such units is rather complex. Whereas the permeability appears to be enhanced in all cases, the influence on diffusivity and solubility depends on both the nature of the parent homopolymer and the size and polarizability of the gas molecule.

## Conclusions

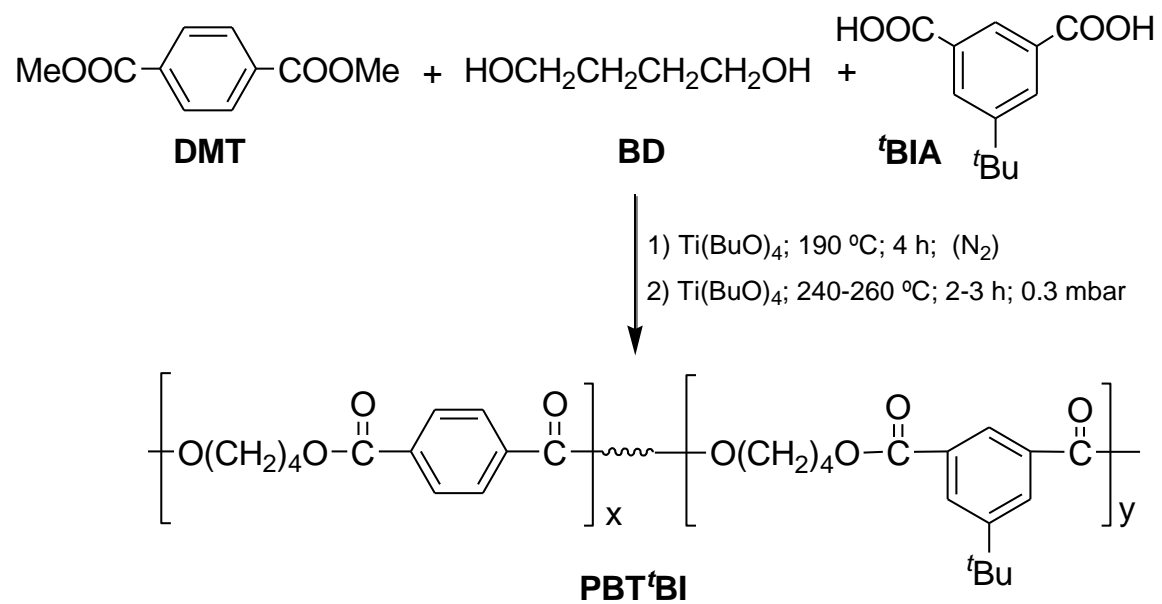
PBT copolymers containing 5-*tert*-butyl isophthalate units at random can be readily prepared in a wide range of compositions by polycondensation from the melt. The composition of the copolymer may be adjusted by choosing the comonomer ratio in the feed. The incorporation of the *tert*-butyl substituted units largely modifies the behavior of the parent polymer according to the disturbing effect that the *tert*-butyl group is expected to have in the packing of the polymer. The most outstanding effect is the notable increase that is observed in  $T_g$ . On the contrary, crystallinity was found to be depressed with a decay in both melting temperature and enthalpy with copolymerization, and consequently mechanical moduli appeared to be weakened. Also the permeability appeared slightly enhanced. The possibility of tuning the crystallizability of these copolymers by adjusting the composition is an interesting approach towards the design of new PBT materials with a better balance between thermal, mechanical and optical properties.

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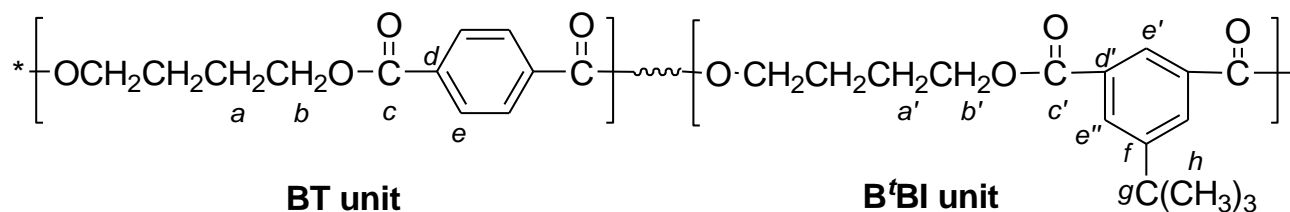


