특별강연 VI

# 액정 고분자 HIQ-40의 열처리에 의한 기체전달 특성 변화

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# The Effect of Thermal Annealing on the Gas Transport Properties of Liquid Crystalline Polymer HIQ-40

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## Introduction

Since the discovery of liquid crystallinity by Reinitzer [1] in 1988 as he studied the melting behavior of cholesteryl benzoate, anisotropic structural ordering in fluid phases has been of considerable interest to chemists, physicists and other scientists. Polymers which exhibit liquid crystallinity either in solution (lyotropic) or in the neat state upon heating (thermotropic) have both theoretical and practical importance [2]. Du Pont's Kevlar, a high modulus polyamide fiber spun from a lyotropic solution, is a prime example of such an application.

But only a few years ago the liquid crystalline polymer (LCP) has applied on gas separation. Chiou and Paul [3] showed the results of gas transport through a random copolyester consisting of HBA and 6-hydroxy-2-naphthoic acid (HNA). Then, poly(p-phenylene terephthalamide) (PPTA) LCP has remarkably high barrier property [4]. And gas permeability of these LCPs is at least an order of magnitude lower than in common glassy polymers such as poly(ethylene terephthalate) (PET) and poly(vinyl chloride) (PVC), and a remarkable barrier polymer polyacrylonitrile (PAN). Cantrell et al. [5] has studied experimentally the influence of thermal annealing on acetone vapor sorption and transport in HIQ-40 LCP. In Cantrell's study the acetone permeability is calculated from the experimental values of solubility and diffusivity.

However, in this study we directly measure the permeability of He, $H_2$, $CO_2$, $O_2$, $N_2$ and $CH_4$ in HIQ-40, a liquid crystalline polymer developed by the Hoechst Celanese Corporation, using the gas permeability cell installed in vacuum oven, and calculate diffusivity from the time lag of gas transport. HIQ-40 LCP films can be prepared with morphologies ranging from isotropic to nematic liquid crystalline by thermal annealing at various temperatures. The density and glass transition temperature of the LCP can be measured by density gradient column and differential scanning calorimeter (DSC) for physical properties of the LCP. We also try to show the relationship between the gas transport properties of HIQ-40 LCP, and kinetic diameter, collision diameter and Lennard-Jones parameter of gas. Then, the gas transport properties of HIQ-40 film can be compared with those of other LCPs.

## Background

In extending our understanding of permeation in glassy and semicrystalline materials to liquid crystalline polymers, the effects of increased rigidity and packing of polymer chains on the transport properties are of special interests as well as are consequences of the presence of impermeable phases [6]. The mechanism by which small gas molecules permeate through rubbury or glassy amorphous polymers involves a solution-diffusion process [7]. The permeability coefficient can be expressed as the product of the diffusivity and solubility coefficients

$$P = D\,S \qquad (1)$$

The diffusion coefficient, D, is associated with the degree of penetrant mobility in the polymer and is lower the stronger the cohesive forces between chains and the more efficiently the polymer chains are packed together. The solubility coefficient, S, is thermodynamic in nature and is determined by the condensability of the gas, the interactions with the polymer, and to some extent the free volume available in the polymer matrix.

HIQ-40 used in this study is a random, all aromatic copolyester which can exhibit both liquid crystalline and isotropic behavior in the melt [5]. It is composed of 40 mole% rigid rod-like p-hydroxybenzoic acid (HBA) units and 30 mole% each of hydroquinone (HQ) and isophthalic acid (IA) units. The "40" suffix refers to the mole% of HBA in the terpolymer. The HBA moieties in HIQ-40 provide the necessary combination of linearity and rigidity to develop liquid crystalline order. However, poly(HBA) is a very high melting point material which is intractable in conventional melt processing operations because it decomposes before melting [8]. Copolymerizing HBA with 27 mole% 6-hydroxy-2-naphthoic acid (HNA), which adds linearity-disrupting rigid HNA kinks to the chain backbone, lowers the melt temperature and is the basis for a commercial, nematic, thermotropic, liquid crystalline copolyester, Vectra$^{R}$, which is melt processible. Tractable nematic LCPs may also be produced by copolymerizing HBA with monomers such as HQ and IA, which are less expensive than HNA. The ether linkage in the hydroquinone group provides a so-called "flexible kink" in the chain backbone which can disrupt chain linearity and increase chain flexibility [9, 10]. The metaconnected phenyl ring of IA comonomer provides a rigid kink in the chain backbone. This combination of flexible HQ linkages and rigid IA kinks, polymerized with rigid rod-like HBA moieties, results in the preparation of random HIQ-40, a soluble thermotropic LCP whose crystalline melting point and isotropization temperature lie below its decomposition temperature.

