

Hydrophilic polyurethaneurea membranes: influence of soft block composition on the water vapor permeation rates

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Abstract

High molecular weight segmented polyurethaneurea (PUU) copolymers based on an aliphatic diisocyanate, bis(4-isocyanatocyclohexyl)methane and mixed hydrophilic and hydrophobic soft segments were prepared. Hydrophilic blocks consisted of poly(ethyleneoxide) (PEO) of molecular weight 1450 g/mol, whereas the hydrophobic blocks were poly(tetramethylene oxide) of molecular weight 2000 g/mol. Ethylene diamine was used as the chain extender. Hard segment contents of the copolymers were kept constant at 18%, whereas PEO contents were varied between 0% and 50% by weight. Water vapor permeation rates (WVPR) of thin films (23–178 μm) cast from dimethylformamide solutions were determined. In studies performed at 23°C and 50% relative humidity, the relationship between PEO content and WVPR followed an S-shaped curve. For copolymers containing up to about 15% by weight of PEO, WVPR were fairly low. This was followed by a region where WVPR increased continuously for membranes containing between 15% and 30% PEO. Further increase in PEO content above 30% did not influence the WVPR substantially. There was also a dramatic increase in WVPR with an increase in temperature from 23°C to 37°C. Activation energy of permeation was determined to be 91.5 kJ for PUU containing 22.0% by weight of PEO. Equilibrium water absorption levels of PUU containing different levels of PEO in their backbone structures followed a similar trend to that of WVPR. Hydrophilic PUUs showed good tensile properties and mechanical integrity even at very high levels of water absorption. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrophilic polyurethanes; Membranes; Water vapor permeability

1. Introduction

Multiphase, segmented polyurethanes (PU) and polyurethaneureas (PUU) consisting of alternating soft and hard segments are one of the most frequently investigated classes of copolymers because of their wide range of properties [1,2]. These polymers find applications in many different fields, such as adhesives, protective coatings, biomaterials, textile fibers, high performance elastomers, etc. Interesting physical, chemical and elastomeric properties of PU and PUU are directly related to the chemical composition of their backbones and resulting microphase separated solid state morphologies which are strongly dependent on the composition, type and molecular weights of the soft and hard segments and the synthetic procedures followed. It is well documented that the strength and high elasticity of PU and PUU are because of the hard domains stabilized by hydrogen bonding [3,4]. Availability of a very large selection of building blocks and flexibility in the synthetic techniques provide opportunities for the preparation of a wide

variety of segmented PU and PUU backbone structures. The selection includes a large number of aliphatic or aromatic diisocyanates and diol or diamine chain extenders as the hard segments and more importantly various dihydroxy or diamine terminated reactive oligomers such as, polyethers, polyesters, polybutadienes, polysiloxanes and polyacrylates, with different molecular weights, as the soft segments. Each of these soft and hard segments impart unique physical and chemical properties to the polyurethanes prepared from them [1].

Hydrophilic polyurethanes are composed of soft segments which are water soluble or highly water swellable. The best examples of such oligomers are poly(ethylene oxide)s of any molecular weight. Oligomers composed of random or block ethylene oxide and propylene oxide units can also be considered as hydrophilic depending on the level of ethylene oxide in their chemical compositions. Hard segments in hydrophilic polyurethanes are made of conventional diisocyanates and organic diols or diamines and they are usually not water soluble. However, in some cases, when carboxylated or sulfonated diols or diamines are used as chain extenders, hard segments may also have

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hydrophilicity [5]. Important applications of hydrophilic polyurethanes include biomaterials, protective wound dressings and water resistant but water vapor permeable textile coatings.