**Scheme I.** Synthesis of poly(butylene terephthalate-*co*-5-*tert*-butyl isophthalate) copolymers.

**Table I.** Compositions, viscosities and molecular weights of polyesters.

Polyester	[DMT/ <sup>t</sup> BIA] <sup>a</sup>	[BT/ B <sup>t</sup> BI] <sup>b</sup>	[ $\eta$ ] <sup>c</sup> (dL·g <sup>-1</sup> )	M <sub>n</sub> <sup>d</sup>	M <sub>w</sub> <sup>d</sup>	PD <sup>d</sup>
PBT	100/0	100/0	1.07	19,900	45,700	2.3
PBT <sub>90</sub> <sup>t</sup> BI <sub>10</sub>	90/10	90.8/9.2	0.69	9,000	25,000	2.5
PBT <sub>80</sub> <sup>t</sup> BI <sub>20</sub>	80/20	79.1/20.9	1.11	19,000	55,000	2.8
PBT <sub>70</sub> <sup>t</sup> BI <sub>30</sub>	70/30	69.6/30.4	1.26	24,000	61,000	2.5
PBT <sub>60</sub> <sup>t</sup> BI <sub>40</sub>	60/40	60.1/39.9	1.19	24,600	53,400	2.1
PBT <sub>50</sub> <sup>t</sup> BI <sub>50</sub>	50/50	50.1/49.9	0.96	22,500	42,500	1.9
PB <sup>t</sup> BI	0/100	0/100	0.77	19,400	37,800	1.9

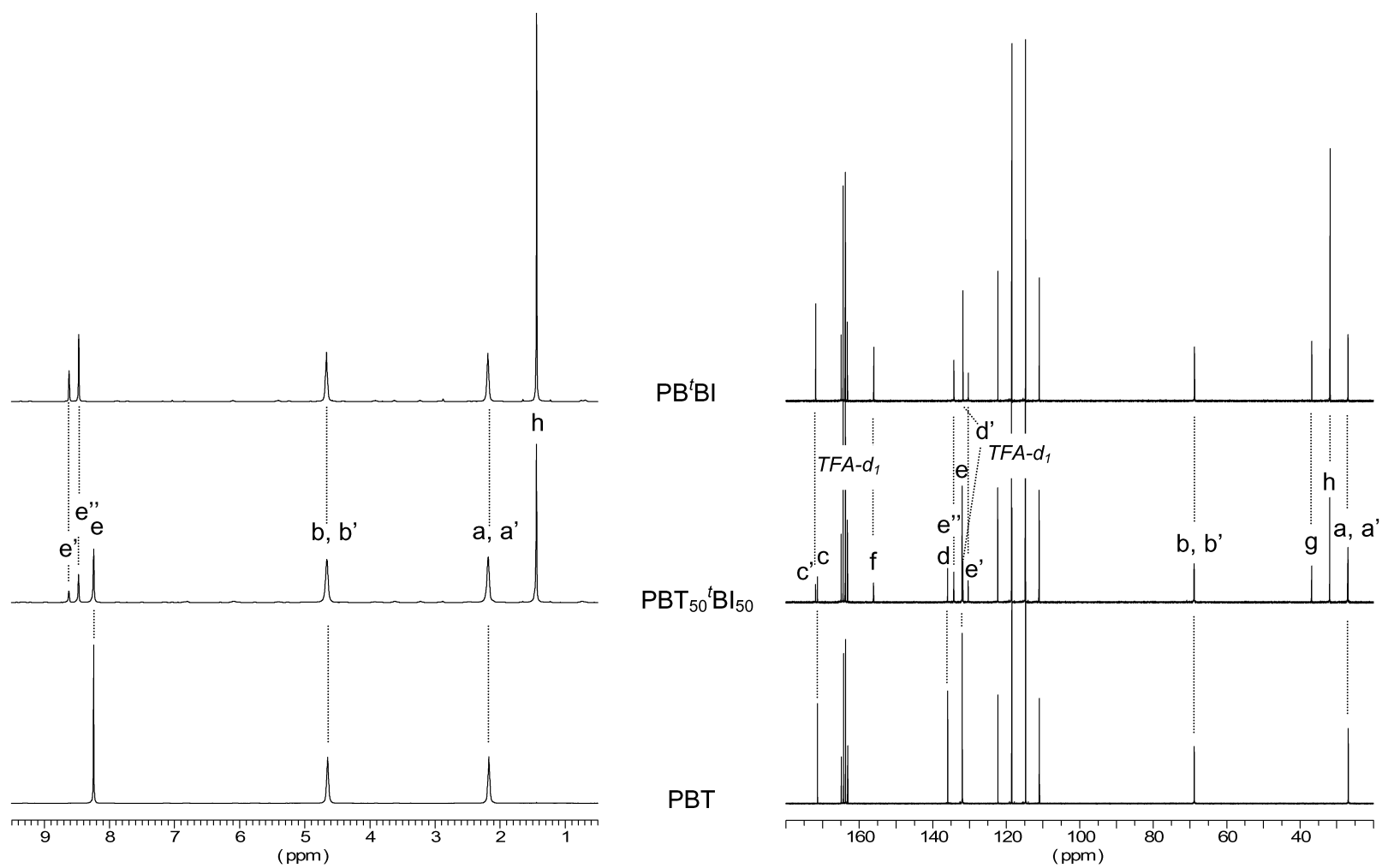
<sup>a</sup> Molar ratio in the feed.<sup>b</sup> Molar composition of the resulting polyester as determined by <sup>1</sup>H NMR.<sup>c</sup> Intrinsic viscosity measured in dichlororoacetic acid at 25 ± 0.1 °C.<sup>d</sup> Average molecular weights and polydispersities measured by GPC.



