

THE EFFECT OF DEGREE OF ACETYLATION ON GAS SORPTION AND TRANSPORT BEHAVIOR IN CELLULOSE ACETATE

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Summary

Cellulose acetate films with degrees of substitution of 1.75, 2.45, and 2.84 were characterized in terms of chemical composition, acetyl group distribution, glass transition, crystallinity, and dynamic mechanical properties. Permeability coefficients for a series of gases, at 1 atm and 35°C, were found to increase with degree of acetylation. Sorption isotherms for CO₂ and CH₄ at 35°C were analyzed in terms of the dual-mode sorption model, and it was shown that conditioning of the films by CO₂ caused an increase in the Langmuir sorption capacity. The permeability of CO₂ was found to increase with pressure above 10 atm due to plasticization. Highly sorbing CO₂ swells the polymer such that interchain interactions are disrupted and segmental mobility increases. Infrared analyses support this conclusion and show that after complete removal of CO₂ and a sufficient relaxation period, the cellulose acetate returned to its original condition. Therefore, the response of the films to plasticization by CO₂ is not only time and pressure dependent but also reversible.

Introduction

Over the past 30 years, membrane-based separation processes have developed into important industrial unit operations [1,2]. Membranes are used in the field of gas separations for recovering hydrogen from process streams, to remove carbon dioxide from methane in enhanced oil recovery and in landfill gas purification, and to produce nitrogen enrichment for blanketing and oxygen enriched air for combustion [3-10]. These applications are possible because of major breakthroughs that include asymmetric membrane structures [11-13], thin-film composites [14], hollow fiber technology [7,15,16], and modularization concepts [3]. While these early developments dealt primarily

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TABLE 1

Permeability coefficients for cellulose acetate reported in previous studies

Reference	Type of film	Temp. (°C)	Permeability, $P \times 10^{10} \left[\frac{\text{cm}^3(\text{STP})\text{-cm}}{\text{sec-cm}^2\text{-cmHg}} \right]$					
			CO ₂	He	H ₂	O ₂	N ₂	CH ₄
26	2.75 DS	30	6.2					
	2.45 DS		5.1					
	2.29 DS		4.5					
	unspecified	25	5.0		8.4	0.68	0.23	
27	unspecified	room temp.	6-21		7-15			
28	unspecified					0.78	0.28	
29	hollow fibers	24		19.9				1.69
	2.44 DS							
30	solution cast	25	5	13			0.17	
31	dense films solution cast	22		13.6			0.14	0.14
	2.41 DS							
32	dense films solution cast	room temp.		20.4		1.22	0.24	
33	dried reverse osmosis membranes	30	4			0.75		
34	solution cast and annealed in water bath	30	4					0.14
	2.45 DS							

with modifying the asymmetric structure of the membrane, research efforts in recent years have focused more on improved membrane materials [17,18]. Studies have shown that the gas transport properties of polymers can be greatly affected by annealing, orientation, blending, conditioning, and through the use of additives [19-23]. The next generations of membranes will undoubtedly involve enhancing performance through tailoring the chemical and physical structure of the polymer to meet specific separation needs [3,17]. In order to develop this type of technology, the relationship between transport properties and the molecular structure of the polymers currently used for gas separations needs to be fully understood.

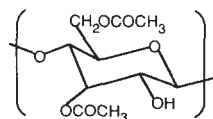
Cellulose acetate has been used as a membrane material for many years in reverse osmosis since it has a high salt rejection [24] and is relatively inexpensive. In fact, it was the first material to be successfully fabricated into an asymmetric membrane [25]. Cellulose acetate is also one of a few polymers currently being used in commercial gas separations [5]. Unfortunately, infor-

mation available in the literature about its sorption and transport properties is somewhat limited and rather confusing. Table 1 contains a brief summary of pure gas permeabilities which have been reported for presumably dense or homogeneous cellulose acetate films, and significantly more information has been published regarding the pure and mixed gas separation performance of asymmetric membranes. The values in Table 1 illustrate the incompleteness and incongruence of the available information, although some recent studies have provided more complete results and analyses of transport in cellulose acetate [34]. Film preparation procedures, including casting conditions, solvent evaporation rate, thermal history, and dryness, as well as the use of truly dense versus collapsed asymmetric films, influence the transport properties. As shown here, prior exposure history to certain gases also affects the results.

This investigation was undertaken in order (1) to provide a more complete analysis of gas sorption and transport behavior in dense cellulose acetate films that have been fully characterized in terms of their molecular, thermal, and mechanical properties; (2) to define the relationship between sorption and transport behavior and the acetyl group content of the polymer; and (3) to gain insight into why cellulose acetate is plasticized by CO_2 and how this effect is influenced by molecular structural changes.

Background

The glucoside repeat units of cellulose, the precursor to cellulose acetate, contain three hydroxyl pendant groups that lead to strong intermolecular hydrogen bonding. The substitution of these hydroxyl groups (OH) with acetyl groups (OCOCH_3) leads to the class of materials known as cellulose acetates [35], e.g.,



The degree of substitution (DS) is the average number of acetyl groups per repeat unit. For example, a fully substituted material has a DS of 3. The bulky nature of the acetyl pendant groups reduces the efficiency of chain packing. They, of course, also reduce the amount of intermolecular hydrogen bonding, thus increasing chain flexibility and mobility [36]. Both factors affect the transport properties of the polymer. The presence of hydroxyl pendant groups as well as acetyl pendant groups in partially substituted cellulose acetates leads to various types and degrees of intramolecular and intermolecular interactions [37]. In this study, infrared analysis has been used to probe these interactions and how they are affected by sorbed CO_2 .

Gas permeation in dense polymers occurs by a solution-diffusion mecha-

nism. This process and the equations used to describe it have been discussed numerous times in the literature [38–46]. The permeability coefficient, P , is defined as the steady-state gas flux, N , divided by a pressure driving force [39]

$$P = \frac{N}{(\Delta p/l)} \quad (1)$$

and is often expressed in units of $10^{-10} \text{ cm}^3 \text{ (STP)·cm}/(\text{cm}^2\text{-sec·cmHg})$ known as barrers. In the simplest case, Fick's law describes the gas flux,

$$N = -D \frac{\partial C}{\partial x} \quad (2)$$

in terms of a concentration gradient of the gas in the polymer and a concentration independent diffusion coefficient, D , while equilibrium sorption follows Henry's law

$$C = k_D p \quad (3)$$

Using eqns. (2) and (3), the permeability coefficient can be identified as the product of the Henry's law solubility coefficient and the diffusion coefficient:

$$P = k_D D \quad (4)$$

This model, in which the permeability is independent of pressure, adequately describes transport of noninteracting penetrants in amorphous polymers above their glass transition temperature. However, in the glassy state, an additional mode of sorption arises because of the nonequilibrium packing of the chains. This sorption process follows a Langmuir-type isotherm and contributes to the total concentration of gas in the polymer as follows

$$C = k_D p + \frac{C'_H b p}{1 + b p} \quad (5)$$

The parameters, C'_H and b , represent the Langmuir capacity and site affinity, respectively [40]. This dual-mode model provides an excellent description of the sorption process in most glassy polymers [23,41,47–50].

Dual-mode theory has also been extended to the transport process, and an expression for the permeability coefficient has been derived [46] for glassy polymers, i.e.,

$$P = k_D D \left[1 + \frac{KF}{1 + b p} \right] \quad (6)$$

in which $K = C'_H b / k_D$ and F is the ratio of the diffusion coefficient for the Langmuir mode to the diffusion coefficient for the Henry's law mode. An important difference between eqn. (4) and eqn. (6) is that the latter predicts that permeability will decrease with increasing pressure. Most gases exhibit some

amount of permeability decrease in glassy polymers. However, there are some exceptions. For example, it is well known that for cellulose acetate the permeability of CO₂ increases with pressure because of plasticization [9,10,17,34,51–53]. Since cellulose acetate is used in commercial separations involving CO₂, it is very important to understand the plasticization process and assess its effect on membrane performance. In this study, the behavior of CO₂ has been investigated in detail, and an attempt has been made to understand plasticization in terms of the molecular structure of cellulose acetate.

Experimental

Some of the inconsistencies in the transport results reported in the literature for cellulose acetate stem from variations in film preparation. In this study, a standard procedure was used to minimize this factor. The cellulose acetates were commercial materials obtained as unplasticized powders from Tennessee Eastman Co. Dense films (3 to 5 mils thick) were prepared by solution casting in a controlled environment. The degrees of substitution, corresponding to the commercial designation, are given in Table 2 for each material, along with the polymer density and the casting solvents used. Initially, about 5 g of polymer was dissolved in 100 ml of solvent. The solution was placed in a glove bag that was purged with nitrogen and then sealed. The solution was poured into glass rings on Teflon-covered glass plates. The rings were used to control film thickness while the Teflon allowed for easy removal of the films. The environment within the glove bag allowed slow, controlled drying of the films and prevented exposure to moisture which can induce asymmetric character. After evaporation for three days, the films were removed and dried for 2 to 3 days in a vacuum oven at room temperature. Finally, the oven temperature was raised to 100°C and held there for 24 hours to ensure complete solvent removal.

Densities of the films were measured by a pycnometer technique using hexane as the displacement fluid to an accuracy of approximately ± 0.003 g/cm³. The results in Table 2 show an expected reduction in density with increasing acetyl content.

The acetyl distribution and actual acetyl content of the films were deter-

TABLE 2

Cellulose acetate films used to investigate sorption and transport

Film designation	1.75 DS	2.45 DS	2.84 DS
Commercial designation	CA 320S	CA 398-30	CA435-75
Casting solvent	2-methoxyethanol	acetone	methylene chloride
Film density (g/cm ³)	1.358	1.327	1.305

mined using previously described techniques [54,55] with some modification. H-NMR data were obtained using a JEOL Model GX-270 NMR spectrometer. The samples were typically run in CDCl_3 at a concentration of 30 mg/ml. Appropriate manipulation of the line broadening and Gaussian factors provided sufficient resolution. Wet chemical analyses were made using a modified hydrolysis procedure [56].

Molecular weights were determined by GPC using three Perkin-Elmer 5 μm columns with pore sizes of 10^{+5} Å, 10^{+3} to 10^{+5} Å, and 100 Å. The solvent was a mixture of methylene chloride and methanol in a 9/1 ratio, and the columns were calibrated with monodisperse polystyrene standards.