Thin, nonporous, hydrophilic polyurethane (dense) membranes may show good permeability to water vapor depending on their chemical composition and bulk morphologies, whereas they are impermeable to liquid water. The driving force for water vapor transmission process is the difference in the water vapor pressure between the two sides of the membrane, which gives rise to a concentration gradient within the membrane. Solubility of the water vapor in the film also plays an important role. The permeant, water vapor, is first adsorbed on the surface of the membrane on the side of highest water vapor concentration. Then it diffuses across by dissolving in the membrane, which is usually called as activated diffusion. Upon arriving to the opposite surface of the membrane, which has a lower vapor pressure, it is desorbed and enters to the surrounding air space as vapor [6].

Rate of transport of low concentration of a low molecular weight permeant through a dense membrane is given by Henry's and Fick's Laws. A linear relationship between the concentration of vapor in equilibrium with the film and the actual concentration of water vapor dissolved in the film is assumed by Henry's Law, as given in Eq. (1), which holds for many polymers:

$$c = Sp \quad (1)$$

where c is the concentration of permeant weight in the membrane. S is the solubility of the permeant in the membrane, and p is the vapor pressure in equilibrium with film.

Fick's Law, as given in Eq. (2), governs the rate of transport of the permeant through the membrane under the existing concentration gradient:

$$q = -D \frac{dc}{dx} \quad (2)$$

where q is the amount of vapor diffusing through unit area per unit time or the permeation rate, D is the diffusion coefficient or diffusivity, specific for the permeant/polymer system, and dc/dx is the concentration gradient of permeant across the membrane.

If D is not a function of concentration, integration across the film thickness l gives:

$$q = D(c_1 - c_2)/l \quad (3)$$

where c_1 and c_2 are the concentrations of permeant at high and low pressure faces of the membrane surface, and l is the membrane thickness.

Substituting values of c_1 and c_2 from Eq. (1), Eq. (3) becomes:

$$q = DS(p_1 - p_2)/l \quad (4)$$

where, p_1 and p_2 are the external partial pressures of the vapor on the high and low pressure sides of the membrane.

(D.S) is termed as the permeability (P). From Eq. (4), it is clear that for ideal systems, permeation rate of permeant is directly proportional with the pressure gradient and inversely proportional with membrane thickness.

During this study, a series of polyurethaneureas based on HMDI/ED hard segments and PEO/PTMO soft segments were prepared. Molecular weights of the copolymers were limited to approximately 35 000 g/mole through the use of *n*-dibutylamine (DBA) chain terminator. Degree of hydrophilicity was controlled by varying the PEO/PTMO ratios in the soft segments. Influence of the soft segment composition of the polymer backbone and temperature on water vapor permeation rates (WVPR) of the membranes produced were determined. Tensile properties of dry and wet films were also investigated.

2. Experimental

2.1. Materials

Cycloaliphatic diisocyanate, bis(4-isocyanatocyclohexyl)methane (HMDI) was obtained from Bayer AG and had a purity better than 99.5% as determined by the back titration of isocyanate end-groups [1]. Poly(ethylene oxide)glycol (PEO) was a product of Union Carbide and had a number average molecular weight of 1450 g/mol. Poly(tetramethylene oxide)glycol (PTMO) with a number average molecular weight of 2000 g/mol was received from Du Pont. Reagent grade ethylene diamine (ED), dibutylamine (DBA) and dimethylformamide (DMF) were obtained from Aldrich. Dibutyltin dilaurate (DBTDL) catalyst was obtained from Witco. Water contents of PEO, PTMO and DMF were determined by Karl Fisher titration and were found to be 320, 250 and 240 ppm respectively. All chemicals and solvents were used as received.