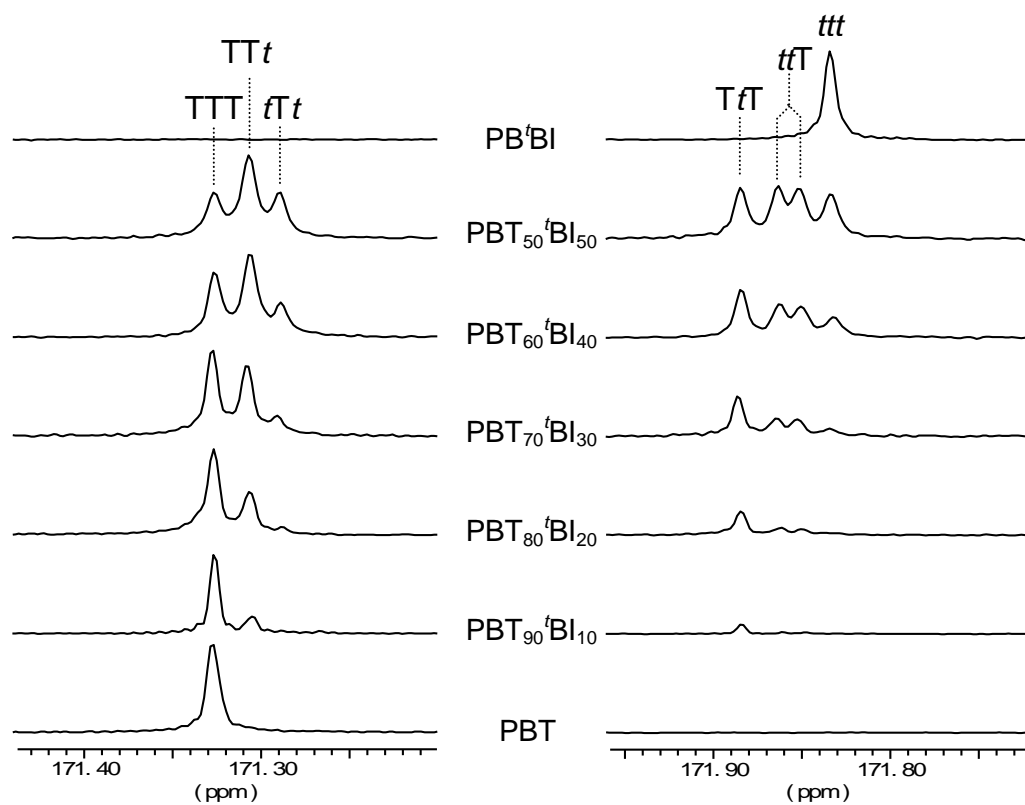
**Scheme II.** Labeling of carbons and protons in the butylene terephthalate units (BT) and butylene 5-*tert*-butyl isophthalate units (B<sup>t</sup>BI) used for the assignment of NMR signals.