Thermal analyses of the films were carried out at the University of Texas using a Perkin-Elmer DSC-7 and TGA-7 and at Eastman Kodak Co. using a Perkin-Elmer DSC-4, both at a heating rate of $20^\circ\text{C}/\text{min}$.

The dynamic mechanical properties of the films were determined using a Polymer Laboratories DMTA Mk II. The samples were dried under vacuum at 60°C and then run in single cantilever bending at a frequency of 1 Hz and a heating rate of $5^\circ\text{C}/\text{min}$. Other mechanical properties were determined in tension according to ASTM D 882 [57] on samples cut from the cellulose acetate films.

Wide-angle X-ray scattering was performed on an a Scintag PAD 5 with a scintillation counter detector using Cu K_α radiation as a source.

Three infrared spectra for the cellulose acetate films were taken: prior to CO_2 exposure, in the presence of CO_2 , and after complete removal of CO_2 . The films were scanned with a Digilab FTS 15/90 FTIR spectrometer. One hundred scans were obtained at a resolution of 2 cm^{-1} . A Harrick Scientific temperature-controlled flow through cell with ZnSe optics was used to mount the films and maintain a CO_2 pressure of 15 atm.

The apparatus and techniques used in the sorption and transport experiments were similar to those described elsewhere [48,58] in greater detail. All measurements were made at 35°C .

Results and discussion

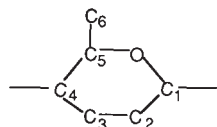
Molecular analysis

The degree of substitution (DS) values determined from H-NMR and hydrolysis are given in Table 3. These results agree very well with the values corresponding to the commercial designations. The samples range from a highly substituted one (2.84 DS) with just over one hydroxyl group in 10 anhydroglucose repeat units, to a low DS value with about 12 hydroxyls in 10 repeat units. It has been shown that strong intermolecular interaction can exist between two hydroxyl groups, between hydroxyl and an acetyl, and between two acetyl groups [37]. For the cellulose acetates with low degrees of substitution, the first two types of interactions will be most prevalent, whereas for the highest

TABLE 3

Molecular characteristics of the cellulose acetate films

	Film designation		
	1.75	2.45	2.84
<i>Degree of substitution</i>			
H-NMR	1.73	2.45	2.88
Hydrolysis	1.77	2.42	2.81
Weight percent acetyl	32.0	39.5	43.5
<i>%-Distribution of anhydroglucose units</i>			
Triacetate	30	57	88
Diacetate and monoacetate	70	43	12
<i>%-Distribution of acetyl groups^a</i>			
C-2 position	32	30	34
C-3 position	31	32	32
C-6 position	37	37	35
<i>Molecular weight (10^3)</i>			
Weight average ($\bar{M}_w$)	157	143	340
Number average ($\bar{M}_n$)	55	73	160
$\bar{M}_w/\bar{M}_n$	2.9	2.0	2.1

^aCarbon atoms in the anhydroglucose units are numbered as follows:

DS film, the acetyl-acetyl interaction will be more common. These interactions contribute to the motions and packing of cellulose acetate chains and thereby affect transport properties. A previous study reported that the flexibility of the chain increases in polar solvents due to the disruption of intermolecular hydrogen bonding [36].

Contrary to other reports [59], the distribution of acetyl groups around the anhydroglucose ring was found to be remarkably uniform as indicated in Table 3. Since all positions are about equally acetylated, the number and type of intermolecular interactions will also be more or less uniformly distributed throughout the polymer.

The molecular weights of the cellulose acetates are given in Table 3. The weight-average molecular weights ($\bar{M}_w$) for the 1.75 DS and 2.45 DS films are relatively similar, while $\bar{M}_w$ for the 2.84 DS is significantly higher. The polydispersity of the three samples is small. Molecular weight can affect the thermal and mechanical properties of polymers [60]; however, it has been shown

that for the molecular weight range of the films in this study, thermal properties are relatively insensitive to molecular weight [61].

Thermal and mechanical analysis

A representative DSC thermogram for a cellulose acetate film is given in Fig. 1. The large broad peak between 50°C and 150°C represents evaporation of water sorbed by the hydrophilic cellulose acetate [62]. The water content prior to heating was estimated to be about 5% by dividing the area of the DSC peak, 113.7 J per gram of film, by the heat of vaporization of water, 2256.3 J/g. TGA (thermogravimetric analysis) also showed a 5% weight loss from the film between 50°C and 150°C. These analyses clearly indicate that cellulose acetate films exposed solely to atmospheric conditions contain about 5%wt. sorbed water. Previous studies found a 3% water content for injection molded samples stored at "room conditions" [62,63].

The films used in the transport experiments were evacuated in the permeation cell for 5 days in order to remove sorbed water. TGA experiments revealed that the water content of the films decreased to less than 1% after 5 days under vacuum. In addition, water desorption was monitored by measuring a daily "leak rate" in the permeation system which decreased to a minimum steady value after five days. Similar procedures were followed for the films used in sorption experiments.

The DSC thermograms shown in Fig. 2 were obtained using cellulose acetate films that had been stored under vacuum at 60°C. The glass transition temperatures (T_g) reported in Table 4 were computed as the midpoint temperature

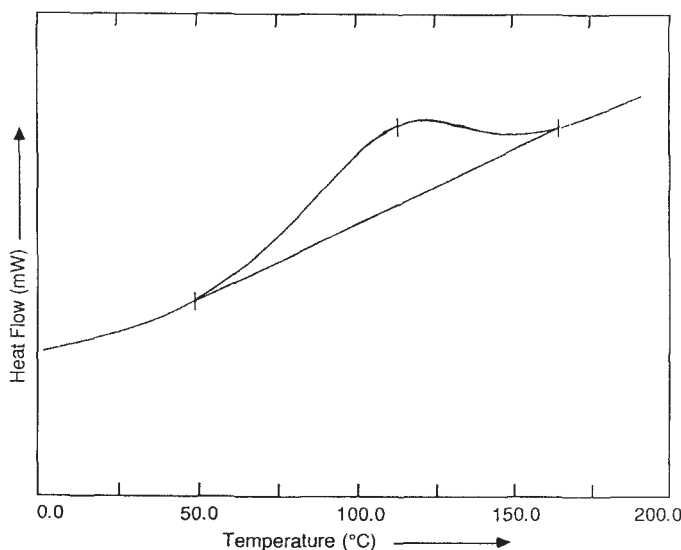


Fig. 1. DSC thermogram for the 2.45 DS cellulose acetate film showing the sorbed water peak.

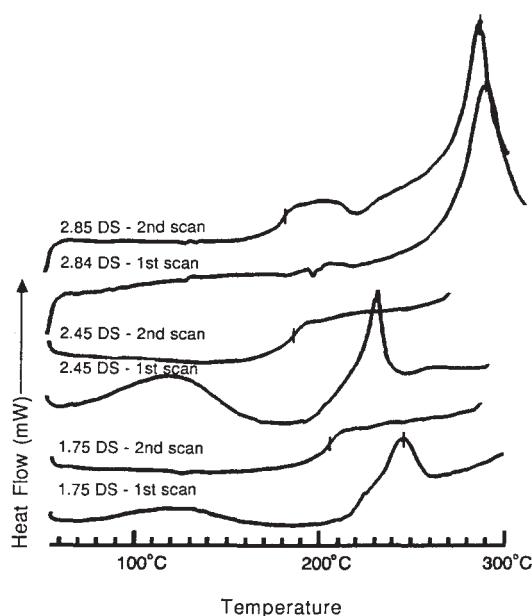


Fig. 2. DSC thermograms for the cellulose acetate films. Heats of fusion were measured from the melting endotherm in the first scan of each material, and glass transition temperatures were taken from the second scan.

of the transition region in the second scans. As many as four other thermal transitions have also been reported in the literature for cellulose acetate [64]. A previous study by Kamide and Saito [61] has shown that the T_g for cellulose acetate varies linearly with the degree of substitution, and values computed using their relationship agree favorably with those found here (see Table 4). Kamide and Saito suggested that for low DS materials, interactions between hydroxyl groups on adjacent polymer chains restrict segmental mobility, thus increasing the T_g of the material.

The melting temperature (T_m) was taken as the peak of the melting endotherm from the first scan of each material. The heat of fusion, calculated from the area under the melting peak, decreases with decreasing acetylation. This is indicative of a decrease in crystallinity. Using melting point depression information [65], the heat of fusion for a perfect cellulose triacetate crystallite has been estimated to be about 8.2 cal/g. Assuming that this heat of fusion applies for all degrees of substitution, crystallinities of the current films ranging from 27% to 52% are calculated. The relatively large range of crystallinities should have a significant effect on the transport properties as discussed later.

Wide-angle X-ray scattering (WAXS) was also used to investigate the crystalline structure of the films. The WAXS patterns shown in Fig. 3 are quite diffuse compared to those of cellulose triacetate fibers [66]. However, the

TABLE 4

Thermal and mechanical properties of the cellulose acetates

	Degree of substitution		
	1.75	2.45	2.84
<i>Thermal properties</i>			
T_g (°C) ^a	205	187	185
T_g (°C) ^b	205–212	198	187
T_g (°C) ^c	214	200	192
T_g (°C) (DMA)	207	298	193
T_m (°C)	245	233	293
ΔH (cal/g)	2.2	3.0	4.3
Crystallinity (%)	27	37	52
<i>Mechanical properties</i>			
Elastic modulus (10^5 MPa)	4.2	4.4	4.9
Tensile strength (10^3 MPa)	6.6	12.7	14.0
Elongation at break (%)	4.0	14.0	17.0

^aMeasured by DSC at Tennessee Eastman.^bMeasured by DSC at University of Texas.^cCalculated from linear relationship reported by Kamide and Saito [61].

WAXS peaks become sharper and more intense as the degree of acetylation increases, which reflects higher levels of crystallinity and possibly larger or more perfect crystallites. These results correspond well with the heat of fusion data.

The mechanical properties of the cellulose acetate films (Table 4 and Fig. 4) are also sensitive to acetyl content. The elastic modulus and ultimate tensile strength increase with DS, while the ultimate elongation decreases. These trends indicate that increasing acetylation produces a stiffer and stronger material. The magnitude of the $\tan \delta$ peak at the glass transition decreases as the degree of acetylation increases, reflecting the reduced fraction of the amorphous phase as shown in Fig. 4.