The synthesis, structure and thermal transitions of HIQ polymers with compositions ranging from HIQ-0 to HIQ-100 have been determined previously by Erdemir et al. [11, 12]. The polymers characterized in these papers were meltpolymerized and then heated to 460 °C for a short time before quenched to ambient conditions. In general, copolyesters with less than approximately 18 mole% HBA do not exhibit a liquid crystalline mesophase because the aspect ratio of rigid moieties is too low to stabilize the liquid crystalline phase [13]. Between 20 and 27 mole% HBA, a nematic mesophase exists over a very narrow temperature range [11]. The thermal stability limit for polymers of all compositions, determined as the temperature at which five percent weight loss had occurred in a nitrogen atmosphere, was

found to be near 450 °C. Polymers with an HBA content of more than 67 mole% were found to have a crystal to nematic mesophase transition temperature which was above the thermal stability limit [11]. Polymers with HBA contents of 33 to 50 mole% (HIQ-33 to HIQ-50) exhibit stable nematogenic behavior. HIQ-33 and HIQ-50 were found to have crystal to nematic mesophase transition temperatures of 307 °C and 375 °C, which are below the thermal stability limit of the polymer. HIQ-33 also exhibited a nematic-isotropic transition at 410 °C while the clearing point of HIQ-50 was not observed below the thermal stability limit of the polymer [5].

Wide angle X-ray diffraction (WAXD) spectroscopy revealed different crystal structures for the two homopolymers, poly(HBA) and poly(p-phenylene isophthalate), poly(HQIA) [11]. HIQ copolymers with compositions ranging from 33 to 50 mole% HBA exhibit X-ray spectra consistent with the presence of low levels of both crystal structures.

**Experimental**

Film casting: HIQ-40 polymer film was prepared by dissolving the polymer in a cosolvent of trifluoroacetic acid (TFAA) and methylene chloride (MC) at a 75/25 weight ratio by the Hoechst-Celanese Corporation. The solid level was 10% by weight. The polymer solution, after filtration, was cast into films. To remove the residual solvents, the films were washed in water for 48 hours followed by drying at room temperature. The as-cast films appeared to be transparent, non-brittle and ranged in thickness from 2.3 to 2.6 mils ( 1 mil = $10^{-3}$ inch).

Film annealing: HIQ-40 polymer films were annealed by the Hoechst-Celanese Corporation as the following method. To prepare the films with various morphology, amorphous as-cast films were heated to different temperatures. The film annealing temperatures were 170 °C, 200 °C, 300 °C and 330 °C. Films heat treated at temperatures up to and including 200 °C were annealed by placing the film in a vacuum oven preheated to the final annealing temperature. The film is left in the oven under vacuum for one hour, and then removed from the oven to be quenched in air at ambient conditions. Films annealed at temperatures above 200 °C were placed in a high temperature oven at ambient conditions under nitrogen. The oven temperature was ramped to the final temperature, which typically took 45 minutes to one hour. Upon reaching the final temperature the oven heater was turned off, and the samples were cooled in the oven by an ambient temperature nitrogen purge stream. Residual solvent TFAA can be checked by FT-IR spectroscopy.

Property Measurement: The permeability coefficients, P, of a series of gases were measured at 35 °C using the standard transient permeation technique employed in this laboratory [14, 15]. The gases used were helium, hydrogen, oxygen, nitrogen, carbon dioxide and methane. Effective diffusion coefficients were estimated using the film thickness, $l$, and the time lag, $\theta$, in the following relationship [16]

$$D = \frac{l^2}{6\theta} \qquad (2)$$

The effective solubility coefficients, S, were then calculated from eq. (1). The "time-lag" method of determining effective diffusion and solubility coefficients in semicrystalline materials

generally gives good agreement with results derived from static sorption measurements [17].

The glass transition temperature ($T_g$) of each polymer film was measured using a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) at a heating rate of 20 °C/min. The samples were heated twice and the $T_g$ was taken as the midpoint of the transition during the second scan. The melting transition temperature ($T_m$) was taken as the center of peak during the second scan, too. The exothermic peak of the polymer samples was shown during the first scan.

The density of polymer film was measured using a density gradient column DC-1 manufactured by Techne Incorporated. Zinc chloride solutions of varying concentrations were added to a graduated cylinder at 30 °C to establish a column of liquid with a linear density gradient. Glass calibration spheres were then introduced into the gradient column. Polymer samples were inserted into the column, and the density of the samples was determined based on the final height of the samples using the calibration graph of density after 24 hours.