**Table II.** Chemical shifts of <sup>1</sup>H and <sup>13</sup>C NMR signals of polyesters PBT and PB<sup>t</sup>BI, and copolyesters PBT<sup>t</sup>BI.

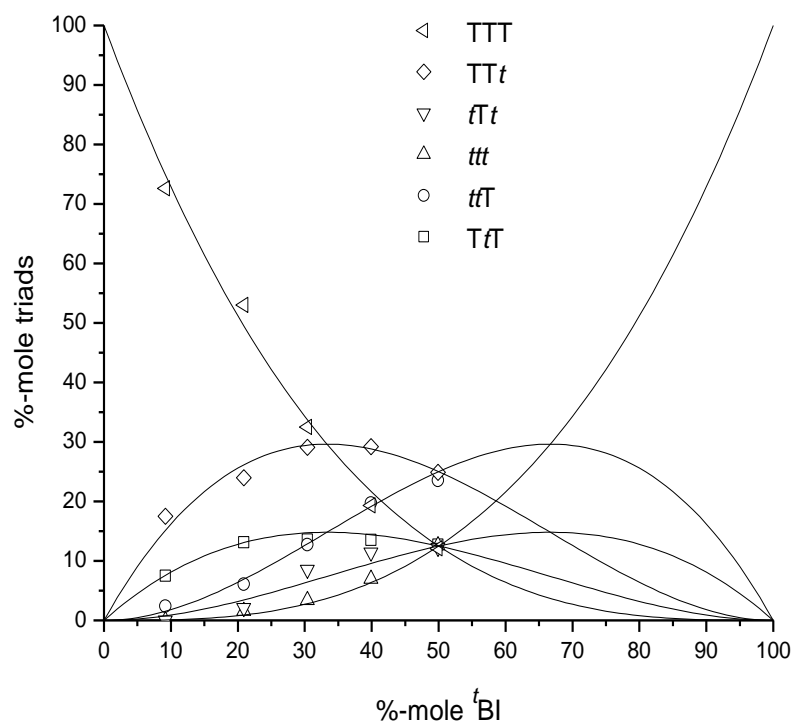
Polyester	a	a'	b	b'	c	c'	d	d'	e	e'	e''	f	g	h
<sup>1</sup> H														
PBT	2.2		4.7						8.3					
PB <sup>t</sup> BI		2.2		4.7						8.6	8.4			1.4
PBT <sup>t</sup> BI	2.2	2.2	4.7	4.7					8.3	8.6	8.4			1.4
<sup>13</sup> C														
PBT	26.9		68.8		171.3		135.9		132.0					
PB <sup>t</sup> BI		26.9		68.7		171.8		131.7		130.3	134.2	156.1	36.8	31.8
PBT <sup>t</sup> BI	26.9	26.9	68.8	68.8	171.3	171.8	135.9	131.7	132.0	130.3	134.2	156.1	36.8	31.8



**Figure 1.** Compared <sup>1</sup>H (left) and <sup>13</sup>C (right) NMR spectra of polyesters.



**Figure 2.** Carbonyl region of the  $^{13}\text{C}$  NMR spectra of polyesters and copolyesters. Left: terephthalate units region; Right: 5-*tert*-butyl isophthalate units region.



**Figure 3.** Distribution of triads as a function of composition copolyester. The Bernoulli statistical functions for the different triad types are plotted as continuous lines.