Gas sorption

Sorption isotherms for CO₂ and CH₄ were measured at 35°C for all three cellulose acetate films. The methane data were obtained for a sample that was not previously exposed to high pressure CO₂, i.e., “unconditioned”. The results shown in Fig. 5 indicate that there is very little difference in the sorption characteristics of the three films. In other words, it appears that the amount of acetylation does not have a significant effect on methane solubility in cellulose acetate. However, a fortuitous combination of effects may be responsible for this. In most semicrystalline polymers, gas sorption and transport occur solely in the amorphous phase [67]. Extensive studies have shown that the effective

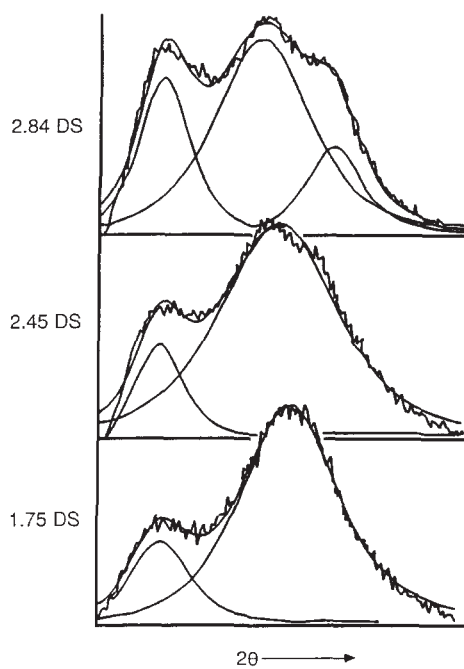


Fig. 3. X-Ray diffraction scans for the cellulose acetate films.

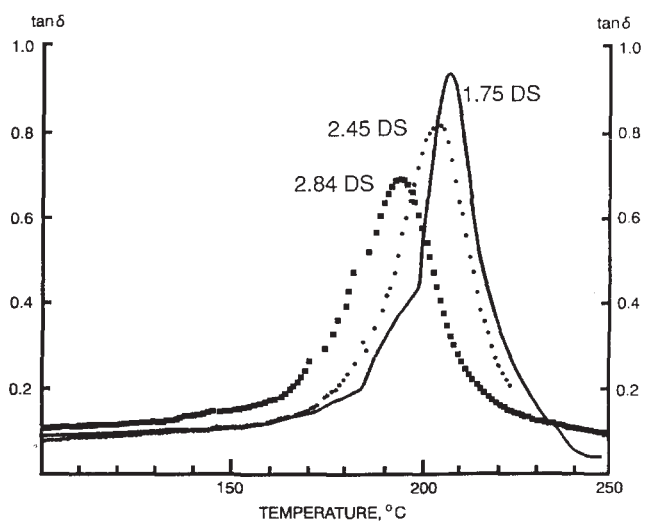


Fig. 4. Dynamic mechanical spectrum at 1 Hz showing the variation in T_g with acetylation.

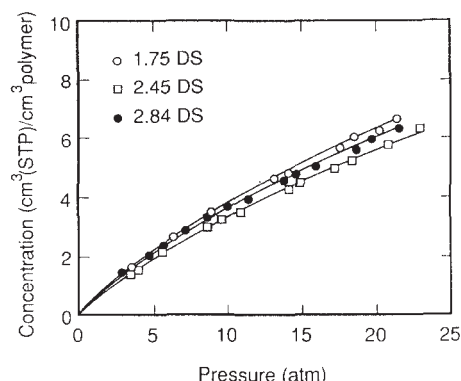


Fig. 5. Sorption isotherms measured at 35°C for CH₄ in the cellulose acetate films.

TABLE 5

Calculation of the intrinsic solubility of methane in cellulose acetate at 18.5 atm

	Film designation		
	1.75	2.45	2.84
Sorbed concentration $\left(\frac{\text{cm}^3(\text{STP})}{\text{cm}^3 \text{ polymer}} \right)$	6.0	5.2	5.6
Density (g/cm ³)	1.358	1.327	1.305
Weight fraction amorphous	0.73	0.63	0.48
Intrinsic solubility $\left(\frac{\text{cm}^3(\text{STP})}{\text{g amorph. polymer}} \right)$	6.0	6.2	8.9

solubility is directly proportional to the amorphous fraction of the polymer [67–72]. Therefore, the intrinsic gas solubility in the amorphous phase (cm³ gas/g amorphous polymer) can be obtained by dividing the overall concentration of sorbed gas (cm³ gas/cm³ polymer) by the density of the polymer and by its amorphous weight fraction. Table 5 gives the results of this calculation for the three cellulose acetate films, using CH₄ sorption at an arbitrary pressure of 18.5 atm (Fig. 5) and the crystallinities listed in table 4. These results show that the 2.84 DS film has a significantly higher intrinsic CH₄ solubility than the other two, i.e., solubility increases with acetylation.

The isotherms in Fig. 5 exhibit the nonlinear concave shape characteristic of other glassy polymers [23,34,47–50] that is well described by the dual sorption model (eqn. 5). The model parameters, k_p , C'_H , and b , listed in Table 6 were calculated using nonlinear regression analysis of the data. Stern and Kul-karni [73] measured methane solubility at 20°C for a 2.4 DS cellulose acetate film which was prepared by drying reverse osmosis membranes. They found

TABLE 6

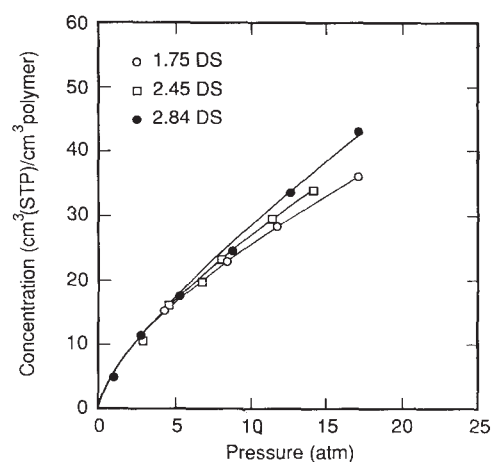
Dual-mode sorption parameters for methane in cellulose acetate

CA film	k_D $\left(\frac{\text{cm}^3(\text{STP})}{\text{cm}^3\text{polymer-atm}} \right)$	C'_H $\left(\frac{\text{cm}^3(\text{STP})}{\text{cm}^3\text{polymer}} \right)$	b (atm ⁻¹)
1.75	0.164	4.908	0.078
2.45	0.190	2.504	0.132
2.84	1.84	3.151	0.134

TABLE 7

Dual-mode sorption parameters for methane at 20°C showing the effect of carbon dioxide exposure

	k_D $\left(\frac{\text{cm}^3(\text{STP})}{\text{cm}^3\text{polymer-atm}} \right)$	C'_H $\left(\frac{\text{cm}^3(\text{STP})}{\text{cm}^3\text{polymer}} \right)$	b (atm ⁻¹)
Prior to CO ₂ exposure	0.061	4.11	0.159
After CO ₂ exposure	0.109	8.28	0.120

Data taken from Stern and Kulkarni [73] assuming a density of 1.33 g/cm³ for the CA sample.Fig. 6. Sorption isotherms measured at 35°C for CO₂ in the cellulose acetate films.

that the methane solubility for unconditioned films was about 50% lower than the solubility in films which had been previously exposed to high pressure CO₂. Their results, given in Table 7, illustrate the effect that CO₂ conditioning can have on the dual mode sorption parameters.

Figure 6 shows carbon dioxide sorption isotherms for the unconditioned cel-

lulose acetate films. Gas solubilities were determined by monitoring the pressure decrease in a sealed chamber containing the polymer. At the beginning of each measurement, gas sorption occurred quickly, but after about 8 hours, the rate of gas uptake by the films slowed considerably. The pressure in the cell continued to decrease slowly for 3 to 4 days, until it appeared to reach a steady, "pseudo" equilibrium. The data in Fig. 6 represent the sorption level at that "pseudo" equilibrium, although it never really attained true equilibrium, i.e., it would probably continue to change slowly with time. The slow changes with time are due to conditioning of the sample by CO_2 .

Chern et al. [74] provide a mechanistic description of the conditioning process of glassy polymers produced by exposure to high pressure gas. They envision the glassy state as having "unrelaxed volume" in the form of small gaps between the polymer chains which are "frozen in" because of the long relaxation times associated with the approach to the equilibrium state. When the polymer is exposed to a highly sorbing penetrant, such as CO_2 , these intersegmental gaps may redistribute. These microvoids are believed to provide sites for Langmuir-type sorption. The sorption at extremely high gas pressures may cause significant swelling of the polymer, and upon removal of the sorbed gas, the volume of the polymer may not fully return to the original value except after very long times [23]. Thus, the conditioning process generates semipermanent changes in the polymer microstructure which result in an increased sorption capacity of the material.

The effect of CO_2 conditioning on subsequent solubility measurements can be seen in Fig. 7 for the 2.84 DS cellulose acetate film. In this illustration, cycle 1 corresponds to sorption measurements made on an unconditioned polymer.

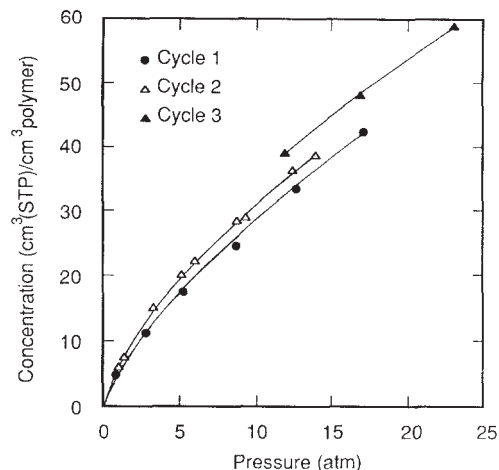


Fig. 7. Sorption isotherms measured at 35°C for CO_2 in the 2.84 DS film, evacuated for 8 days between the first and second cycles and for 3 days between the second and third cycles.

After that cycle was completed, the film was evacuated for 8 days, and then a second sorption isotherm, cycle 2, was measured. The results for this cycle agree extremely well with CO₂ solubility data reported by Sada et al. [34] for a solution-cast dense cellulose acetate film prepared similarly to those in this study. The same experimental procedure was followed for all three films, and the dual-mode parameters calculated for both cycles, unconditioned and conditioned, are listed in Table 8. The parameter values changed significantly after conditioning. For example, the Langmuir capacity, C'_H , was increased for all three films, but the Henry's law constant, k_D , was decreased by conditioning. The first observation is consistent with conclusions drawn by Wonders and Paul [23] regarding CO₂ conditioning of polycarbonate. As previously mentioned, upon exposure to high pressure CO₂, there is an increase or redistribution of the free volume in which Langmuir-type sorption occurs. After removing the gas, the extremely slow relaxation time of the glass prevents the material from returning to its original state within the time scale of the experiments. Therefore, the increase in Langmuir sites remains. The second observation, that k_D decreases after conditioning, may reflect changes in the packing efficiency for some chain segments or changes in interactions with the gas after the conditioning process.

