

# Gas permeability of cupric ion containing HTPB based polyurethane membranes

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## Abstract

For the purpose of oxygen enrichment from air, the gas permeability and selectivity of an ionic polyurethane membrane was under investigation. Membranes of ionic polyurethane were prepared by step-growth polymerization of hydroxyl terminated polybutadiene (HTPB) and 4,4'-dicyclohexylmethane diisocyanate ( $H_{12}$ MDI). The ionic group was introduced by adding *N*-methyl-diethanolamine (MDEA) as the chain extender of which the tertiary amines were complexed with cupric ions. The effect of hard segment content, polymerization method, peroxide introduction, and the amount of cupric ion on gas permeability were investigated. It was found that the binding of hard segment and the flexibility of soft segments had subtle effects on gas permeability. Membranes of the same composition were synthesized through two different procedures, one- and two-stage polymerization. The former contains large hard segment of cluster aggregation and flexible soft segments had a higher gas permeation rate. When a crosslinker, benzoyl peroxide, was added, the crosslinkage within soft segments hindered cluster formation by hard segment aggregation, the permeability increased. Furthermore,  $CuCl_2$  addition enhanced hard segment aggregation, more hard segments formed cluster aggregates and less dispersed in soft segment region, which also increased permeability. However, excess  $CuCl_2$  addition resulted in  $CuCl_2$  piling up in the soft segment region, which restricted the movement of soft segments and therefore reduced the gas permeability.

**Keywords:** Polyurethane membrane; Hydroxyl terminated polybutadiene; Gas permeability; Ionomer

## 1. Introduction

PU materials have been used to separate oxygen from air. The effect of chemical composition and membrane morphology has been extensively studied. McBride et al. [1] measured diffusion coefficients and activation energy of a series of PU block copolymers of different types of soft segment. Knight and

Lyman [2] studied the influence of the chemical composition of PUs and polyurethane-urea on the gas permeability. Pegoraro et al. [3] measured the diffusion coefficient and its dependence on the structure of PUs with bifunctional, polyfunctional polyols and different chain extender. Hsieh et al. [4] reported that the gas and vapor permeability depended on the type of polyol, molecular weight of polyol and hard segment content. Gallano and Lam [5] reported that the most important factor in diffusion is the molecular weight of soft segment. The effect of chemical composition on the gas permeability may be due to

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the degree of phase segregation and to the nature of chain packing.

Polymer ionomers have become more and more popular for using in gas separation. Sakai et al. [6] prepared Nafion–silver microcomposite membranes having significantly improved  $O_2/N_2$  selectivity ratio because of the affinity between oxygen and silver. Lai and co-workers [7,8] reported that the gas permeability of PC–DMF– $CuCl_2$  or PMMA–DMF– $CuCl_2$  membranes were significantly improved as compared to pure PC or PMMA membranes.

It was due to the use of a chain extender having asymmetrical structure and the presence of the ionic component, PU ionomers exhibit different morphology in comparison to their respective PUs with similar composition. However, there are not enough studies on the morphology of PU ionomers. Some polyurethane ionomers were prepared by incorporating a chain extender containing tertiary amines and then reacting with alkyl halides [9] or glycolic acid [10]. Others are formed by the use of sulfonate containing chain extender [11] or by the addition of  $LiClO_4$  to polyurethane [12,13]. It has been proposed that there are two types of ionic aggregates, termed multiplets and clusters. A multiplet is a group of a few tightly bounded ion pairs, and a cluster, formed at higher ion content, is a domain. The effect of multiplet and cluster on membrane permeability has never been studied.

The purpose of this study is to understand the effect of membrane microstructure on the gas permeability. Polyurethane membranes were prepared by step-growth polymerization of hydroxyl terminated polybutadiene (HTPB) and 4,4'-dicyclohexylmethane diisocyanate ( $H_{12}$ MDI). A tertiary amine functional group was introduced by adding *N*-methyl-diethanolamine (MDEA) as the chain extender. The HTPB– $H_{12}$ MDI–MDEA based polyurethanes were synthesized by two different polymerization methods, namely one- and two-stage processes. The one-stage polymerized PUs were shown to have longer hard segments than the corresponding two-stage PUs [14,15]. It is difficult for long hard segment to disperse in the soft segment and thus made polymers had distinct hard and soft segment domains, that is, lower homogeneity. The membrane microstructure was altered by adding ben-

zoyl peroxide (BPO) as a modifier to the HTPB soft segments. The PU ionomers are obtained by adding the cupric chloride to PU solutions. The effect of hard segment content, addition of BPO and cupric chloride, as well as annealing treatment on gas permeability and selectivity were studied. HBI values, IR wavenumber shift, glass transition temperature and thermogravimetric analysis were used for the identification of phase segregation and chain flexibility.