2.2. Preparation of polyurethaneurea copolymers

A two-step procedure was followed during the preparation of copolymers. First step was the formation of isocyanate terminated prepolymers, followed by the addition of DBA to control the molecular weight (aimed at 35 000 g/mol). The second step was the chain extension with ED to form high molecular weight copolymers. Typical procedure for the preparation of PUU with a PEO content of 22.0% by weight was as follows: A four-neck, flat bottomed 1000 ml pyrex reaction kettle fitted with an overhead stirrer, addition funnel, thermometer and dry nitrogen inlet, was charged with 24.7 g of HMDI (94.1 mmol), 90.0 g of PTMO (45.0 mmol) and 33.0 g of PEO (22.8 mmol). The system was heated up to 80°C in an oil bath and stirred. Reaction was started by the addition of 0.005 g of DBTDL catalyst in 1 ml of toluene. The reaction was monitored by FTIR spectroscopy using a Nicolet Impact 400D spectrometer. Prepolymer formation was completed in two hours. Isocyanate content of the prepolymer was determined [1]. This was

Table 1
Chemical compositions of polyurethaneurea segmented copolymers

Sample code	HMDI (g)	PEO (g)	PTMO (g)	DBA (g)	ED (g)
PUU.00	24.40	0	123.0	1.13	1.57
PUU.07	24.45	10.50	112.5	1.13	1.43
PUU.14	24.45	21.00	102.0	1.13	1.32
PUU.18	24.75	27.00	96.00	1.13	1.35
PUU.22	24.70	33.00	90.00	1.12	1.30
PUU.25	24.90	37.50	85.50	1.10	1.28
PUU.27	24.85	40.50	82.50	1.09	1.27
PUU.34	25.00	51.00	72.00	1.09	1.18
PUU.42	24.90	63.00	60.00	1.09	0.92
PUU.50	25.20	75.00	48.00	1.08	0.79

mostly around 96%–98% of the theoretical amount. Remaining isocyanate was lost as a result of side reactions, which are typical in these systems [1,7]. Then the prepolymer was dissolved by adding 300 g of DMF into the reactor and the solution was cooled down to room temperature. At this point 1.12 g of DBA (8.67 mmol) in 25 g DMF was added to control the molecular weight of the polymer to be formed. For chain extension 1.30 g ED (21.62 mmol) was dissolved in 50 g of DMF and introduced into the addition funnel. ED solution was added dropwise into the reactor, at room temperature and high molecular weight polymers were obtained. Towards the end of the chain extension process as the viscosity of the reaction medium increased, 75 g more DMF was added for dilution. Table 1 gives the detailed compositional data on PUU copolymers prepared and characterized in this study.

2.3. Membrane preparation

Membranes with controlled thicknesses were cast on either polydimethylsiloxane coated release paper or poly(ethylene terephthalate) sheets from DMF solution using a Doctor's blade. In order to prepare pinhole free films, DMF was first very slowly evaporated at room temperature. Then the temperature was increased to 120°C and kept there for 2 h. Final traces of DMF was removed by keeping the membranes in vacuum oven at 60°C overnight. Membranes thus obtained were examined under light microscope to ensure they were pinhole free.

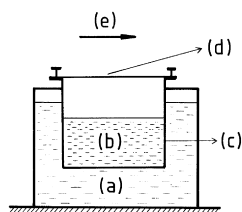


Fig. 1. Schematic representation of the set-up used in the measurement of WVPR. (a) Thermostated water bath, (b) deionized, triple distilled water, (c) permeability cup, (d) polyurethaneurea membrane and (e) air flow with a velocity of 4 m/s.

2.4. Measurement of water vapor permeation rate (WVPR)

WVPR was measured according to ASTM method E 96-80B. Round bottomed stainless steel cups with a diameter of 65 mm and a height of 50 mm were filled with deionized, triple distilled water to about half depth. Membranes were placed over the top of the cups, secured with a metal ring and were clamped to ensure perfect sealing. The cups were placed in a constant temperature bath at the desired temperature (23°C, 27°C, 30°C or 35°C). During all WVPR measurements air surrounding the membranes had a constant temperature of 23°C and 50% relative humidity. An air flow with a velocity of 4 m/s over the sample was also maintained. Fig. 1, schematically shows the setup used during these measurements. Samples were conditioned in the environment for 24 h before the measurements. WVPR were determined by periodically measuring the weight loss in the cups using an analytical balance. On the average 4 different samples were used for each WVPR measurement, which is expressed in units of (g/m²/24 h).