A comparison of the sorption results for CO₂ and CH₄, Table 6 and Table 8 respectively, indicates that sorption of CO₂ is substantially more affected by the acetyl content of the polymer than is the case for methane. In fact, an analysis of the CO₂ data similar to that for CH₄ in Table 5 suggests significantly greater differences in intrinsic CO₂ sorption than is shown by the isotherms in Fig. 6. The film with the highest acetylation, 2.84 DS, and the highest intrinsic solubility of CO₂ is the most susceptible to conditioning by CO₂. For this film, the Langmuir sorption capacity, C'_H , undergoes an almost four-fold increase after conditioning as compared to a less than 10% change in C'_H for

TABLE 8

Dual-mode sorption parameters for carbon dioxide in cellulose acetate at 35°C

Ca film		k_D $\left(\frac{\text{cm}^3(\text{STP})}{\text{cm}^3\text{polymer-atm}} \right)$	C'_H $\left(\frac{\text{cm}^3(\text{STP})}{\text{cm}^3\text{polymer}} \right)$	$b \text{ (atm}^{-1}\text{)}$
1.75	cycle 1	1.138	21.11	0.215
	cycle 2	0.996	22.87	0.275
2.45	cycle 1	1.572	14.62	0.303
	cycle 2	1.362	22.58	0.248
2.84	cycle 1	2.176	6.67	1.056
	cycle 2	1.647	19.63	0.291

the 1.75 DS film. This issue will be discussed further in the section on permeation results.

It has been suggested [49,75,76] that highly soluble penetrants have a greater conditioning effect on polymers than lower sorbing penetrants. Figures 5 and 6 show that CO_2 is much more soluble in cellulose acetate than is CH_4 . Stern and Kulkarni [73] found no significant conditioning effect when cellulose acetate films were exposed to high pressure methane. Figure 8 shows that CO_2 sorption in cellulose acetate is much greater than that in polycarbonate and polysulfone [23,49]. This may explain several unusual features of cellulose acetate, relative to those for these two polymers, including the tendency for the CO_2 sorption level to slowly creep upwards with time for cellulose acetate, but not for the others. These facts may reflect extensive changes in cellulose acetate caused by CO_2 sorption, such as disruptions in chain to chain interactions. These points will be elaborated on in the discussion of the unusual permeation behavior of CO_2 in cellulose acetate.

Conditioning is not only pressure dependent but also a time-dependent phenomenon, and the amount of time the polymer is allowed to relax between solubility measurements is an important variable. Stern and Kulkarni suggested that the rate of depressurization after exposure to high pressure CO_2 may have an effect on the extent of conditioning observed. Some evidence for the time dependence of sorption and desorption has been given by Kamiya et al. [77] in a study of high pressure sorption in polysulfone and polycarbonate. The films used in this study were evacuated for 8 days between the first and second CO_2 sorption isotherm cycles, which is twice the time it took for each individual solubility measurement to reach "pseudo" equilibrium. However, a third sorption cycle shown in Fig. 7 for the 2.84 DS material was taken after

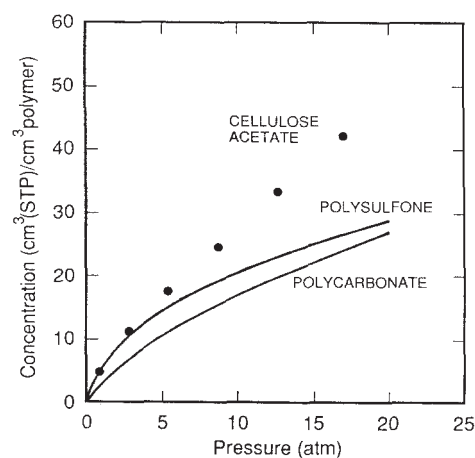


Fig. 8. Comparison of sorption isotherms measured at 35 °C for CO_2 in cellulose acetate (2.84 DS), polycarbonate [23], and polysulfone [49].

just 3 days of evacuation from the second cycle. The solubility levels in the third cycle are higher than either of the previous two cycles. Therefore, in order to compare results from one study involving high pressure CO₂ to the next, it is imperative to know the entire CO₂ exposure history of the polymer. The current results suggest that the nature of this time dependence and the extent to which high pressure exposure to a penetrant affects the glassy state can vary greatly from one polymer to another.

Gas permeation

Pure gas permeability coefficients for He, H₂, N₂, O₂, CH₄, and CO₂, were measured at 1 atmosphere and 35°C for each cellulose acetate film, with the results summarized in Table 9. The values obtained for He, N₂, and CH₄ are similar to those in Table 1 published by Gantzel and Merten [31] for a dense cellulose acetate film with 2.41 DS; however, their measurements were made at a lower temperature than used here. Figure 9 clearly shows that the permeation rate for each gas increases with acetyl content. However, since crystallinity reduces the overall permeation rate for a semicrystalline polymer [67], the intrinsic permeability coefficients for the amorphous phase of the cellulose acetates would be even higher than the values given in Table 9. Because of this, the intrinsic amorphous phase permeability increases even more with increasing acetylation than shown in Fig. 9. Since replacing hydroxyl groups with bulkier acetyl groups causes a decrease in intermolecular hydrogen bonding and opens up the structure of the polymer, it is reasonable to expect a strong increase in permeation rates with degree of acetylation.

For most of the gases, the permeability coefficients were either independent of pressure or there was a small decrease with increasing pressure as predicted by dual mode theory (eqn. 6) for glassy polymers. The pressure dependence of the methane permeability coefficient for all three films is illustrated in Fig. 10. Carbon dioxide was the only gas that showed an increase in permeability with

TABLE 9

Permeability coefficients for cellulose acetate at 1 atm and 35°C

Gas	Permeability, $P \times 10^{10} \left[\frac{\text{cm}^3(\text{STP})\text{-cm}}{\text{sec-cm}^2\text{-cmHg}} \right]$ at degree of substitution		
	1.75	2.45	2.85
He	9.34	16.0	19.6
H ₂	6.05	12.0	15.5
CO ₂	1.84	4.75	6.56
O ₂	0.32	0.82	1.46
N ₂	0.057	0.15	0.23
CH ₄	0.052	0.15	0.20

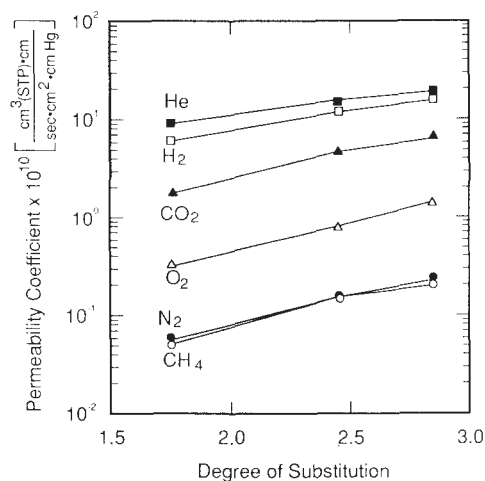


Fig. 9. Effect of degree of acetylation on gas permeation in cellulose acetate at 35°C and 1 atm.

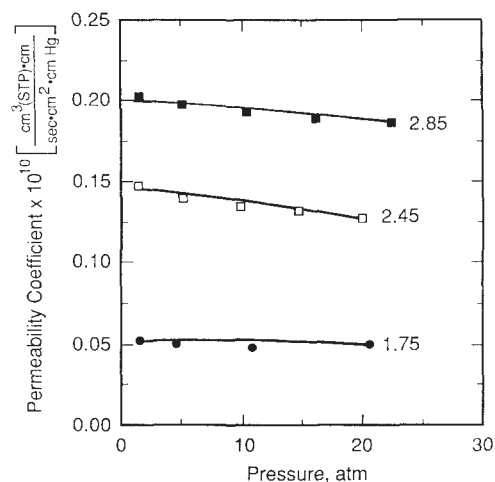


Fig. 10. Effect of pressure on CH₄ permeability in the cellulose acetate films.

pressure, and additional experiments were performed to examine more fully this unusual behavior as described later.

Ideal separation factors, defined as the ratio of pure gas permeability coefficients, are listed in Table 10 for three gas pairs. For most membrane materials, the selectivity is lower the higher the permeability. This trend is also observed for the films in this study. However, for gas pairs which have similar molecular sizes (i.e., CO₂/CH₄ and O₂/N₂), the selectivity varies much less with acetylation than for the He/CH₄ pair. Since increasing acetylation does

TABLE 10

Ideal separation factors for cellulose acetate at 35°C and 1 atm

Degree of substitution	Selectivity, P_A/P_B		
	$P_{\text{He}}/P_{\text{CH}_4}$	$P_{\text{O}_2}/P_{\text{N}_2}$	$P_{\text{CO}_2}/P_{\text{CH}_4}$
1.75	181.0	5.5	35.6
2.45	114.3	5.5	31.1
2.84	98.0	6.4	32.8

not detract from the separation performance of the polymer and improves the mechanical properties (Table 4), it appears that the 2.84 DS polymer would be more attractive than the other two for commercial applications.

In this study, an ideal separation factor of about 32 was found for CO_2/CH_4 ; values reported in the literature for dense cellulose acetate films are only slightly lower, about 27–28 [34,78]. Preliminary mixed gas permeation investigations using a 50/50 mixture of CO_2 and CH_4 gave an actual selectivity of about 32 to 34 at a CO_2 partial pressure of about 10 atm. However, further experiments at higher pressures are needed to draw decisive conclusions about mixed gas behavior. Previous studies of CO_2/CH_4 mixed gas permeation rates for high flux asymmetric cellulose acetate membranes revealed lower separation factors in the range 20 to 22 [51,79], which remained constant up to a CO_2 partial pressure of 18 atm [51].

Carbon dioxide behavior

As mentioned previously, the permeation behavior of CO_2 in cellulose acetate is unusual, compared to many other glassy polymers, in that after a certain pressure, the permeability coefficient begins to increase [9,10,34,51–53]. This is illustrated in Fig. 11 for the 2.84 DS cellulose acetate film. From 1 to about 10 atm, the permeability decreases in accordance with the dual mode theory of transport. Above 10 atm, the permeability coefficient increases with pressure due to the onset of plasticization by the CO_2 . The high concentration of sorbed penetrant leads to increased segmental motions, and, consequently, the transport rate of the penetrant is also enhanced.