## 2. Experimental

### 2.1. Materials

The chemicals used in this study were 4,4'-dicyclohexylmethane diisocyanate ( $H_{12}$ MDI, Desmodur W of Mobay), hydroxyl terminated polybutadiene (equivalent weight 1370 g, R-45M of ARCO), *N*-methyl-diethanolamine (MDEA) as chain extender and dibutyltin dilaurate (DBTDL) as catalyst. Benzoyl peroxide (BPO) was used as a cross-linking agent. Cupric chloride was used as complexation reagent. DMF and toluene were used as solvent.

### 2.2. Preparation of polyurethane membrane

The two-stage polyurethanes were polymerized first by a –NCO terminated prepolymer and then chain extended with MDEA under 25 wt% solid content after a theoretical –NCO content had reached. Detailed procedures for polymerization had been reported in a previous publication [16]. The one-stage PUs were prepared by adding proper amount of HTPB, MDEA and solvent mixture of DMF and toluene to a reaction vessel under nitrogen atmosphere and then add a suitable amount of diisocyanate for condensation polymerization.

Uncrosslinked membranes were prepared by pouring the solution mixture onto a glass plate to a thickness of 600  $\mu$ m. The solvent in the casting solution was evaporated by degassing at 50°C for 24 h. The dried PU membranes were peeled from the plate after it had been immersed in deionized water for several hours.

Crosslinked membranes were prepared by adding 1.0 wt% (based on solid PU content) of BPO to PU solution (15 wt% solid content) in a closed vessel at 60°C for 6 h. Benzoyl peroxide was decomposed

first and activated the double bonds of HTPB soft segment. This active site then reacted with other HTPB chain [17]. Then the crosslinkage between HTPB soft segments was formed. All the other membrane preparation steps were the same as that of uncrosslinked membranes.

Ionized membranes were prepared by adding cupric chloride to the above crosslinked PU solutions. The dried ionized membranes were peeled from the plate after it had been put in the refrigerator to the frozen state for several hours.

Membranes of different compositions in this study are denoted, for example by 11211-1C-1/3Cu or 187-2C-1/4Cu. The numbers 11211 and 187 represent the equivalent ratio of HTPB/H12MDI/MDEA = 1/12/11 and 1/8/7, respectively. 1C and 2C means one- or two-stage polymerized and then crosslinked by BPO. 1/3Cu or 1/4Cu means the addition of 1/3 or 1/4 mole ratio of cupric chloride with MDEA content to the PU composition, respectively. All these membranes were then put in oven under vacuum at 70°C for 48 h for further degassed the solvent residue. Finally, the samples were kept under vacuum, at room temperature for at least 5 days prior to property testing.

### 2.3. Gas permeation measurement

Oxygen and nitrogen permeabilities of membranes were determined by using the Yanaco GTR-10

gas permeability analyzer. Detailed procedures for measuring the gas permeation had been reported in a previous publication [18]. The gas permeability was determined by the following equation:

$$P = \frac{ql}{(p_1 - p_2)At}$$

where  $P$  is the gas permeability [ $\text{cm}^3(\text{STP}) \text{cm}/\text{cm}^2 \text{s cm Hg}$ ],  $q$  is the volumetric flow rate of gas permeation [ $\text{cm}^3(\text{STP})/\text{s}$ ],  $l$  is the membrane thickness (cm),  $p_1$  and  $p_2$  are the upstream and downstream pressures (cm Hg) and  $A$  is the effective membrane area ( $\text{cm}^2$ ).