2.5. Determination of water absorption at 23°C

Polymer films with dimensions of 5.0 × 5.0 × 0.1 cm were prepared on glass plates by casting from DMF solutions. Solvent was first slowly evaporated under an IR lamp in a hood and then in a vacuum oven at 75°C until constant weight was reached. These films were then immersed into distilled water in a constant temperature bath at 23°C and kept there until equilibrium water absorption levels were reached. Percent water absorption was determined gravimetrically by weighing the water saturated films after removing excess water on the film surfaces with a paper towel.

2.6. Tensile tests

Stress–strain behavior of PUU films, under dry conditions or when completely saturated with water, were determined using an Instron Model 4411 Universal Tester at room temperature. Dog-bone samples were tested with a crosshead speed of 2 cm/min. Films for these tests, at a thickness of about 1 mm, were cast onto glass plates from DMF solution. Solvent was first slowly evaporated under an IR lamp in a hood and then in a vacuum oven at 75°C until constant weight was reached. Dog-bone samples were cut from these films using a standard die.

3. Results and discussion

High molecular weight hydrophilic polyurethaneurea copolymers with mixed PEO/PTMO soft segments and HMDI/ED hard segments were prepared. Hard segment contents of these copolymers were constant at 18.0% by weight. PEO content of the backbone was varied between 0% and 50% by weight. Table 1 gives the chemical compositions of PUU copolymers synthesized. Progress and

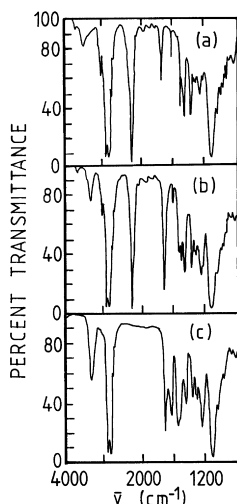


Fig. 2. FTIR spectra of reactants and products at various stages of polymerization reaction. (a) Initial reaction mixture, (b) prepolymer and (c) final polyurethaneurea product.

completion of polymerization reactions were monitored by FTIR spectroscopy. Fig. 2(a) gives the FTIR spectrum of prepolymer mixture for polymer PUU.22, which shows a very strong isocyanate ($\text{N}=\text{C}=\text{O}$) peak at 2260 cm^{-1} and a broad hydroxyl (OH) peak centered around 3400 cm^{-1} . At the end of the prepolymer formation (Fig. 2(b)), as expected, hydroxyl peak has completely disappeared and the intensity of the isocyanate peak has been somewhat reduced. In contrast, as expected, two major peaks due the formation of urethane groups ($\text{NH}-\text{CO}-\text{O}$) have appeared. These are, the sharp peak at 1750 cm^{-1} , caused by carbonyl ($\text{C}=\text{O}$) absorption and another strong peak at 3300 cm^{-1} caused by ($\text{N}-\text{H}$) stretching of the urethane group. Fig. 2(c) gives the FTIR spectrum of the chain extended, final product. As expected, the isocyanate peak has completely disappeared.

Fig. 3 gives the WVPR of $25\text{ }\mu\text{m}$ thick membranes prepared from polymers containing different levels of PEO. These measurements were done at 23°C . It is interesting to note that the change in WVPR with respect to PEO/PTMO ratio in the soft segments follow an S-shaped curve. As explained later, we believe this is directly related to the change in the solid state morphologies of the continuous soft

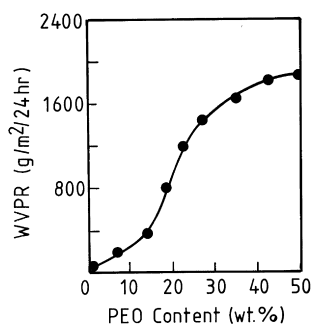


Fig. 3. A plot of the Water Vapor Permeation Rates of polyurethaneurea membranes against the Poly(ethylene oxide) content of the copolymer.