Plasticization effects are common in rubbery polymers [80,81]. For cellulose acetate, the high solubility of CO_2 may swell the polymer to such an extent that intermolecular interactions are disrupted. As a result, mobility of the acetyl and hydroxyl pendant groups, as well as small-scale main chain motions, would increase thereby enhancing the gas transport rates.

It was also observed that as the film was held at a constant pressure of 10 atm, the permeability increased slowly with time (Fig. 11). Permeability measurements were taken at 10 atm until it appeared that a steady value had been

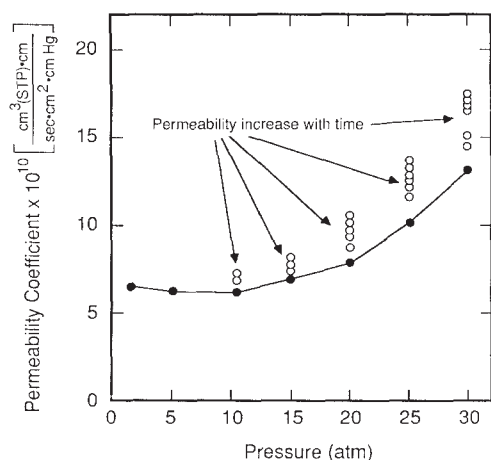


Fig. 11. Effect of pressure on CO_2 permeability in the 2.84 DS cellulose acetate film at 35°C . Open circles represent the increase in permeability with time at a constant pressure.

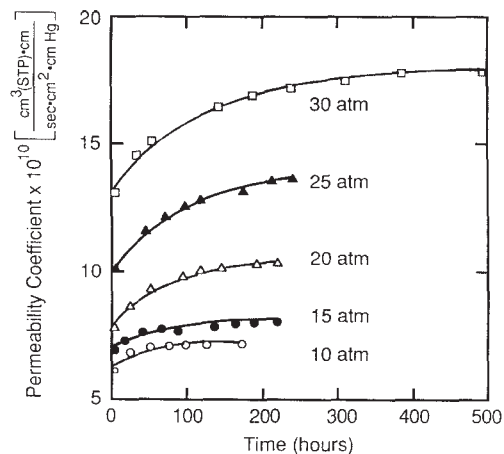


Fig. 12. Time dependence of CO_2 permeability in the 2.84 DS cellulose acetate film.

reached. Then the pressure was increased to 15 atm and held there while the permeability increase was again monitored with time. The time dependence of the permeability coefficient is illustrated in Fig. 12. At each pressure, the permeability increased with time until it seemed to reach a "pseudo" equilibrium, or a plateau; however, it never really stopped creeping up slowly with time. This type of time dependence, also observed in CO_2 solubility measurements, is related to the conditioning effect of CO_2 . Chiou and Paul [82] observed similar behavior for CO_2 in poly(methyl methacrylate). They noted that the amount of conditioning experienced by the polymer was affected by

the length of time it was exposed to CO₂. Evidently, the highly sorbing gas dilates the polymer, allowing the chain segments to move slowly towards a new organizational state.

All of the data shown in Figs. 11 and 12 were taken continuously, i.e., with no depressurization between the measurements. At 30 atm, the CO₂ permeability coefficient for the 2.84 DS film increased in time by almost 40% to a final level about 3 times the initial permeability coefficient measured at 1 atm. After the permeability reached a "pseudo" equilibrium at 30 atm, the pressure was decreased very slowly, at a rate of approximately 5 atm per day. The depressurization cycle for the 2.84 DS film is shown in Fig. 13. At each 5 atm interval, the upstream pressure was held constant for approximately four time lags while the permeability was measured. As the pressure decreased from 30 atm to about 20 atm, the permeability coefficient continued to increase. Below 20 atm, the permeability began to decrease upon further lowering of the pressure. At 1 atm the permeability coefficient was about 70% higher than the value measured initially at 1 atm for the cellulose acetate film. After the permeation "loop" was completed, the film was evacuated for about 10 days. At the end of this period, the CO₂ permeability at 1 atm had decreased to a value only about 30% higher than the initial 1 atm permeability. Upon further evacuation, the permeability continued to approach the initial value.

A similar hysteretic behavior was reported by Jordan et al. [83] for high pressure CO₂ permeation in polycarbonate and by Kamiya et al. [77] for high pressure sorption in polysulfone and polycarbonate. However, in the study by Jordan et al., much greater pressures (about 55 atm) and longer time scales were required to induce such plasticization effects in polycarbonate. They also

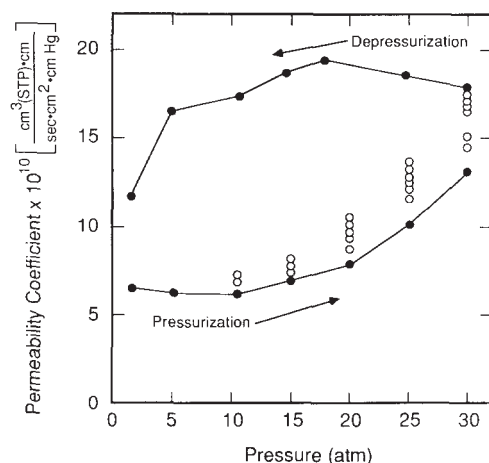


Fig. 13. Pressurization and depressurization cycles showing the hysteretic response of CO₂ permeability in the 2.84 DS cellulose acetate film.

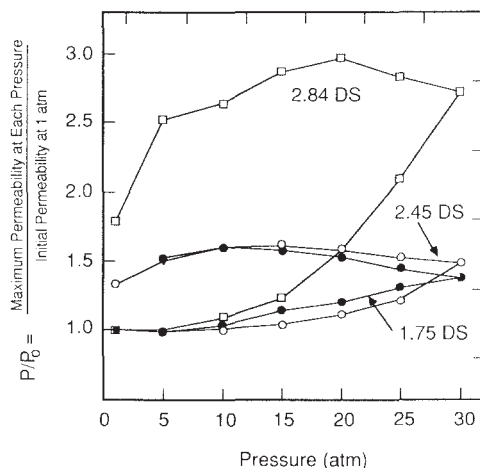


Fig. 14. Comparison of CO₂ permeation in the three cellulose acetate films.

found that the CO₂ permeability coefficient for polycarbonate continued to increase during depressurization over the entire pressure range, and it remained at a “semipermanent” steady value as long as the penetrant was in the film (for at least two months). In other words, the polycarbonate did not exhibit the same type of relaxation phenomena on depressurization as the cellulose acetate did. Subsequent evacuation of the polycarbonate to remove the CO₂ resulted in permeation values approaching those for the unconditioned starting material.

The pressure dependence of the CO₂ permeability exhibited a similar hysteric response for all three cellulose acetate films as shown in Fig. 14. In order to compare the results for the three films on a similar scale, a “relative” permeability coefficient can be defined as the maximum permeability measured at each pressure divided by the initial permeability at 1 atm, or P/P_0 . It is apparent from Fig. 14 that the cellulose acetate with the largest amount of acetylation, 2.84 DS, experienced the greatest amount of plasticization. Whereas, the response was practically the same for the other two materials. This agrees with the sorption results, in that conditioning with CO₂ affected the solubility for the 2.84 DS sample much more than the other two. The explanation for this no doubt relates to the higher intrinsic solubility of CO₂ in its amorphous phase and perhaps to the higher proportion of weaker, and more easily disrupted, acetayl-acetyl interactions compared to hydroxyl-hydroxyl and hydroxyl-acetyl interactions that exist at lower degrees of substitution.

Interactions in cellulose acetate

Attempts have been made to characterize the intermolecular interactions of the pendant groups of cellulose acetate with each other and with solvent mol-

ecules [37,84,85]. Kamide et al. [37] used nuclear magnetic resonance and infrared spectroscopy to analyze the effects of acetylation on interactions between the cellulose acetate and polar solvents. Their study included samples with 0.49 to 2.92 degrees of substitution. From an infrared analysis, they proposed three types of interactions between pendant groups of neighboring polymer chains: hydroxyl-hydroxyl (or hydrogen bonding), hydroxyl-acetyl, and acetyl-acetyl (see Fig. 15). Interactions with acetyl groups stems from the dipolar nature of the carbonyl. Addition of a polar solvent to cellulose acetate can weaken the interactions between pendant groups due to new polar interactions between pendant groups and the solvent.

Of the three types of pendant group interactions, they found that the acetyl-acetyl interaction is the weakest, with the other two being of more comparable strength. This was confirmed by Kamide and Saito [61] in their analysis of the relation between the amount of acetylation and the glass transition. As a result, the 2.92 DS material, which has very few hydroxyl groups, has intermolecular interactions weak enough to be completely solvated by a polar solvent. For the 2.46 DS cellulose acetate, the extent of disruption of the stronger hydroxyl-acetyl and hydroxyl-hydroxyl interactions will depend on the polarity of the solvent and its propensity to interact with the pendant groups.

The reasoning of Kamide et al. can be applied to the cellulose acetate samples used in this study. For each sample, Table 3 lists the percentage of anhydroglucose units which are fully substituted (triacetate) and those which have 1 or 2 hydroxyl groups in the repeat unit. The 2.84 DS cellulose acetate has approximately 1 to 2 hydroxyl groups for every 10 repeat units, indicating that the acetyl-acetyl interaction predominates, with only an occasional hydroxyl-hydroxyl or hydroxyl-acetyl interaction. Consequently, it appears that the weaker interactions and more open structure of the 2.84 DS cellulose acetate

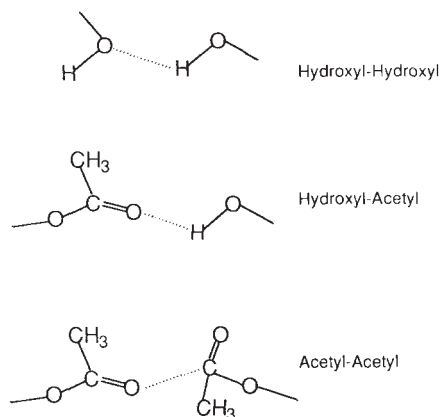


Fig. 15. Various types of interactions between the cellulose acetate pendant groups (Kamide et al. [37]).

would be more susceptible to the plasticizing influence of CO_2 . It has been suggested that CO_2 somehow interacts with the carbonyl, $\text{C}=\text{O}$, part of the ester unit of the acetyl group, since other glassy polymers which are also plasticized by CO_2 have a carbonyl group as a common structural feature, e.g., poly(methyl methacrylate), poly(ethyl methacrylate), and nylon-6 [76,82,86,87]. For the 2.45 DS film almost half of the repeat units (43%) have at least one hydroxyl group and the percentage is even greater for the 1.75 DS film. These hydroxyl groups are involved in stronger interactions with acetyl groups and other hydroxyl groups, resulting in a tighter polymer structure. Therefore, CO_2 still affects these materials but not to as great an extent as the 2.84 DS film.

