



Properties of polyurethanes derived from poly(diethylene glycol terephthalate)

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ARTICLE INFO

Keywords:

Polyurethane elastomers
Poly(diethylene glycol terephthalate)
Thermal analysis
Mechanical analysis
Dielectric spectroscopy
Gas permeability

ABSTRACT

The synthesis of linear and crosslinked polyurethanes based on α,ω -dihydroxypolydiethylene glycol terephthalate (PDET) is described. Prior to the preparation of these materials, a PDET polymer was obtained by conventional condensation reaction between dimethyl terephthalate and diethylene glycol, and a well-characterized fraction of PDET with number average molecular weight of $3,650 \text{ g mol}^{-1}$ was chosen for the synthesis of the polyurethanes. Specifically, three polyurethanes were prepared: a pure linear polyurethane by reaction of PDET with 4,4'-diphenylmethane diisocyanate (MDI), a chain extended polyurethane obtained with MDI, PDET and 1,4-butanediol as chain extender, and a crosslinked polyurethane synthesized from PDET and a polyfunctional isocyanate. Thermal, mechanical, dielectric and gas transport properties of the polyurethanes were studied, showing excellent performance. In particular, rubber-like flexible materials were obtained with elongation values over 1000%, due to the low glass transition temperature of PDET. Furthermore, it was observed that these materials, in particular the crosslinked polyurethane, behave as gas barriers.

1. Introduction

Polyurethanes (Pus) are considered excellent materials with physical properties going from very flexible to very rigid. Usually, they are synthesized by a combination of a macroglycol, which is a polyfunctional glycol consisting of a relatively long chain, a polyisocyanate and a chain extender or crosslinker (if functionality is 2 or greater than 2, respectively) comprised of a short chain polyol or polyamine. The macroglycol chains constitute the so-called soft segment whereas the chains built by reaction of isocyanate and the chain extender constitute the hard segment. Due to their synthetic flexibility based on the reaction components, their properties can be very different and easily controllable, leading to useful materials with a variety of applications such as flexible and rigid foams, coatings, elastomers and adhesives [1–3].

The low glass transition temperatures of typical macroglycols such as aliphatic polyethers and polyesters impart great flexibility to the chains leading to polyurethane elastomers able to exhibit high or low elongations, depending on their molecular weight and the proportion of the hard segment. When aromatic polyesters such as polyols derived from phthalic, isophthalic and terephthalic acids are used as macroglycols, their chemical structure produces rigid polyurethanes. For this reason,

aromatic polyester macroglycols are used exclusively in rigid foams by the polyurethane industry [4]. Notably, elastomeric polyurethanes derived from aromatic polyesters have been hardly studied.

Networks based on hydroxyl end-linked poly(diethylene glycol terephthalate) (PDET) and poly(diethylene glycol isophthalate) (PDEI) have been subject of research by our group [5–9]. The statistical properties of PDET were studied in detail and the interpretation of the results using the rotational isomeric state model indicates a prevalence of *gauche* over *trans* states about the carbon-carbon methylene bonds in these chains [10–13]. The results were confirmed by NMR spectroscopic analysis of PDET, showing that the amount of $\text{CH}_2 - \text{CH}_2$ bonds in the *gauche* state represents approximately 90% of the population [14]. The preference of the moiety $\text{O} - \text{CH}_2 - \text{CH}_2 - \text{O}$ for *gauche* states likely induces to fold back of the chain on itself, leading to more coiled chains than initially expected [10]. As a result, PDET enhances the elastomeric properties of the networks prepared from this polymer. Also, the configurational properties and dielectric relaxations of networks of PDEI at different elongations ratios were studied and showed relatively high modulus and high chain extensibilities without rupture even at elongation ratios greater than 800%. Thus, both macrodiols polyesters, PDET and PDEI, exhibit adequate characteristics for use in the

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preparation of polyurethanes (with especial properties) due to their relatively low glass transition temperatures ($<20\text{ }^{\circ}\text{C}$) compared to other aliphatic-aromatic polyesters. Despite the regular structure of both polymers, they do not crystallize from the melt, and crystallization is only possible from very dilute solutions in appropriate solvents. This characteristic enables the preparation of linear or crosslinked amorphous polyurethanes by reaction of α,ω -dihydroxy PDET or PDEI polymers with di or tri-isocyanates.

A revision of the work cited above prompted us to further investigate the polyurethanes that incorporate aromatic rings to the macromolecular structure in order to attain a better understanding of the properties and, in turn, improve the applicability of these polymers where elastomeric behavior is required. In particular, three polyurethanes were prepared with low number average molecular weight PDET ($M_n = 3,650\text{ g}\cdot\text{mol}^{-1}$) and their thermal, mechanical and dielectric properties were evaluated. In addition, the gas transport coefficients of O_2 , N_2 and CO_2 for the three polymers were determined. Prior to this study, an extensive characterization of the PDET was carried out in order to obtain model linear polymers and networks with the indicated M_n between crosslinks.

2. Experimental

2.1. Materials

4,4'-Diphenylmethane diisocyanate (MDI) in the form of flakes was donated by Merquinsa (now Lubrizol Advanced Materials Spain SL, Montmeló, Spain). MDI was purified by short path distillation at approximately $110\text{ }^{\circ}\text{C}$ and $4\cdot 10^{-1}$ mbar using a vacuum sublimator connected to a cryostat at $-15\text{ }^{\circ}\text{C}$ and stored in vacuum until use. Since MDI tends to dimerize, the purified MDI was used within 10 days after purification.

Aliphatic polyisocyanate based on hexamethylene diisocyanate (TriHDI) with commercial name Vestanat® HT2500/100 and an equivalent weight of $192.7\text{ g}\cdot\text{eq}^{-1}$ was donated by Evonik Industries (Germany). This polyisocyanate contains isocyanurate groups as polyfunctional sites and is a mixture of species with a mean functionality between 3 and 4.