### 2.4. Properties measurements

#### 2.4.1. Infrared spectroscopy

JASCO-FTIR 310E was used for the infra-red spectra measurement. The peak due to bonded C=O stretching is centered at  $1700 \text{ cm}^{-1}$  and that due to free C=O stretching is centered at about  $1717 \text{ cm}^{-1}$ . While the peak of bonded N–H stretching is at  $3320 \text{ cm}^{-1}$  and that of free N–H stretching is at  $3442 \text{ cm}^{-1}$ . Hydrogen bonded carbonyl bands will correspond to those groups that are in the interior of hard segments, while the free bands may correspond to those groups in the hard segment domains or in the soft domains or at the interface [19]. In the butadiene-containing polyurethanes, hydrogen bonding oc-

Table 1  
Infrared adsorbance, wavenumber of C=O and N–H groups

Composition	Wavenumber ( $\text{cm}^{-1}$ ) of bonded N–H	Wavenumber ( $\text{cm}^{-1}$ ) difference	Wavenumber ( $\text{cm}^{-1}$ ) of bonded C=O	$\frac{A_{\text{C=O, bonded}}}{A_{\text{C=O, free}}}$
143-2	3320.8	0	1700.9	0.9849
143-1	3320.8	0	1700.9	0.9978
143-2-1/3Cu	3330.4	9.6	1704.8	0.9294
143-1-1/3Cu	3336.2	15.4	1706.7	1.0165
187-2	3320.8	0	1700.9	1.0181
187-1	3320.8	0	1700.9	1.1266
187-2-1/3Cu	3332.4	11.6	1702.8	0.9829
187-1-1/3Cu	3342.0	21.2	1704.8	1.1325
187-1C	3320.8	0	1702.8	0.9602
187-1C-1/3Cu	3342.4	21.6	1706.8	0.9856
11211-2	3320.8	0	1700.9	1.2329
11211-1	3320.8	0	1700.9	1.2975
11211-2-1/3Cu	3332.4	11.6	1702.8	1.2178
11211-1-1/3Cu	3342.0	21.2	1704.8	1.2975

Table 2  
Glass transition temperature of soft and hard segment

Composition	$T_{gs}$ (°C)	$T_{gh}$ (°C)	$\Delta T_g$ (°C)
143-1	-78.4	-	-
143-1C	-72.5	-	-
143-1C-1/3Cu	-58.5	78.1	136.6
143-2	-74.8	-	-
143-2C	-70.6	-	-
143-2C-1/3Cu	-47.9	71.6	119.5
187-1	-76.8	72.0	148.8
187-1C	-70.3	75.2	145.5
187-1-1/3Cu	-50.1	98.7	148.8
187-2	-71.6	69.5	141.1
187-2C	-67.4	73.7	141.1
187-2C-1/3Cu	-38.3	85.6	123.9
11211-1	-72.7	73.4	146.1
11211-1C	-68.2	75.0	143.2
11211-1C-1/3Cu	-47.4	108.3	155.7
11211-2	-66.9	71.9	138.8
11211-2C	-64.3	74.2	138.5
11211-2C-1/3Cu	-35.1	98.5	133.6

curs only between urethane segments of C=O and N–H group since the carbonyl in the urethane linkage and the urethane alkoxy oxygen are the only available proton acceptors.

The extent of the carbonyl absorption group participating in hydrogen bonding is expressed by hydrogen bonding index (HBI), which is defined as the relative absorbances of the two carbonyl peaks [20].

$$\text{HBI} = \frac{A_{\text{C=O, bonded}}}{A_{\text{C=O, free}}}$$

where  $A_{\text{C=O, bonded}}$  and  $A_{\text{C=O, free}}$  are the absorbance of bonded and free carbonyl groups, respectively.

Table 1 shows the HBI value, wavenumber and wavenumber shift of bonded C=O and bonded N–H groups.

#### 2.4.2. Differential scanning calorimeter

A Du Pont 9000 instrument was used for DSC measurement, using liquid nitrogen for cooling and with a heating rate of 10°C/min in temperature range between -120 and 150°C. Effect of polymerization method, crosslinking, hard segment content and cupric ion ionization on the distribution and morphology of hard and soft segment and hence affect the glass transition temperature of soft segment ( $T_{gs}$ ) and hard segment ( $T_{gh}$ ) as shown in Table 2.  $\Delta T_g$  is the difference between  $T_{gh}$  and  $T_{gs}$ .

#### 2.4.3. Thermogravimetric analysis

A Du Pont 951 was used for TGA measurement with a heating rate of 20°C/min in the temperature range from 50 to 600°C. A three-step degradation was observed in all these two types of membranes of three different compositions. It is stable up to 300°C and the polymer remains almost intact in the first step. The quantity of gaseous components, mainly water, released in this step is relatively small.