FTIR analysis

Infrared (IR) analyses have been used extensively to investigate the molecular structure of polymers and polymer blends [88–95]. For cellulose and its esters, the IR peak assignments and a complete interpretation of the IR spectra have already been published [96]. In this study, infrared analysis was used to probe the effect of CO_2 on intermolecular interactions in the polymer.

The IR spectra of the 2.45 DS and 2.85 DS films were examined before, during, and after exposure to CO_2 . After the initial scan, CO_2 gas was introduced into the IR cell containing the cellulose acetate film, and a pressure of about 15 atm was maintained for 4 days. Another IR scan was taken in the presence of the gas. Then the pressure was slowly released, and the cell was purged with nitrogen. After a long period of time, enough for complete removal of the CO_2 and relaxation of the film, a third IR scan was taken. Similar patterns were observed for both CA films, and the spectra illustrated in Fig. 16 are for the 2.45 DS sample. Part (b) of this figure is the spectrum of the film taken in the presence of CO_2 . The absorption bands appearing at 2350 cm^{-1} and 665 cm^{-1} , in addition to the two “doublet” peaks at 3715 cm^{-1} and 3610 cm^{-1} are characteristic of CO_2 gas [97]. The hydroxyl ($3000\text{--}3600\text{ cm}^{-1}$) and carbonyl ($1700\text{--}1800\text{ cm}^{-1}$) regions of cellulose acetate show some changes upon sorption of CO_2 .

Figure 17(a) shows the carbonyl ($\text{C}=\text{O}$) absorption band for the acetyl pendant group of the 2.45 DS film, before and during CO_2 exposure. It is obvious that the presence of CO_2 causes a shift in the carbonyl peak by about 4 cm^{-1} to a higher wave number with a slight increase in absorbance. Kamide et al. [37] also found a shift in the carbonyl peak for a 2.46 DS cellulose acetate due to the presence of certain solvents. They associate the band at 1748 cm^{-1} to $\text{C}=\text{O}$ stretching for carbonyls that are not hydrogen bonded, i.e., not involved in acetyl–hydroxyl interactions, but are involved with interactions between other acetyl groups. The IR shifts were then attributed to weakening of these interactions by solvents. This interpretation is supported by more recent studies of polymer blends in which at least one component contained carbonyl groups [93–95]. Jo et al. [94] found a similar shift in the carbonyl peak for

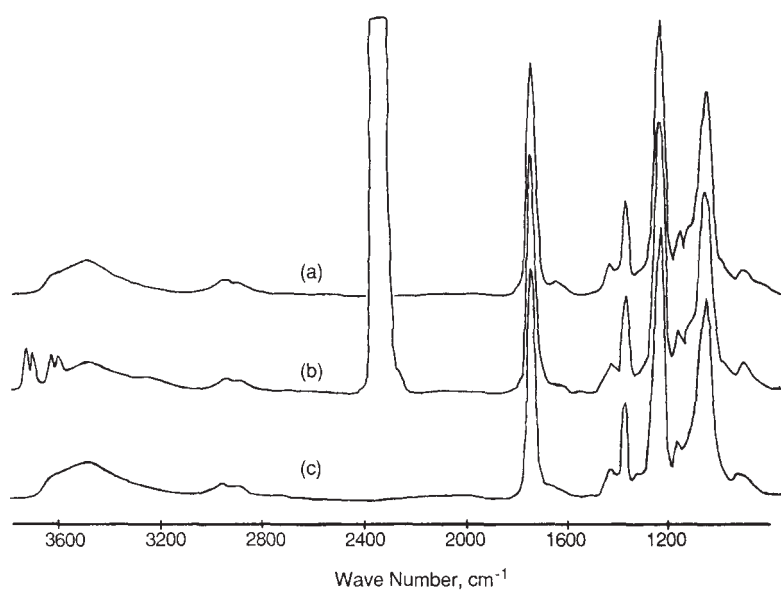


Fig. 16. Infrared spectra for the 2.45 DS cellulose acetate film (a) before, (b) during, and (c) after exposure to CO_2 .

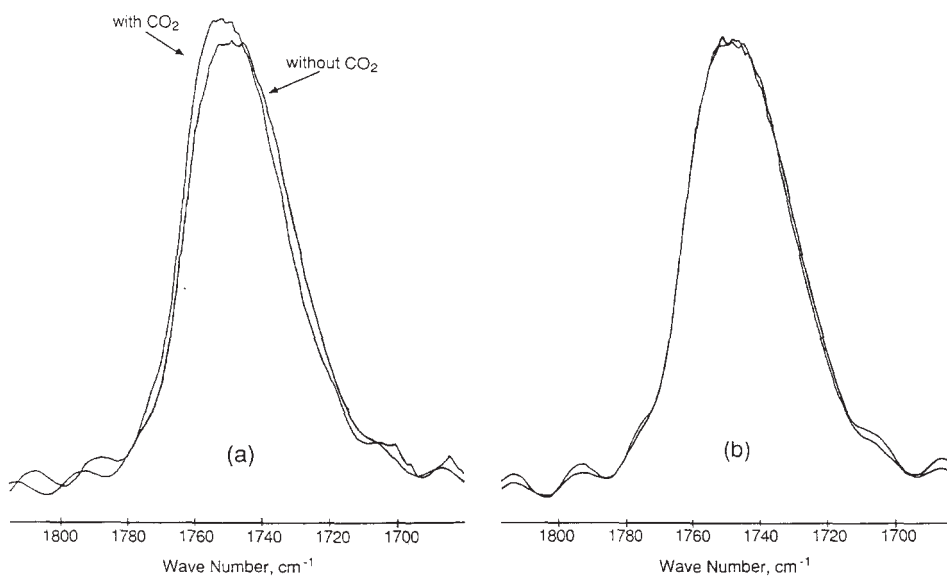


Fig. 17. Change in the carbonyl band position of the 2.45 DS film caused by the presence of CO_2 (a), and comparison of the carbonyl band before and after CO_2 exposure (b).

poly(methyl methacrylate), or PMMA, upon the addition of styrenic polymers. They, too, postulated that dipole-dipole associations existed among the carbonyls in PMMA and that the carbonyl peak observed was a composite of both "free" and "self-interacting" carbonyls. Addition of an inert component would disrupt the dipole-dipole interactions and increase the population of "free" carbonyls, as reflected by a small shift (about 5 cm^{-1}) to a higher frequency and an increase in peak intensity. Cruz-Ramos and Paul [95] provide further evidence for this, using IR analysis of low molecular weight analogs that simulate blends of poly(vinyl chloride) with ethylene/vinyl acetate copolymers.

The similarity between the results outlined above and those shown in Fig. 17(a) for cellulose acetate seem to provide adequate proof that CO_2 disrupts the dipolar interactions between acetyl groups, thereby increasing the amount of unassociated or "free" acetyls. After removal of the CO_2 and enough time for the polymers chains to fully relax, the carbonyl absorption band shifts back to the original position, as shown in Fig. 17(b). From the equivalence of the peaks measured before and after CO_2 exposure, it appears that the acetyl groups become "re-associated", and the plasticizing effect of CO_2 is reversible.

Carbon dioxide also affects the IR spectra of cellulose acetate in the hydroxyl region. The broad hydroxyl band shown in Fig. 18 between 3700 cm^{-1} and 3400 cm^{-1} represents a combination of various degrees of intermolecular and intramolecular hydrogen bonding. The bands at 2950 cm^{-1} and 2890 cm^{-1} are C-H stretches [96]. As previously mentioned, the sharp "doublet" or split peaks

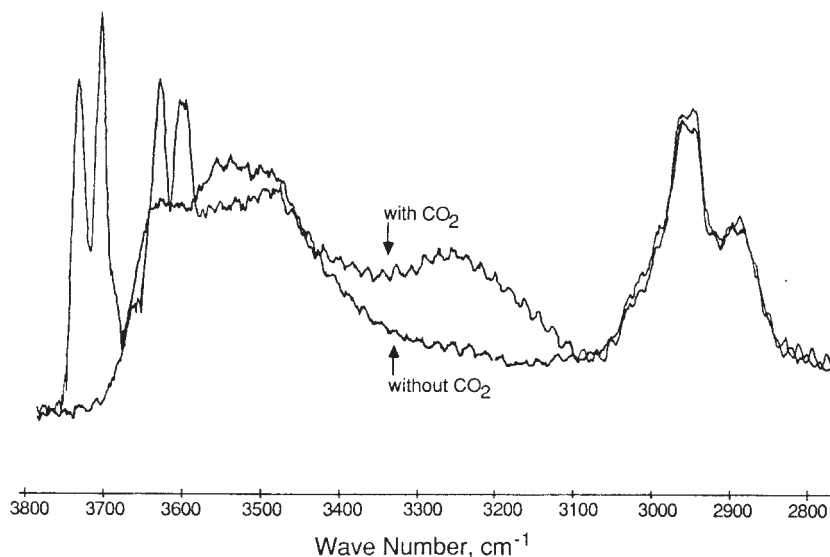


Fig. 18. Infrared scan showing the effect of CO_2 in the hydroxyl region of the 2.84 DS cellulose acetate film.

at 3715 cm^{-1} and 3610 cm^{-1} are due to CO_2 gas. Two other obvious differences can be seen in the spectrum during CO_2 exposure. First, there is a small decrease in the height of the broad band from 3475 cm^{-1} to 3575 cm^{-1} , and second, a new peak appears at 3250 cm^{-1} . A possible explanation for the first observation is that sorbed CO_2 disrupts some of the hydrogen bonding in the polymer thus reducing the peak absorbance. If so, the appearance of the new peak may be due to subsequent interaction of the “free” hydroxyls with the CO_2 molecules. In their study, Kamide et al. concluded that dissolution of cellulose acetate involved interactions between the solvent molecules and the hydroxyls which become more pronounced for lower DS polymers. It is also known that the interaction between OH and C=O groups on the *same* molecule (or chelation) is observed in IR spectra as a broad band between 3200 cm^{-1} and 2500 cm^{-1} [98]. Therefore, it seems reasonable to conclude that the new peak in the cellulose acetate spectrum is related to a “new environment” for the hydroxyl groups in the presence of CO_2 , possibly even an interaction between the OH and CO_2 . It is also interesting that this new peak disappears after complete removal of CO_2 , thus supporting the conclusion that plasticization by CO_2 is reversible.