1,2-Dichloroethane (DCE) was supplied by Scharlau (Barcelona, Spain) and dried by distillation from phosphorus pentoxide. *N,N*-Dimethylacetamide, purchased from Scharlau (Barcelona, Spain), was vacuum-distilled from isocyanates (commercial polymeric MDI) in order to eliminate residual water and amines that would unbalance the stoichiometry on the synthesis of the polyurethane. Distillation temperature was kept below $60\text{ }^{\circ}\text{C}$ to avoid solvent decomposition, and the distilled solvent was used immediately. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) and tin (II) 2-ethylhexanoate (known as stannous octoate, SnOct_2) were supplied by Sigma Aldrich Química S.L. (Madrid, Spain) and used as received. 1,4-Butanediol (BD), purchased from Sigma Aldrich Química S.L. (Madrid, Spain), was dried over magnesium sulfate, distilled and stored blanketed with nitrogen until use.

2.2. Synthesis of PDET diol

Poly(diethylene glycol terephthalate) (PDET) was obtained by the standard melt phase procedure from dimethyl terephthalate and diethylene glycol, in the presence of isopropyl titanate. The initial mole ratio of diester to glycol was 1:2.2. The polycondensation reaction proceeded in two steps. In the first step the ester interchange was complete after 2–3 h at $160\text{--}180\text{ }^{\circ}\text{C}$ with elimination of the theoretical amount of methanol; the second step, the polycondensation, was carried out at $230\text{--}250\text{ }^{\circ}\text{C}$ under vacuum (0.7 mbar). The polymer was dissolved in chloroform and precipitated several times with methanol in order to remove low molecular weight species and cyclic oligomers. The polymer was fractionated at $30\text{ }^{\circ}\text{C}$ using chloroform/methanol as solvent-nonsolvent system. A fraction of nominal molecular weight $3,650\text{ g}\cdot\text{mol}^{-1}$ was used to prepare the linear and crosslinked polyurethanes.

2.3. Synthesis of PDET + MDI

The synthesis of the linear non-segmented polyurethane was performed in solution, in a 25 mL round bottom flask. Briefly, 1.5 g of $3,650\text{ g}\cdot\text{mol}^{-1}$ molecular weight PDET diol (0.411 mmol) and 0.103 g (0.411 mmol) of MDI were dissolved in 3 mL DCE at $80\text{ }^{\circ}\text{C}$, one drop of SnOct_2 added, and the solution stirred by magnetic spin at $80\text{ }^{\circ}\text{C}$ for 5 h. During reaction, when viscosity was too high to allow stirring, solvent was added. After 5 h reaction time, a total of 12 mL of DCE were added. The solution was allowed to cool at room temperature, diluted with DCE and casted onto a Teflon sheet at $40\text{ }^{\circ}\text{C}$ overnight. Films for the characterization of the physical properties were obtained as follows: the appropriate amount of the resulting polymer to obtain a film of 50 to $100\text{ }\mu\text{m}$ thickness was dissolved in HFIP and the solution casted onto a leveled Teflon sheet enclosed with a glass ring within a fume cupboard; the film was covered with a conical funnel to protect it from dust and to avoid an excessively fast solvent evaporation and allowed to stand for 2 days at ambient temperature; then the film was released from the Teflon sheet and dried further 24 h in vacuum.

2.4. Synthesis of PDET + MDI + BD

The synthesis procedure for this linear segmented polyurethane with a 30% hard segment content was done in two steps. In a 25 mL round bottom flask 1.5 g of PDET diol of $3,650\text{ g}\cdot\text{mol}^{-1}$ (0.411 mmol) and 0.5 g (2 mmol) of MDI were dissolved in 3 mL DCE at $80\text{ }^{\circ}\text{C}$, one drop of SnOct_2 added, and the solution stirred at $80\text{ }^{\circ}\text{C}$ for 15 min. Then 5 mL of anhydrous DMAc and 0.143 g BD (1.589 mmol) were added, and the solution stirred at $80\text{ }^{\circ}\text{C}$ for further 4.5 h. The solution was allowed to cool at room temperature and casted onto a Teflon sheet at $80\text{ }^{\circ}\text{C}$ overnight. Films for the characterization of the physical properties were prepared as described previously for PDET + MDI.

2.5. Synthesis of PDET + TriHDI

The synthetic procedure was as follows. In a 25 mL round bottom flask 1 g of PDET diol of $3,650\text{ g}\cdot\text{mol}^{-1}$ (0.274 mmol , 0.548 meq) and 0.1056 g (0.548 meq) of the polyisocyanate based on hexamethylene diisocyanate or triHDI were dissolved in 5 mL DCE at $60\text{ }^{\circ}\text{C}$, two drops of SnOct_2 added, and the solution stirred at $60\text{ }^{\circ}\text{C}$ for 90 min. The stirring was stopped and the solution let to stand for several minutes until all the bubbles disappeared. The solution was casted onto a leveled Teflon sheet enclosed with a glass ring covered with a conical funnel within a fume cupboard and the solvent evaporated at ambient temperature for 18 h. The film was put in a heated vacuum desiccator without vacuum and cured with the following protocol: from 30 to $50\text{ }^{\circ}\text{C}$, the temperature was increased in successive steps of $5\text{ }^{\circ}\text{C}$ and from 50 to $80\text{ }^{\circ}\text{C}$ in steps of $10\text{ }^{\circ}\text{C}$. At each stage, the temperature was maintained for 1 h. After the last stage, the temperature was raised to $100\text{ }^{\circ}\text{C}$ and maintained for 5 h. The crosslinked film was extracted by immersing the film in a covered crystallizing dish with 60 mL chloroform for 3 h. The 8 cm diameter film swelled to a diameter of approximately 18 cm. The extracted film was dried overnight at ambient temperature and then at vacuum and ambient temperature for further 5 h. The dry extracted film was used for all the measurements.