A rapid weight loss starts at approximately 300 up to 500°C, the main quantity of gaseous components, e.g., water, carbon monoxide and methane are split off. Decomposition of step 2 corresponds to the urethane bonding breaking and step 3 is the polyol decomposition [21]. In this degradation stage random chain scission occurs. It can be assumed that a coalescence of chains to form ribbons occurs in this stage [22]. Almost complete decomposition was ob-

Table 3  
Decomposition temperature and residue of thermogravimetric analysis

Composition	Decomposition temperature (°C)		Residue (wt%)
	2nd step	3rd step	
143-1-1/3Cu	458	480	15.0
143-2-1/3Cu	445	499	14.3
187-1-1/3Cu	441	461	14.5
187-2-1/3Cu	430	482	14.0
11211-1-1/3Cu	378	452	13.8
11211-2-1/3Cu	369	473	13.5

served at about 500°C. Table 3 shows the decomposition temperature at 2nd and 3rd step and wt% of residue.

### 3. Result and discussion

#### 3.1. Effect of one- or two-stage polymerization method

Fig. 1 shows that the gas permeabilities of two-stage polymerized PUs are all lower than those of the corresponding one-stage ones. It was shown that one-stage polymerized PU contained hard segments of greater length [14]. Therefore, PUs prepared by one-stage polymerization exhibited a higher degree of microphase segregation as the interaction between hard segments increased with hard segment length. This can also be shown by the hydrogen bonding index (HBI) and glass transition temperature of polymers. Higher HBI values indicates stronger interaction between hard segments. Table 1 shows the HBI values of PUs of various hard segment contents, with or without addition of  $\text{CuCl}_2$  or BPO. It is clear that the HBI values of one-stage polymerized PUs were always higher than those of two-stage ones, no mat-

ter what additives or modifiers were added. Comparing the glass transition temperatures of both hard and soft segment ( $T_{\text{gs}}$  and  $T_{\text{gh}}$ ), we also found that one-stage polymerized PUs had lower values of  $T_{\text{gs}}$  and higher  $T_{\text{gh}}$  as shown in Table 2. The above information indicate that the one-stage polymerized PUs had more hard segments forming aggregates and less dispersing in soft segment region. On the contrary, the two-stage polymerized PUs contained more hard segments dispersing in soft segment region. This implies that the soft segments of one-stage polymerized PUs are more flexible than those of two-stage ones. It may be the reason why one-stage PUs have larger gas permeability and nearly the same separation factors compared with the two-stage counterparts. These results are in agreement with the previous report of PU membranes with 1,4-BD as chain extender [16], but are different from that reported by Abouzahr and Wilkes [15] who indicated that polymerization method has no effect on the polyether based PUs.

#### 3.2. Effect of hard segment content

The higher the hard segment content was, the lower was the gas permeability and the higher was the separation factor, which are shown in Fig. 1. These results of HTPB based PU membranes are contradictory to those of conventional polyol based PU membranes reported by Hsieh et al. [4]. McBride et al. [1] reported that an increase in the hard segment content resulted in an increase in the activation energy, which may be the suitable explanation for the above result.

It was suspected that two effects may be introduced by the increase of hard segment content. One effect was the enlargement of hard segment of cluster aggregate and the other was the restriction of the movement of soft segments, which could be shown by the HBI and  $T_{\text{g}}$  values. As is shown in Table 1, the HBI values increased with the increase of hard segment content. The increase of HBI values indicated that the intermolecular attraction between hard segments increased. Table 2 shows that the  $T_{\text{gs}}$  and  $T_{\text{gh}}$  increased as the hard segment increased. The increase of  $T_{\text{gh}}$  indicated that the increase of hard segment content increased the intermolecular attrac-