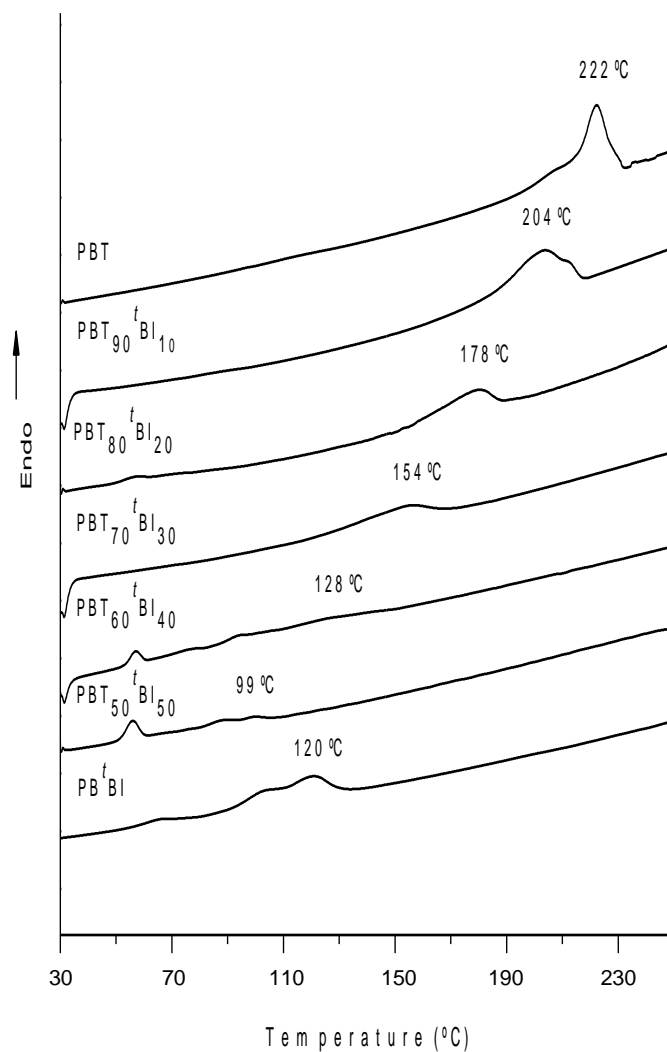
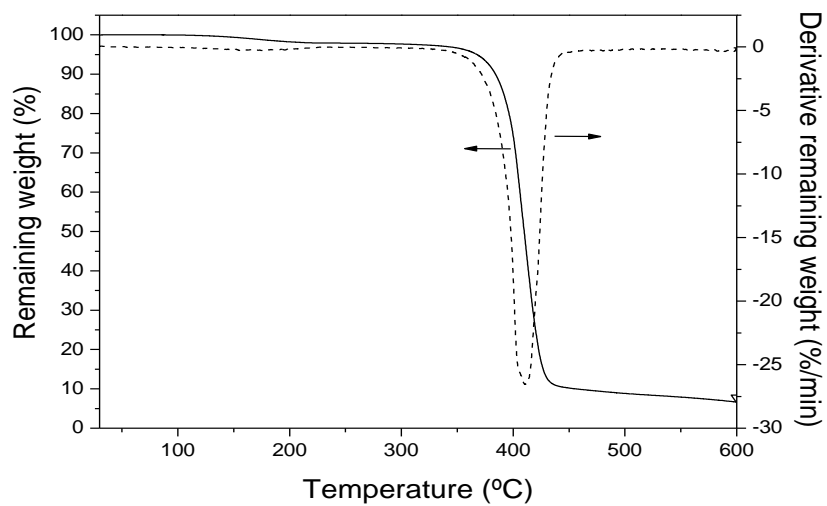




**Table III.** Microstructure of PBT<sup>t</sup>BI copolyesters.<sup>a</sup>

Copolyester	T-centered triads (% mol)			<sup>t</sup> BI-centered triads (% mol)			Av. seq. length		R
	tTt	tTT <sup>d</sup>	TTT	TtT	ttT <sup>d</sup>	ttt	n <sub>T</sub>	n <sub>tBI</sub>	
PBT <sub>90</sub> <sup>t</sup> BI <sub>10</sub>	0	17.5	72.6	7.5 <sup>b</sup>	2.4	0	10.3	1.1	0.98
	(0)	(15.2)	(74.9)	(7.6) <sup>c</sup>	(1.5)	(0)	(10.8)	(1.1)	(1.00)
PBT <sub>80</sub> <sup>t</sup> BI <sub>20</sub>	2.1	24.0	53.0	13.1	6.1	1.6	5.6	1.3	0.96
	(3.5)	(26.2)	(49.5)	(13.1)	(6.9)	(0.9)	(4.8)	(1.3)	(1.00)
PBT <sub>70</sub> <sup>t</sup> BI <sub>30</sub>	8.5	29.1	32.5	13.6	12.7	3.4	3.0	1.5	1.00
	(6.4)	(29.5)	(33.7)	(14.7)	(12.8)	(2.8)	(3.3)	(1.4)	(1.00)
PBT <sub>60</sub> <sup>t</sup> BI <sub>40</sub>	11.4	29.2	19.3	13.5	19.7	7.0	2.3	1.7	1.02
	(9.6)	(28.8)	(21.7)	(14.4)	(19.1)	(6.3)	(2.5)	(1.7)	(1.00)
PBT <sub>50</sub> <sup>t</sup> BI <sub>50</sub>	12.2	24.9	12.1	12.7	23.5	12.6	2.0	2.0	1.00
	(12.5)	(25.0)	(12.6)	(12.5)	(25.0)	(12.4)	(2.0)	(2.0)	(1.00)