Conclusion

The purpose of this study has been to examine gas sorption and transport in dense cellulose acetate films which have been fully characterized in terms of molecular, thermal, and mechanical properties. The results indicate that acetylation is an important factor in determining transport characteristics. Replacing hydroxyl groups with the bulkier acetyl groups opens up the polymer structure and reduces the extent of hydrogen bonding. Thus, the densities of the films decrease and permeabilities increase with a higher degree of acetylation. The intrinsic gas solubilities in the amorphous phase of cellulose acetate are also higher for the 2.84 DS film than for the other two.

The sorption isotherms for CO_2 and CH_4 are well described by the dual mode sorption model for glassy polymers. Conditioning of the films by CO_2 causes an increase in the Langmuir site capacity. CO_2 also causes significant plasticization of all three materials, as evidenced by the increase in CO_2 permeability with pressure. The highly sorbing gas dilates the polymer structure and interferes with interactions between pendant groups. This allows greater mobility of the chain segments and higher diffusion rates. The acetyl–acetyl attractions, which are the most prevalent type in the 2.84 DS film, are weaker than either the acetyl–hydroxyl or hydroxyl–hydroxyl interactions. Thus, the acetyl–acetyl interactions are more easily disrupted. This seems to account for the greater plasticization response of the 2.84 DS film. The hysteretic behavior of the CO_2 permeability upon depressurization indicates that plasticization is, for the most part, reversible.

Infrared analyses confirmed the conclusion that CO₂ interferes with interactions involving the carbonyl functionality and hydroxyl groups. After removal of the CO₂ and complete relaxation of the chains, it appears that the films return to their original condition.

Acknowledgments

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References

- 1 H.K. Lonsdale, The growth of membrane technology, *J. Membrane Sci.*, 10 (1982) 81-181.
- 2 H.J. Strathmann, Membrane separation processes, *J. Membrane Sci.*, 9 (1981) 121-189.
- 3 E.R. Beaver and C.J. Patton, Membranes for generating nitrogen: gas processing applications, paper presented at the AIChE Spring National Meeting, Houston, TX, April 1987.
- 4 W.J. Schell, Commercial applications for gas permeation membrane systems, *J. Membrane Sci.*, 22 (1985) 217-224.
- 5 J.E. Kurz and R.S. Narayan, New developments and applications in membrane technology, paper presented at the AIChE Spring National Meeting, New Orleans, LA, April 1986.
- 6 H. Yamashiro, M. Hirajo, W.J. Schell and C.F. Maitland, Hydrogen purification with cellulose acetate membranes, paper presented at the Europe-Japan Congress on Membranes and Membrane Processes, Stresa, Italy, June 1984.
- 7 W.J. Schell and C.D. Houston, in: T.E. Whyte, Jr., C.M. Yon and E.H. Wagener (Eds.), *Industrial Gas Separations*, ACS Symp. Ser. No. 223, American Chemical Society, Washington, DC, 1983, p, 125.
- 8 W.A. Bollinger, D.L. MacLean and R.S. Narayan, Separation systems for oil refining and production, *Chem. Eng. Prog.*, (Oct. 1982) 27-32.
- 9 W.M. Mazur and M.C. Chan, Membranes for natural gas sweetening and CO₂ enrichment, *Chem. Eng. Prog.*, (Oct. 1982) 38-43.
- 10 A.B. Coady and J.A. Davis, CO₂ recovery by gas permeation, *Chem. Eng. Prog.*, (Oct. 1982) 44-49.
- 11 S. Loeb and S. Sourirajan, Sea water demineralization by means of an osmotic membrane, *Adv. Chem. Ser.*, 38 (1962) 117-132.
- 12 H. Strathmann, K. Kock, P. Amar and A.K. Baker, The formation mechanism of asymmetric membranes, *Desalination*, 16 (1975) 179-203.
- 13 W.J. Schell, Separation of coal hydrogasification gases by permselective membranes, *ACS, Div. Fuel Chem., Prepr.*, 20 (1975) 253-259.
- 14 J.E. Cadotte, R.S. King, R.J. Majerle and R.J. Petersen, Interfacial synthesis in the preparation of reverse osmosis membranes, *J. Macromol. Sci., Chem.*, A15 (1981) 727-755.

- 15 I. Cabasso, in: D.R. Lloyd (Ed.), *Materials Science of Synthetic Membranes*, ACS Symp. Ser. No. 269, American Chemical Society, Washington, DC, 1985, p. 306.
- 16 R.J. Gardner, R.A. Crane and J.F. Hannan, Hollow fiber permeator for separating gases, *Chem. Eng. Prog.* (Oct. 1977) 76-78.
- 17 R.T. Chern, W.J. Koros, H.B. Hopfenberg and V.T. Stannett, in: D.R. Lloyd (Ed.), *Materials Science of Synthetic Membranes*, ACS Symp. Ser. No. 269, American Chemical Society, Washington, DC, 1985, p. 25.
- 18 H.H. Hoehn, in: D.R. Lloyd (Ed.), *Materials Science of Synthetic Membranes*, ACS Symp. Ser. No. 269, American Chemical Society, Washington DC, 1985, p. 82.
- 19 A.H. Chan and D.R. Paul, Effect of sub- T_g annealing of CO₂ sorption in polycarbonate, *Polym. Eng. Sci.*, 20 (1980) 87-94.
- 20 M.J. El-Hibri and D.R. Paul, Effects of uniaxial drawing and heat-treatment on gas sorption and transport in PVC, *J. Appl. Polym. Sci.*, 30 (1985) 3649-3678.
- 21 Y. Maeda and D.R. Paul, Selective gas transport in miscible PPO-PS blends, *Polymer*, 26 (1985) 2055-2063.
- 22 Y. Maeda, Ph.D. Dissertation, The University of Texas at Austin, 1985.
- 23 A.G. Wonders and D.R. Paul, Effect of CO₂ exposure history on sorption and transport in polycarbonate, *J. Membrane Sci.*, 5 (1979) 63-75.
- 24 C.E. Reid and E. Breton, Water and ion flow across cellulosic membranes, *J. Appl. Polym. Sci.*, 1 (1959) 133-143.
- 25 H. Finken, in: D.R. Lloyd (Ed.), *Materials Science of Synthetic Membranes*, ACS Symp. Ser., 269, American Chemical Society, Washington, DC, 1985 p. 245.
- 26 H.J. Bixler and O.J. Sweeting, in: O.J. Sweeting (Ed.), *The Science & Technology of Polymer Films*, Vol. 2, John Wiley & Sons, New York, NY, 1971.
- 27 K. Kammermeyer, Silicone rubber as a selective barrier, *Ind. Eng. Chem.*, 49 (1957) 2685-1686.
- 28 V. Stannett and M. Szwarc, The permeability of polymer films to gases - A simple relationship, *J. Polym. Sci.*, 16 (1955) 89-91.
- 29 D.R. Seok, S.G. Kang and S. Hwang, Separation of helium and hydrocarbon mixtures by a two-membrane column, *J. Membrane Sci.*, 27 (1986) 1-11.
- 30 W. Pusch and A. Tanioka, Structure investigations of homogeneous cellulose acetate membranes by gas permeation measurements, *Desalination*, 46 (1983) 425-434.
- 31 P.K. Gantzel, and U. Merten, Gas separations with high-flux cellulose acetate membranes, *Ind. Eng. Chem.*, 9 (1970) 331-332.
- 32 A. Kakuta, O. Ozaki and M. Ohno, Gas permeation in freeze dried cellulose acetate membrane, *J. Polym. Sci., Polym. Chem.*, 16 (1978) 3249-3257.
- 33 S.A. Stern, S.K. Sen and A.K. Rao, The permeation of gases through symmetric and asymmetric (Loeb-type) cellulose acetate membranes, *J. Macromol. Sci., Phys. B10* (1974) 507-528.
- 34 E. Sada, H. Kumazawa, Y. Yoshio, S.T. Wang and P. Xu, Permeation of carbon dioxide through homogeneous dense and asymmetric cellulose acetate membranes, *J. Polym. Sci. Polym. Phys.*, 26 (1988) 1035-1048.
- 35 F.W. Billmeyer, Jr, *Textbook of Polymer Science*, John Wiley & Sons, New York, NY, 1984, Ch. 15.
- 36 K. Kamide and M. Saito, Cellulose and cellulose derivatives: recent advances in physical chemistry, *Adv. Polym. Sci.*, 83 (1987) 1.
- 37 K. Kamide, K. Okajima and M. Saito, Nuclear magnetic resonance study of thermodynamic interactions between cellulose acetate and solvent, *Polym. J. (Tokyo)*, 13 (1981) 115-125.
- 38 D.R. Paul, Gas sorption and transport in glassy polymers, *Ber. Bunsenges. Phys. Chem.*, 83 (1979) 294-302.