2.6. Characterization

Solution NMR spectra were recorded at room temperature in a Varian Unity Plus 400 instrument (Palo Alto, CA, USA) using deuterated chloroform (CDCl_3) as solvent. Spectra were referenced to the residual solvent signals at 7.26 ppm.

Molecular weights of the polymers were determined by size exclusion chromatography (SEC) in a Perkin Elmer gel permeation chromatograph (Series 200 LC pump) equipped with a refractive index detector (IR 200a). A set of ResiPore columns (Polymer Laboratories)

conditioned at 70 °C were used to elute samples at the flow rate of 0.3 mL·min⁻¹ of HPLC-grade *N,N*-dimethylformamide (DMF) with LiBr (0.1 wt%). Polystyrene standards (Polymer Laboratories) were used for calibration.

The thermal transitions of the samples were analyzed by DSC on a Mettler Toledo DSC 822e calorimeter (Schwerzenbach, Switzerland) equipped with a liquid nitrogen accessory. Disc samples cut from films weighing approximately 5–6 mg were sealed in aluminium pans. Samples were heated, from 25 °C to 80 °C at a rate of 10 °C·min⁻¹, cooled to –60 °C at a rate of –10 °C·min⁻¹, maintained for 5 min at this temperature and re-heated at a rate of 10 °C·min⁻¹ from –60 °C to 80 °C for PDET + MDI and PDET + TriHDI and from –60 °C to 220 °C for PDET + MDI + BD. The segmented polymer PDET + MDI + BD was subjected to another cooling-heating cycle (220 °C to –60 °C and to 220 °C). Glass transition temperatures (T_g) were taken as the midpoint of the transition, and melting points (T_m) from the maximum of the melting endotherm.

Tensile properties were measured in a MTS Synergie 200 testing machine (Eden Prairie, MN, USA) equipped with a 100 N load cell. Type 4 dumbbell test pieces (according to ISO 37) were cut from the samples. A cross-head speed of 5 mm·min⁻¹ was used. Strain was measured from cross-head separation and referred to 12 mm initial length. A minimum of 5 samples were tested for each material.

2.7. NMR gas solubility measurements

To measure the gas solubility with NMR, 0.45 g of polymer membrane strips less than 2 mm wide and approximately 15 mm long were placed inside a 10 mm o.d. NMR tube modified for studies at moderately pressurized gases. In addition, a standard consisting of a sealed glass capillary with a known amount of labeled ¹³C(1) acetic acid was placed in the tube.

Prior to fill the tube at a given pressure with ¹³CO₂, the air was removed by vacuum. The gas pressure was monitored with a transducer working in the range 0–10 bar.

The NMR measurements were performed in a Bruker Avance™ 400 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany) equipped with a 89 mm wide bore, 9.4 T superconducting magnet (¹³C Larmor frequency at 100.61 MHz). The reported data were acquired at 30 ± 0.1 °C. The 90° radiofrequency (rf) pulse length was 12.5 μs for ¹³C. An inversion-recovery pulse sequence was used to estimate the longitudinal relaxation times, T_1 , of sorbed gas. Solubility measurements were performed as described previously [15]. The ¹³C NMR spectra were referenced to ¹³C(1) acetic acid (178.1 ppm), secondary to tetramethylsilane (TMS, 0.0 ppm). For each spectrum, gas peak area was measured, corrected for the signal intensity reduction due to T_i , and normalized to the corresponding peak area of the standard, ¹³C(1).

2.8. Permeation measurements

A laboratory-made permeator, described elsewhere [16,17], was used for permeation measurements. Briefly, it consists of a gas cell in which the polymer membrane is placed in the centre, separating the high-pressure or upstream chamber from the low-pressure or downstream chamber. High vacuum was generated in the permeation device by means of an Edwards molecular turbo-pump and the whole arrangement was thermostatically controlled at 30 °C by means of a water bath. Before performing the measurements, vacuum was maintained overnight in the permeation device to remove the last traces of solvent and gas in the membrane, and to reach a low pressure (about 10⁻³ mbar). Subsequently, gas contained in a reservoir was allowed to flow into the downstream chamber and the evolution of the pressure of the gas in this chamber was monitored with a MKS Baratron type 627B absolute pressure transducer working in the pressure range 10⁻⁴ – 1 mbar. Pressure in the upstream chamber was measured with a Gometrics transducer to control the gas pressures at which the experiments are

performed, which varied between 0.1 and 5 bar in this work. Three independent experiments were performed for each membrane and gas.

The permeability, P , and diffusion, D , coefficients were determined from the curves measuring the pressure increase at the downstream side, once the steady state conditions were reached. The value of P in barrers {1 barrer [10⁻¹⁰ cm³(STP) cm/(cm² s cmHg)]} can be calculated by the equation

$$P = 3.59 \frac{VL}{p_0 A T} \lim_{t \rightarrow \infty} \left(\frac{dp(t)}{dt} \right) \quad (1)$$

where V is the volume of the downstream chamber, L is the membrane thickness and A is the permeation area, all given in units of the cgs system, and p_0 (the gas pressure in the upstream chamber) and $p(t)$ in cmHg. The diffusion coefficient D , in cm²/s, was estimated using the Daynes-Barrer method [18,19]. Plots of $p(t)$ against t in the steady state are straight lines intercepting the abscissa axis at

$$D = \frac{L^2}{6\theta} \quad (2)$$

where θ is the time lag in seconds. Once permeability and diffusion coefficients are determined, the apparent solubility coefficients can be calculated directly from the P/D ratio. It should be pointed out that S corresponds to the true solubility coefficient only when the gas sorption in the polymer membrane obeys Henry's law.