segment matrices in PUU copolymers as the PEO/PTMO ratio is changed [8]. It is well known that interesting properties of segmented PUU are as a result of good phase separation between moderately polar polyether soft segments and extremely polar polyurea hard segments [2–4]. A good measure of the polarity of a group or a molecule is the value of its cohesive energy density (CED) or the solubility parameter (δ) which is the square root of CED [9]. Solubility parameters for moderately polar poly(ethylene oxide) and poly(tetramethylene oxide) are 9.0 and $8.6\text{ (cal/cm}^3)^{1/2}$ respectively [9]. Solubility parameters for highly polar and strongly hydrogen bonding urethane and urea groups are 14.2 and $16.8\text{ (cal/cm}^3)^{1/2}$ respectively [9]. Such a high difference between solubility parameters of polyether soft segments and polyurethane and/or polyurea hard segments give rise to phase separation between these segments in the solid state. PUUs prepared in this work contain about 18.0% hard and 82.0% soft segments by weight. As a result, the solid state morphology of these PUUs consists of a continuous matrix of soft segments with hard segment domains scattered in this matrix. Hard segments provide the mechanical strength and integrity to these membranes, whereas the permeability to the water vapor is related to the PEO content of the continuous soft segment matrix. This is clearly seen in Fig. 3, where, Sample PUU.00 containing only PTMO as the soft segment shows an extremely low WVPR value of less than $50\text{ g/m}^2/24\text{ h}$. This is expected, since PUU.00 has no hydrophilic character. As the PEO content in PUU is increased up to around 15% by weight WVPR also increases slowly. However, when the PEO content of PUUs are further increased to above 15% by weight there is a dramatic increase in WVPR. This strongly indicates that within the soft matrix composed of PEO and PTMO, when PEO content is less than 15% by weight, the soft matrix is dominated by PTMO continuous phase, with PEO distributed in it [8]. As the amount of PEO is increased, a co-continuous PEO and PTMO morphology forms in the soft matrix giving rise to a substantial increase in WVPR. Absorption of water vapor by PEO segments will further enhance the phase separation in the soft matrix since the polarity difference will be greater between PTMO and PEO phases. It is very difficult to directly observe this morphological change by microscopy, differential scanning calorimetry or dynamic mechanical thermal analysis, since T_g and T_m values of PEO and PTMO are very close to each other. T_g and T_m for PEO, which are molecular weight dependent, are reported to be around -65°C and 50°C respectively for low molecular weight oligomers [10]. For PTMO, T_g and T_m values are reported as -80 and 50°C [11]. In the absence of water, PEO and PTMO oligomers which have similar solubility parameter values also show partial miscibility when mixed. This also suggests that in copolymers containing low levels of PEO, it will be dissolved/distributed within continuous PTMO matrix. In contrast, as PEO content of the soft segment is increased above a critical level and the system is brought in contact with water or water vapor, moisture will

Table 2
Tensile properties of polyurethaneurea copolymers before and after water absorption

Sample code	Absorbed water (% by weight)	Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PUU.00		4.15	33.1	900
PUU.00	2	4.10	31.7	920
PUU.22		3.80	31.0	1000
PUU.22	25	3.60	24.1	1100
PUU.34		3.45	29.0	1100
PUU.34	74	2.00	9.45	1750
PUU.42		3.45	27.6	1000
PUU.42	110	1.15	3.52	2000

Table 3
Relationship between membrane thickness and WVPR for PUU.22 membranes

Membrane thickness (μm)	$1/\text{thickness } (\mu\text{m})^{-1}$	WVPR ($\text{g}/\text{m}^2/24 \text{ h}$)
23	0.0435	1400
36	0.0278	1180
51	0.0196	1000
114	0.0088	750
178	0.0056	480

mainly be absorbed by PEO in the system. This will dramatically change the polarity of PEO domains and force them to phase separate from PTMO, resulting in a co-continuous PEO/PTMO soft matrix. From our results, this phenomenon seems to be taking place when about 15% by weight of PEO is incorporated into our copolymers.