- 39 D.R. Paul and G. Morel, in: Kirk Othmer Encyclopedia of Chemical Technology, John Wiley & Sons, New York, NY, Third Edition, Vol. 15, 1981.
- 40 W.R. Vieth, J.M. Howell and J.H. Hsieh, Dual sorption theory, *J. Membrane Sci.*, 1 (1976) 177-220.
- 41 R.T. Chern, W.J. Koros, B. Yui, H.B. Hopfenberg and V.T. Stannett, Selective permeation of CO₂ and CH₄ through Kapton® polyimide: Effects of penetrant competition and gas-phase nonideality, *J. Polym. Sci., Polym. Phys.*, 22 (1984) 1061-1084.
- 42 D.R. Paul and W.J. Koros, Effect of partially immobilizing sorption on permeability and the diffusion time lag, *J. Polym. Sci. Polym. Phys.*, 14 (1976) 675-685.
- 43 J.H. Petropoulos, Quantitative analysis of gaseous diffusion in glassy polymers, *J. Polym. Sci.*, 8 (1970) 1797-1801.
- 44 S.A. Stern and V. Saxena, Concentration-dependent transport of gases and vapors in glassy polymers, *J. Membrane Sci.*, 7 (1980) 47-59.
- 45 W.J. Koros, Ph.D. Dissertation, The University of Texas at Austin, 1977.
- 46 W.J. Koros, D.R. Paul and A.A. Rocha, Carbon dioxide sorption and transport in polycarbonate, *J. Polym. Sci., Polym. Phys.*, 14 (1976) 687-702.
- 47 A.H. Chan, W.J. Koros and D.R. Paul, Analysis of hydrocarbon gas sorption and transport in ethyl cellulose using the dual sorption/partial immobilization models, *J. Membrane Sci.*, 3 (1978) 117-130.
- 48 W.J. Koros, A.H. Chan and D.R. Paul, Sorption and transport of various gases in polycarbonate, *J. Membrane Sci.*, 2 (1977) 165-190.
- 49 A.J. Erb and D.R. Paul, Gas sorption and transport in polysulfone, *J. Membrane Sci.*, 8 (1981) 11-22.
- 50 W.J. Koros and D.R. Paul, CO₂ sorption in poly(ethylene terephthalate) above and below the glass transition, *J. Polym. Sci., Polym. Phys.*, 16 (1978) 1947-1963.
- 51 C.G. Wensley and S.Z. Jakabhazy, High performance gas separation membranes, paper presented at the AIChE Winter National Meeting, Atlanta, GA, March 1984.
- 52 B.S. Minhas, T. Matsuura and S. Sourirajan, Formation of asymmetric cellulose acetate membranes for the separation of carbon dioxide-methane gas mixtures, *Ind. Eng. Chem. Res.*, 26 (1987) 2344-2348.
- 53 S.Y. Lee, B.S. Minhas and M.D. Donohue, Effect of composition and pressure on permeation through cellulose acetate membranes, paper presented at the AIChE Summer National Meeting, Minneapolis, MN, August 1987.
- 54 C.M. Buchanan, J.A. Hyatt and D.W. Lowman, Two-dimensional NMR of polysaccharides: Spectral assignments of cellulose triesters, *Macromolecules*, 20 (1987) 2750-2754.
- 55 T. Miyamoto, Y. Sato, T. Shibata, H. Inagaki and M. Tanahashi, ¹³C Nuclear magnetic resonance studies of cellulose acetate, *J. Polym. Sci., Polym. Chem.*, 22 (1984) 2363-2370.
- 56 ASTM Standard Methods, Vol. 6.02, 1987.
- 57 ASTM Standard Methods, Vol. 8.01, sec. 8, 1987.
- 58 A.C. Puleo, Ph.D. Dissertation, The University of Texas at Austin, 1988.
- 59 C.J. Malm, L.J. Tanghe and B.C. Laird, Primary hydroxyl groups in hydrolyzed cellulose acetate, *J. Amer. Chem. Soc.*, 72 (1950) 2674-2678.
- 60 T.G. Fox and P.J. Flory, The glass temperature and related properties of polystyrene — Influence of molecular weight, *J. Polym. Sci.*, 14 (1954) 315-319.
- 61 K. Kamide and M. Saito, Thermal analysis of cellulose acetate solids with total degrees of substitution of 0.49, 1.75, 2.46, and 2.92, *Polym. J.*, 17 (1985) 919-928.
- 62 M. Scandola and G. Ceccorulli, Viscoelastic properties of cellulose derivatives. 1. Cellulose acetate, *Polymer*, 26 (1985) 1053-1057.
- 63 G. Ceccorulli, M. Pizzoli and M. Scandola, Influence of water on the secondary relaxations of cellulose acetate, *Polym. Commun.*, 27 (1986) 228-230.

- 64 J.H. Daane and R.E. Barker, Jr., Multiple glass transitions in cellulose 2.5 acetate, *Polym. Lett.*, 2 (1964) 343-347.
- 65 L. Mandelkern and P.J. Flory, Melting and glassy state transitions in cellulose esters and their mixtures with diluents, *J. Amer. Chem. Soc.*, 73 (1951) 3206-3212.
- 66 A.M. Hindeleh and D. Johnson, Correlation of crystallinity and physical properties of heat-treated cellulose triacetate fibres, *J. Polym.*, 11 (1970) 666-680.
- 67 A.S. Michaels and R.B. Parker, Jr., Sorption and flow of gases in polyethylene, *J. Polym. Sci.*, 41 (1959) 53-71.
- 68 A.S. Michaels and H.J. Bixler, Solubility of gases in polyethylene, *J. Polym. Sci.*, 50 (1961) 393-412.
- 69 A.S. Michaels and H.J. Bixler, Flow of gases through polyethylene, *J. Polym. Sci.*, 50 (1961) 413-439.
- 70 A.S. Michaels, W.R. Vieth and J.A. Barrie, Solution of gases in polyethylene terephthalate, *J. Appl. Phys.*, 34 (1963) 1-12.
- 71 A.S. Michaels, W.R. Vieth and J.A. Barrie, Diffusion of gases in polyethylene terephthalate, *J. Appl. Phys.*, 34 (1963) 13-20.
- 72 A.S. Michaels, H.J. Bixler and H.L. Fein, Gas transport in thermally conditioned linear polyethylene, *J. Appl. Phys.*, 35 (1964) 3165-3178.
- 73 S.A. Stern and S.S. Kulkarni, Solubility of methane in cellulose acetate — Conditioning effect of carbon dioxide, *J. Membrane Sci.*, 10 (1982) 235-251.
- 74 R.T. Chern, W.J. Koros, E.S. Sanders, S.H. Chen and H.B. Hopfenberg, in: T.E. Whyte, Jr., C.M. Yon and E.H. Wagener (Eds.), *Industrial Gas Separations*, ACS Symp. Ser. No. 223, American Chemical Society, Washington, DC, 1983, p. 47.
- 75 A.H. Chan and D.R. Paul, Influence of history on gas sorption, thermal, and mechanical properties of glassy polycarbonate, *J. Appl. Polym. Sci.*, 24 (1979) 1539-1550.
- 76 J.S. Chiou, J.W. Barlow and D.R. Paul, Plasticization of glassy polymers by CO₂, *J. Appl. Polym. Sci.*, 30 (1985) 2633-2642.
- 77 Y. Kamiya, T. Hirose, K. Mizoguchi and Y. Naito, Gravimetric study of high-pressure sorption of gases in polymers, *J. Polym. Sci., Polym. Phys.*, 24 (1986) 1525-1539.
- 78 K. Haraya, K. Obata, T. Hakuta and H. Yoshitome, The permeation of gases through asymmetric cellulose acetate membranes, *J. Chem. Eng. Jpn.*, 19 (1986) 431-436.
- 79 D.L. Ellig, J.B. Althouse and F.P. McCandless, Concentration of methane from mixtures with carbon dioxide by permeation through polymeric films, *J. Membrane Sci.*, 6 (1980) 259-263.
- 80 M.S. Suwandi and S.A. Stern, Transport of heavy organic vapors through silicone rubber, *J. Polym. Sci., Polym. Phys.*, 11 (1973) 663-681.
- 81 H. Odani, M. Uchikura and M. Kurata, Permeation of gas mixtures through polymer membranes, *Polym. Prepr.*, 24 (1983) 81-82.
- 82 J.S. Chiou and D.R. Paul, Effects of CO₂ exposure on gas transport properties of glassy polymers, *J. Membrane Sci.*, 32 (1987) 195-205.
- 83 S.M. Jordan, W.J. Koros and G.K. Fleming, The effects of CO₂ exposure on pure and mixed gas permeation behavior: Comparison of glassy polycarbonate and silicone rubber, *J. Membrane Sci.*, 30 (1987) 191-212.
- 84 P. Clement, Solvation et gonflement des polymères cellulosiques, *Ann. Chim.*, 12 (1947) 420-451.
- 85 R.U. Lemieux and J.D. Stevens, Substitutional and configurational effects on chemical shift in pyranoid carbohydrate derivatives, *Can. J. Chem.*, 43 (1965) 2059-2070.
- 86 J.S. Chiou and D.R. Paul, Sorption and transport of CO₂ in PVF₂/PMMA blends, *J. Appl. Polym. Sci.*, 32 (1986) 2897-2918.
- 87 J.S. Chiou and D.R. Paul, Gas sorption and permeation in poly(ethyl methacrylate), *J. Membrane Sci.*, 45 (1989) 167-189.

- 88 P.C. Painter, M.M. Coleman and J.L. Koenig, *The Theory of Vibrational Spectroscopy and its Application to Polymeric Materials*, John Wiley & Sons, New York, NY, 1982.
- 89 J.L. Koenig, *Chemical Microstructure of Polymer Chains*, John Wiley & Sons, New York, NY, 1980.
- 90 J.H. Keighley, in: D.W. Jones (Ed.), *Introduction to the Spectroscopy of Biological Polymers*, Academic Press, New York, NY, 1976, Chap. 2.
- 91 M.M. Coleman and E.J. Moskala, FTIR studies of polymer blends containing the poly(hydroxy ether of bisphenol A) and poly(ϵ -caprolactone), *Polymer*, 24 (1983) 251-257.
- 92 M.M. Coleman and P.C. Painter, Fourier transform infrared spectroscopy: Probing the structure of multicomponent polymer blends, *Appl. Spectrosc. Rev.*, 20 (1984) 255-346.
- 93 J.Y. Lee, P.C. Painter and M.M. Coleman, Hydrogen bonding in polymer blends — Blends involving polymers containing methacrylic acid and ether groups, *Macromolecules*, 21 (1988) 346-354.
- 94 W.H. Jo, C.A. Cruz and D.R. Paul, FTIR investigation of interactions in blends of PMMA with a styrene/acrylic acid copolymer and their analogs, *J. Polym. Sci., Polym. Phys.*, 27 (1989) 1057-1076.
- 95 C.A. Cruz-Ramos and D.R. Paul, Evaluation of interactions in EVA-PVC blends using model compounds, *Macromolecules*, 22 (1989) 1289-1300.
- 96 J. Blackwell and R.H. Marchessault, in: N.M. Bikales and L. Segal (Eds.), *Cellulose and Cellulose Derivatives*, Vol. 5, Wiley-Interscience, New York, NY, 1971, Chap. 13.
- 97 G. Herzberg, *Molecular Spectra and Molecular Structure*, Van Nostrand Reinhold, New York, NY, 1945.
- 98 K. Nakanishi and P.H. Solomon, *Infrared Absorption Spectroscopy*, Holden-Day, Oakland, CA, 1977, Chap. 2.