<sup>a</sup> Experimental values obtained from <sup>13</sup>C RMN data, calculated values for a random copolymer in brackets.



**Figure 4.** Top: TGA trace and derivative curve for copolyester  $\text{PBT}_{90}\text{tBI}_{10}$ . Bottom: compared DSC traces for polyesters PBT,  $\text{PBtBI}$  and copolyesters  $\text{PBT}^t\text{BI}$ .



**Table IV.** Compared thermal and mechanical properties of polyesters and copolyesters.

Polyester	DSC		TGA		Tensile test <sup>e</sup>		
	T <sub>g</sub> <sup>a</sup> (°C)	T <sub>m</sub> <sup>b</sup> (°C) ( $\Delta H_m$ J·g <sup>-1</sup> ) <sup>b</sup>	T <sub>d</sub> <sup>c</sup> (°C)	RW <sup>d</sup> (%)	E (MPa)	$\sigma_{max}$ (MPa)	$\gamma$ (%)
PBT	32	222 (53.9) 222 (45.3)	379/407	8	1676 ( 61)	55.2 (3.2)	6.5 (0.6)
PBT <sub>90</sub> <sup>t</sup> BI <sub>10</sub>	30	204 (54.1) 206 (37.4)	382/407	7	-	-	-
PBT <sub>80</sub> <sup>t</sup> BI <sub>20</sub>	33	178 (26.2) 178 (25.2)	385/410	7	1476 (93)	44.4 (3.8)	482.6 (49)
PBT <sub>70</sub> <sup>t</sup> BI <sub>30</sub>	42	154 (20.2)	390/412	9	1237 (16)	38.2 (2.3)	457.4 (34)
PBT <sub>60</sub> <sup>t</sup> BI <sub>40</sub>	47	128 (4.1)	384/408	8	1269 (62)	35.4 (0.7)	217.0 (40)
PBT <sub>50</sub> <sup>t</sup> BI <sub>50</sub>	48	99 (4.1)	386/415	9	1327 (149)	45.7 (5.9)	12.2 (8.6)
PB <sup>t</sup> BI	59	120 (28.2)	385/410	7	1557 (80)	44.1 (1.8)	4.0 (0.3)

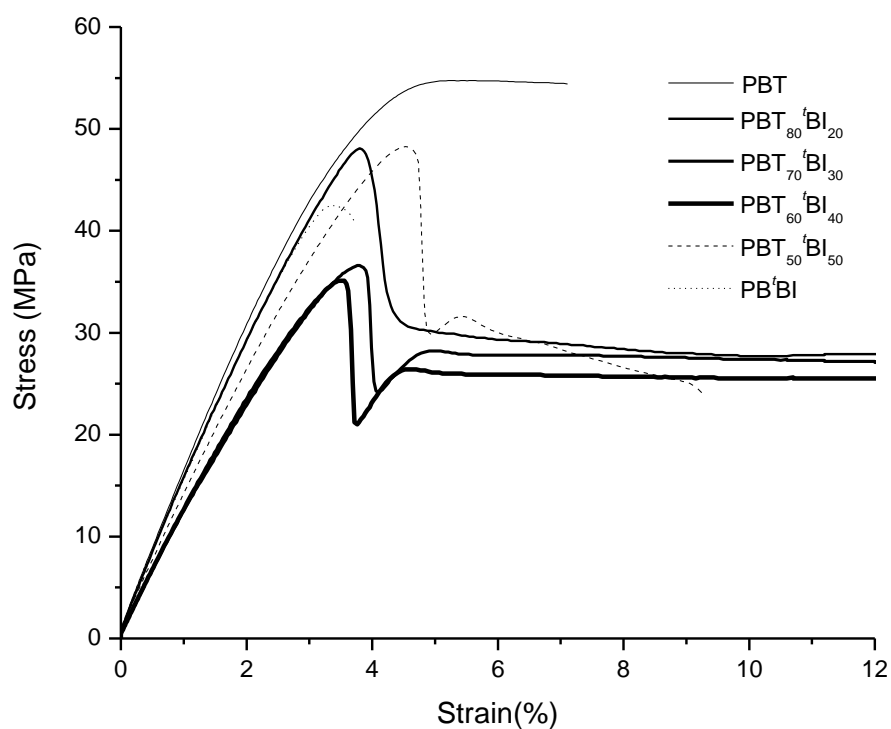
<sup>a</sup> Glass temperature determined by DSC at heating from quenched samples.