2.9. Dielectric spectroscopy measurements

The experimental dielectric behavior of the linear and crosslinked polyurethanes was studied in the frequency domain with a Novocontrol broadband dielectric spectrometer (Hundsagen, Germany) consisting of an Alpha analyzer to carry out measurements from 0.1 to 1 × 10⁷ Hz. The device was coupled to a Quatro temperature controller with a thermal stability ≤ ± 0.1 °C. Molded disk shaped samples of about 0.1 mm thickness and 20 mm diameter were inserted between two gold-plated flat electrodes. The measurements were carried out in inert N₂ atmosphere from –100 to + 150 °C in 1 or 5 °C intervals.

3. Results and discussion

3.1. Molecular weight determination of PDET diol

In the synthesis of polyurethanes, a step-growth polymerization, it is important to determine precisely the molecular weight of the reactants in order to have a balanced stoichiometry and achieve a high molecular weight during polymerization. The molecular weight of macrodiols is usually calculated in industry by titration following the appropriate standard [20,21]. However, the standard needs a very high amount of polyol for the determination when the hydroxyl number is low (or the equivalent weight high). For example, the determination of the hydroxyl number of a macrodiol with a molecular weight of 2,000 g·mol⁻¹ needs 20 g of sample, and the determination of the hydroxyl number of a macrodiol with a molecular weight of 3,500 g·mol⁻¹ needs 35 g of sample. When working with research products synthesized at laboratory scale, they are obtained usually in small quantities and titration following the standard is not an option. NMR is an alternative method that uses a very small amount of sample and there are already standards based on NMR for the determination of primary hydroxyl groups in polyether polyols [22]. Proton NMR has been routinely used to determine the molecular weight of macrodiols [23–25]. In general, the values obtained with NMR are very close to the values obtained by titration for low molecular weights (up to 2,500 g·mol⁻¹ approximately), but they tend to be overestimated when macrodiols with higher molecular weight are characterized [26].

Proton NMR was used to determine the number average molecular weight of PDET diol. As shown in Fig S1 (Supporting Information), two

peaks were observed in the aromatic region and four signals in the aliphatic region. These signals were assigned according to published results [27], and the details can be found in the [Supporting Information](#). From the integrals of the well resolved signals at 3.65 and 4.51 ppm, a molecular weight of $5,460 \text{ g}\cdot\text{mol}^{-1}$ was calculated. If the integrals of the slightly overlapping peaks in the aromatic region were used, the calculated molecular weight was $4,400 \text{ g}\cdot\text{mol}^{-1}$. A wide discrepancy between these values was observed and, in both cases, the calculated molecular weight was higher than anticipated. As already mentioned, when macrodiols of relatively high molecular weight are characterized by proton NMR, the calculated value tends to be overestimated.

An indirect method was used to determine more precisely the molecular weight of PDET diol. Approximately 1.5 g of PDET diol were reacted with the equivalent amount of MDI in 3 mL DCE. A PDET molecular weight of approximately $5,500 \text{ g}\cdot\text{mol}^{-1}$ was estimated for the initial reaction, but it was reduced sequentially by 10% in the following reactions. In the course of the reaction, if the molecular weight of the polymer increased substantially, the magnetic stirring bar stopped and it was necessary to add some solvent to maintain the stirring. It was assumed that the reaction requiring the highest amount of solvent would have the precise stoichiometric ratio hydroxyl/isocyanate needed to produce the polymer with the highest molecular weight and, therefore, the molecular weight of PDET would be the value assumed for that particular reaction. In total, five reactions were carried out and the optimal polymer in terms of molecular weight (confirmed by SEC measurements) was obtained for a PDET molecular weight of approximately $3,650 \text{ g}\cdot\text{mol}^{-1}$ (see Table S1, in [Supporting Information](#)), which was taken as the actual molecular weight of PDET diol.

3.2. Synthesis of polyurethanes

Two linear polyurethanes (PDET + MDI and PDET + MDI + BD) and one crosslinked polyurethane (PDET + TriHDI) were synthesized from PDET diol. The reaction of PDET diol with MDI produced a linear non-segmented polyurethane with the diisocyanate molecules merely linking the PDET chains. Reaction of PDET diol with MDI and BD produced a linear segmented polyurethane with the soft segments consisting of PDET chains and the hard segments being formed by the reaction of MDI and BD. A 30% hard segment content (hard segment content being defined as $(\text{MDI} + \text{BD})/\text{total polymer}) \times 100$) was chosen in order to have the lowest amount of hard segment that will produce a polyurethane with a phase separated morphology and elastomeric behavior. It is accepted that a minimum molar ratio diisocyanate:chain extender 2:1 is needed to produce a phase separated morphology and, for a 30% hard segment content, the molar ratio is 4.87:3.87, well above 2:1, thus long hard segments will be produced to drive phase separation. The reaction of PDET diol with HDI polyisocyanate produced a crosslinked, non-segmented polyurethane. Non-segmented polyurethanes (PDET + MDI and PDET + TriHDI) are expected to exhibit a single-phase morphology whereas segmented polyurethane (PDET + MDI + BD) is expected to display a phase-separated morphology. All polyurethanes were translucent, nearly transparent, as seen in [Fig S2](#). This is expected in the case of the single-phase polyurethanes, and in the case of the phase-separated polyurethane (PDET + MDI + BD) the transparency is because the size scale of the morphology (tenths to a hundred nanometers) is smaller than the wavelength of visible light.

For the linear polyurethanes, the molecular weight reached during synthesis was high enough to obtain good films. SEC measurements confirmed the high molecular weight for these polymers: $M_n = 281,000$ and $M_w = 536,000$ for the non-segmented polyurethane PDET + MDI; and $M_n = 105,000$ and $M_w = 170,000$ for the segmented polyurethane PDET + MDI + BD with a 30% hard segment content.