This is also strongly supported by Fig. 4, which shows the equilibrium water absorption of PUUs with different PEO contents, at 23°C. Amount of water absorbed increases linearly but with a fairly small slope up to about 15% by weight of PEO in the PUUs. Then there is still a linear relationship between water absorbed and PEO content of the copolymer, however, the slope is much steeper. Similar behavior was also observed by other researchers in polyurethanes prepared from HMDI, varying ratios of PTMO/PEO soft segments and chain extended with 1,4-butanediol [12].

Table 2 gives the tensile properties of several PUUs at

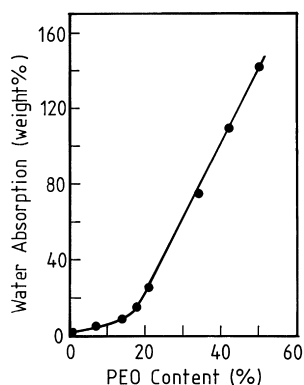


Fig. 4. Equilibrium water absorption of polyurethaneurea membranes at 23°C as a function of their Poly(ethylene oxide) content.

room temperature before water absorption and after completely saturated with water. As it is clearly seen from Table 2, under ambient conditions all polymers display similar values for initial tensile modulus, tensile strength and elongation at break. Moduli values for these polymers, before saturation with water, are between 3.45 and 4.15 MPa, tensile strengths between 27.6 and 33.1 MPa and elongation at break between 900% and 1100%. This is expected since they all have the same hard and soft segment contents and very similar polymer molecular weights. When saturated with water, not much change is observed in PUU made of all PTMO as the soft segment since it only absorbs around 2% of water by weight. In contrast, in water saturated PEO containing PUUs as the amount of PEO in the system is increased substantial reductions in tensile strengths and increases in the elongation at break values are observed. The change in tensile moduli values are somewhat smaller. This is an expected behavior, because, in segmented polyurethaneureas the modulus is directly related to the type and amount of hard segment in the copolymer [2]. In contrast, tensile strength and elongation at break are dependent on the combined effects of hard and soft segments or more precisely the overall morphology of the copolymer. The dramatic drop in the tensile strength of PEO containing wet polymers is as a result of the plasticization effect of water, which is mainly absorbed by PEO soft segments. Water can also interact with urea hard segments through hydrogen bonding [2,13–15], and weakens their strengths as physical crosslinks, but to a smaller extent. Therefore, the net result of the water plasticization is a dramatic weakening in the soft matrix and thus in the tensile strengths of the

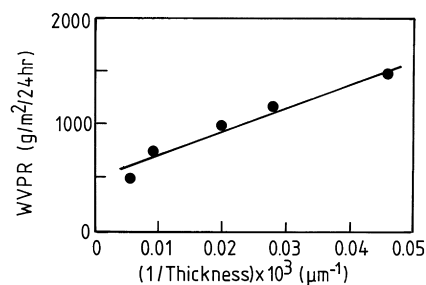


Fig. 5. Relationship between the Water Vapor Permeation Rates and Membrane Thickness for PUU.22 membranes.

Table 4

Water vapor permeation rates as a function of temperature and water vapor pressure for PUU.22 membranes with a thickness of 115 μm

Temp. ($^{\circ}\text{C}$)	Water vapour pressure (kPa)		ΔP (kPa)	WVPR ($\text{g}/\text{m}^2/24 \text{ h}$)	$\ln(\text{WVPR})$	$1/T (1/\text{K})10^3$
	P_{cup}	$P_{\text{surrounding}}$				
23	2.809	1.404	1.405	750	6.620	3.378
27	3.565	1.404	2.161	1320	7.185	3.333
30	4.243	1.404	2.839	1820	7.505	3.300
35	5.623	1.404	4.219	2900	7.972	3.247

copolymers, and a somewhat smaller reduction in the tensile moduli. However, even PUU.42 films which absorbs 110% by weight water when saturated, show very good mechanical integrity. This is mainly because of the extremely strong hydrogen bonding in the urea hard segments [16].