**Results and Discussion**

As the results of DSC scan the glass transition temperature of HIQ-40 films exists between 127 and 135 °C, which is a good agreement with the values of Canrell et al. [5]. A broad exotherm, associated with the melting of the conventional three-dimensional crystallites in HIQ-40, is centered between approximately 314 - 343 °C. The as-cast film of HIQ-40 and the film annealed at 170 °C exhibited an exothermic peak in the temperature of 148 and 170 °C respectively during the first DSC scan. The development of this peak seems to result from isotropic to nematic ordering complementing low levels of conventional crystalline ordering, quite analogous to cold-crystallization of conventional non-liquid crystalline copolyesters. The second scan of DSC did not exhibit the exothermic peak since the structural order was asymptotically developed during the first scan. No exothermic peak was observed during the first scan of the thermally treated HIQ-40 films annealed above 200 °C because the thermal annealing at the high temperatures presumably developed the order.

The density of HIQ-40 films determined experimentally using the density gradient column is compared with the results of Cantrell et al. [18]. The as-cast film which was not annealed has the lowest density value, which means to be the highest fractional free volume. The density increases as the annealing temperature rises to 300 °C, and then drops a little in the film annealed at 330 °C. This observation suggests that the three dimensional crystallites have developed in the samples treated at the temperature less than 300 °C, but melted in the sample annealed at 330 °C.

Gas permeability through HIQ-40 was measured at various upstream pressures and at the same temperature, 35 °C. The permeability coefficients for the larger penetrant molecules decreased with increasing upstream pressure as the same as expected for glassy polymers and as predicted by the frequently used dual mode sorption model. As the annealing temperature rises to 300 °C, the gas permeability decreases and then increases a little in the film annealed at 330 °C in case of all gases except methane. Figure 1 shows clearly the dimensionless gas permeability, which is defined as permeability of annealed film over permeability of as-cast film, versus the annealing temperature. Acetone permeability measured by Cantrell et al. [5] also is plotted as dotted line compared with the permeability of other gases in the same figure. The dimensionless permeability decreases remarkably to 200 °C near the glass transition temperature, which is approximately 130 °C, and then the

change is not large from 200 °C to 330 °C. The crystal to nematic transition in HIQ-40 polymer occurs at approximately 315 °C. The reduction in density of annealed films from 300 °C to 330 °C suggest that the film annealed at 330 °C has lower levels of three dimensional crystallinity than the film annealed at 300 °C.

Time lag of gas permeability by diffusion is investigated as various experimental conditions. Hydrogen and helium gas has small molecular size compared with the pore size of films, and the time lag of these two gases could not be observed. The time lag of the largest gas, methane in this experiment, has the larger value than those of other gases, because it is related with the diffusion of gas. The diffusion coefficient of HIQ-40 films can be obtained from this time lag and the film thickness using the equation (2). The diffusion coefficient of various gases decreases to 300 °C, and then increases a little in the film annealed at 330 °C. Figure 2 shows the dimensionless diffusion coefficient, which is defined as diffusion coefficient of annealed film over diffusion coefficient of as-cast film, versus the annealing temperature. Acetone diffusion coefficient measured by Cantrell et al. [5] also is plotted as dotted line in the same figure. Methane and acetone diffusion coefficients, which is larger gases than oxygen, nitrogen, and carbon dioxide, reduce from 300 °C to 330 °C. In these two gases the gas size seems to be more dominant than the change of fractional free volume by melting the crystalline structure of HIQ-40 polymer.

Solubility of HIQ-40 polymer films can be obtained from the permeability and diffusion coefficient using the equation (1). The dimensionless solubility, which is defined as solubility of annealed film over solubility of as-cast film, is plotted according to the annealing temperature in Figure 3. The solubility of oxygen, nitrogen and carbon dioxide intends to decreases as the annealing temperature increases, but the solubility of methane and acetone increase a little from 300 °C to 330 °C. This observation might be related with the molecular size of gas.

Figure 4 shows the linear relation between solubility of various polymers and force constant of Lennard-Jones potential, $\varepsilon/k$ [19]. $\varepsilon/k$ could explain and predict well the solubility of HIQ-40 liquid crystalline polymer (as-cast film) as well as glassy polymers, for example polycarbonate (PC), tetramethyl polycarbonate (TMPC), hexafluoro polycarbonate (HFPC), and tetramethyl hexafluoro polycarbonate (TMHFPC) [20].

Gas permeability, diffusion coefficient and solubility of unannealed HIQ-40 polymer film are compared with the values of other liquid crystalline polymers [21] in Table 7 ~ 9. Poly(ethylene terephthalate) (PET) has the similar values with the unannealed HIQ-40 film, but Vectra has much lower values than those of the unannealed HIQ-40 film. The gas permeability of each liquid crystalline polymer decreases in sequence of He, $H_2$, $CO_2$, $O_2$, $N_2$, and the diffusion coefficient and solubility decreases in sequence of $CO_2$, $O_2$, $N_2$.