In the case of crosslinked polyurethane, the gel content measured by extraction with chloroform was 93% and, consequently, the crosslinking reaction with triHDI was considered efficient. In order to obtain a good film free of bubbles, it was important to balance the viscosity of the

solution and, therefore, the molecular weight of the pre-polymerized material, before casting. If the viscosity was too low, the solution would not form a film and extensive cratering would take place. At the opposite end, with a solution of high viscosity, bubbles would form during the solvent evaporation that it could not be eliminated. In addition, the rate of evaporation of the solvent should be slow enough to allow the stripping of the solvent without bubble formation. With the conditions detailed in the experimental section, the viscosity of the solution (or the degree of polymerization) was high enough to obtain a good film and the procedure for solvent evaporation slow enough to avoid the formation of bubbles.

3.3. Thermal properties

Non-segmented polyurethanes PDET + MDI (linear) and PDET + TriHDI (crosslinked) showed a single T_g at low temperature, 1.1°C and 4.0°C respectively. The absence of any other transition and the low value of T_g indicate that both materials are soft with a homogeneous single-phase morphology. The slightly higher T_g observed for the network with respect to the linear material could be due to restrictions on the motion of the chains imposed by the crosslinks.

The segmented polyurethane PDET + MDI + BD showed a T_g at low temperature associated to the amorphous PDET soft segment and a melting endotherm at high temperature related to the semi-crystalline MDI + BD hard segment, as shown in [Fig S3](#) in [Supporting Information](#). These results are indicative of a phase-separated morphology. In the first heating cycle, the T_g had a value of 16.3°C and the broad melting endotherm spanned from approximately 90 to 190°C . In the cooling cycle from 220°C , a crystallization peak for the hard segment with a minimum at 136.6°C and a T_g for the soft segment were observed. In the second heating cycle, the T_g had a value of 32.7°C , 15°C above the value observed in the first heating cycle, and the melting endotherm with multiple maxima was observed between 140 and 211°C , with the maximum at 169.3°C and peak area equal to the peak area of the crystallization exotherm determined in the cooling cycle.

The increase in the value of the T_g and the shift to higher temperatures of the melting endotherm could be explained assuming an improvement of the phase separation after cooling from the melt. After casting from solution, the hard segment crystallized in a more disordered state than when crystallized from the melt. The increased ordering of the hard segments from the melt produced larger crystals leading to a higher melting point and, concurrently, hindering the motion of the soft segments and increasing the value of T_g . Considering that crystallites could act as multifunctional crosslinking points and reinforcing nanofillers in the phase separated polyurethane compared to the single-point crosslinks in PDET-TriHDI networks, the influence of the hard segment domains on limiting chain motions could exceed that of crosslinks and, consequently, the value of the T_g could be higher for the PDET + MDI + BD polymer than for the PDET-TriHDI network. This improvement in phase separation with thermal treatment has been found in linear segmented poly(ether-urea)s [28] and poly(ether-imide)s [29]. Similarly, in very early studies of thermal treatment on linear segmented polyurethanes molded or cast from solution [30], a shift to higher temperatures of the multipeak endotherm corresponding to the melting of hard segment regions was observed.

The PDET chains for all the polymers derived from the PDET with a molecular weight of $3,650 \text{ g}\cdot\text{mol}^{-1}$ in this study were amorphous. Pure PDET chains have been shown to be able to crystallize from dilute solutions resulting in 20 to 33% crystallinity with a melting point of up to 84°C [31]. It has also been shown that the same chains are not able to crystallize from the melt. In the polymers of this study, PDET chains were not able to crystallize even from solution during casting of the films. The value of T_g for completely amorphous PDET materials was 2°C , as obtained by DSC with extrapolation at zero heating rate, which is similar to the value found for the non-segmented polyurethanes PDET + MDI and PDET + TriHDI.

3.4. Mechanical properties

The mechanical properties in tension for the prepared polyurethanes are listed in Table 1, and representative stress-strain curves are shown in Fig. 1.

All the polyurethanes showed fair to good mechanical properties. Non-segmented polyurethanes presented the typical curve for a soft elastomeric polymer with a very low Young modulus. The curves for these polyurethanes were superimposable up to approximately 400% strain, and above this strain value, the crosslinked polymer PDET + TriHDI increased its stress values with respect to the linear polymer PDET + MDI at the same strain values due to crosslinking. Crosslinking leads to a higher tensile stress value and a lower strain value at failure. The shape of the curve was different for the linear segmented polyurethane PDET + MDI + BD. At low strain values, stress built up rapidly until a yield point was reached at approximately 35% strain and, from this point, stress grew almost linearly with strain until rupture. This shape is typical for polyurethanes with phase separated morphology. As indicated earlier, for thermal properties, the phase-separated hard segments act as multifunctional physical crosslinks and a reinforcing nanofiller, increasing the Young modulus more than 10 times respect to the non-segmented polyurethanes and the tensile strength.

3.5. Dielectric measurements

Knowledge of molecular dynamics in the vicinity of the glass transition is paramount to understand better the vitreous state of a material and its macroscopic properties. In the case of polymers, broadband dielectric spectroscopy is powerful tool to study relaxations allowing their analysis in a wide interval of frequencies and temperatures.