Table 3 gives the WVPR of PUU.22 as a function of membrane thickness in a fairly broad range of 23 to 178 μm . As expected from Eq. (4), there is an inverse linear relationship between water vapor permeability and film thickness, which is clearly shown in Fig. 5. This also indicates that at 23 $^{\circ}\text{C}$ and 50% relative humidity, under fairly mild conditions, the system behaves ideally.

Table 4 gives the data on the change of WVPR as a function of temperature for PUU.22 membranes with a constant thickness of 115 μm . As expected, WVPR increases as the temperature is increased. Actual driving force in this process is the increase in the vapor pressure of the water inside the heated permeability cups when compared with the atmosphere surrounding the system, which has a constant temperature of 23 $^{\circ}\text{C}$ and constant relative humidity of 50%, during measurements. As predicted by Eq. (4), and shown in Fig. 6, linear relationship is obtained when WVPR is plotted against the vapor pressure difference on two sides of the membranes.

Using data in Table 4 we also constructed an Arrhenius type plot between permeation rates (WVPR) and temperature. As shown in Fig. 7, this data shows almost a perfect fit to Arrhenius relationship. From the slope of the line, activation energy (E_a) for diffusion of water vapor through PUU.22 membranes is calculated to be 91.5 kJ. This is a

fairly small activation energy indicating that such PUU membranes show very high permeability to water vapor.

4. Conclusions

Segmented, hydrophilic polyurethaneurea copolymers were prepared from HMDI, a mixed PTMO/PEO soft segment and ED chain extender. Overall molecular weights were limited to 35 000 g/mole through the use of DBA chain terminator. Hard segment contents (HMDI + ED + DBA) of the copolymers were kept constant at 18% by weight. Level of hydrophilicity was controlled by varying the amount of PEO in the copolymer from zero to 50% by weight.

Water vapor permeabilities of membranes prepared from these copolymers showed very good fit to Fick's Law, such that there was a linear relationship between WVPR and ΔP (the vapor pressure difference between the two sides of the membrane) and an inverse linear relationship between WVPR and membrane thickness. Polymer with no PEO in its backbone was practically non-permeable to water vapor. As the amount of PEO in the system is increased, first there was a gradual and then (after about 15% of PEO in the backbone) a sharp increase in WVPR. A very similar trend was also observed between PEO content and equilibrium water absorption of these copolymers. Activation energy of water vapor permeation for membranes containing 22% by weight of PEO was determined to be 91.5 kJ. Membranes showed very good mechanical strength and

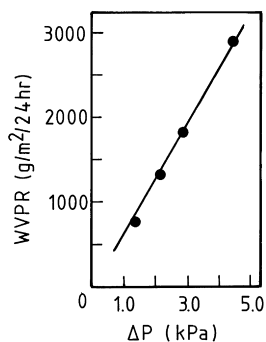


Fig. 6. A plot of the Water Vapor Permeation Rates of PUU.22 membranes against the difference in water vapor pressure between the cup and the surrounding.

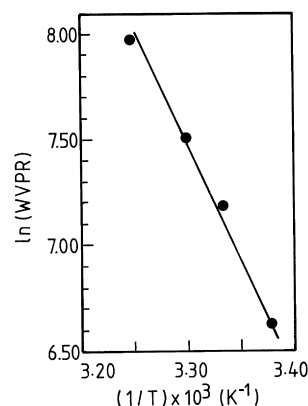


Fig. 7. Arrhenius Plot for PUU.22 membranes.

integrity in dry form or when saturated with water as indicated by tensile test results.

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