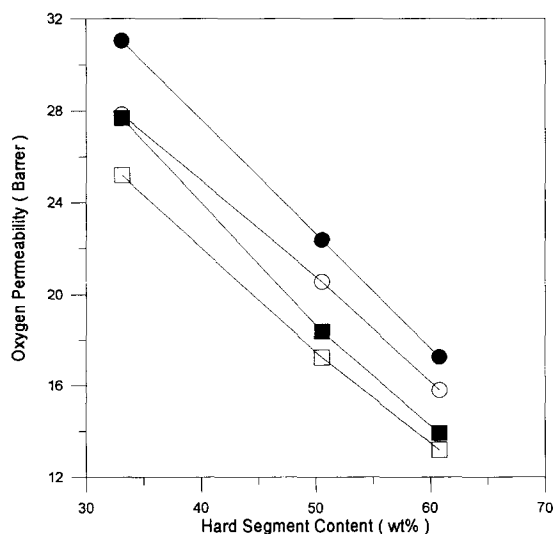


Fig. 1. Effect of polymerization method and crosslinkage on the gas permeability. (○) One-stage and uncrosslinked, (□) two-stage and uncrosslinked, (●) one-stage and crosslinked, (■) two-stage and crosslinked.

tion between hard segments. The increase of  $T_{gs}$  indicated the decrease of soft segment mobility.

The area enlargement of hard segment domain and the flexibility decrease in soft segments may explain why the gas permeability decreased as the hard segment content increased.

### 3.3. Effect of benzoyl peroxide addition

The oxygen permeabilities and separation factors of one-stage polymerized membranes containing 1.0 wt% of BPO were slightly higher than that the ones without BPO, which are shown in Fig. 1. Nitrogen permeabilities, which are not shown in the figure, has the same trend as observed in oxygen.

The addition of BPO might cause crosslinkage between soft segments and introduce benzoyl groups in the soft segment packing area. Crosslinkage usually results in a decrease in membrane permeability, however, it was not the case in this particular membrane. From the HBI measurement shown in Table 1, we found that the HBI value decreased after BPO was introduced. This indicates that the crosslinkage between soft segments hindered the hydrogen bonding among hard segments, which might be the reason why the permeability increased after BPO introduced.

Although the packing among hard segments became looser after BPO addition, the mobility of both hard and soft segments decreased. The DSC studies, which is shown in Table 2, revealed that the glass transition temperatures of both hard and soft segments increased after BPO addition. This might explain why the separation factor did not fall with the elevation of permeability.

### 3.4. Effect of cupric chloride content of one-stage polymerized PU ionomers

PU ionomers were prepared by complexing cupric ion with the tertiary amine of MDEA. It was due to poor membrane formation, our studies were restricted to membranes containing cupric chloride lower than 1/2  $\text{CuCl}_2$  to MDEA molar ratio. Crosslinked, one-stage polymerized membranes with various cupric chloride contents were under investigation. The membrane permeabilities of the ones containing lower than 1/5 molar ratio of cupric ions

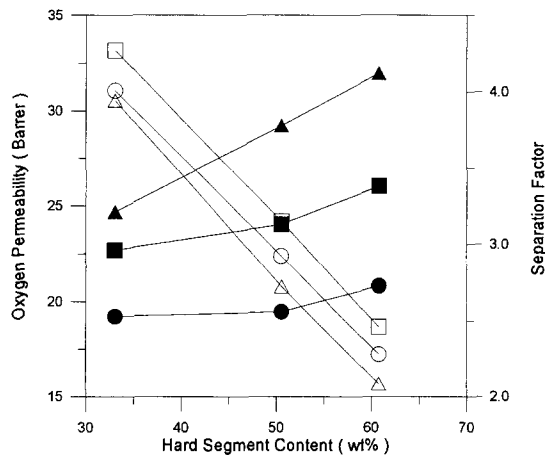


Fig. 2. Effect of cupric chloride content on the gas permeability (open symbol) and separation factor (close symbol) of one-stage polymerized PUs. (○) (●) Crosslinked, (□) (■) crosslinked and 1/4 molar ratio of cupric chloride complexed, (△) (▲) crosslinked and 1/3 molar ratio of cupric chloride complexed.

were essentially the same as the one without any cupric ion complexation. As were shown in Fig. 2, the gas permeability of membranes containing 1/4  $\text{CuCl}_2$ /MDEA molar ratio were higher than those of zero cupric chloride content. However, the membrane with 1/3 molar ratio of cupric chloride had a slightly lower permeability. Since the cupric ion interacts with the tertiary amine of MDEA as well as the carbonyl and secondary amine in urethane linkage [23], a suitable amount of cupric ion addition may enhance the binding between hard segments, and subsequently enlarge the void volume in soft segment domains and increase the flexibility of soft segments. This may explain why gas permeability of crosslinked PU increased after 1/4 molar ratio of  $\text{CuCl}_2$  was added. The increase of HBI and  $\Delta T_g$  shown in Tables 1 and 2 supports the above arguments, respectively. As the  $\text{CuCl}_2$  content increased, excess  $\text{CuCl}_2$  filled up the void space. This may contribute to the decrease in gas permeability of membranes containing 1/3 molar ratio of  $\text{CuCl}_2$ .