## Conclusions

The HIQ-40 polymer used in this study is the glassy random copolyester composed of 40 mole% p-hydroxybenzoic acid (HBA), 30 mole% hydroquinone (HQ) and 30 mole% isophthalic acid (IA). The HIQ-40 thin films with morphologies ranging from amorphous to nematic liquid crystalline are prepared by thermal annealing. As the results of DSC scan the glass transition of HIQ-40 films exists between 127 and 135 °C, and the melting transition point is centered between 314 -343 °C. As the liquid crystalline structure is developed more, permeability, diffusivity and calculated solubility of various gases seem to be decreased

remarkably near the glass transition temperature, and then the change is not large. The thin film annealed at 300 °C, which has the highest rate of liquid crystalline, the lowest density and the highest fractional free volume, shows the minimum values of permeability and diffusion coefficient. The values of permeability and diffusion coefficient seems to be increased a little in the film annealed at 330 °C. This observation suggests that the three dimensional crystallites have developed in the films treated at the temperature less than 300 °C, but melted in the film annealed at 330 °C.

The gas permeability seems to be brought into closer relation with the kinetic diameter of gas than the collision diameter. Force constant of Lennard-Jones potential has the linear relation with solubility of HIQ-40 liquid crystalline polymer (as-cast film) as well as other glassy polymers. Poly(ethylene terephthalate) has the similar values with the as-cast HIQ-40 film.

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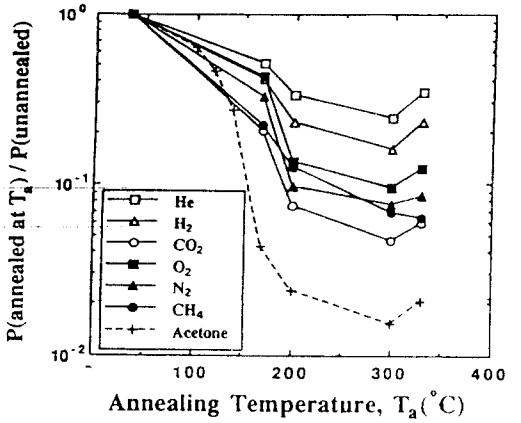


Figure 1. The effect of thermal annealing temperature on dimensionless permeability of HIQ-40 polymer films.

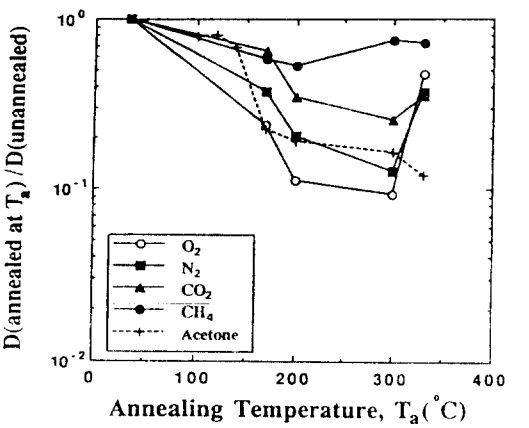


Figure 2. The effect of thermal annealing temperature on dimensionless diffusion coefficient of HIQ-40 polymer films.

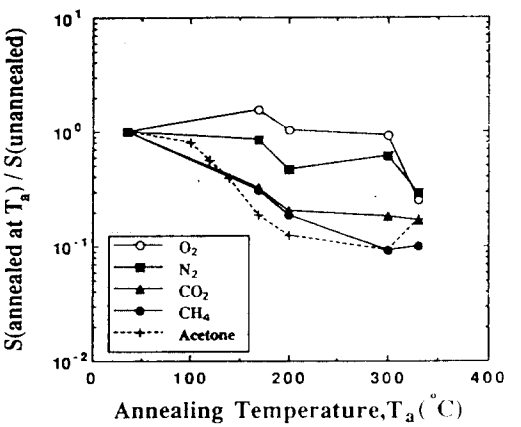


Figure 3. The effect of thermal annealing temperature on dimensionless solubility of HIQ-40 polymer films.

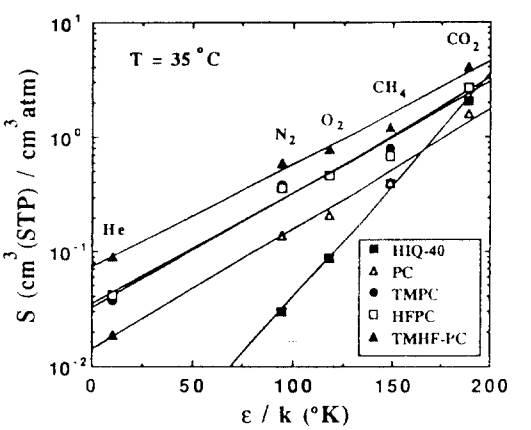


Figure 4. Relation between solubility and force constant of Lennard-Jones potential.