The treatment of relaxations using dielectric permittivity measurements is usually made by means of the empirical equations developed by Havriliak-Negami [32–34], where the complex permittivity, $\epsilon^*(\omega)$, is given by:

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{(\epsilon_0 - \epsilon_\infty)}{[1 + (i\omega\tau_{HN})^\alpha]^\beta} - i \frac{\sigma}{\epsilon_0\omega^s} \quad (3)$$

where $\omega = 2\pi f$ is the angular frequency with the frequency f in Hz, ϵ_0 and ϵ_∞ are the permittivity in the vacuum and the limiting high frequency permittivity, respectively, σ is the DC conductivity due to interfacial electrode polarization, s is a fitting parameter usually close to a value of one and τ_{HN} is a time characteristic associated to the relaxation studied, in this case to the glass transition. The exponents $0 < \alpha \leq 1$ and $0 < \beta \leq 1$ represent the departure of a Debye type relaxation where both exponents are equal to the unity, a unique relaxation time is supposed for all the molecules and a plot of the imaginary part of the permittivity ϵ'' vs the real part ϵ' gives a semicircle. A more complete description of the dielectric properties was given by Cole-Cole [35,36] ($\beta = 1$) and Cole-Davidson [37,38] ($\alpha = 1$) and subsequently by Havriliak-Negami as indicated above. After extracting the imaginary part ϵ'' from equation (3) the following equation is obtained [39]

$$\epsilon''(\omega) = r^{-\beta/2} [(\epsilon_0 - \epsilon_\infty) \sin(\beta\theta)] + \frac{\sigma}{\epsilon_0\omega^s} \quad (4)$$

Table 1

Glass transition temperature, activation energies for the α relaxation and mechanical properties in tension for the PDET derived polyurethanes.

Polyurethane	Tensile stress, MPa	Tensile strain, %	Young modulus, MPa	T_g , K	E_a , kJ/mol
PDET + MDI	9.3 ± 1.8	2490 ± 70	2.34 ± 0.13	282	15.4
PDET + TriHDI	21 ± 5	1800 ± 110	2.1 ± 0.6	280	12.9
PDET + MDI + BD	26 ± 2	1270 ± 130	24 ± 3	280	7.6

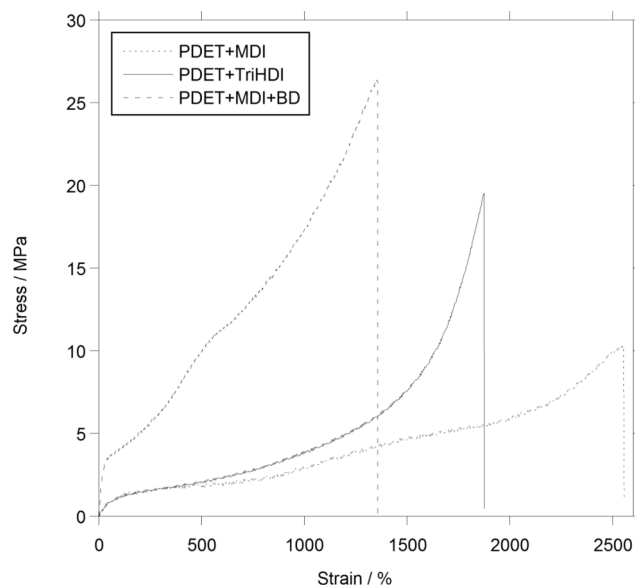


Fig. 1. Tensile stress–strain curves for the PDET based polyurethanes PDET + MDI (dotted line), PDET + TriHDI (solid line) and PDET + MDI + BD (dashed line).

where

$$r = \left[1 + (\omega\tau_0)^\alpha \cos\left(\frac{\pi}{2}\alpha\right) \right]^2 + \left[(\omega\tau_0)^\alpha \sin\left(\frac{\pi}{2}\alpha\right) \right]^2 \quad (5a)$$

$$\theta = \arctan \left[\frac{(\omega\tau_{HN})^\alpha \sin\left(\frac{\pi}{2}\alpha\right)}{1 + (\omega\tau_{HN})^\alpha \cos\left(\frac{\pi}{2}\alpha\right)} \right] \quad (5b)$$

An example of the variation of ϵ'' with the frequency for the membranes studied at different temperatures is illustrated in Fig. 2, where the relaxations associated to the glass transition, as well as straight lines at low frequencies due to conductivity effects are shown.

On the other hand, the relaxation time τ_{max} associated with the maximum at the α -relaxation is given by [40]

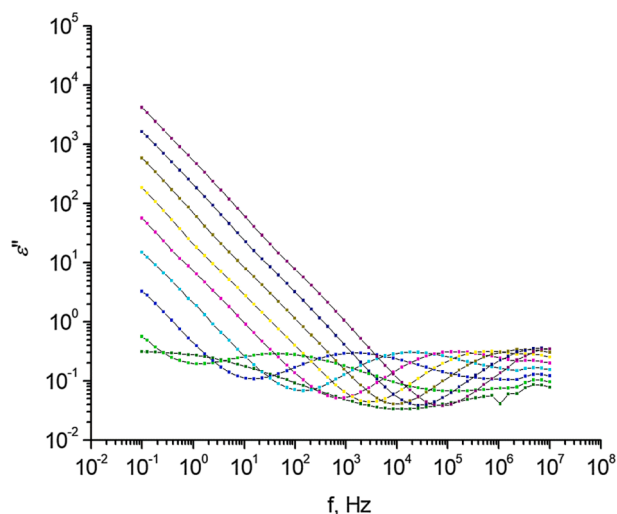


Fig. 2. Variation of the imaginary dielectric permittivity with frequency corresponding to a sample of PDET + MDI, at temperatures between 20 and 100 °C. The temperature interval is 10 °C.

$$\tau_{max} = \tau_{HN} \left[\frac{\sin\left(\frac{\pi\alpha\beta}{2\beta+2}\right)}{\sin\left(\frac{\pi\alpha}{2\beta+2}\right)} \right]^{1/\alpha} \quad (6)$$

These relaxation times can be used to determine their temperature dependence and, consequently, the activation energy associated to the glass transition for the different membranes. An example is shown in Fig. 3.