Cupric ion has high oxygen affinity and therefore the introduction of cupric ion can enhance the separation factor [2,3]. Fig. 2 shows that membranes containing either 1/4 or 1/3  $\text{CuCl}_2$ /MDEA molar ratio has higher separation factors than the ones without  $\text{CuCl}_2$  addition.

### 3.5. Effect of cupric chloride addition to two-stage polymerized PUs

Compared with one-stage polymerized PUs, the addition of cupric chloride to two-stage ones induced different effects on gas permeability. Fig. 3 shows that the addition of  $\text{CuCl}_2$  of either 1/4 or 1/3 molar ratio reduced the gas permeability. This puzzling result can partly be explained by the HBI and  $\Delta T_g$  values. The HBI and  $\Delta T_g$  values of two-stage PU ionomers were all lower than those of the ones without ion complexation as shown in Tables 1 and 2. The reduction in HBI and  $\Delta T_g$  indicates the increase of microphase homogeneity, i.e., the amount of hard segment dispersed in soft segment region increased, which may responsible for the decrease of gas permeability. The exact reason why the HBI and  $\Delta T_g$  values of one-stage polymerized PUs increased but those of two-stage ones decreased is still unknown. This must relate to the length of hard segments. One-stage polymerized PUs contain longer hard segments, while two-stage ones shorter. It may be that  $\text{CuCl}_2$  was unable to disrupt the hydrogen bonding between long hard segments but formed shell-like cluster surround the hard segment bundles. However, cupric ion complexed with tertiary amine in MDEA and disrupted the hydrogen bonding be-

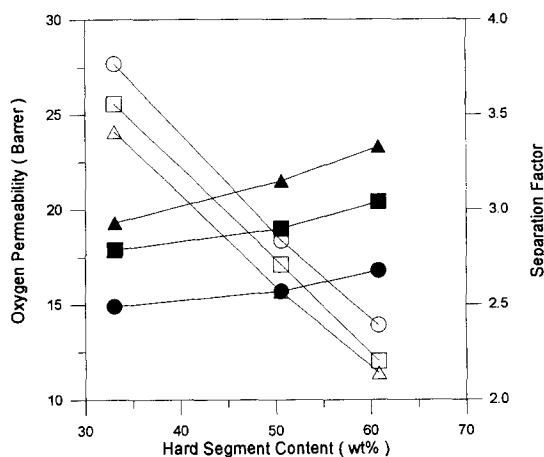


Fig. 3. Effect of cupric chloride content on the gas permeability (open symbol) and separation factor (close symbol) of two-stage polymerized PUs. (○) (●) Crosslinked, (□) (■) crosslinked and 1/4 molar ratio of cupric chloride complexed, (△) (▲) crosslinked and 1/3 molar ratio of cupric chloride complexed.

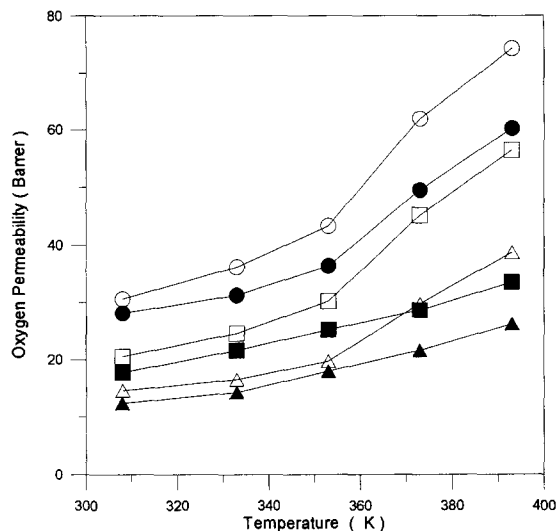


Fig. 4. Effect of temperature on the gas permeability. (○) 143-1C-1/3Cu, (□) 187-1C-1/3Cu, (△) 11211-1C-1/3Cu, (●) 143-2C-1/3Cu, (■) 187-2C-1/3Cu, (▲) 11211-2C-1/3Cu.

tween short hard segments and made the hard segments become more compatible with the soft ones. This may be the reason why HBI and  $\Delta T_g$  values of two-stage PUs went opposite direction after  $\text{CuCl}_2$  addition as compared with one-stage PUs.