<sup>b</sup> Melting temperature and enthalpy (in brackets) measured by DSC from samples coming directly from synthesis. Second row, values observed in the second heating scan.

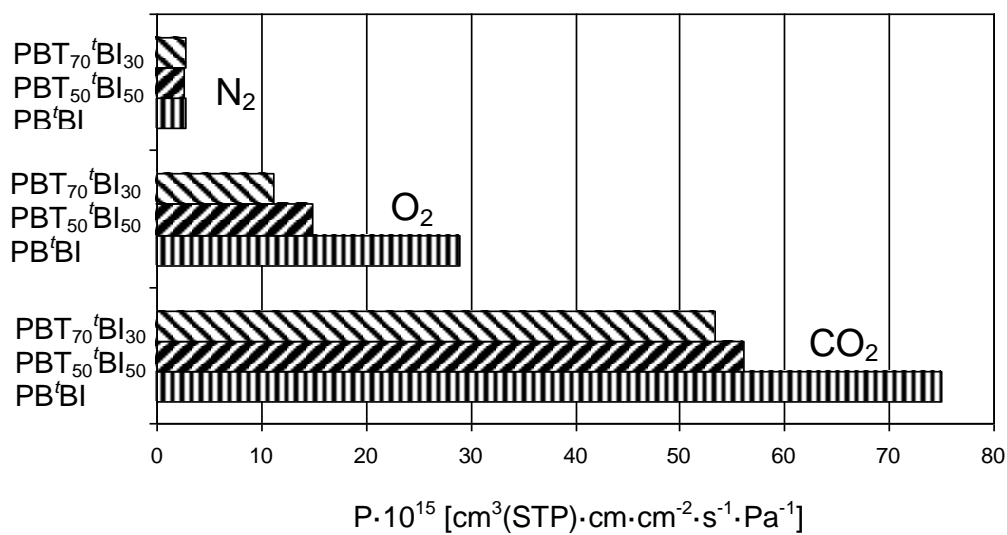
<sup>c</sup> Temperatures for a 10% of weight loss and for maximum decomposition rate.

<sup>d</sup> Weight left after heating at 550 °C.

<sup>e</sup> Standard deviations, in brackets.



**Figure 5.** Compared stress-strain curves for polyesters and copolyesters.



**Figure 6.** Compared permeabilities of polyesters.

**Table V.** Gas transport properties of polyesters at 25 °C.

Polyester	$P \cdot 10^{15} [\text{cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}]$			$Ps^a$		$D \cdot 10^9 [\text{cm}^2 \cdot \text{s}^{-1}]$			$S \cdot 10^7 [\text{cm}^3(\text{STP}) \cdot \text{cm}^{-3} \cdot \text{Pa}^{-1}]$		
	$N_2$	$O_2$	$CO_2$	$O_2/N_2$	$CO_2/O_2$	$N_2$	$O_2$	$CO_2$	$N_2$	$O_2$	$CO_2$
PBT <sub>70</sub> <sup>t</sup> BI <sub>30</sub>	2.78	11.1	53.4	4.0	4.8	2.89	13.8	4.73	9.64	8.16	113
PBT <sub>50</sub> <sup>t</sup> BI <sub>50</sub>	2.58	14.9	56.1	5.8	3.8	2.68	13.5	3.54	9.72	11.1	160
PB <sup>t</sup> BI	3.51	28.9	75.0	8.2	2.6	12.3	28.6	8.34	2.87	10.1	90.6

<sup>a</sup> Permselectivity is defined as  $P_A/P_B$ .