Similarly, relaxation times can also be obtained from the variation of the dielectric modulus with temperature at low frequencies. The complex dielectric modulus is defined by

$$M^*(\omega) = \frac{1}{\epsilon^*} = M'(\omega) + iM''(\omega) \quad (7)$$

or the inverse of the permittivity, and consequently includes both real and complex dielectric permittivity parameters. Thus, M'' can be used to eliminate electrode polarization effects.

The characteristic time of a given relaxation could also be determined from plots of M'' at varying frequency and its dependence with temperature. Fig. 4 shows an example for the pure polyurethane PDET-MDI which exhibits a behavior similar to that observed for the relaxation times determined from the loss permittivity, as both correspond to the same relaxation. Values of the so-called laboratory glass transition temperature [41] for a relaxation time of 100 s were calculated using the Vogel-Vulcher-Tamman equation to the experimental relaxation times.

$$\tau = \tau_0 \exp\left(\frac{A}{T - T_0}\right) \quad (8)$$

where τ is the relaxation time at the measurement temperature T , and τ_0 , A and T_0 are fitted parameters. T_0 is the Vogel temperature, and A may be considered as an apparent activation energy ($A = E_a R$, R constant of gases) of the α relaxation.

The non-linear analysis of the data according to Equation (8) allows to determine the desired parameters and the corresponding T_g at $\tau = 100$ s, as it is shown in the example of Fig. 3.

Also, the isochronal graphical curves (Fig S4 and S5 in Supporting Information), could be used to determine the glass transition temperatures at low frequencies. However, the observed changes of M' and M'' with temperature and frequency show a complex pattern and this behavior is currently not well understood.

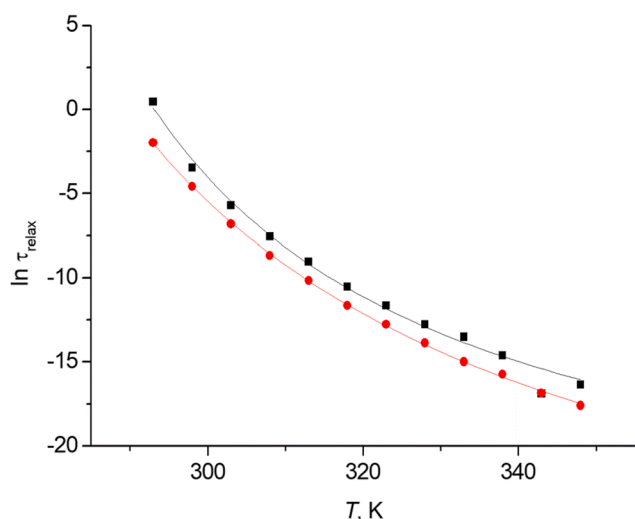


Fig. 3. Variation of the natural logarithm of the relaxation times, obtained from the imaginary components of permittivity (black, squares) or modulus (red, circles) with temperature for PDET + MDI. The continuous lines were obtained by fitting of the experimental points to the Vogel-Fulcher-Tamman equation.

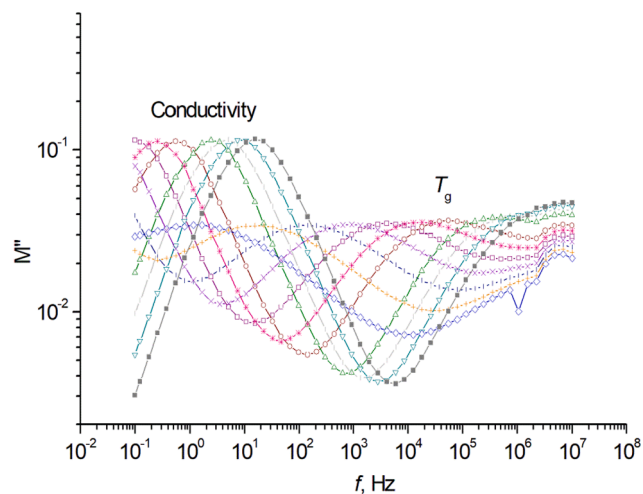


Fig. 4. Variation of the imaginary dielectric modulus M'' with frequency corresponding to a sample of PDET + MDI, at temperatures between 20 and 75 °C, at intervals of 5 °C.

A comparison of the relaxation times corresponding to M'' (Fig. 5) for the three polyurethanes studied to determine the T_g and calculate the corresponding activation energies associated to the α relaxation was performed. The values of T_g and the activation energy, for the different polyurethanes are shown in Table 1. The glass transition temperatures corresponding to these polyurethanes are very similar, which could be anticipated if we take into consideration that the long segment of the PDET is present in all polymers. However, the values of the activation energy of the α -relaxation are very different. It seems that the decreasing of the values of E_a is associated to a decrease of the theoretical flexibility originated by crosslinking or by introducing a hard segment in the macromolecular chain. We consider that more studies are needed to assess this apparently anomalous result and determine its consistency.

3.6. Gas transport coefficients

The permeability and diffusivity coefficients were calculated from the curves measuring the pressure increase at the downstream side, as

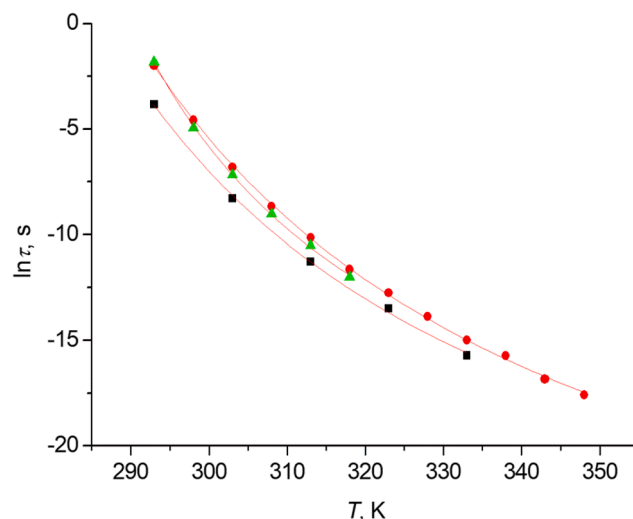


Fig. 5. Relaxation times obtained from the imaginary part of the dielectric modulus M'' as a function of temperature for the three polyurethanes derived from PDET, (red) PDET + MDI, (black) PDET + TriHDI and (green) PDET-MDI-BD. The continuous lines correspond to the fitting of the experimental points to the Vogel-Fulcher-Tamman equation.

indicated in the methods. Fig S6 in Supporting Information illustrates an example.