PU ionomers membranes by one-stage polymerization had a higher 2nd decomposition temperature and a lower 3rd step decomposition temperature than those made by two-stage polymerization, which is shown in Table 3. The 2nd decomposition temperature is related to the decomposition of hard segments, while the 3rd decomposition temperature is related to the soft ones. The decomposition data supported that the binding of hard segments of one-stage polymerized PU ionomers were stronger than those of two-stage ones.

### 3.6. The effect of the operating temperature

Fig. 4 shows that the oxygen permeability increased as temperature increased. Nitrogen permeability, which is not shown in this figure, also increased so that the separation factor decreased. The increase in gas permeabilities of one-stage polymerized membranes were higher than those of two-stage ones. This may be explained by the soft segment

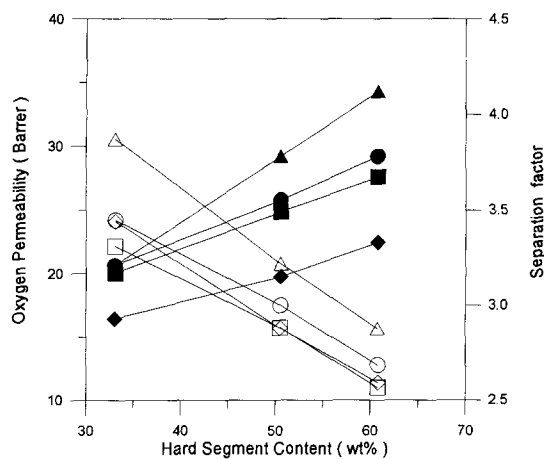


Fig. 5. Effect of annealing on the gas permeability (open symbol) and separation factor (close symbol) of crosslinked and 1/3 molar ratio of cupric chloride complexed membranes. (○) (●) One-stage, annealed. (□) (■) two-stage, annealed. (△) (▲) one-stage, without annealing. (◇) (◆) two-stage, without annealing.

mobility. As we mentioned before, the soft segments of one-stage polymerized PUs had higher mobility than those of two-stage ones. The difference in soft segment flexibility would be more profound at higher temperature, which resulted in the enlargement of gas permeability differences between one- and two-stage polymerized PU membranes.

### 3.7. PU ionomers after annealing treatment

Fig. 5 shows that the annealing treatment reduced the gas permeability and also the separation factor of one-stage polymerized PU ionomers. However, it increased the separation factor of two-stage polymerized ones without any sacrifice in gas permeability. The effect of annealing treatment on gas permeability can also be explained by the soft segment flexibility. One-stage polymerized PUs contained flexible soft segments, therefore, annealing treatment had stronger effect. On the other hand, two-stage polymerized ones had soft segments already orderly packed. Annealing treatment could no longer make it denser. We had no idea about the effect of annealing treatment on separation factors. It has to do with the distribution of cupric ion in complexed form or in chloride salt form, and how its oxygen binding efficiency varies with respect to the form it exists.

## 4. Conclusions

The gas permeabilities of crosslinked HTPB–HMMDI–MDEA based PU membranes are all higher than that of uncrosslinked ones and decreased as the hard segment increased. The gas permeability of membranes with 1/4 molar ratio of cupric chloride are higher than those without cupric chloride, while the gas permeability of membranes containing 1/3 molar ratio of cupric chloride are lower. All the above results can be explained by the flexibility of soft segments and the cluster aggregation of hard segments. The decrease in size and the disruption in packing of hard segment cluster aggregates would increase the membrane permeability. The increase of the amount of hard segments dispersed in soft segment region would decrease the mobility of soft segments and subsequently reduce the gas permeability.

By manipulating the way of polymerization, the degree of crosslinking and the amount of cupric addition, a separation factor of 4.12 and gas permeability of 15.67 barrers can be obtained by 11111-1c-1/3Cu membrane.

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