In Table 2 all the results corresponding to the diffusion of different gases studied in the three polymer membranes are shown.

The solubility coefficients S of these membranes were in the range between 0.005 and 0.013 cm³ (STP)/(cm³ cmHg), in reasonable agreement with the value determined for ¹³C₂O₂ by NMR spectroscopy, $S = 0.018$ cm³ (STP)/cm³ cmHg, a 30 °C and 3.7 bar for the crosslinked membrane (Fig S7 in Supporting Information).

For these membranes with small values of permeability, the most reliable results might be those of permeability, whereas the other transport coefficients (D , S) are strongly dependent of the measurement procedure. On the other hand, we could not measure the diffusion coefficients of ¹³C dioxide by NMR due to the low value of its solubility coefficient and, especially, because the transverse relaxation time T_2 is shorter than 1 ms.

The values for permeability are comparable to the values found for PET. In literature, PET permeability is in the range 0.029–0.13 barrer for O₂, and in the range of 0.14–0.69 barrer for CO₂. In one specific case, the values given are 0.128 barrer for O₂, 0.69 barrer for CO₂ and 0.03 barrer for N₂ [42], and in a recent work, the values determined for a 23 μm film of PET were 0.022 barrer for O₂ and 0.12 barrer for CO₂. [43] If we compare the values in Table 2 with the lowest values measured for PET, it is clear that the crosslinked polymer PDET + TriHDI shows permeability values similar to those of PET and that linear polymers have values an order of magnitude higher for O₂ and approximately twice for CO₂. Still, values for linear polymers are very low.

Poly(ethylene terephthalate) (PET) is one of the most widely used barrier polymers for food and beverage packaging because its gas permeability is low enough to significantly prolong the shelf life of packaged products. High barrier polymers are most generally crystalline or glassy amorphous. It is difficult to find an elastomeric polymer with high barrier polymers. Values in Table 2 allow for the classification of these elastomeric PDET based polyurethanes as barrier polymers. In particular, the crosslinked polyurethane shows the lowest values of permeability. This difference in gas barrier performance between the crosslinked and the linear materials could be attributed to the presence of crosslinks in the former which might reduce the free volume and hinder the molecular mobility.

Butyl rubber is well known among elastomers for its superior gas barrier characteristics. Measured permeabilities for butyl rubber are 1.28 barrer for O₂, 5.00 barrer for CO₂ and 0.324 barrer for N₂ [44]. These values are approximately an order of magnitude higher than for the elastomeric PDET based polyurethanes, thus the barrier properties of these polymers are among the best for elastomers. Recently an elastomeric polymer based on poly(ethylene 2,5-furandicarboxylate) modified with 40% weight of an aliphatic polycarbonate diol presented values close to PET and PDET + TriHDI, 0.053 barrer for O₂ and 0.20 barrer for CO₂ [43], but with significantly lower extensibility (203%) than PDET + TriHDI.

4. Conclusions

Two high molecular weight linear and one fully crosslinked PDET-based polyurethanes were prepared. Thermal properties showed that, for the linear polyurethane without chain extender and the crosslinked polyurethane, a single phase-morphology with T_g below ambient temperature was obtained. For the linear polymer with chain extender, a phase-separated morphology was obtained with amorphous PDET soft segment and partially crystalline hard segment. The dielectric measurements unveiled complex spectra and similar values of T_g for the α relaxation in all samples. Mechanical properties of the polyurethanes were fair to good, with elastomeric behavior and very high strain at break as shown by the stress-strain curves. Elastomeric PDET based polyurethanes can be classified as gas barrier polymers with permeability values similar to PET and one order of magnitude lower than butyl

Table 2

Permeability and diffusion coefficients of O₂, N₂ and CO₂, in PDET membranes at 30 °C.^a

Membrane	P_{O_2} , barrer	P_{N_2} , barrer	P_{CO_2} , barrer	$D_{O_2} \times$ 10^8 , cm ² /s	$D_{N_2} \times$ 10^8 , cm ² /s	$D_{CO_2} \times$ 10^8 , cm ² / s
PDET + MDI	0.16	0.02	0.46	0.22	0.036	0.52
PDET + MDI + BD	0.19	0.05	0.51	0.58	0.23	0.38
PDET + TriHDI	0.018	0.008	0.17	0.16	0.11	0.16

^a The measurements were carried out at different pressures, although the values of the permeation coefficients were practically independent of pressure due to the amorphous nature of the membranes and also due to operating at higher temperatures than the glass transition. The estimated error in these measurements is 5%.

rubber.

CRedit authorship contribution statement

Ángel A. Marcos-Fernández: Conceptualization, Methodology, Investigation, Writing. **Rodrigo Navarro:** Investigation. **Esperanza Benito:** Investigation. **Julio Guzmán:** Conceptualization, Methodology, Investigation, Writing. **Leoncio Garrido:** Investigation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors acknowledge the financial support of the Ministry of Economy and Competitiveness (MINECO) grants MAT2017-87204-R and RTI2018-096636-J-100 and Consejo Superior de Investigaciones Científicas (CSIC) grant 201960E004.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2021.110576>.

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